Spectroscopy
Spectra 1

Introduction

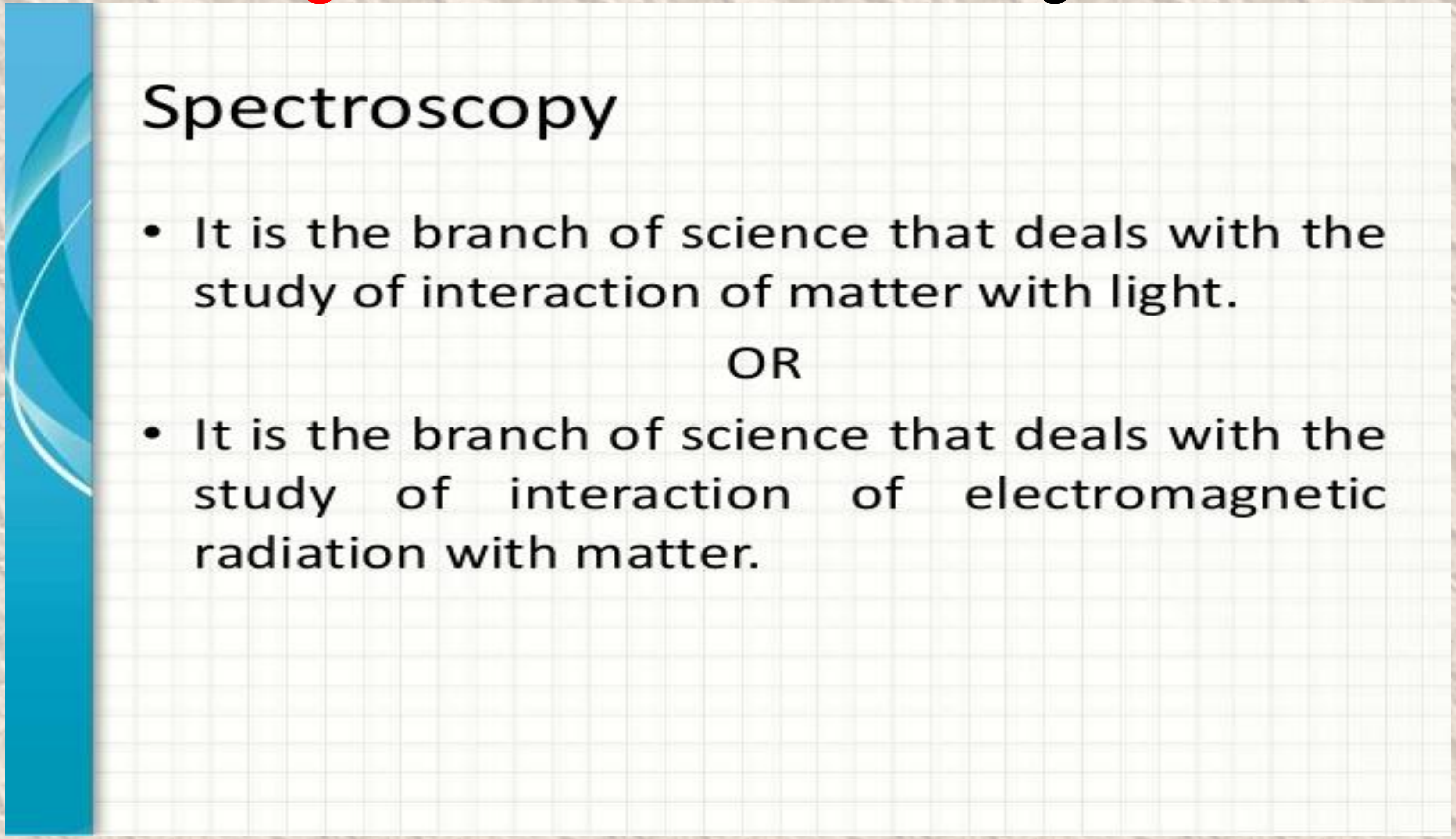
- For synthesis of new compound we use "4" methods of spectral method to make identification for the structure of the compound.

➡ These four methods are:

- **(1)** Ultra Violet (U.V) **(2)** Infrared (I.R)
- **(3)** Mass spectrometry (M.S)
- **(4)** Nuclear Magnetic Resonance (N.M.R)

Spectroscopy

The light is a beams of electromagnetic waves



Spectroscopy

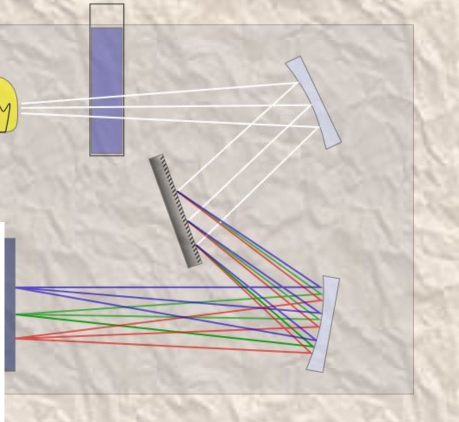
- It is the branch of science that deals with the study of interaction of matter with light.

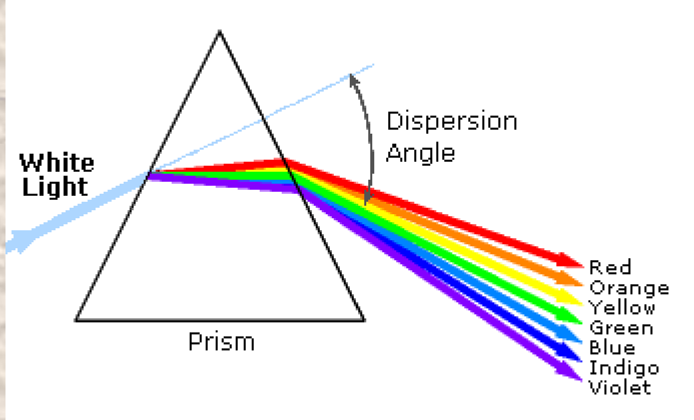
OR

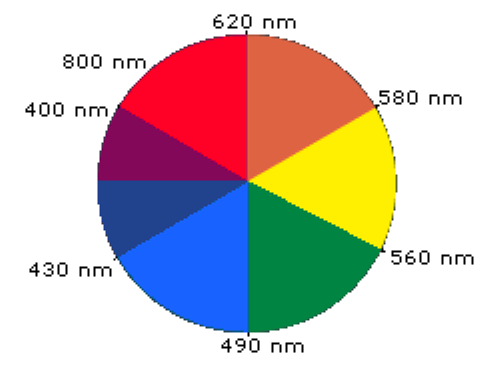
- It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

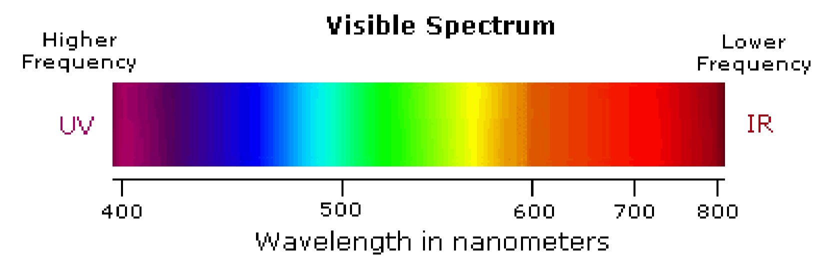
- ❖ **Idea**:
  - Compound which we want to identify absorb an energy with a certain wave length causes excitation and then it will emit this energy which pass to detector and pass to plotter to plot a chart. .
-

UV-Vis spectroscopy
Electronic absorption spectroscopy

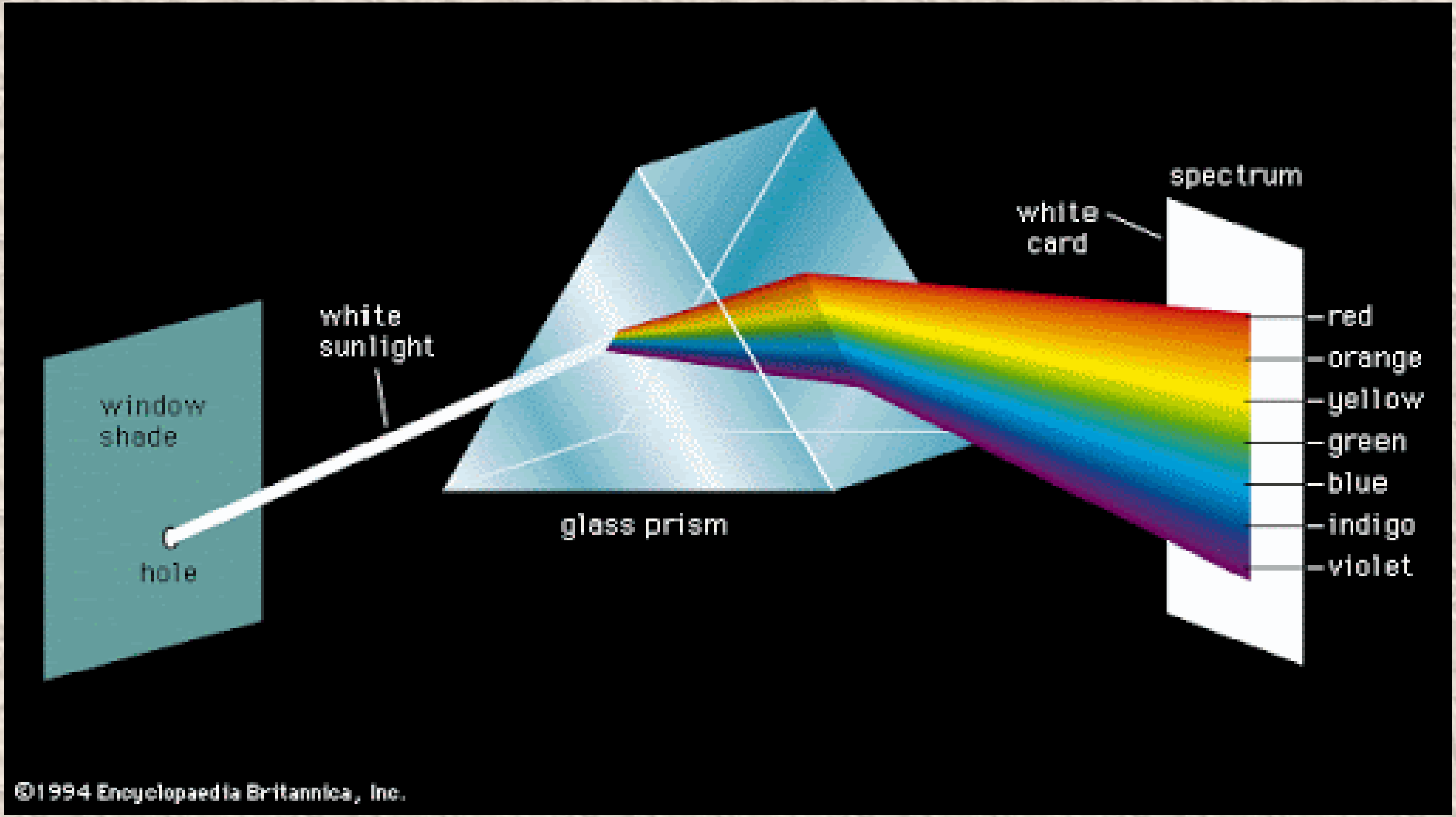


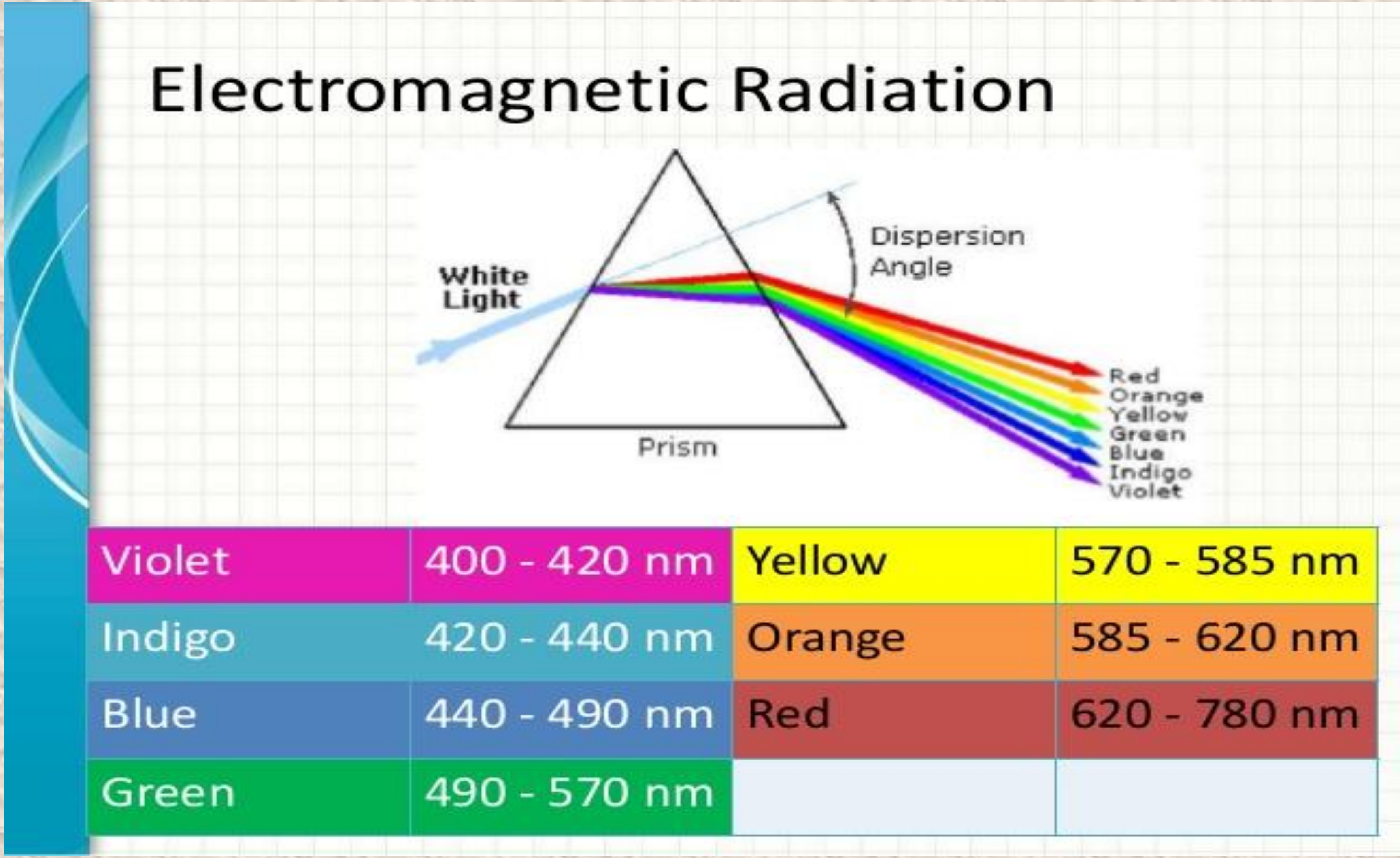






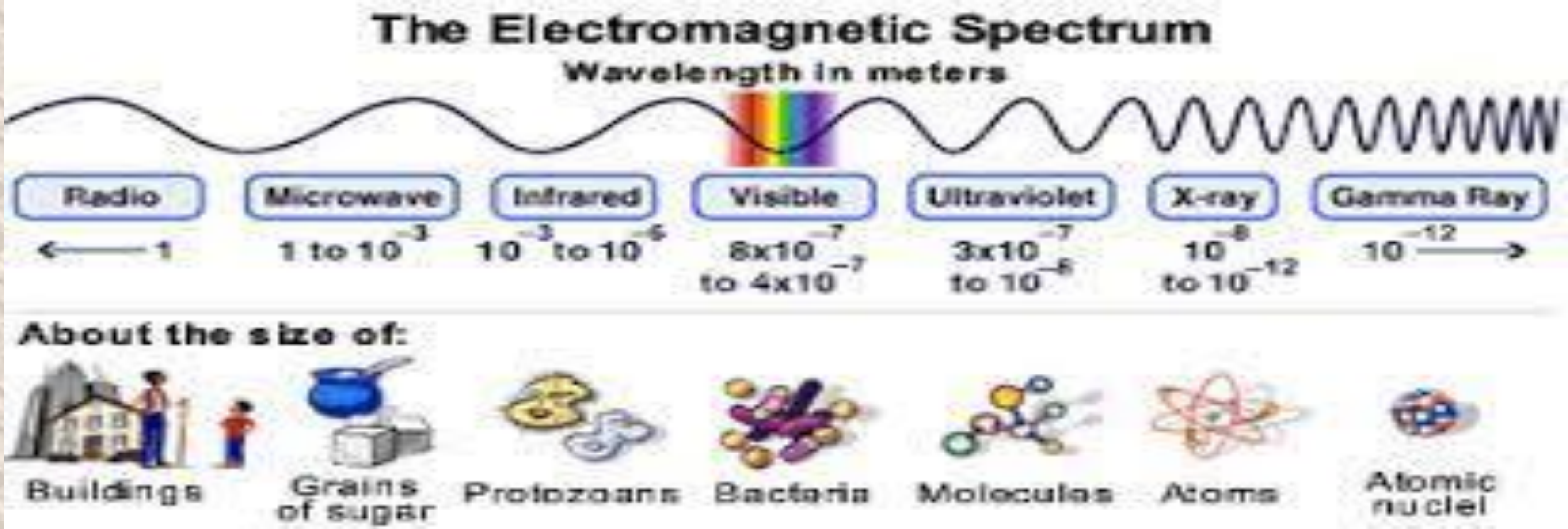
- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm


white sunlight
window shade
hole
glass prism
spectrum
white card
red
orange
yellow
green
blue
indigo
violet



Electromagnetic Radiation

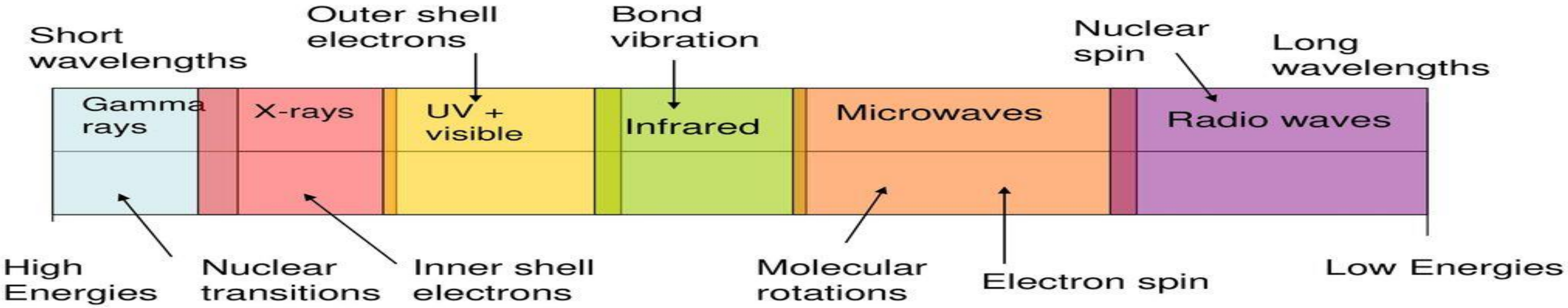
Violet	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm
Green	490 - 570 nm		

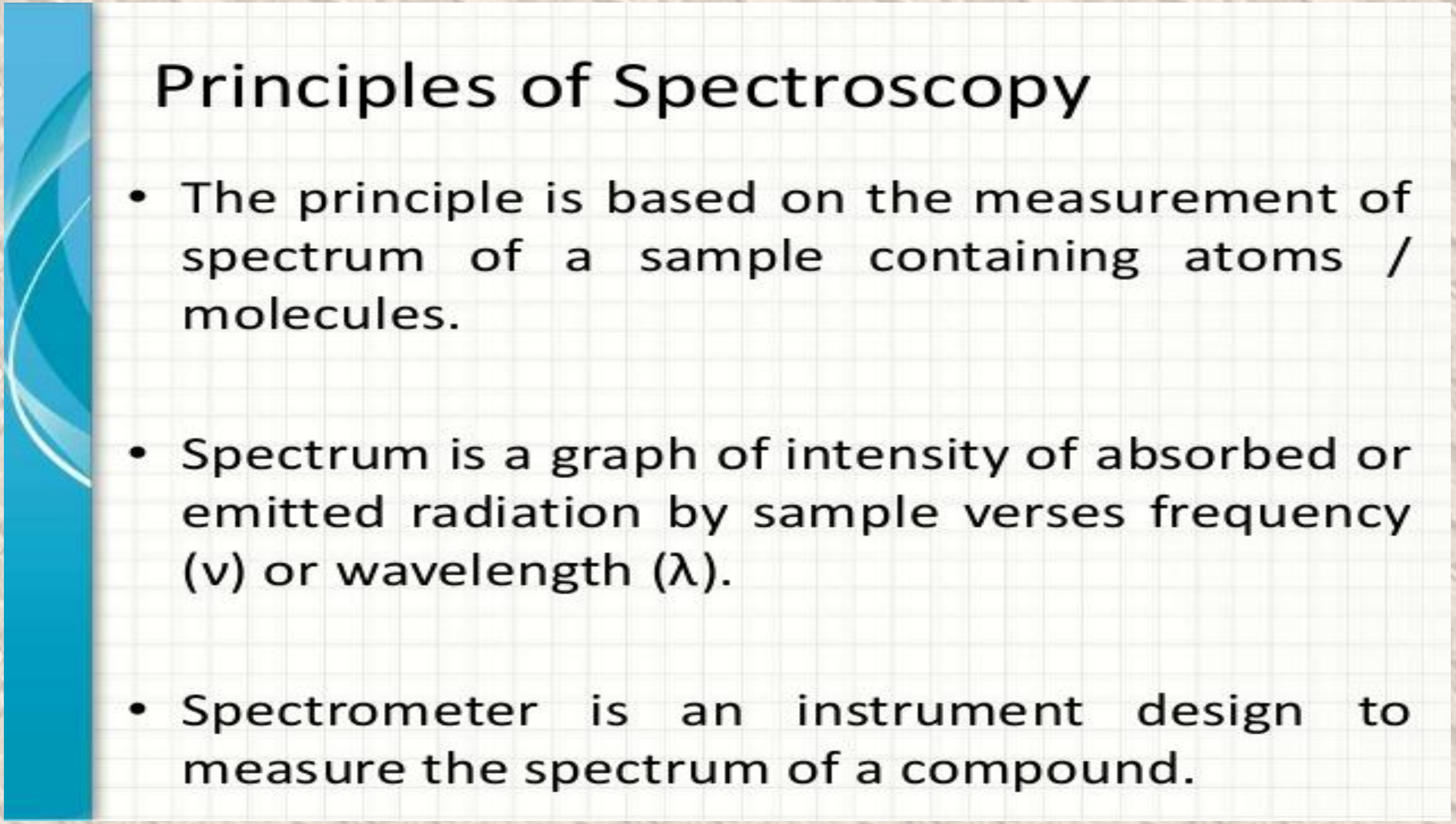


Spectroscopy

Regions of the Electromagnetic Spectrum

1. Many regions are defined as much by the mechanism of the transitions (e.g. outer shell electron) as by the frequency or energy of the transitions



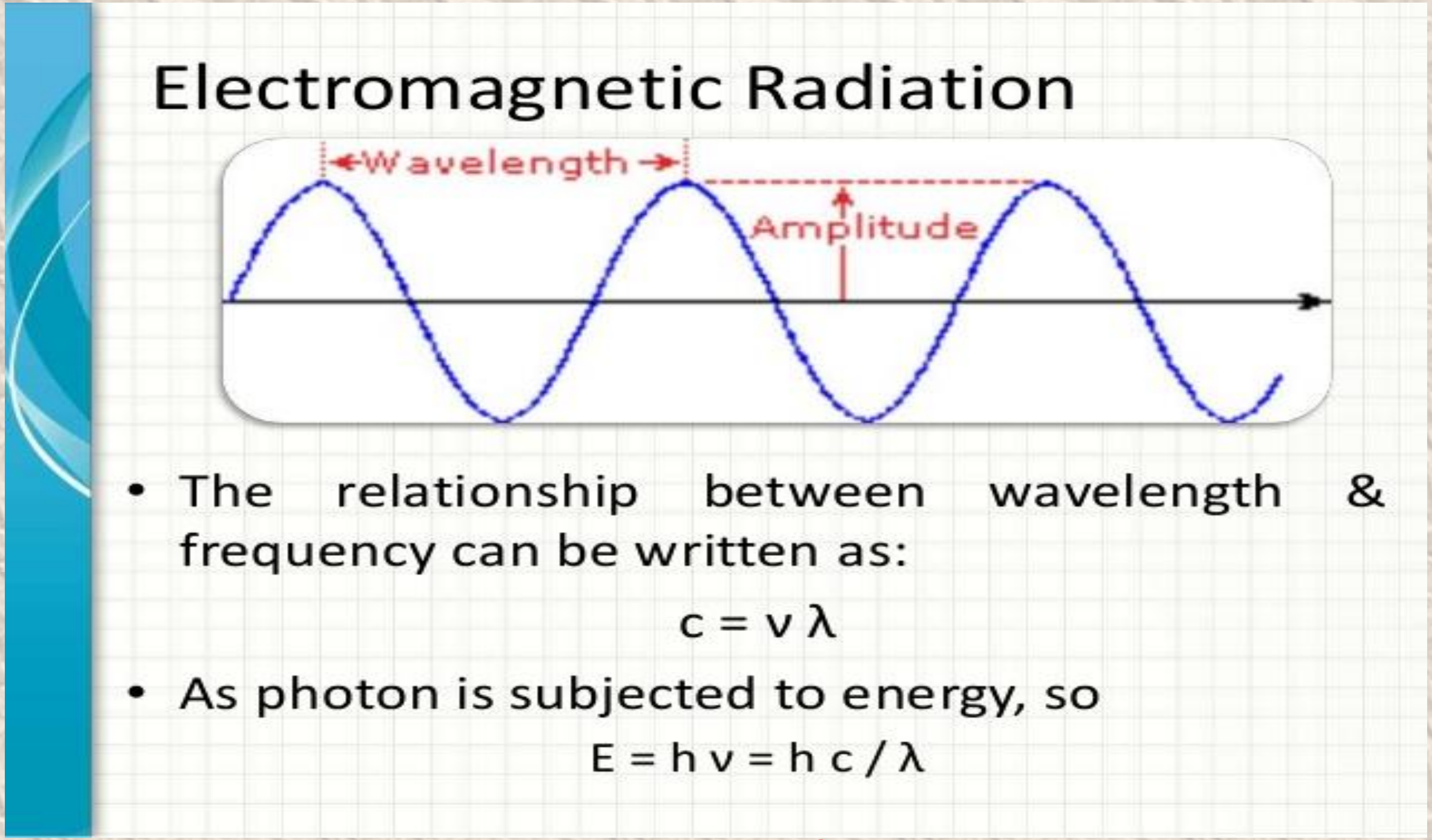


Principles of Spectroscopy

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.

- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (v) or wavelength (λ).

- Spectrometer is an instrument design to measure the spectrum of a compound.



Electromagnetic Radiation

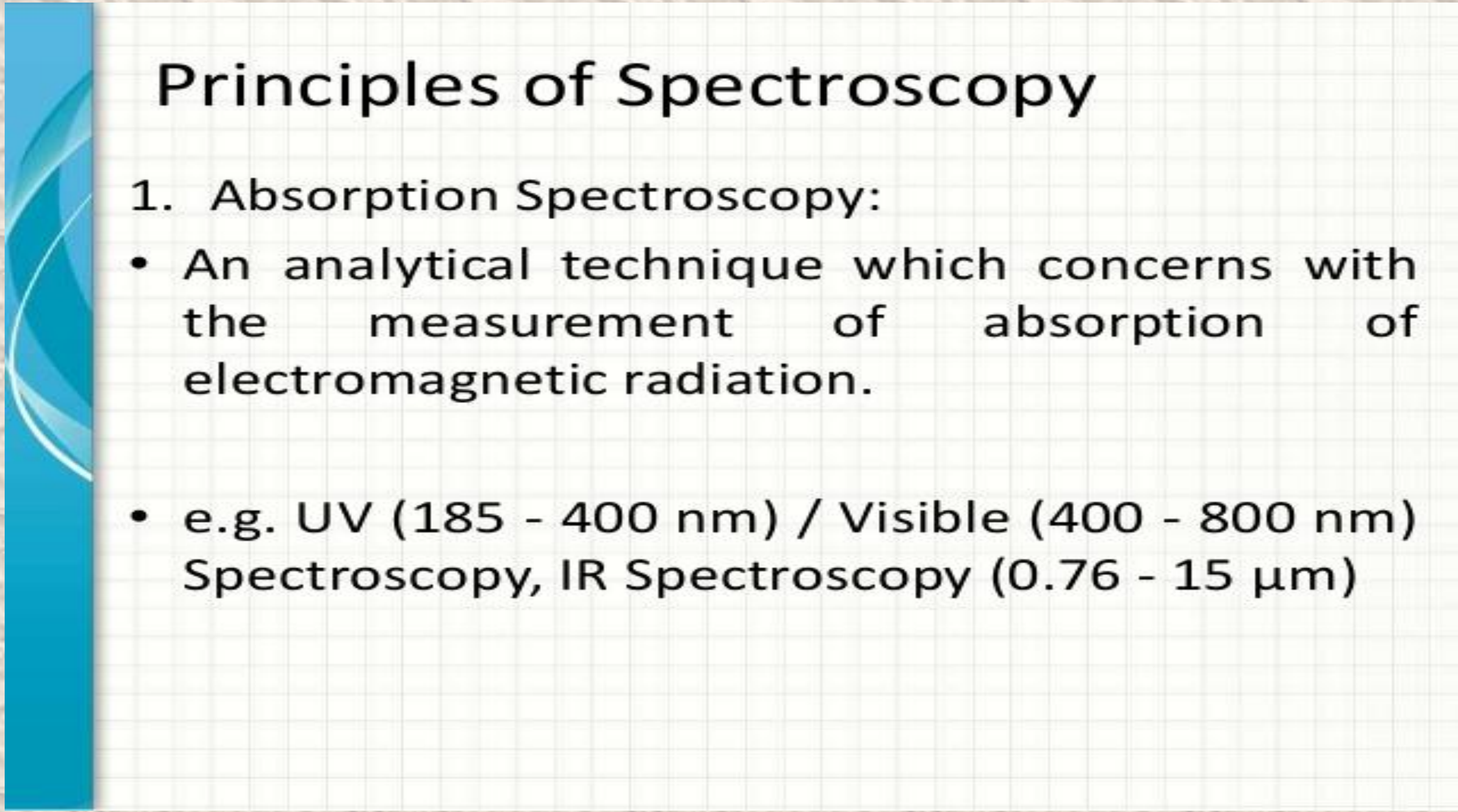
- The relationship between wavelength & frequency can be written as:

$$c = \nu \lambda$$

- As photon is subjected to energy, so

$$E = h \nu = h c / \lambda$$

$$E \ \alpha \ \lambda$$



Principles of Spectroscopy

1. Absorption Spectroscopy:

- An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

- e.g. UV (185 - 400 nm) / Visible (400 - 800 nm) Spectroscopy, IR Spectroscopy (0.76 - 15 µm)

Principle

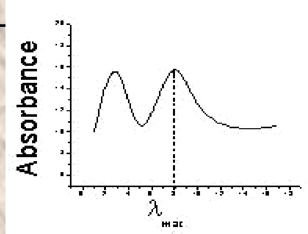
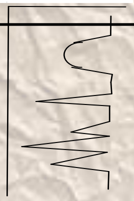
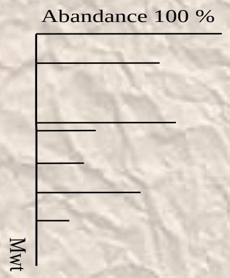
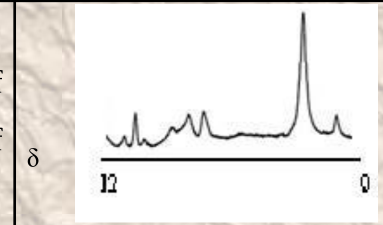
- The UV radiation region extends from 10 nm to 400 nm and the visible radiation region extends from 400 nm to 800 nm.

  Near UV Region: 200 nm to 400 nm

  Far UV Region: below 200 nm

- Far UV spectroscopy is studied under vacuum condition.
- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane.

Spectroscopic Techniques:

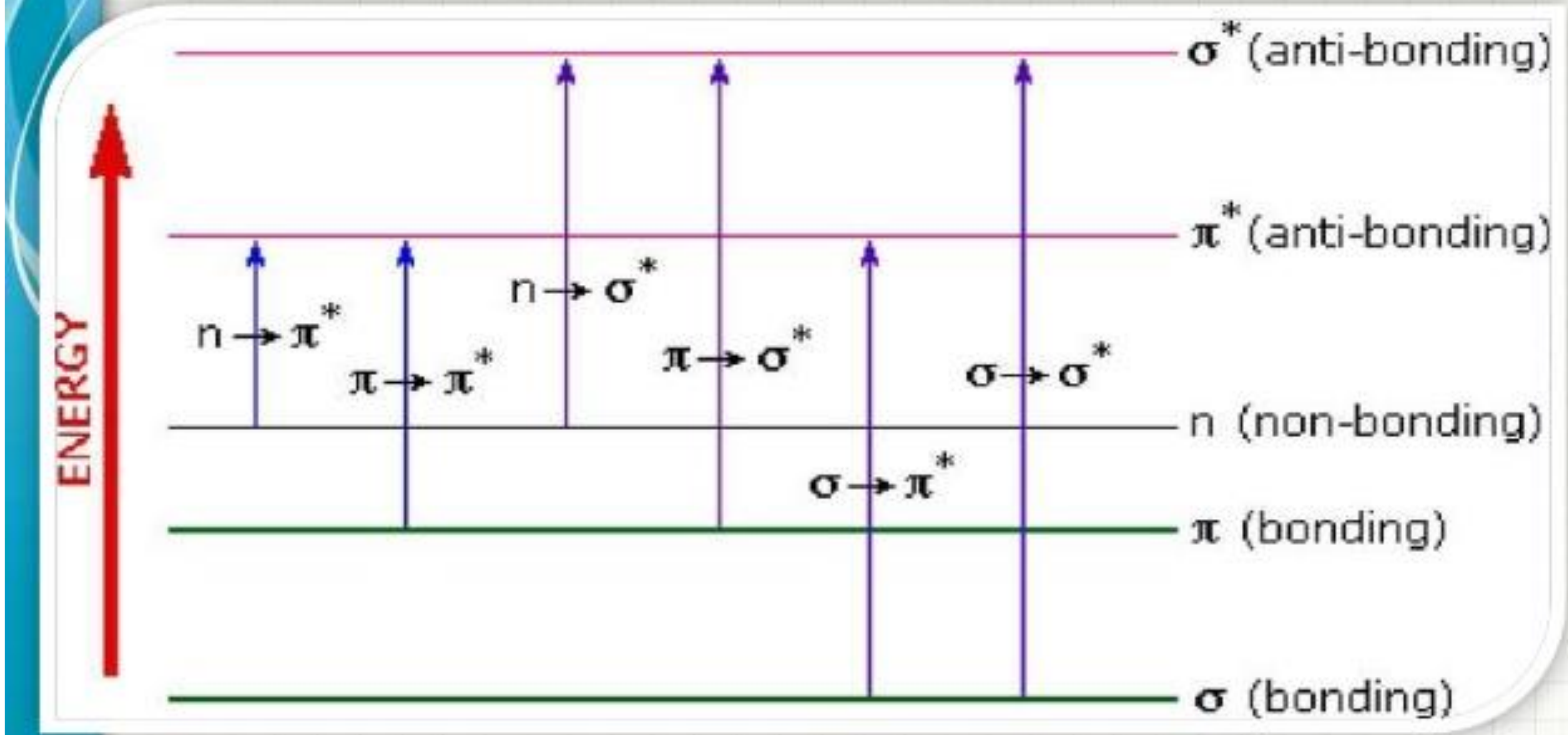
Type of technique	Effect of this "E" on the molecule	Shape of chart	Uses of this technique
U.V.	Cause changes in the electronic energy levels within a molecule Excitation of elec. from lower level [illegible]her level		Identify for conjugation (= - =)
I.R	Vibration for bond between two atoms		Identify for the function J/gps in the molecule
M.S	Fragmentation of the molecule to small parts		Identify through wt. and M.wt. of some fragment to identify the structure
N.M.R	Microwave cause resonance of nucleus of atom under effect of strong magnet		Identification for the types of "H" in the compound and the structure

Chromophores is the atoms or groups responsible to absorption

N, S, Osuch as;

C=O, C=C, C-C, C=N, C=s

The possible electronic transitions can graphically shown as:

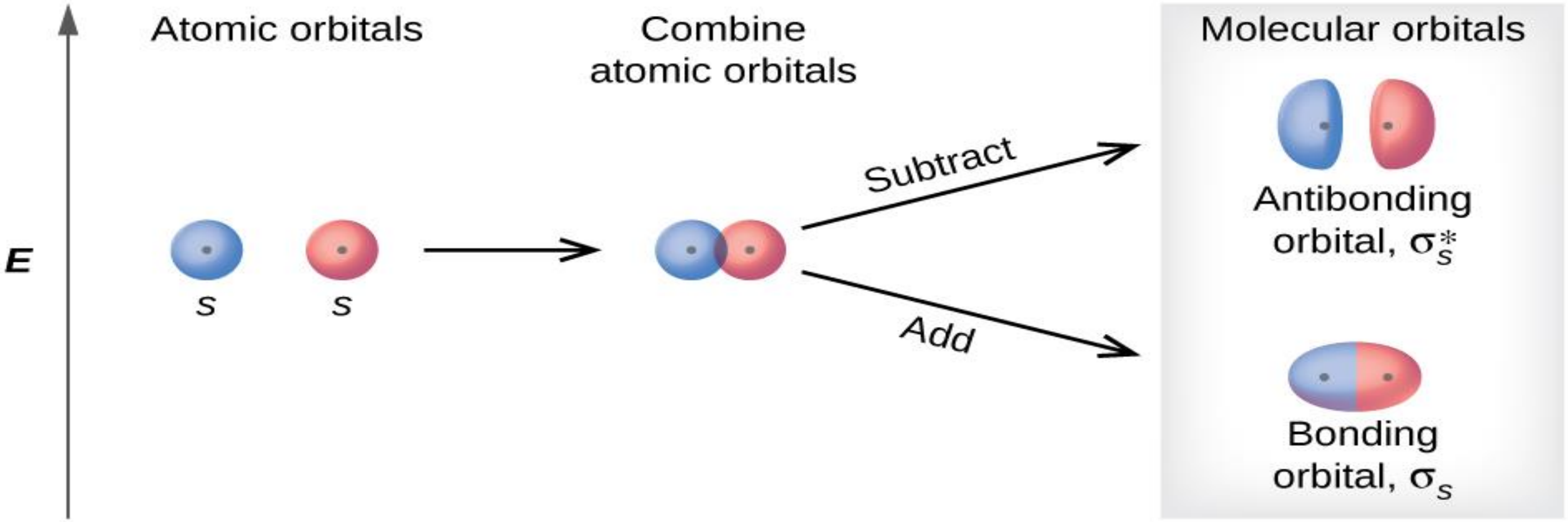


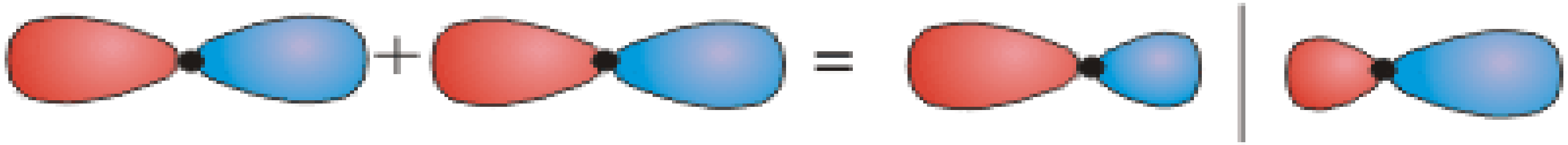
The possible electronic transitions are

1. $\sigma \rightarrow \sigma^*$ transition
2. $\pi \rightarrow \pi^*$ transition
3. $n \rightarrow \sigma^*$ transition
4. $n \rightarrow \pi^*$ transition
5. $\sigma \rightarrow \pi^*$ transition
6. $\pi \rightarrow \sigma^*$ transition

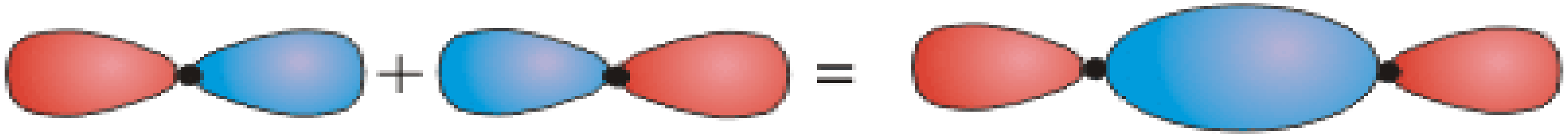
1 • σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.
- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

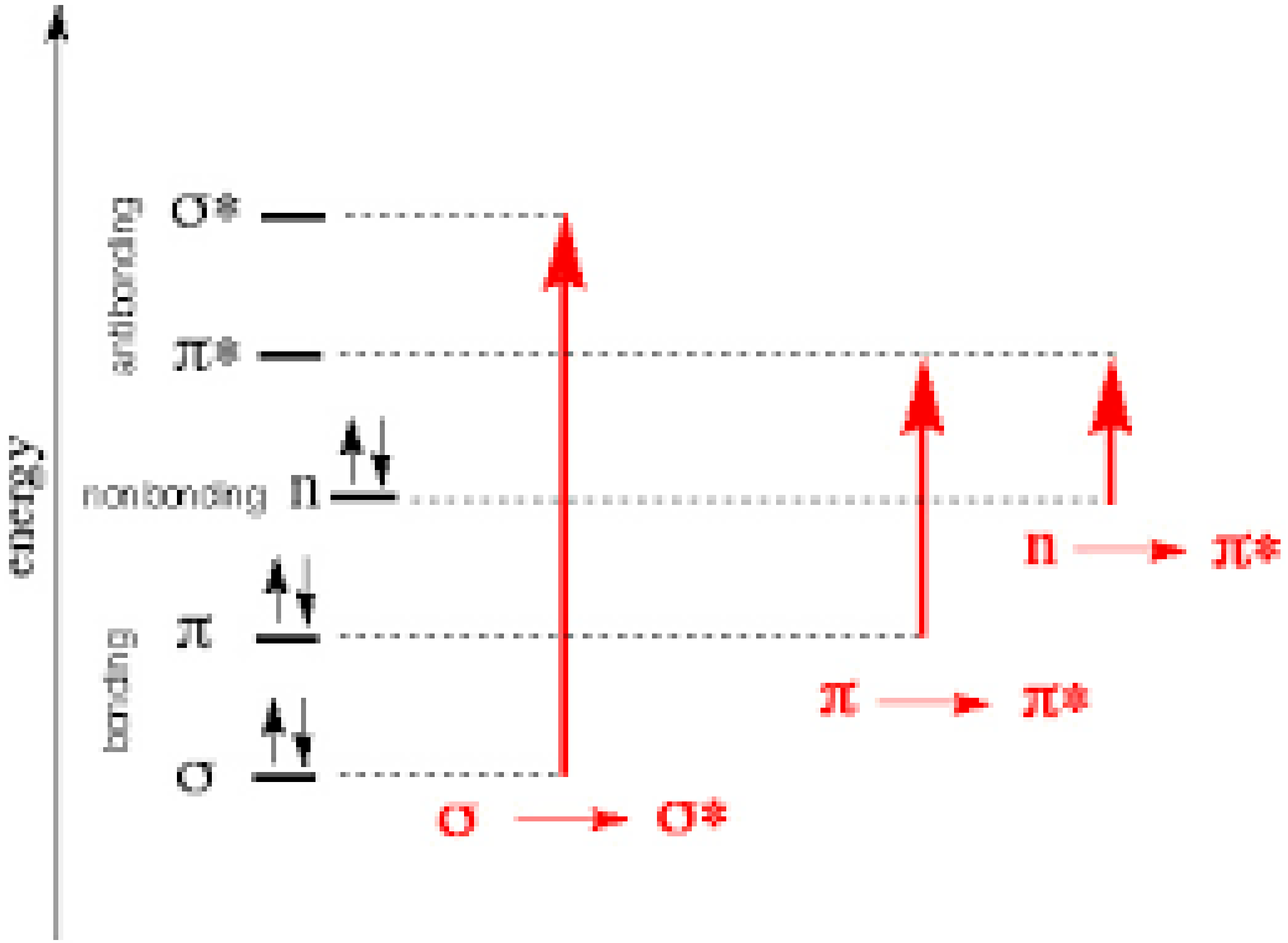




out of phase combination = σ* MO



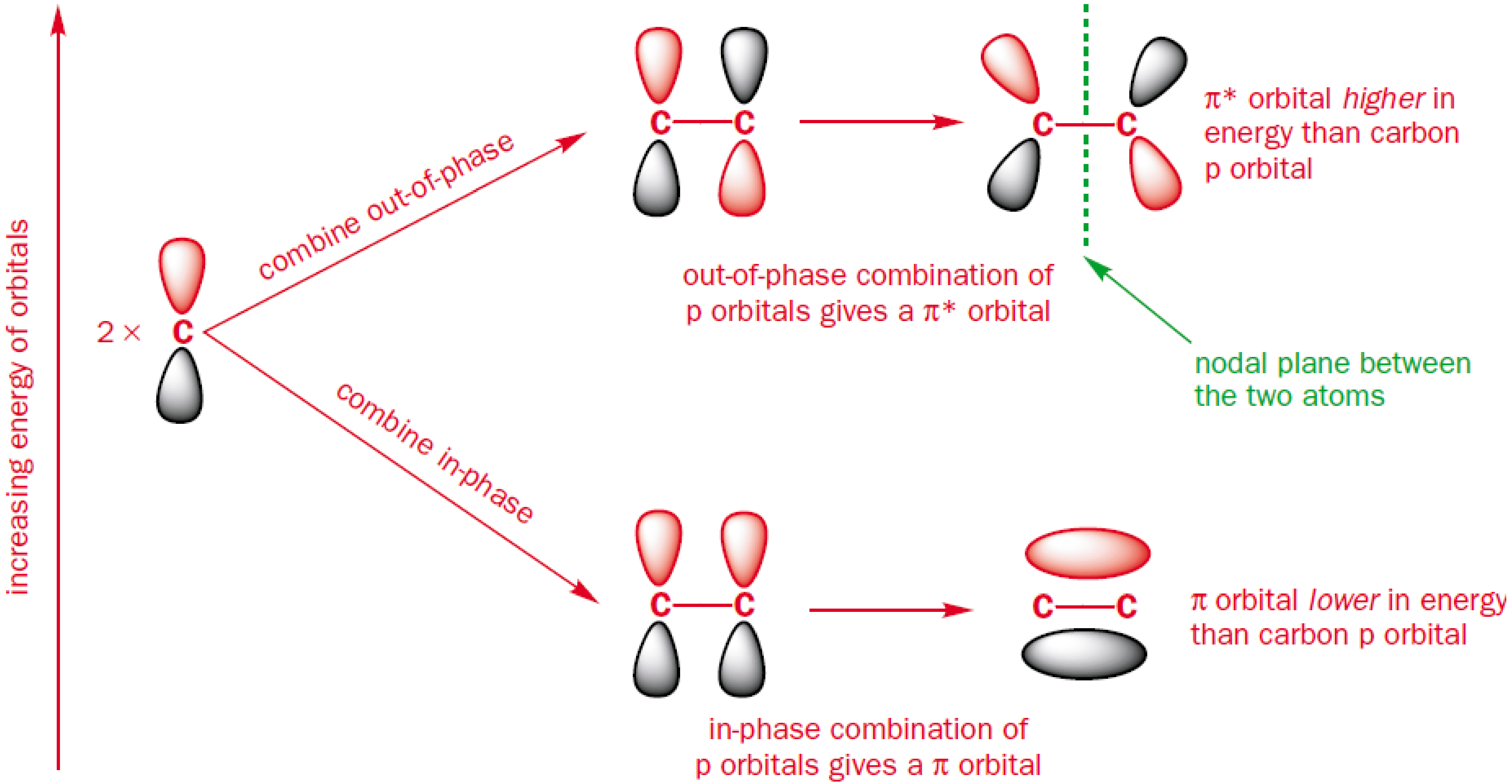
in-phase combination = σ MO


energy
antibonding
σ*
π*
nonbonding
n
bonding
π
σ
σ → σ*
π → π*
n → π*

2

• $\pi \rightarrow \pi^*$ transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π^*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.


increasing energy of orbitals
2 × C
combine out-of-phase
combine in-phase
C—C
C—C
π* orbital *higher* in energy than carbon p orbital
out-of-phase combination of p orbitals gives a π* orbital
nodal plane between the two atoms
C—C
C—C
π orbital *lower* in energy than carbon p orbital
in-phase combination of p orbitals gives a π orbital

4 • n → π* transition

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.

- Compounds containing double bond involving hetero atoms ($C=O$, $C\equiv N$, $N=O$) undergo such transitions.

- n → π* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

Chromophore

The part of a molecule responsible for imparting color, are called as chromospheres.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions.

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

Chromophore

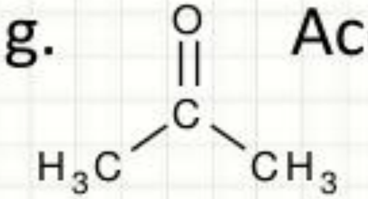
To interpretate UV – visible spectrum following points should be noted:

1. Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.

2. Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

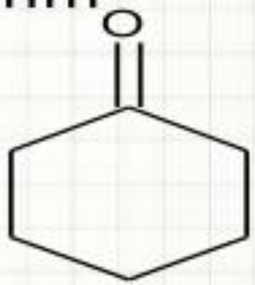
Chromophore

e.g.



Acetone which has λ_{max} = 279 nm

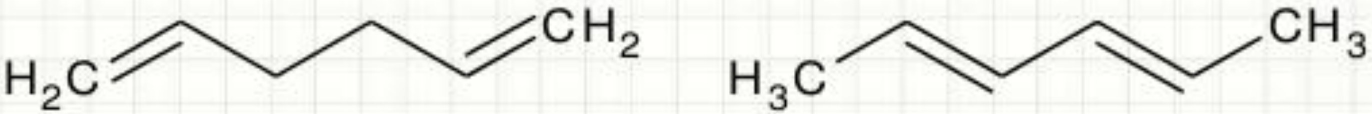
and that cyclohexane has λ_{max} = 291 nm.



When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm

2,4 - hexadiene has λ_{max} = 227 nm



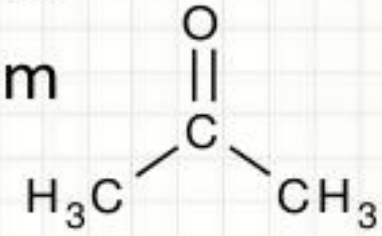
Chromophore

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

e.g. Ethylene has λ_{max} = 171 nm

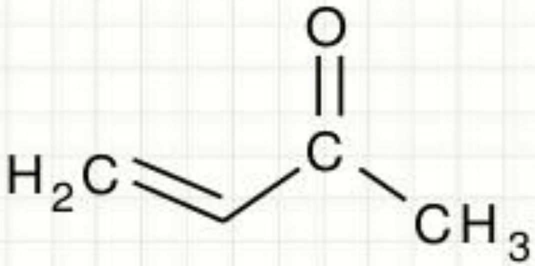
Acetone has λ_{max} = 279 nm

$H_2C{=}CH_2$



$H_3C-C(=O)-CH_3$

Crotonaldehyde has λ_{max} = 290 nm



Auxochrome

The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

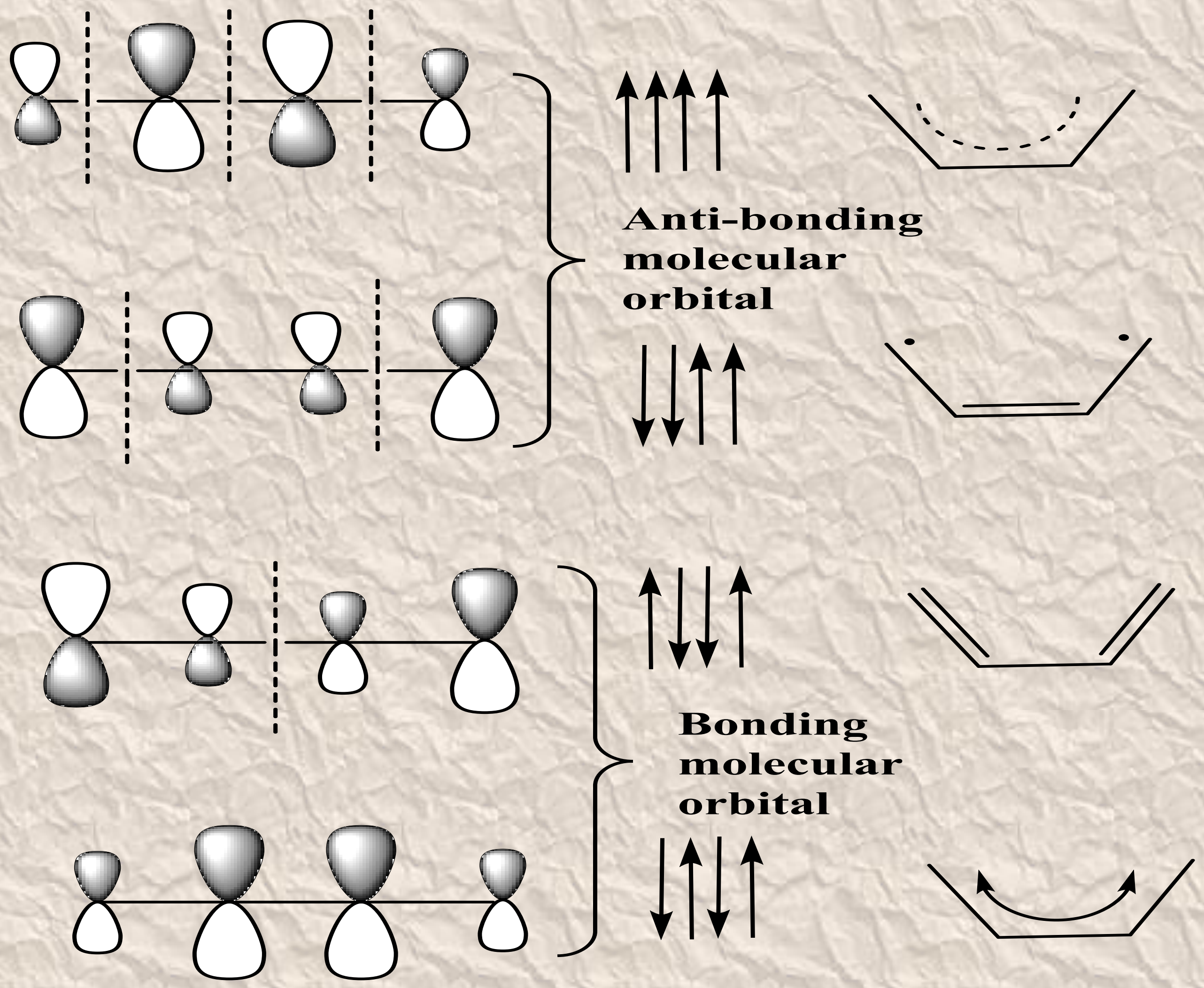
Auxochrome

e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm

Aniline λ_{max} = 280 nm

The π- π* transitions in π-molecular orbitals of 1,3-butadiene.



HUMO π_4

LUMO π_3

Anti-bonding molecular orbital

HOMO π_2

LOMO π_1

Bonding molecular orbital

π - Molecular orbitals of 1,3-butadiene

Chromophore

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

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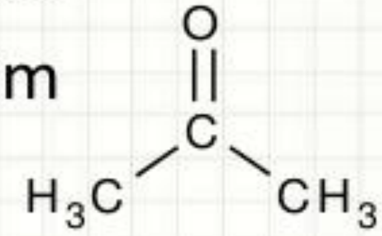

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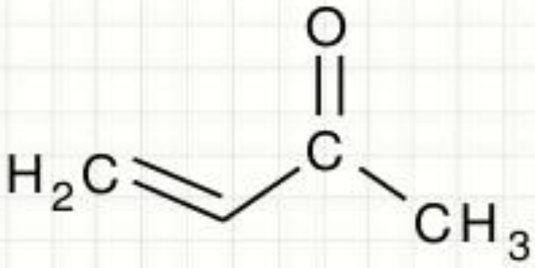
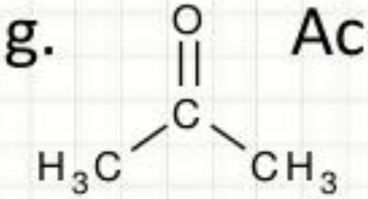


Chromophore

e.g. 

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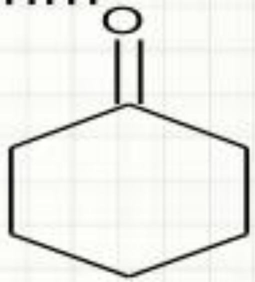

and that cyclohexane has λ_{max} = 291 nm.

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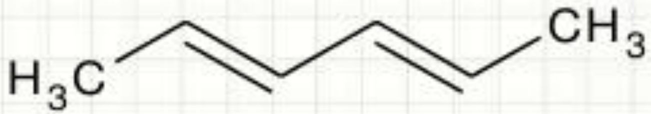
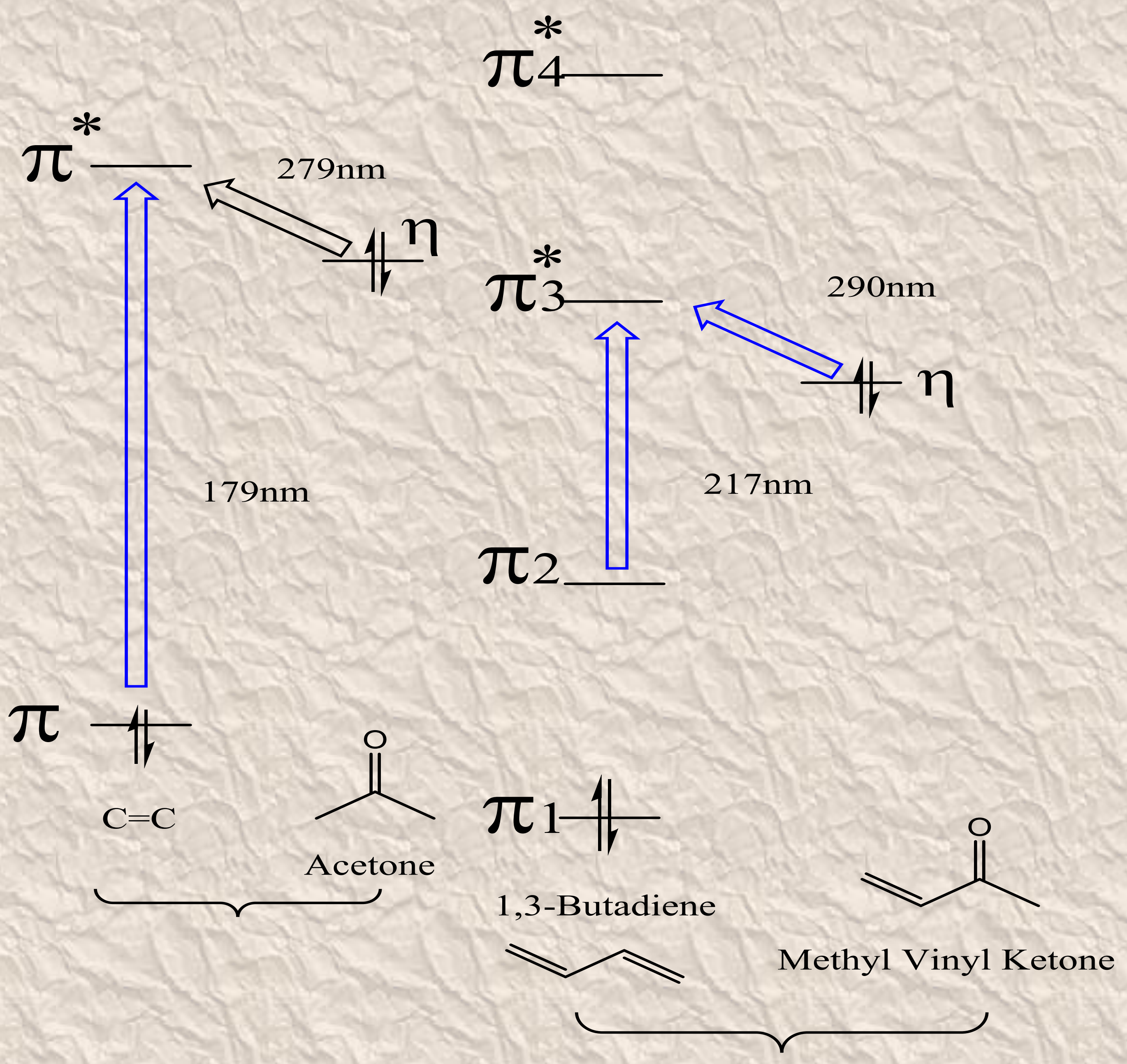




The Electronic Transitions of C=C, Acetone, 1,3-butadiene and Methyl vinyl ketone

Auxochrome

The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Auxochrome

e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm

Aniline λ_{max} = 280 nm

FOLLOW THE ULTRA-VIOLET SPECTROSCOPY

Woodward-Fieser rules

- In this lesson we discuss a few examples of how we can utilize the **Woodward-Fieser** rules to determine the wavelength of maximum absorption for some molecules. **You have to** read up the first two sections on the **Woodward rules to calculate the λmax for conjugated dienes** and **the Woodward rules to calculate the λmax for α,β-unsaturated carbonyl compounds**.

The Numerical values for Woodward-Fieser rules are in the following tables:

S	Conjugated polyenes	Base absorption (nm)
1	Homoannular diene	253
2	Heteroannular diene	214
	Function	
3	Alkyl	5
4	-OCOR	0
5	-OR	6
6	-SR	30
7	-Cl, -Br	5
8	-NR_2	60
9	Extended conjugation	30
10	**Exocyclic double bond**	5

It is recommended that you learn on how to apply these values on the structures and then you have to calculate the λmax value.

In these sample problems you will be shown the structure, then the structure is highlighted to show you key features which would affect the λmax of the molecule. Then the table will show you the solutions on how to solve to get the wavelength of maximum absorption, with a final calculated λmax using the Woodward-Fieser rules. In some cases if we have an observed λmax for comparison, it may be given as well.

Example 1

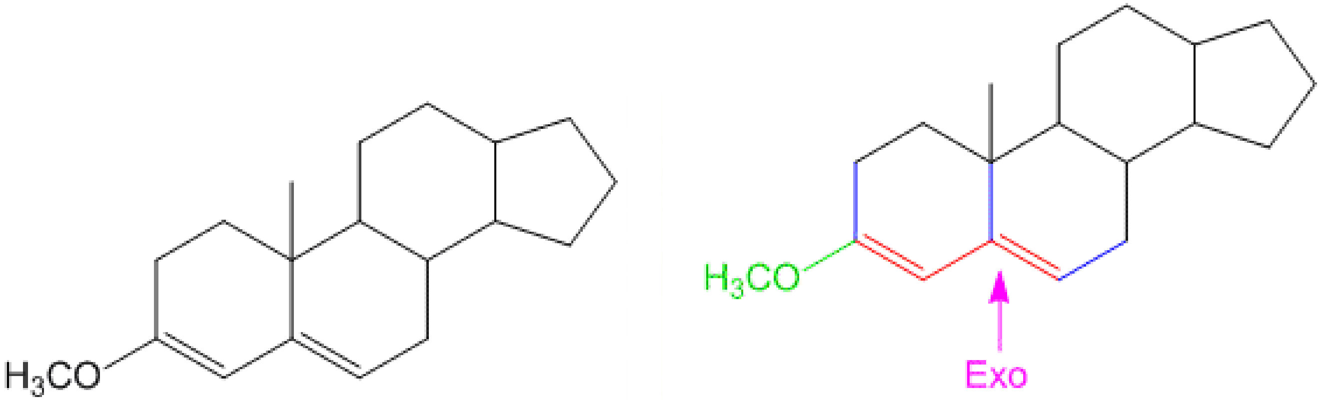
2,4-dimethylpenta-1,3-diene

Woodward Component	Contribution
Parent base- Heteroannular Diene	+ 214 nm
Substituents- 3 alkyl groups	3 x 5 = 15 nm
Calculated λmax	**229 nm**

Example 2

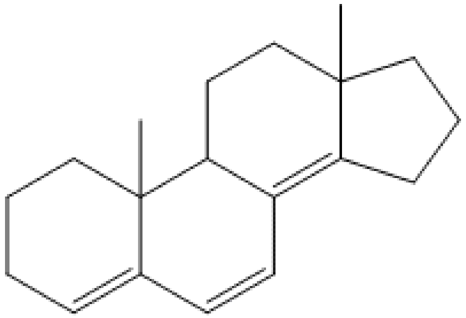
Name of Compound	1-methylcyclohexa-1,3-diene
Woodward Component	**Contribution**
Parent base- Homoannular Diene	+ 253 nm
Substituents- 3 alkyl groups	3 x 5 = + 15 nm
Calculated λmax	**268 nm**

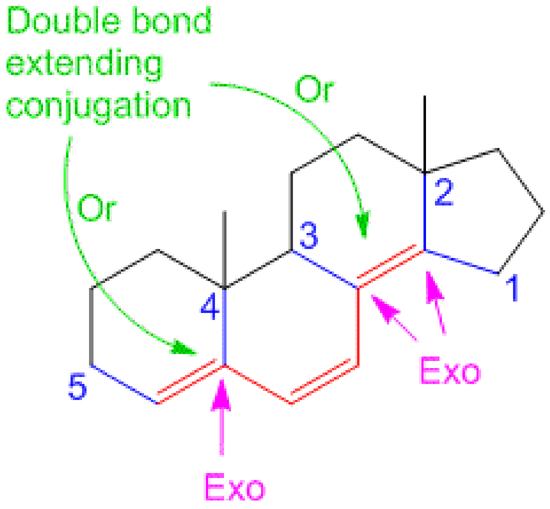
Example 3



Name of Compound	3-methoxy-10-methyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene
Woodward Component	**Contribution**
Parent base- Heteroannular Diene	214 nm
Substituents- 3 alkyl groups	3 x 5 = 15 nm
1 alkoxy group	+ 6 nm
Exocyclic Double Bond	+ 5 nm
Calculated λmax	**240 nm**

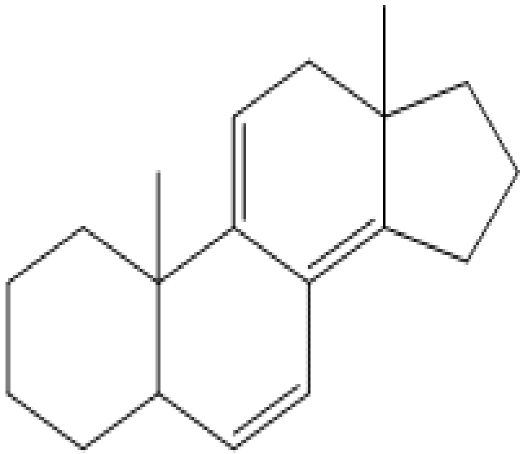
Example 4





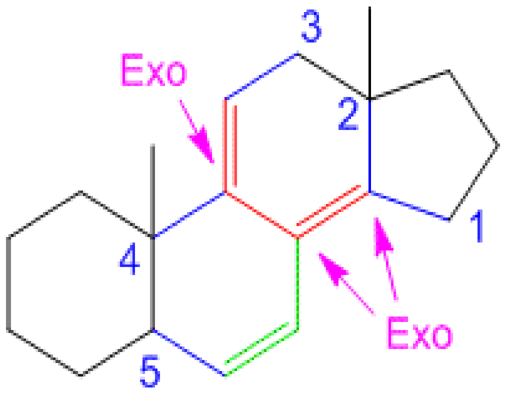
Name of Compound	10,13-dimethyl-2,3,9,10,11,12,13,15,16,17-decahydro-1H-cyclopenta[a]phenanthrene
Woodward Component	**Contribution**
Parent base- Heteroannular	+ 214 nm
Substituents- 5 alkyl groups 1 Double bond extending conjugation	5 x 5 = + 25 nm + 30 nm
3 Exocyclic Double Bond	+ 15 nm
Calculated λmax	**284 nm**

Example 5



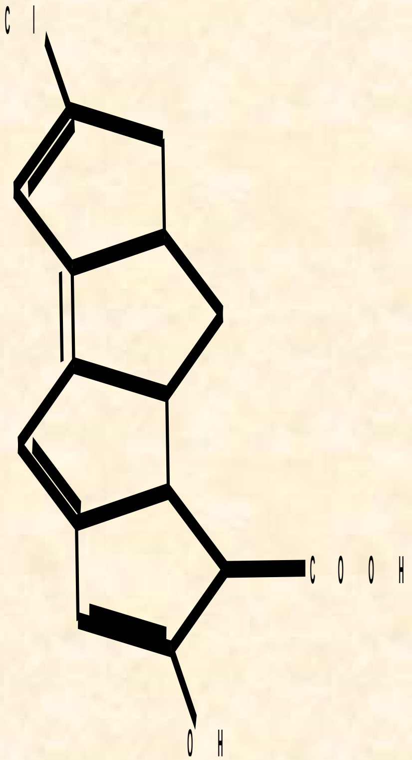
Note- In this example the molecule **contains both, a homoannular diene system and a heteroannular diene** system. In such a molecule the core chromophore is considered to be the homoannular system and accordingly the calculations are performed.

Homoannular system



Component	**Contribution**
Parent base- Homoannular	+ 253 nm
Substituents– 5 alkyl substituents	5 x 5 = + 25 nm
Double bond extending conjugation	+ 30 nm
3 Exocyclic double bonds	3 x 5 = + 15 nm
Calculated λ_{max}	**323 nm**

Parent base- α,β-unsaturated carbonyl compound cyclohexenone	+ 214 nm
Substituents: 5 alkyl group	+ 25 nm
Cl	5
OH	+ 6 nm
Other Effects: 2 Double bonds extending conjugation	+ 60 nm
3 Exocyclic double bond	+ 15 nm
Calculated λ_{max}	325 nm



Calculation of the λmax of α,β-unsaturated carbonyl compounds

In this lesson we discuss a few examples of how we can utilize the **Woodward-Fieser** rules to determine the wavelength of maximum absorption for some molecules. **The Woodward rules to calculate the λmax for α,β-unsaturated carbonyl compounds**.

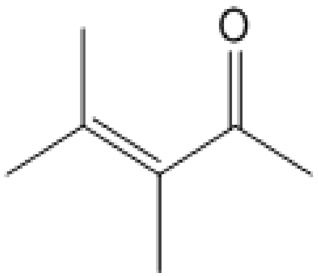
The Numerical values for Woodward-Fieser rules are in the following tables:

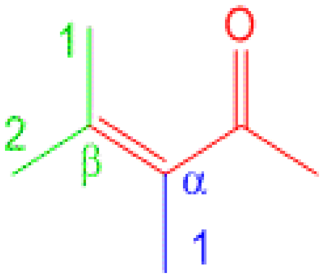
S	α , β- Unsaturated parent	Base absorption (nm)
1	Acyclic or six membered or higher ring ketones	215
2	Five-membered ring ketone	205
3	Aldehydes	210
4	Carboxylic acids and esters	195
5	Extended conjugation	30
6	Homodienic component	39
7	**Exocyclic double bond**	5

S	Substituent	α	β	γ or higher
1	Alkyl (R-)	10	12	18
2	Hydroxyl (-OH)	35	30	50
3	Alkoxyl (RO-)	35	30	17
4	Acetoxyl (CH_3COO-)	6	6	6
5	Dialkylamino (-NR_2	-	95	-
6	Chloro (Cl-)	15	12	-
7	Bromo (Br-)	25	30	-
8	**Alkylthio (RS-)**	-	85	-

It is recommended that you learn on how to apply these values on the structures and then you have to calculate the λmax value.

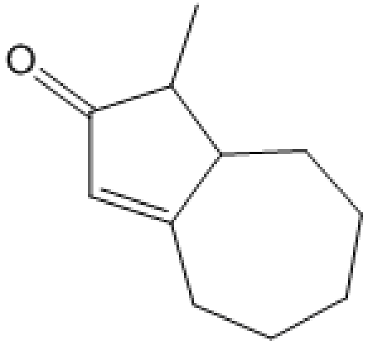
In these sample problems you will be shown the structure, then the structure is highlighted to show you key features which would affect the λmax of the molecule. Then the table will show you the solutions on how to solve to get the wavelength of maximum absorption of α,β-unsaturated carbonyl compounds, with a final calculated λmax using the Woodward-Fieser rules. In some cases if we have an observed λmax for comparison, it may be given as well.

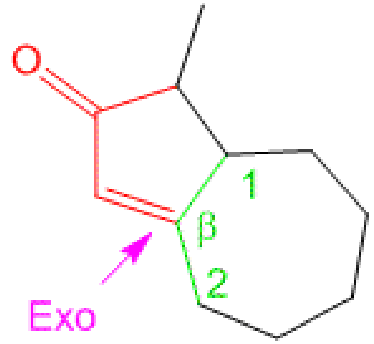




Name of Compound	3,4-dimethylpent-3-en-2-one
Component	**Contribution**
Parent base- α,β-unsaturated carbonyl compound	+ 215 nm
Substituents at α-position- 1 alkyl group	+ 10 nm
Substituents at β-position- 2 alkyl groups	2 x 12 = 24 nm
Calculated λ_{max}	**249 nm**

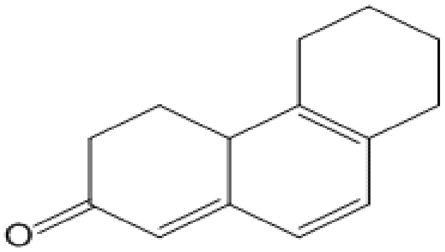
Example 1

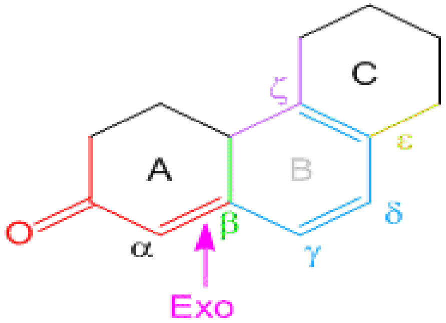




Name of Compound	1-methyl-4,5,6,7,8,8a-hexahydroazulen-2(1H)-one
Component	**Contribution**
Parent base- cyclopentenone	+ 205 nm
Substituents at α-position	0
Substituents at β-position- 2 alkyl groups	2 x 12= + 24 nm
1 Exocyclic Double Bond	+ 5 nm
Calculated λ_{max}	**234 nm**

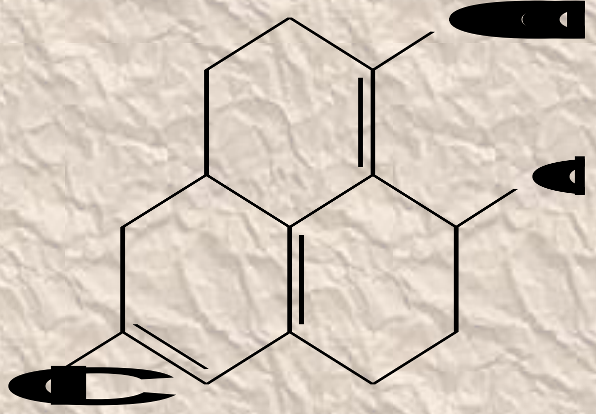
Example 2



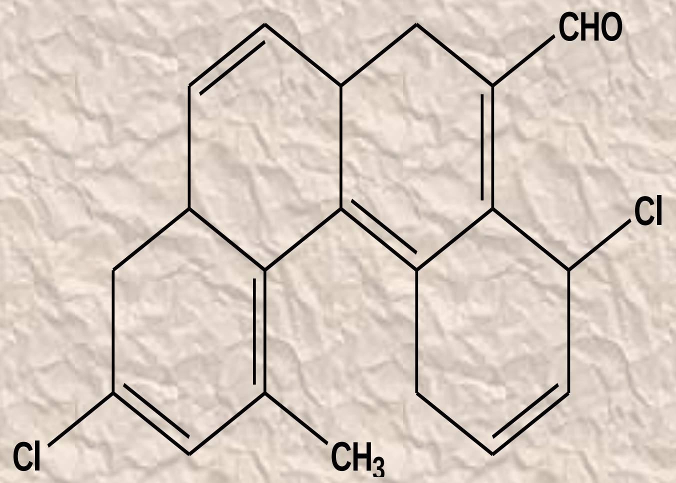


Name of Compound	4,4a,5,6,7,8-hexahydrophenanthren-2(3H)-one
Component	**Contribution**
Parent base- α,β-unsaturated carbonyl compound cyclohexenone	+ 215 nm
Substituents at α-position:	0
Substituents at β-position: 1 alkyl group	+ 12 nm
Substituents at γ-position: 3 alkyl group	3 x 18 = + 54 nm
Other Effects: 2 Double bonds extending conjugation	2 x 30 = + 60 nm
Homoannular Diene system in ring B	+ 35 nm
1 Exocyclic double bond	+ 5 nm
Calculated λ_{max}	**381 nm**

Parent base- α,β-unsaturated carbonyl compound cyclohexenone	+ 195 nm
Substituents at α-position:	+ 10nm
Substituents at β-position: 1 alkyl group	+ 12 nm
Substituents at γ-position: 3 alkyl group	3 x 18 = + 54 nm
γ- Cl	0
Other Effects: 2 Double bonds extending conjugation	2 x 30 = + 60 nm
Homoannular Diene system in ring B	+ 35 nm
2 Exocyclic double bond	+ 10nm
Calculated λ_{max}	376 nm



Parent base- α,β-unsaturated carbonyl compound Aldehyde	+ 210 nm
Substituents at α-position:	+ 10nm
Substituents at β-position: 1 alkyl group	+ 12 nm
Substituents at γ-position: 4 alkyl group	4 x 18 = + 72 nm
γ- CH3	+18
γ- Cl	0
Other Effects: 2 Double bonds extending conjugation	3 x 30 = + 90 nm
Homoannular Diene system in ring B, D	2 x 39 nm
4 Exocyclic double bond	+ 20nm
Calculated λ_{max}	510 nm



IR

Infrared Spectroscopy

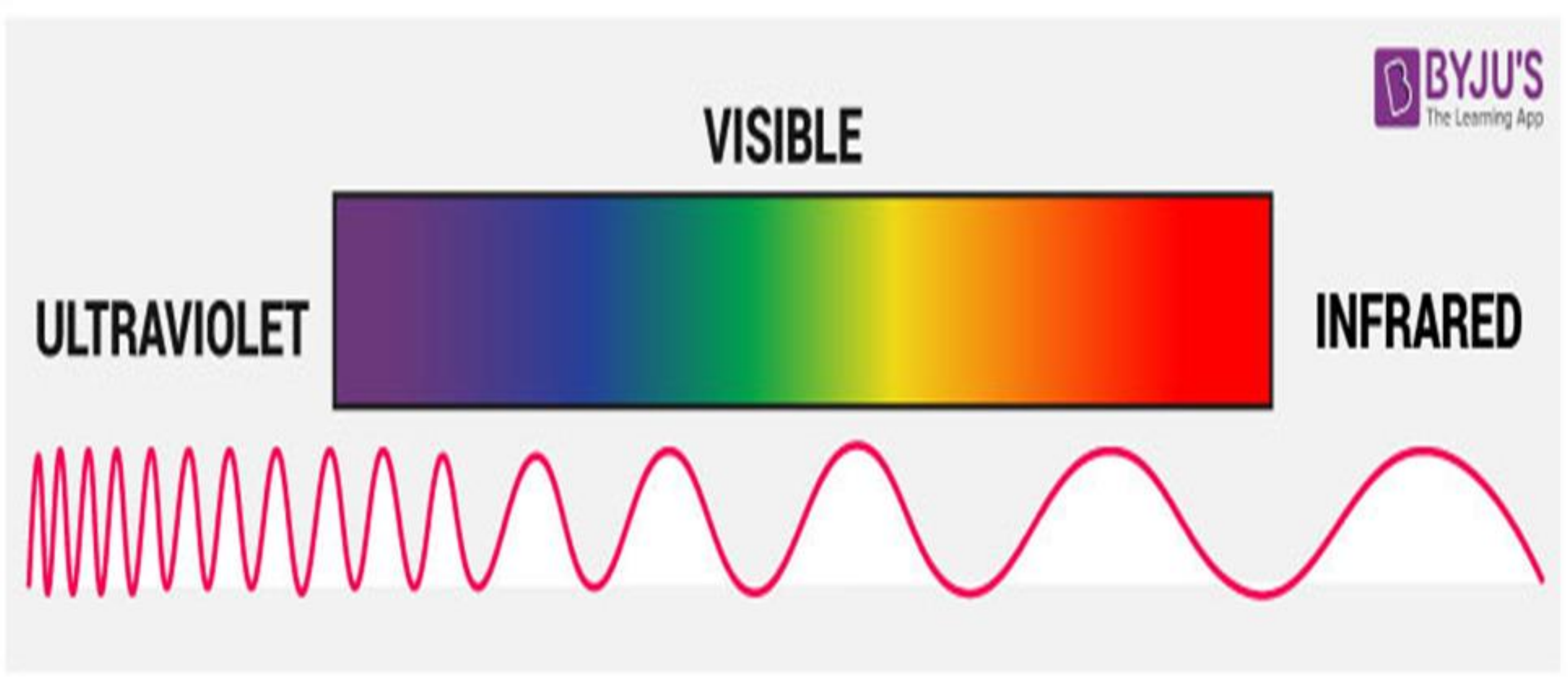
Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. The IR spectroscopy theory utilizes the concept that molecules tend to absorb specific frequencies of light that are characteristic of the corresponding structure of the molecules.

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemical substances. Samples may be solid, liquid, or gas. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer to produce an infrared spectrum.

Typical units of frequency used in IR spectra are wave numbers, with the symbol cm−1. Units of IR wavelength are commonly given in micrometers (formerly called "microns"), symbol µm, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. Two-dimensional IR is also possible.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near- (0.75- 2.5 µm , mid- (2.5- 16 µm) and far- infrared (25- 1000 µm), named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm−1 (0.7–2.5 µm wavelength) can excite overtone or harmonic molecular vibrations. The mid-infrared, approximately 4000–400 cm−1 (2.5–25 µm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm−1 (25–1000 µm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule. Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.


VISIBLE
ULTRAVIOLET
INFRARED
BYJU'S
The Learning App

There are two types of vibrational motions:

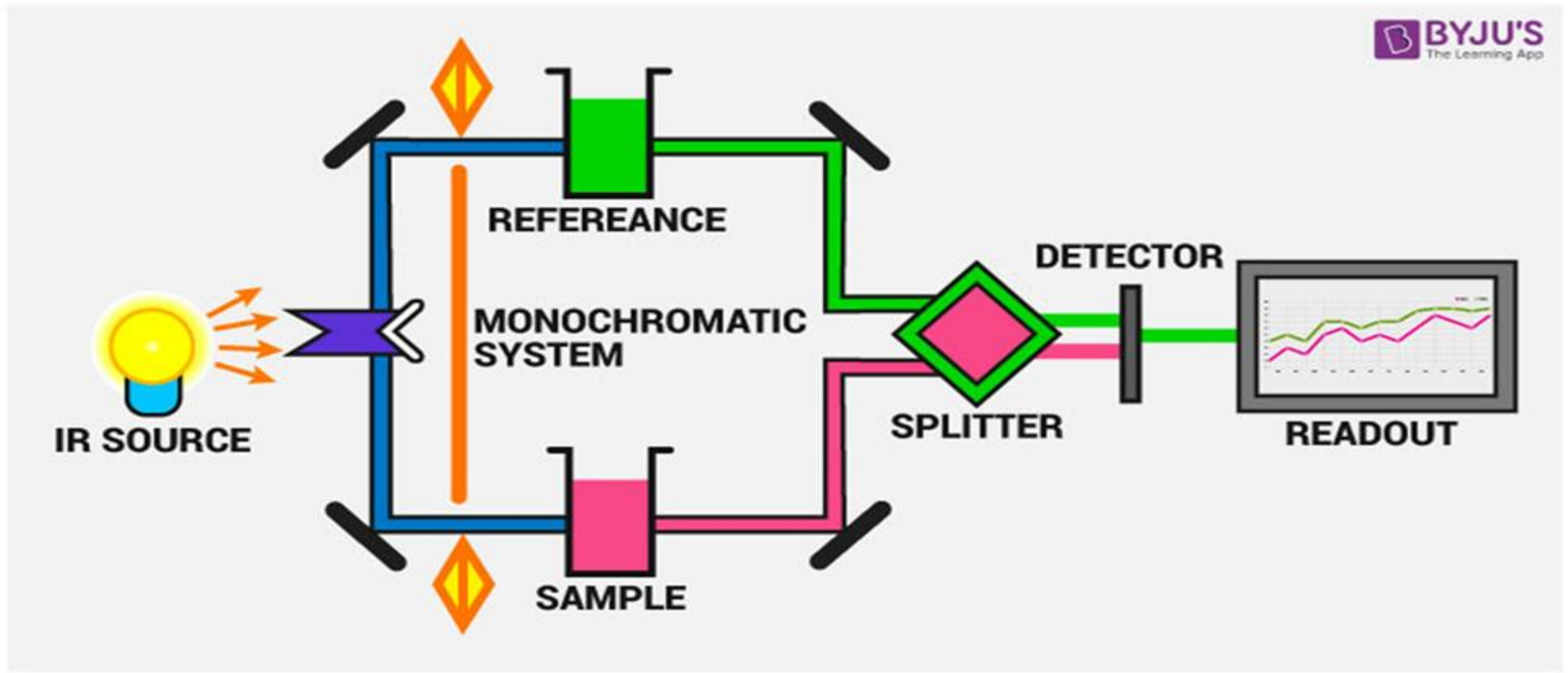
A) Stretching deformation: It is a vibrational motion of a bond along the bond axis within a molecule (Ʋ).

B) Bending deformation: It is a vibrational motion of a bond perpendicular to the bond axis within a molecule (δ).

Normal modes: A molecule can vibrate in many ways, and each way is called a vibrational mode. Linear molecules have 3N - 5 degrees of vibrational modes whereas nonlinear molecules have 3N - 6 degrees of vibrational modes (also called vibrational degrees of freedom). As an example H2O, a non-linear molecule, will have 3 × 3 - 6 = 3 degrees of vibrational freedom, or normal modes.

IR Spectroscopy Instrumentation

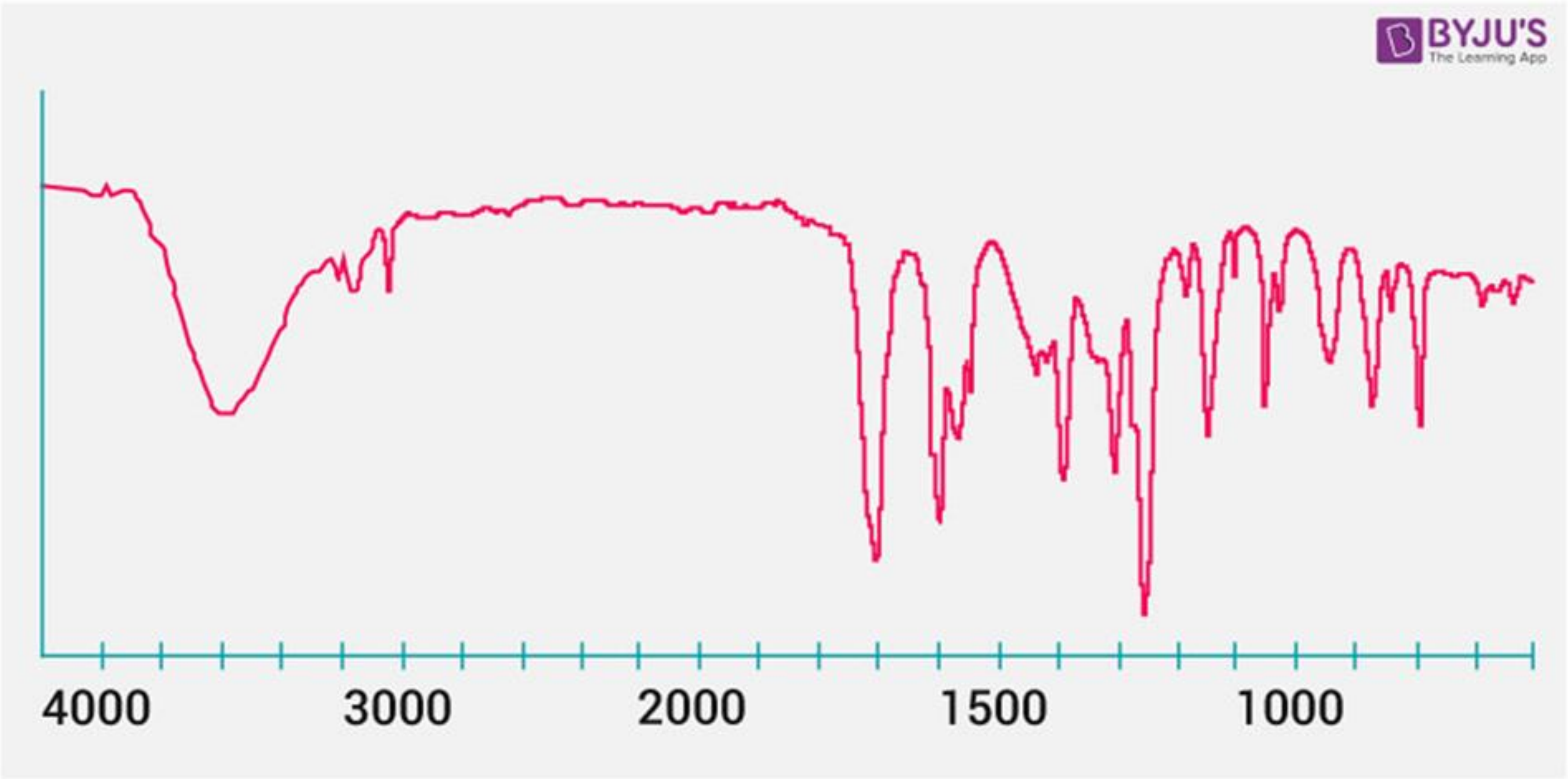
The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference ant the sample respectively.



Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

Graph of the IR spectrum

Given below is a sample of typical Infrared Absorption Frequencies.



CHARACTERISTIC ABSORPTION BANDS

The IR Spectrum Table is a chart for use during infrared spectroscopy. The table lists IR spectroscopy frequency ranges, appearance of the vibration and absorptions for functional groups.

IR Spectrum Table by Frequency Range

Use the following table when you already know the frequency of your material. Find the frequency range in the first column on the left side of the chart and corresponding values in adjacent columns. (يحفظ الجدول كاملا)

Frequency Range	Absorption (cm^{-1})	Appearance	Group	Compound Class	Comments
4000-3000 cm^{-1}	3650	weak, broad	O-H stretching	alcohol	free
	3350-3310	medium	N-H stretching	secondary amine	
	3500-2500	strong, broad	O-H stretching	carboxylic acid	usually centered on 3000 cm^{-1}
	3610	weak, broad	O-H stretching	phenol	intramolecular bonded
	3400, 3350	strong, broad	NH2 stretching	Amino group	
cm^{-1}	2980, 2890	strong, sharp	C-H stretching	C-H (CH_3, CH_2, CH) aliphatic	
	3030	medium	C-H stretching	C-H aromatic	
	2700	medium	C-H stretching	O=C-H aldehyde	doublet
	2600-2550	weak	S-H stretching	thiol	
	2349	strong	O=C=O stretching	carbon dioxide	
	2275-2250	strong, broad	N=C=O stretching	isocyanate	

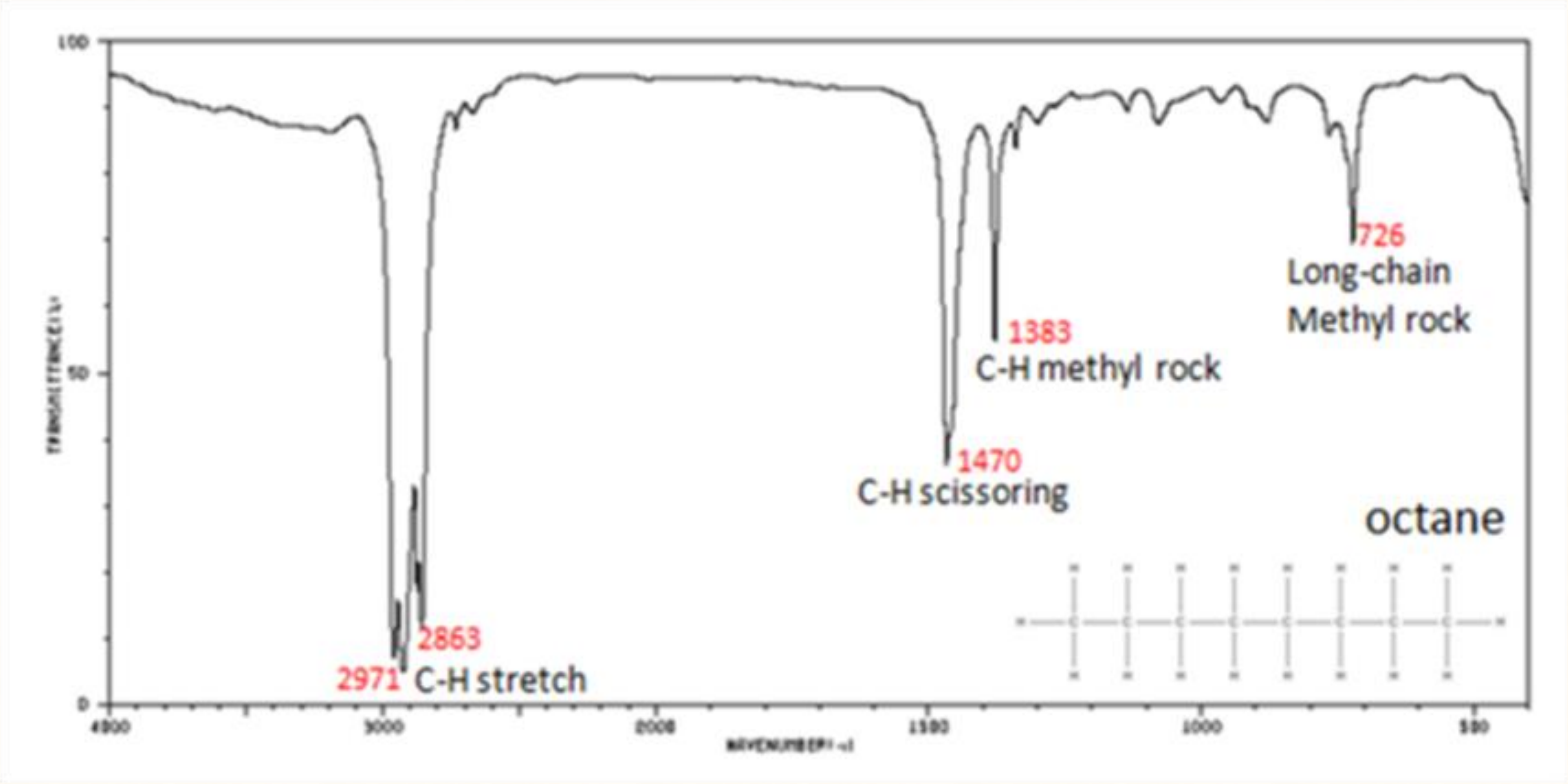
2220	weak	CΞN stretching	nitrile	
2260-2190	weak	CΞC stretching	alkyne	disubstituted
2175-2140	strong	S-CΞN stretching	thiocyanate	
2160-2120	strong	N=N=N stretching	N3 azide	
2150		C=C=O stretching	ketene	
2145-2120	strong	N=C=N stretching	carbodiimide	
2140-1990	strong	N=C=S stretching	isothiocyanate	
2000-1900	medium	C=C=C stretching	allene	
2000		C=C=N stretching	ketenimine	
2000-1650	weak	C-H bending	C-H aromatic compound	overtone

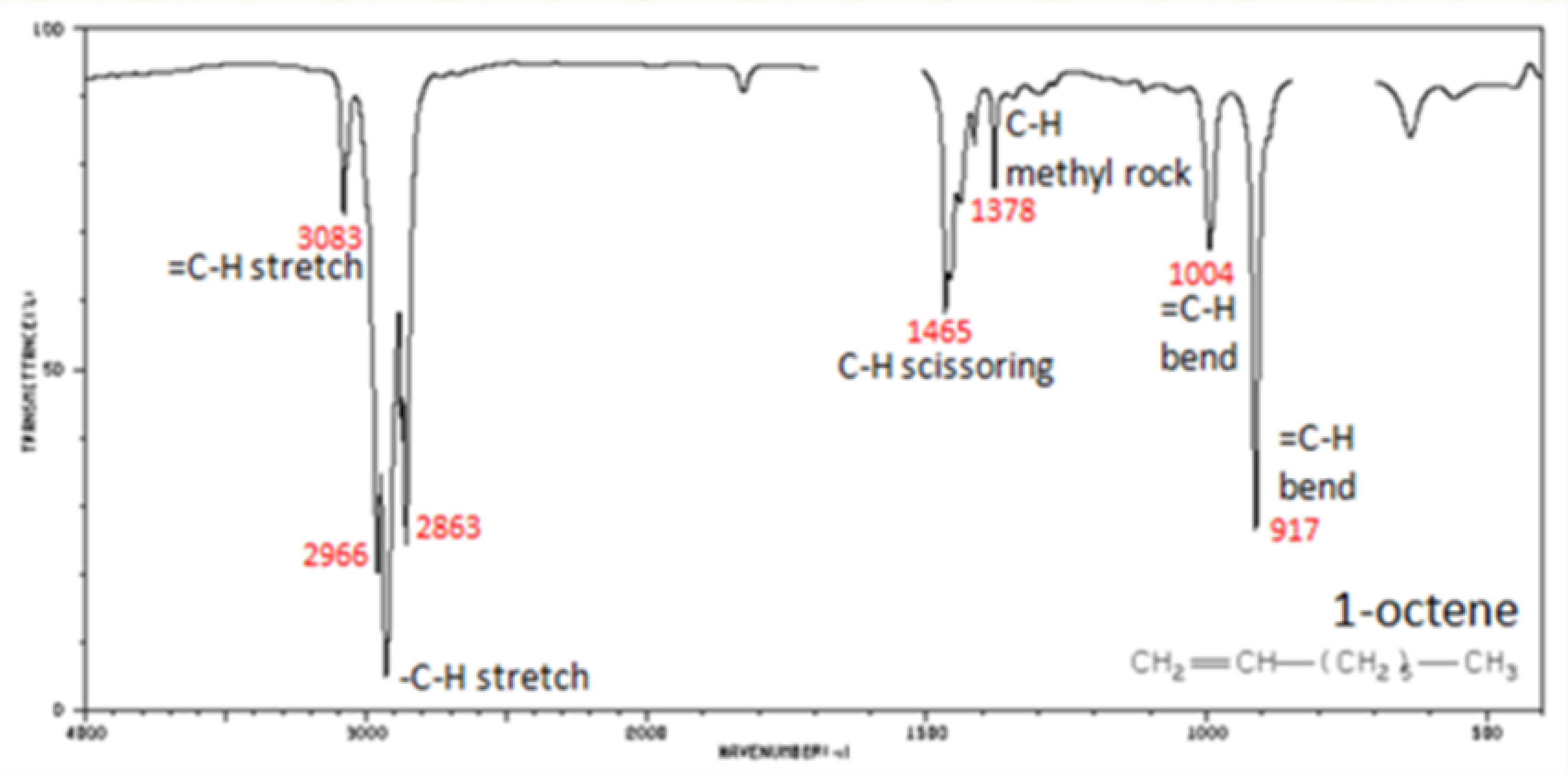
1820, 1760	strong	C=O stretching	anhydride	
1815-1785	strong	C=O stretching	O=C-X acid halide	
1760	strong	C=O stretching	carboxylic acid	monomer
1735	strong	C=O stretching	esters	6-membered lactone
1750	strong	C=O stretching	δ-lactone	γ: 1770
1745	strong	C=O stretching	cyclopentanone	
1720	strong	C=O stretching	aldehyde	
1725	strong	C=O stretching	aliphatic ketone	or cyclohexanone or cyclopentenone
1690	strong	C=O stretching	CONH$_2$ primary amide	
1620	medium	C=N stretching	imine / oxime	
1640	strong	C=O stretching	secondary amide	

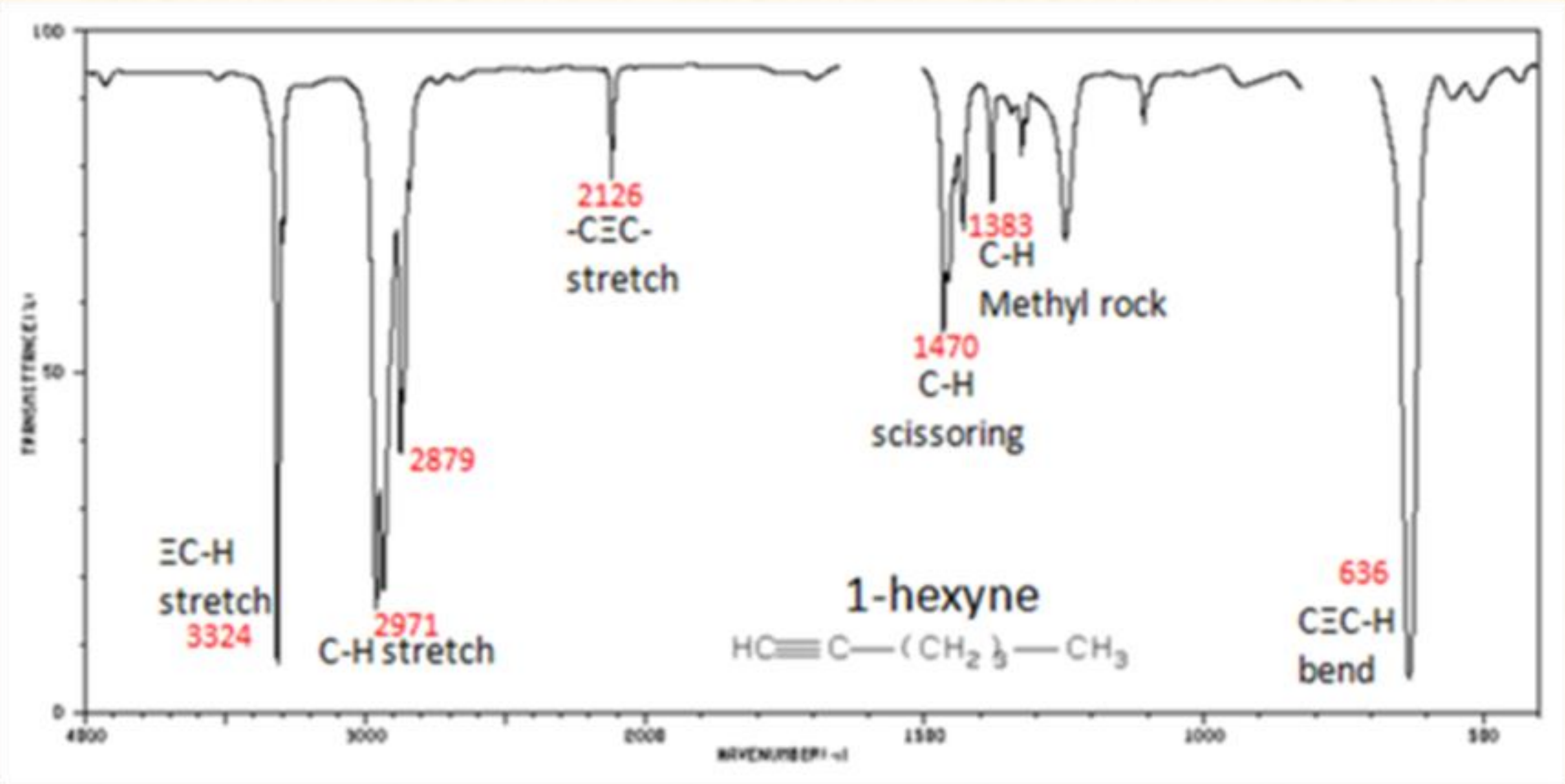
1630	strong	C=O stretching	tertiary amide	
1650	strong	C=O stretching	δ-lactam	
1678-1668	weak	C=C stretching	alkene	disubstituted (trans)
1662-1626	medium	C=C stretching	alkene	disubstituted (cis)
1650-1600	medium	C=C stretching	C=C-C=C conjugated alkene	
1620-1610	strong	C=C stretching	C=C-C=O α,β-unsaturated ketone	
1550-1500	strong	N-O stretching	NO_2 nitro group	
1415-1380	strong	S=O stretching	SO_4 sulfate	
1200-1185				

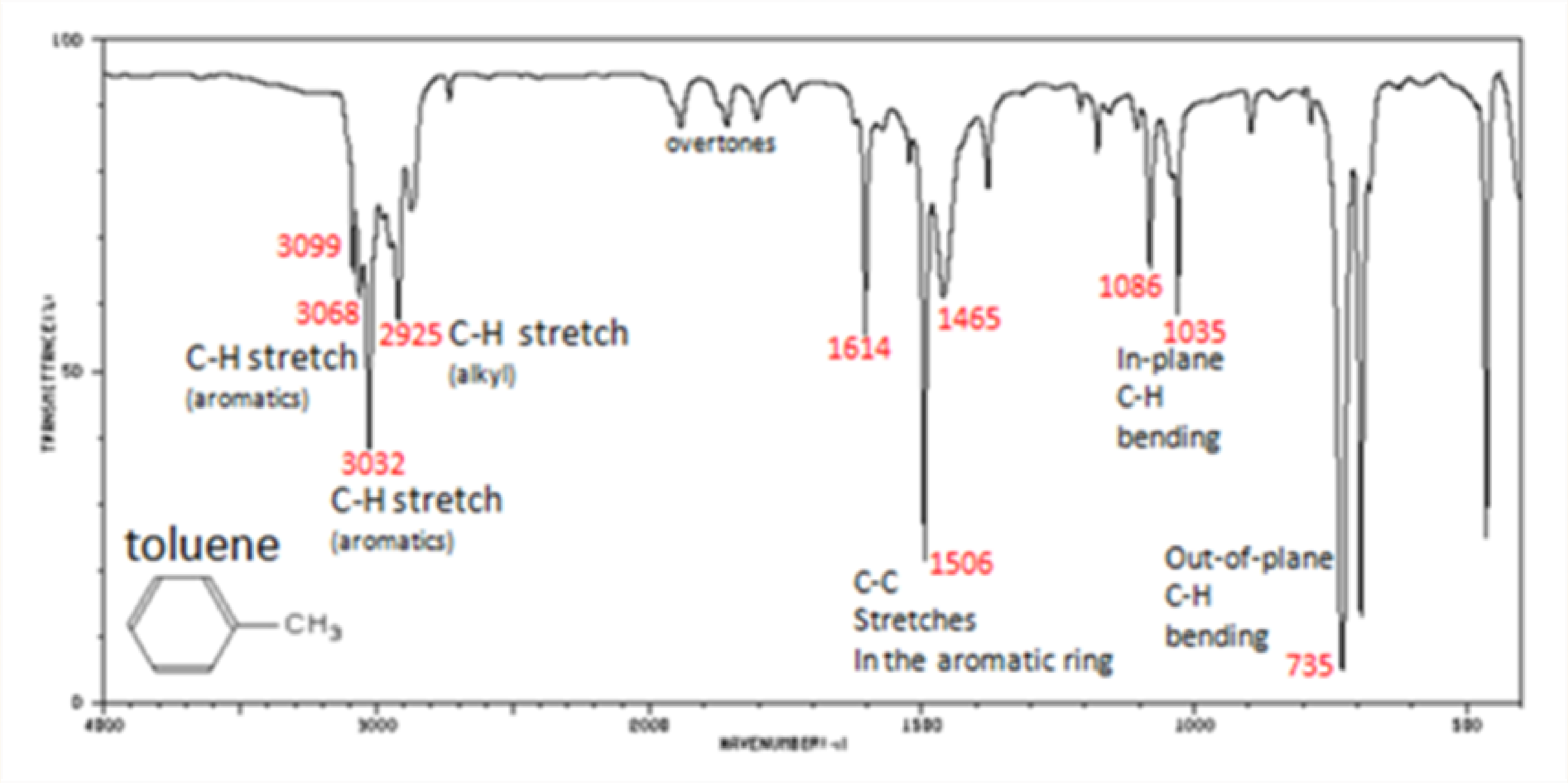
1410-1380	strong	S=O stretching	SO_2Cl sulfonyl chloride	
1204-1177				
1400-1000	strong	C-F stretching	fluoro compound	
1372-1335	strong	S=O stretching	sulfonate	
1370-1335	strong	S=O stretching	SO_2NH_2 sulfonamide	
1170-1155				
1350-1342	strong	S=O stretching	SO_3H sulfonic acid	anhydrous
1070-1030	strong	S=O stretching	sulfoxide	
690-515	strong	C-Br stretching	halo compound	
600-500	strong	C-I stretching	halo compound	
880	strong	C-H bending	1,2,4-trisubstituted benzene	
860	strong	C-H bending	1,3-disubstituted benzene	
780	strong	C-H bending	1,4-disubstituted or	
780	strong	C-H bending	1,2,3-trisubstituted benzene	
755	strong	C-H bending	1,2-disubstituted benzene	
700	strong	C-H bending	monosubstituted	
			benzene derivative	

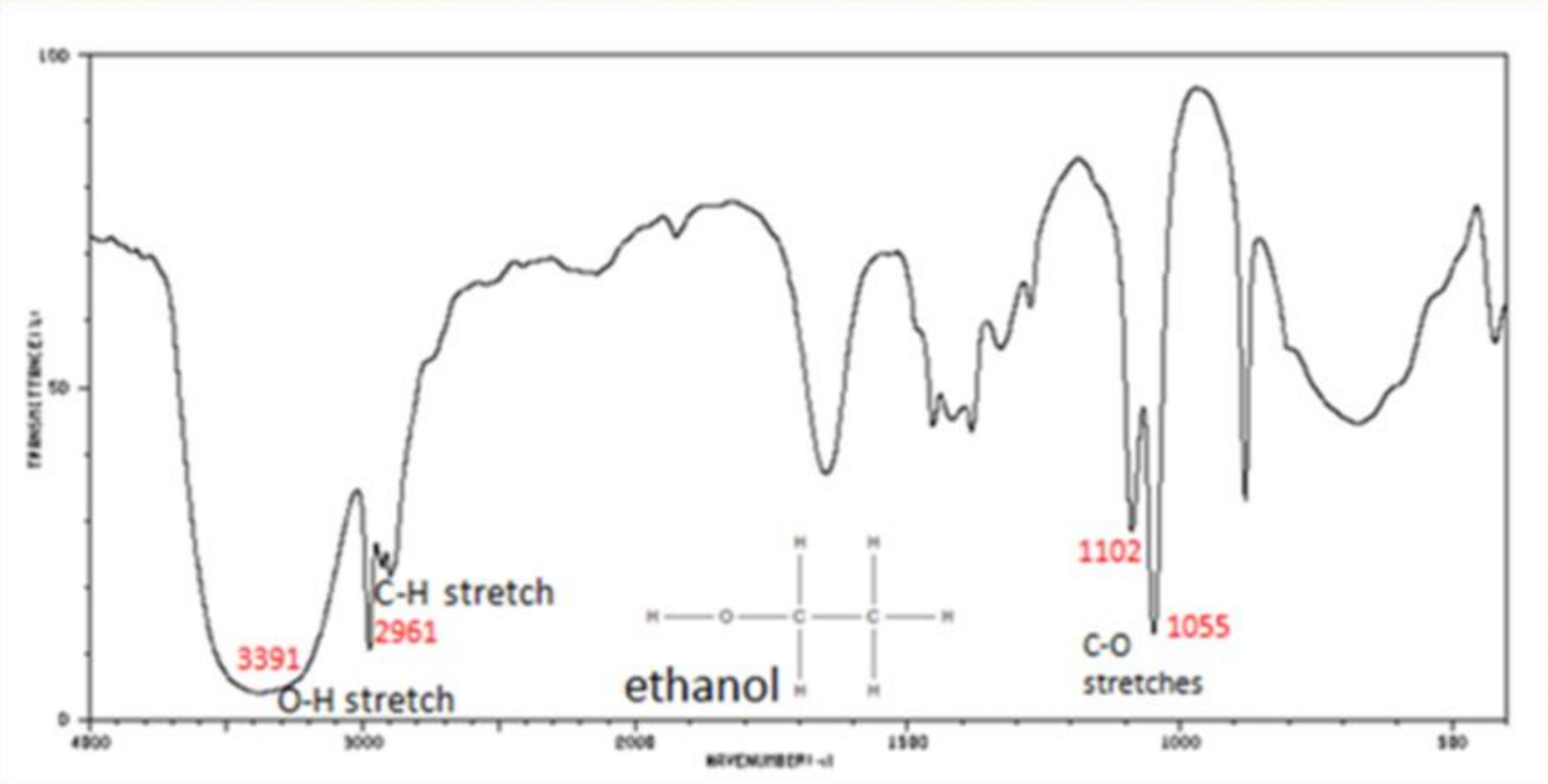
Examples

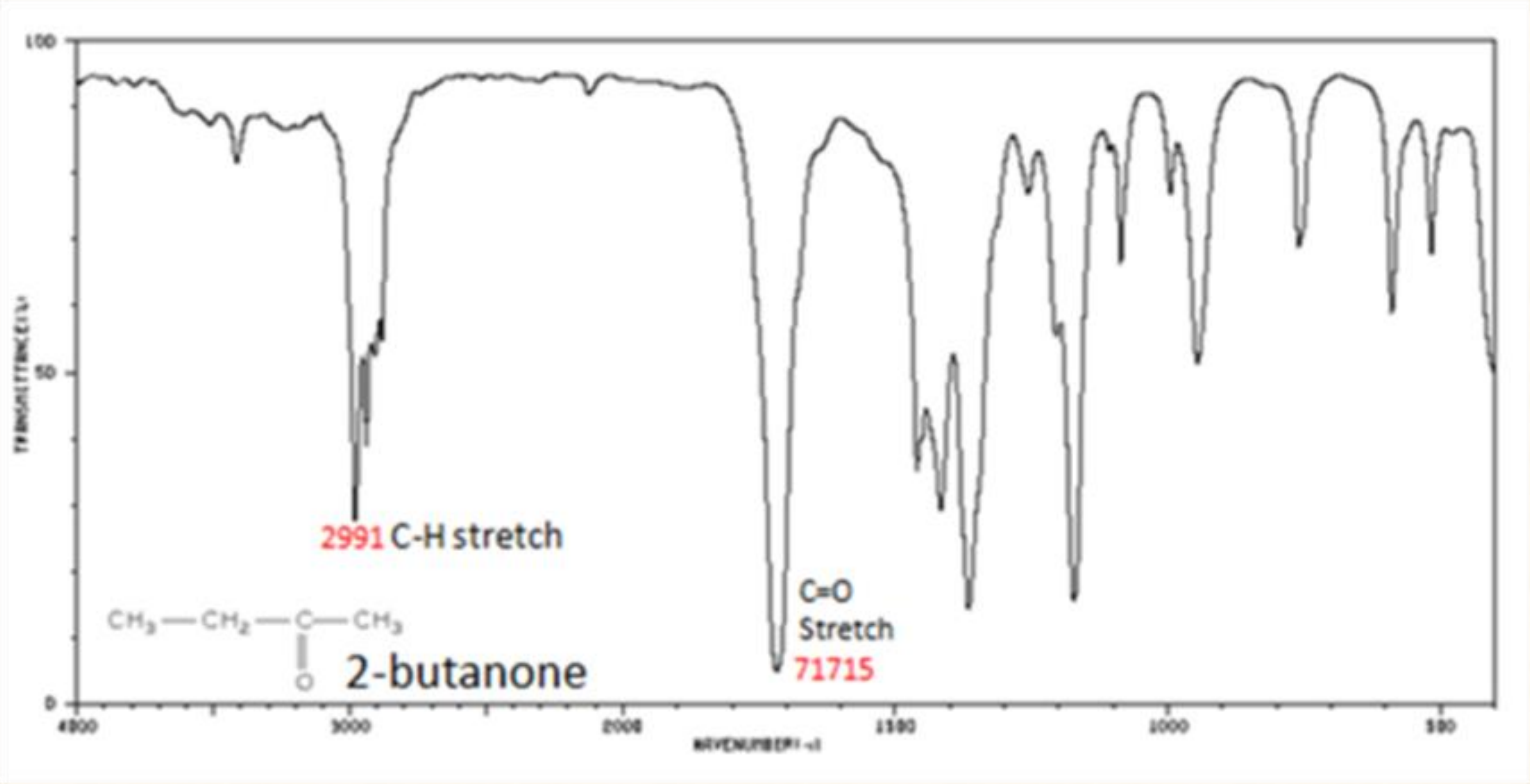

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
2971
2863
C-H stretch
1470
C-H scissoring
1383
C-H methyl rock
726
Long-chain
Methyl rock
octane

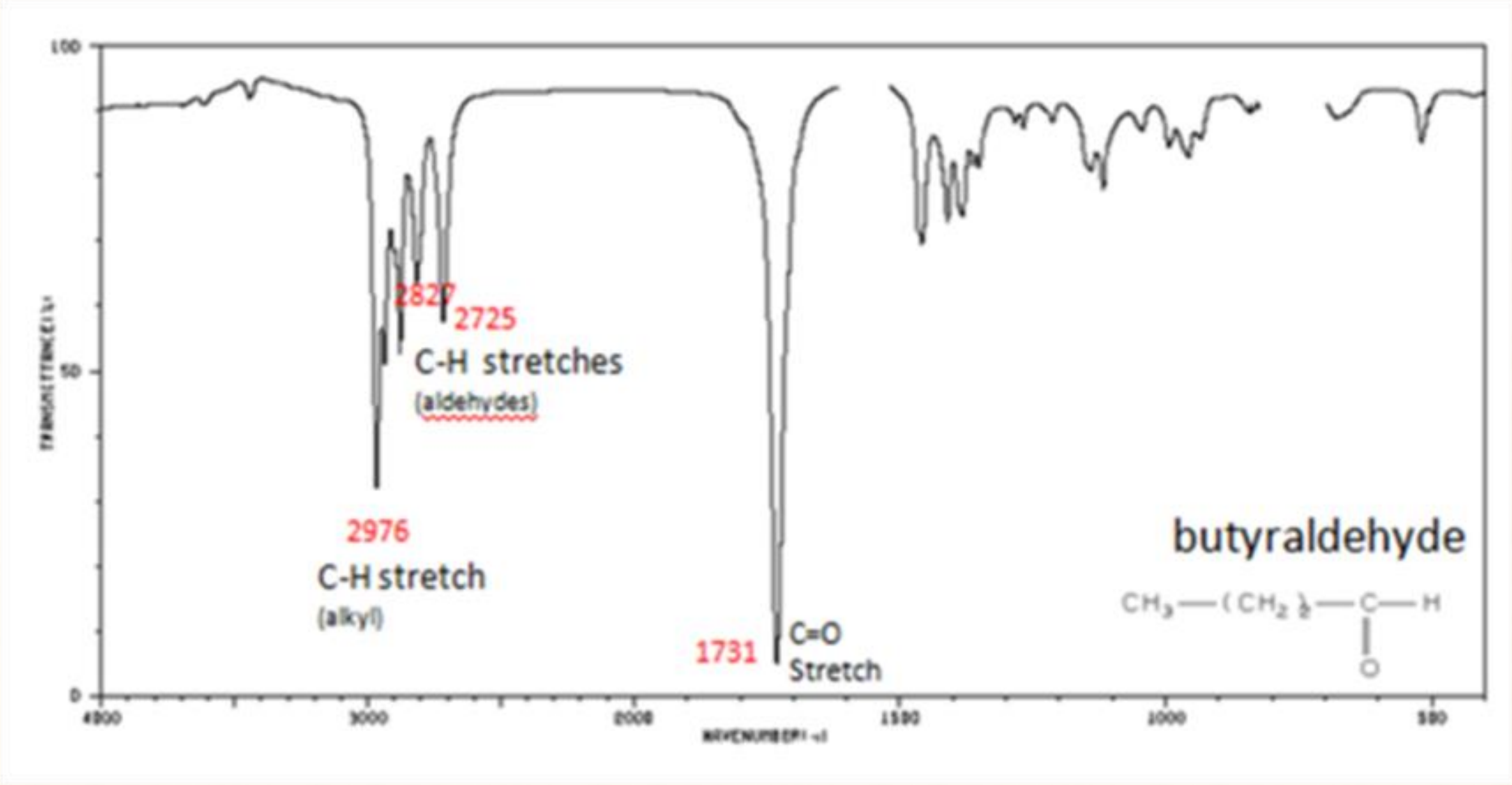

100
50
0
4000
3000
2000
1500
1000
500
3083
=C-H stretch
2966
2863
-C-H stretch
1465
C-H scissoring
1378
C-H
methyl rock
1004
=C-H
bend
=C-H
bend
917
1-octene
CH2═CH—(CH2)5—CH3

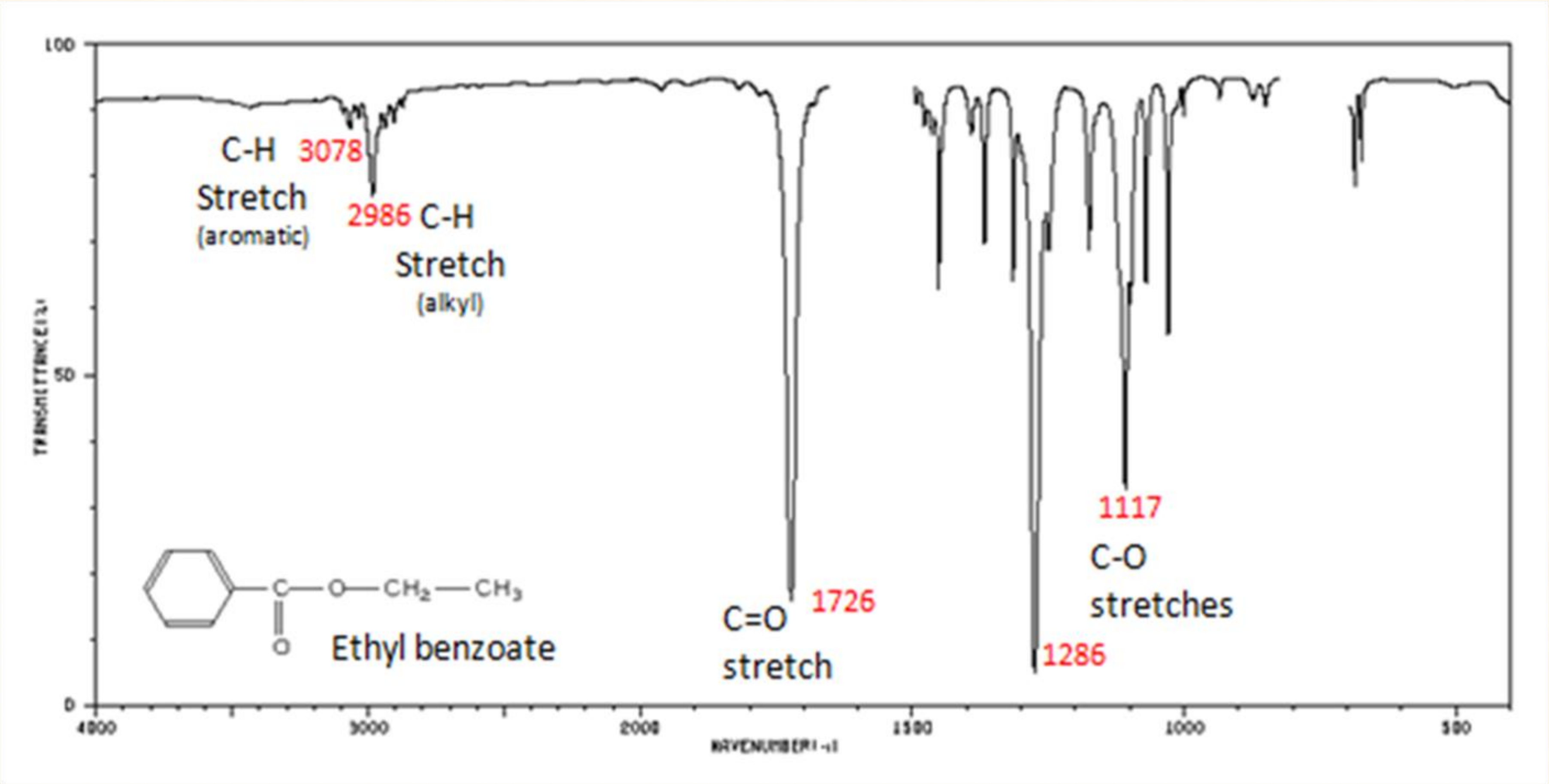

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
2126
-C≡C-
stretch
1383
C-H
Methyl rock
1470
C-H
scissoring
2879
≡C-H
stretch
3324
2971
C-H stretch
1-hexyne
HC≡C—(CH$_2$)$_3$—CH$_3$
636
C≡C-H
bend


100
50
0
4000
3000
2000
1500
1000
500
overtones
3099
3068
C-H stretch
(aromatics)
2925
C-H stretch
(alkyl)
3032
C-H stretch
(aromatics)
toluene
CH_3
1614
1465
1506
C-C
Stretches
In the aromatic ring
1086
1035
In-plane
C-H
bending
Out-of-plane
C-H
bending
735

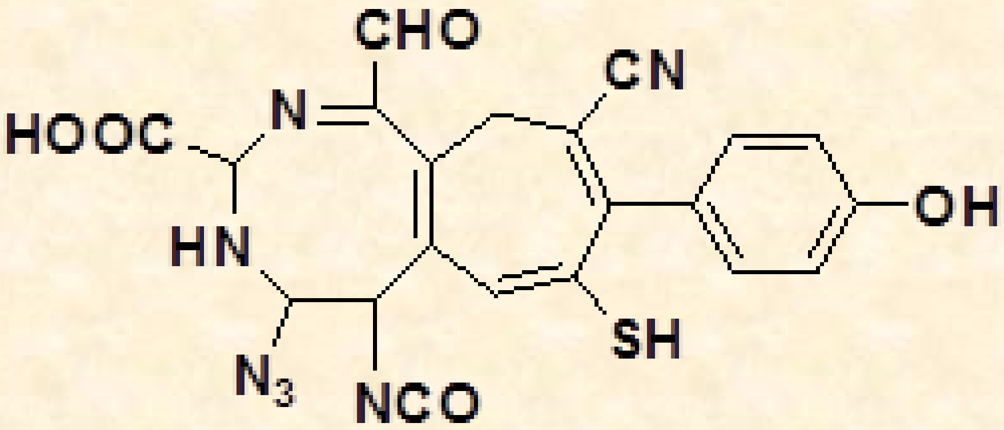

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
3391
O-H stretch
C-H stretch
2961
ethanol
H
O
C
1102
1055
C-O
stretches


100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
2991 C-H stretch
C=O
Stretch
71715
CH$_3$—CH$_2$—C—CH$_3$
O
2-butanone


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[cm-1]
2827
2725
C-H stretches
(aldehydes)
2976
C-H stretch
(alkyl)
1731
C=O
Stretch
butyraldehyde
CH3—(CH2)2—C—H
O


100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
C-H
3078
Stretch
(aromatic)
2986
C-H
Stretch
(alkyl)
C=O
stretch
1726
1286
1117
C-O
stretches
C
O
CH2
CH3
O
Ethyl benzoate

Indicate the expected IR bands for the following compound:



The Answer:

-CN 2220 cm-1, NH 3350-3310 cm-1, C=O (COOH) 1760 cm-1, carboxylic -OH 2500-3500 cm-1, -SH 2600-2550 cm-1, -CHO 2700 cm-1, 1720 cm-1, CH 2980, 2890 cm-1, N3 2160-2120 cm-1, NCO 2275-2250 cm-1 , C=N 1620 cm-1, OH 3610 cm-1, CH aromatic 3030 cm-1.

SOUTH VALLY UNIVERSITY

FACULTY OF SCIENCE

INTRODUCTION TO THE CHEMISTRY OF ALICYCLIC COMPOUNDS

By

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Chemistry Department, Faculty of Science,
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For 3rd Science Students

2022/ 2023

Author's preface

The chemistry of *alicyclic* compounds is important class of organic chemistry that studies the aliphatic cyclic compounds in their physical and chemical behavior because they react and behave in ways highly dependent on their stereochemistry.

The chemical reactions of *alicyclic* compounds require an understanding of their reaction mechanism and the stereochemistry of the molecules.

This book discussed the nomenclature of the different types of *alicyclic* compounds, physical properties, stereochemistry and methods of preparation and reactions of *alicyclic* compounds.

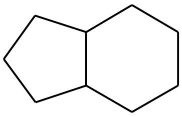
This book is designed to understanding of basic conceptual of the chemistry of *alicyclic* compounds in separated units and chapters with questions and exercises. Answers are given at the end of each chapter.

When this study has been completed the reader should be able to:

1. Demonstrate a scientific framework of organic chemistry knowledge in the chemistry of *alicyclic* compounds.
2. Demonstrate a working knowledge of the fundamental concepts of the chemistry of aliphatic cyclic compounds to allow further study of chemistry.
3. Define various kinds of *alicyclic* isomers.
4. Demonstrate the ability to name and draw structures of several types of *alicyclic* compounds.

I acknowledge the help I have from many sources during the preparation of this book.

Author
Dr. Ahmed M. Abo-Bakr



INTRODUCTION

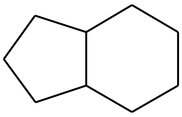
This course presents a brief introduction to the chemistry of alicyclic compounds, it is necessary to understand some of the language used to describe the stereochemistry of alicyclic compounds.

cyclic compound any one of a class of compounds whose molecules contain a number of atoms bonded together to form a closed chain or ring. If all of the atoms that form the ring are carbon, the compound is said to be carbocyclic; if not, the compound is called heterocyclic.

Alicyclic compounds behave chemically like the open-chain aliphatic compounds.

This course is aimed at providing the students with theoretical, usable knowledge that will allow them to carry out research and development in alicyclic chemistry. The course improves the student's ability to solve synthetic problems in alicyclic chemistry.

The author will discuss in this course some important topics Include types of aliphatic cyclic compounds, nomenclature, the physical properties, the stereochemistry and the methods of preparation of different types of alicyclic compounds.



GENERAL OBJECTIVES OF THIS COURSE

1-The student will be able to demonstrate a scientific framework of organic chemistry knowledge in the chemistry of alicyclic compounds.

2-The student will be able to demonstrate a working knowledge of the fundamental concepts of the chemistry of aliphatic cyclic compounds to allow further study of chemistry.

3-The student will be able to define various kinds of alicyclic isomers.

4-The student will be able to demonstrate the ability to name and draw structures of several types of alicyclic compounds.

ASSESSMENT OF LEARNER OUTCOMES

The student will be evaluated by means of classroom participation, homework problems, exams, quizzes, and the final exam.

OBJECTIVES OF EACH LESSON

Lesson 1:

- **a- The student will be able to identify and define the several types of aliphatic rings.**
- **b- The student will be able to name and draw structures of several types of alicyclic compounds.**

Lesson 2:

- **a- The student will be able to identify the naturally occurrence of many common rings.**

b- The student will be able to identify the physical properties of many common rings.

c- The student will be able to know the classification of momocyclic system.

d- The student will be able to know the different theories that discuss the stability of alicyclic compounds.

Lesson 3:

a- The student will be able to demonstrate the ability to name and draw structures of several kinds of alicyclic isomers.

b- The student will be able to know how to designate the geometrical isomers as *cis*- or *trans* in the substituted rings.

Lesson 4:

a- The student will be able to identify the different conformations of cycloalkanes.

b- The student will be able to draw the different shapes of the common rings.

c- The student will be able to identify the different conformations of cyclohexane.

Lesson 5:

a- The student will be able to know the different methods of preparation of alicyclic compounds.

b- The student will be able to identify the mechanisms of some reactions.

Lesson 6:

a- The student will be follow the different methods of preparation of alicyclic compounds with explanation the mechanisms of some reactions.

Lesson 7:

- a- The student will be able to know the physical properties of cyclopropane and its derivatives.
- b- The student will be able to know the different methods of preparation of cyclopropane and its derivatives.

Lesson 8:

- a- The student will be able to know the physical properties of cyclobutane and its derivatives.
- b- The student will be able to know the different methods of preparation of cyclobutane and its derivatives.

Lesson 9:

- a- The student will be able to know the physical properties of cyclopentane and its derivatives.
- b- The student will be able to know the different methods of preparation of cyclopentane and its derivatives.

Lesson 10:

- a- The student will be able to know the physical properties of cyclohexane and its derivatives.
- b- The student will be able to know the different methods of preparation of cyclohexane and its derivatives.

Lesson 11:

- a- The student will be able to know the physical properties of cycloheptane and its derivatives.
- b- The student will be able to know the different methods of preparation of cycloheptane and its derivatives.

Lesson 12:

- a- The student will be able to know the different methods of preparation of bicyclic compounds, spirans and fused rings.

Unit 1

Lesson 1: Basic Concepts

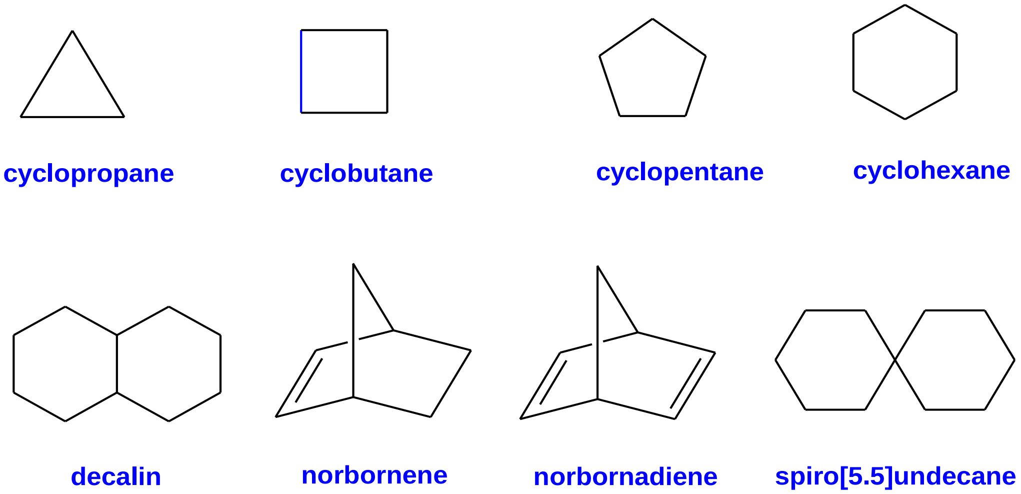
1.1 Introduction

Alicyclic compounds are class of organic compounds whose molecules contain one or more rings and all of the atoms that form the ring are carbon.

The term "Alicyclic compound" means that "An organic compound that is both aliphatic and cyclic". Also, these compounds called *closed chain compounds, carbocyclic compounds and/or cycloalkanes.*

Alicyclic compounds behave chemically like the open-chain aliphatic compounds, but many cyclic compounds exhibit the special properties characteristic of the aromatic compounds. The saturated Alicyclic hydrocarbons have the general formula C_nH_{2n} (the same as that of the alkenes); they do not contain a double bond but possess a ring structure, and when the molecular formula of a saturated hydrocarbon corresponds to the general formula C_nH_{2n-2} , then the compound contains two rings; if to C_nH_{2n-4}, three rings, etc.

Simple Alicyclic compounds are cyclopropane, cyclobutane, cyclopentane and cyclohexane. A polycyclic cycloalkane is decalin. Bicyclic alkanes are norbornene and norbornadiene. Spiro compounds have bicyclic connected through one carbon atom is spiro[5.5]undecane (Fig. 1.1).


cyclopropane cyclobutane cyclopentane cyclohexane

decalin norbornene norbornadiene spiro[5.5]undecane

Fig. 1.1

1.2 Nomenclature

There are many rules used in the nomenclature of alicyclic compounds according to the I.U.P.A.C system are listed as follows:

A- Monocyclic compounds:

The saturated monocyclic hydrocarbons take the name of the corresponding open chain saturated paraffins, preceded by the prefix ***cyclo-***, such as cyclobutane and cyclohexane, and if the cyclic hydrocarbon is unsaturated, the prefix ***cyclo-*** is followed by the name of the corresponding alkene, such as cyclopentene and 1,3-cyclohexadiene (Fig. 1.2).

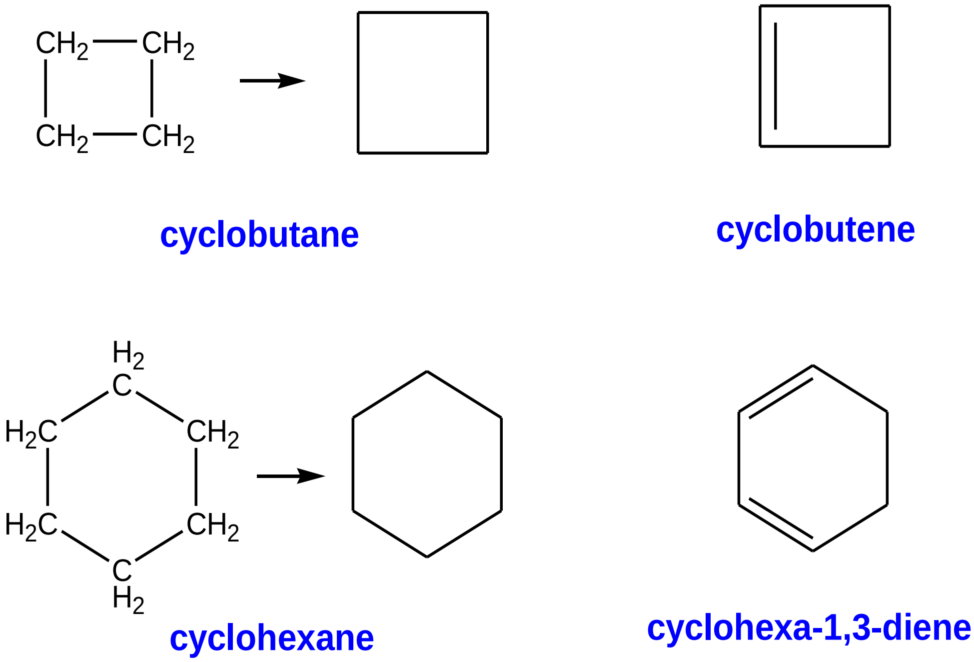
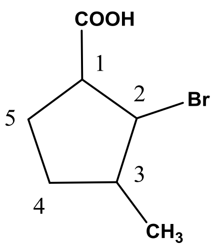
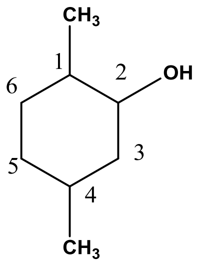


Fig. 1.2

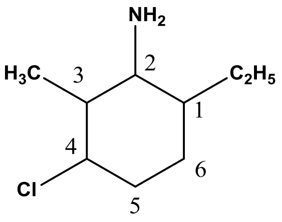
When a monocyclic hydrocarbon has a long and complex side chain, the open chain is named according to the I.U.P.A.C system, and the ring is regarded as a substituent, see examples in (Fig. 1.3).



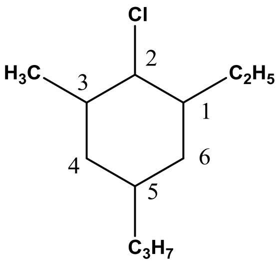
2-bromo-3-methyl-cyclopentane carboxylic acid



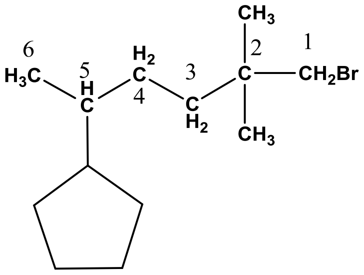
1,4-dimethyl-2-cyclohexanol



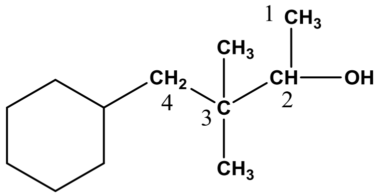
4-chloro-1-ethyl-3-methyl-2-cyclohexylamine



2-chloro-1-ethyl-3-methyl-5-propyl-cyclohexane



1-bromo-5-cyclopentyl-2,2-dimethyl-hexane



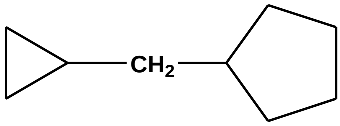
4-cyclohexyl-3,3-dimethyl-2-butanol

Fig. 1.3

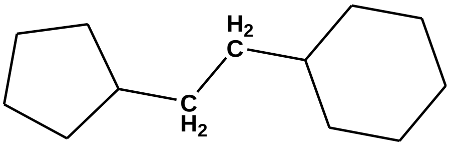
B- Bicyclic system:

Bicyclic system may be divided into the following types:

1- Bicyclic compounds with isolated rings separated by a chain of carbons: The naming of this type is as the following examples;

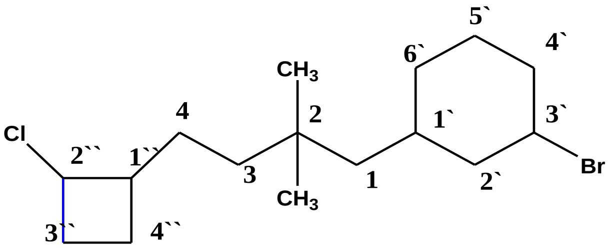


cyclopropylcyclopentylmethane

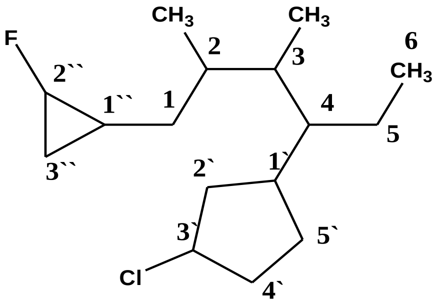


cyclopentylcyclohexylethane

If the carbon chain in between the two rings was more complicated, then the main chain is numbered as usual and the two rings being substituents and the carbon atoms in each ring are given primed numbered (Fig. 1.4).



2,2-dimethyl-1-(3`-bromocyclohexyl)-4-(2``-chlorocyclobutyl)-butane

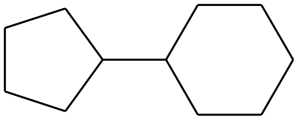


2,3-dimethyl-4-(3`-chlorocyclopentyl)-1-(2``-flourocyclopropyl)-hexane

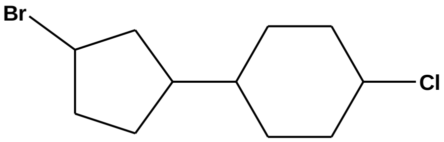
Fig. 1.4

2- Bicyclic compounds with rings connected by singly carbon-carbon bond:

In this type, the name of the smaller ring will be the first followed by the larger ring, e.g.,



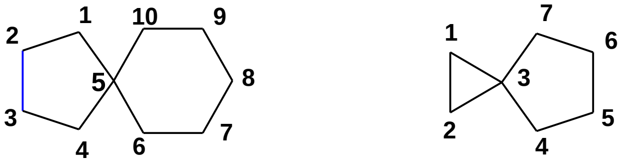
cyclopentyl-cyclohexane



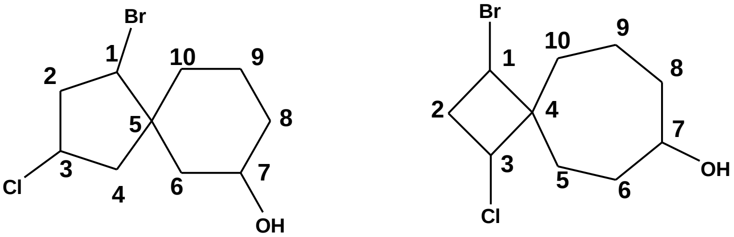
1-(3`-bromocyclopentyl)-4-chloro-cyclohexane

3- Bicyclic compounds with rings having one common atom (Spirans):

A spiro compound is a bicyclic organic compound with rings connected through one atom called a quaternary carbon "**spiro carbon**". The rings can be different in nature or identical. All spiro compounds have the prefix ***spiro*** followed by square brackets containing the number of atoms in the smaller ring and the number of atoms in the larger ring excluding the spiro atom itself, then the name of alkane corresponding to the total number of carbon atoms, sees examples in (Fig.1.5).



Spiro[4.5]decane Spiro[2.4]heptane

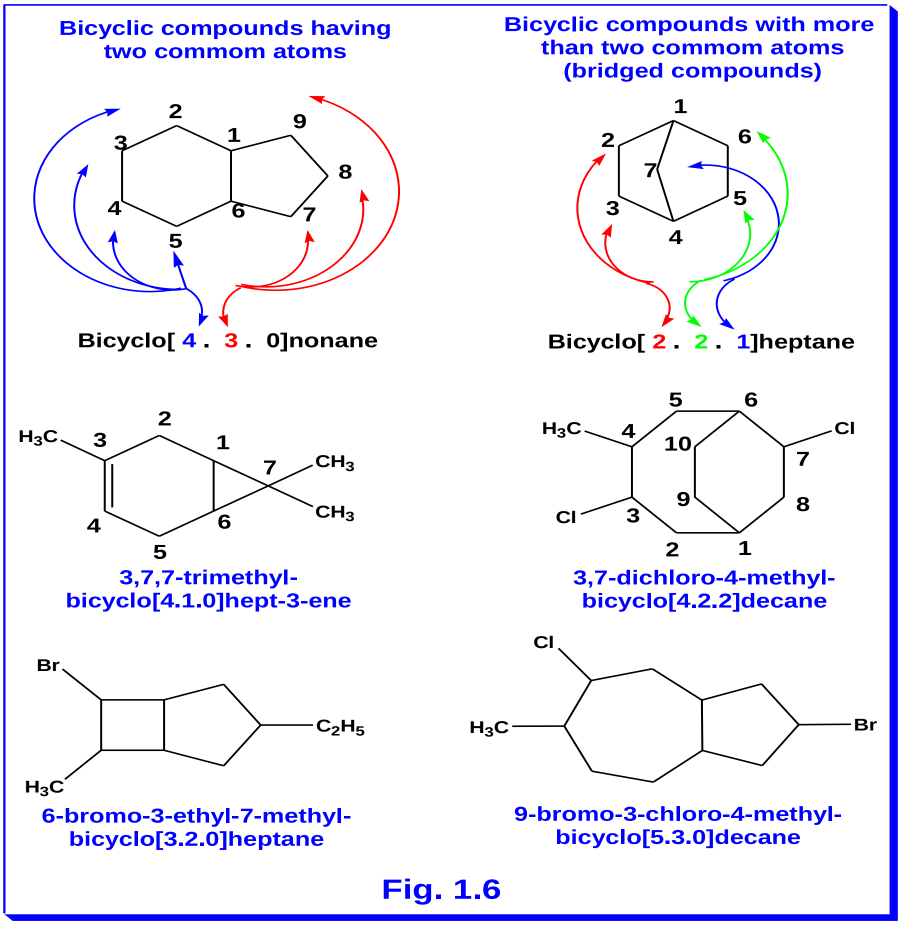


1-Bromo-3-chloro-spiro[4.5]decan-7-ol 1-Bromo-3-chloro-spiro[3.6]decan-7-ol

Fig. 1.5

4- Bicyclic compounds with rings having two or more common atoms:

According to the I.U.P.A.C system, the naming of these compounds is by taken the prefix "***bicyclo***" followed by the name of the alkane containing the same total number of carbon atoms, in between them square brackets containing three numbers, the first and the second indicate the number of atoms in the larger ring and the number of atoms in the smaller ring respectively excluding the common atoms, and the third is to express the number of carbons (**bridge atoms**) in between the two tertiary carbon atoms (**bridgeheads**) which connect the two rings (Fig.1.6).



Bicyclic compounds having two commom atoms

Bicyclo[4 . 3 . 0]nonane

Bicyclic compounds with more than two commom atoms (bridged compounds)

Bicyclo[2 . 2 . 1]heptane

3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene

3,7-dichloro-4-methyl-bicyclo[4.2.2]decane

6-bromo-3-ethyl-7-methyl-bicyclo[3.2.0]heptane

9-bromo-3-chloro-4-methyl-bicyclo[5.3.0]decane

Fig. 1.6

Unit 1

Lesson 2: General properties of alicyclic compounds

2.1 Occurrence and physical properties

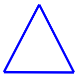
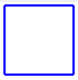
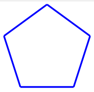
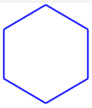
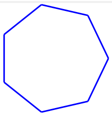
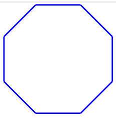
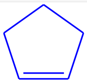
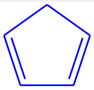
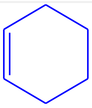
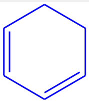
Five and six membered paraffins occur in petroleum (The naphthenes); three, four and five membered rings occur in terpenes which are the most important class of alicyclic compounds.

Many cyclic acids also occur in petroleum; these are known as the naphthenic acids and are mainly cyclopentane derivatives. Some cyclopentene derivatives of the fatty acids occur naturally, and are important in medicine.

Alicyclic hydrocarbons are light liquids (cyclopropane and cyclobutene are gases) which are immiscible with water and miscible in all proportions with the nonpolar solvents.

Some of physical properties of the lower and medium-sized alicyclic hydrocarbons are listed in (Table. 2.1).

Table 2.1

S	Name	Formula	Melting point °C	Boiling point °C	Density g/cm^3
1.	Cyclopropane		-126.6	-34.4	0.72
2.	Cyclobutane		-91	12.5	0.703
3.	Cyclopentane		-93.3	49.5	0.751
4.	Cyclohexane		6.5	81.4	0.779
5.	Cycloheptane		-12	118.1	0.809
6.	Cyclo octane		14.3	148	0.835
7.	Cyclopentene		-93.3	44.2	0.772
8.	1,3-cyclopentadiene		-8.5	42.5	0.802
9.	Cyclohexene		-103.7	83	0.810
10.	1,3-cyclohexadiene		-98	80.5	0.84

2.2 Classification of monocyclic system

Monocyclic systems can be classified according to the number of carbon atoms in the ring into four main types, the first is the small rings as three and four-membered rings. The second is the common rings which refer to the five-, six-, and seven-membered rings. The rings contains eight to eleven carbon atoms called the medium rings, and the rings have more than eleven carbons is the large rings. These types shown in the following (Diagram 2.2):

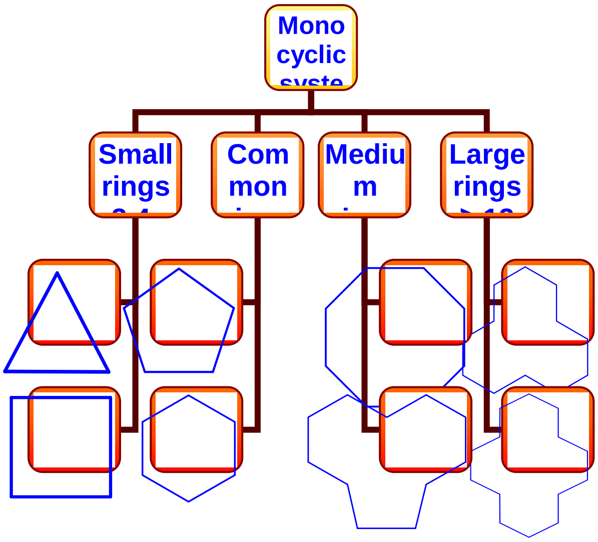


Diagram 2.2

Many chemical properties depend on the class of cycloalkane, and the difference in behavior has been explained largely in terms of steric strain.

2.3 Baeyer's strain theory (1885):

Baeyer point out that in cycloalkanes the valency angle can be altered from the normal tetrahedral value (109º 28`) of the carbon atom, and this cause a strain (α) in the molecule, consequently the greater deviation from the normal angle, the greater strain. Thus, according to Baeyer, five- and six-membered rings are the most stable because they have the least strain (or distortion) from the normal tetrahedron value. Also, Baeyer assumed that all the rings are planar, so the stain for each ring-size can be calculated, e.g., in cyclopropane, the angles of an equilateral triangle are 60º (Fig. 2.3), the stain in cyclopropane can be calculated as follows:

$$\boldsymbol{(\alpha) = 1/2\,(109^{o}\,28` - 60) = +\,24^{o}\,44`}$$

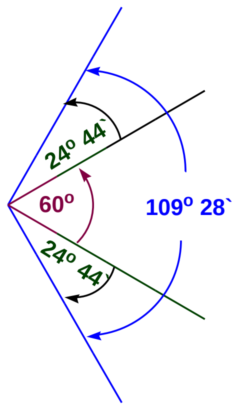


Fig. 2.3

A list of strains (distortions) can be explained in (Table 2.4).

Table 2.4

S	***No. of carbon atoms in the ring***	***Angle between valency bonds***	***Distortion (Strain)***	***Heat of combustion in kJ/CH2***	***Total strain (kJ)***
1.	**3**	**60º**	**24º 44`**	**697**	**120**
2.	**4**	**90º**	**9º 44`**	**685**	**112**
3.	**5**	**108º**	**0º 44`**	**664**	**35**
4.	**6**	**120º**	**-5º 16`**	**659**	**12**
5.	**7**	**128º 34`**	**-9º 33`**	**662**	**35**
6.	**8-11**	**135º-147º 16`**	**-12º 46`-- 18º 54`**	**661-665**	**32-88**

When the carbon valences are forced together, the stain is said to be positive (+), when forced apart it is negative (-).

From the list of strains, it can be conclude that according to Baeyer's strain theory:

- Because the deviation of the bond angles in cyclopropane is greater than in cyclobutane, the strain in cyclopropane is greater than in cyclobutane, so cyclopropane is less stable than cyclobutane.
- Due to the bond angle in cyclopentane is (108º), which is very similar to the tetrahedral angle (109º 28`), cyclopentane should be free of angle strain, where the

stain in cyclopentane (α) = 0° 44`. Hence, cyclopentane must posses the lowest energy and the highest stability.

- The bond angle in the planar cyclohexane is (120°), which is larger than the tetrahedral angle, so, the strain (α) = - 5° 16`. Also the stain in cycloheptane will be (α) = - 9° 33`.
- From the results shown in (Table 2.4), the stability increase up from the three- to six-membered ring, then decreases from seven to the eleven-membered rings, according to the values of heats of combustion.

2.4 The analysis of Baeyer's strain theory

- Baeyer's strain theory is based on a mechanical concept of valence, and this led to wrong conclusions on the assumption that all the rings are planar, where the physical methods and the quantum mechanical calculations shown that all rings (except cyclopropane) are not planar (See pages 30 and 31) and also do not permit very large distortion of bond angles.
- If cyclopropane was an equilateral triangle, the bond angle would be (60°). This value is impossible, since, the carbon valency angle never be less than (90°). Furthermore, according to Coulson *et al.* calculation has shown that the smallest carbon valency angle is (104°), and in cyclopropane, the carbon hybridized orbitals are not pointing towards one another in the same straight line, and

linked together with (bent) bonds. Hence, cyclopropane molecule being in the state of strain.

Unit 1

Lesson 3: Stereochemistry of Alicyclic compounds

3.1 Types of isomers in alicyclic compounds

There are many types of isomerism are known for alicyclic compounds as shown in the following diagram (3.1):

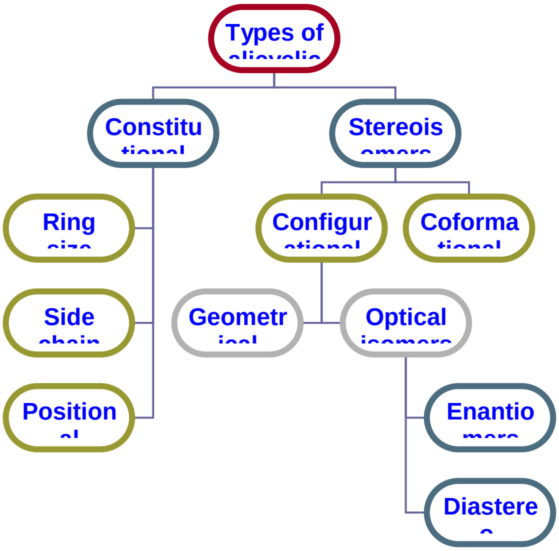


Diagram 3.1

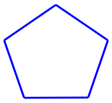
3.2 Constitutional isomers:

Constitutional isomers are isomers that differ because their atoms are connected in a different order.

Types of constitutional isomers in alicyclic compounds:

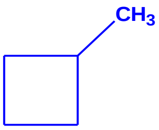
I- Ring size isomers:

Ring size isomers are compounds have the same molecular formula but differ in the ring size, e.g.,



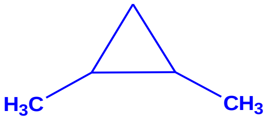
Cyclopentane

MF: C_5H_{10}



Methyl-cyclobutane

C_5H_{10}

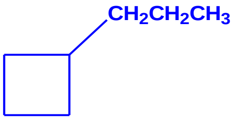


1,2-Dimethyl-cyclopropane

C_5H_{10}

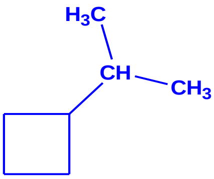
II- Side chain isomers:

Side chain isomers are compounds have the same molecular formula but differ in the side chain structure, e.g.,



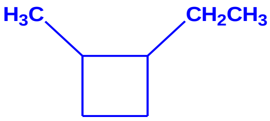
Propyl-cyclobutane

MF: C_7H_{14}



Isopropyl-cyclobutane

C_7H_{14}

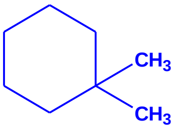


1-Ethyl-2-methyl-cyclobutane

C_7H_{14}

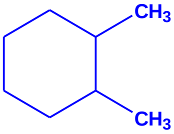
III- Positional isomers:

Positional isomers are compounds have the same molecular formula but differ in the relative arrangement of the substituents connected to the ring, e.g.,



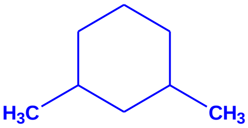
1,1-Dimethyl-cyclohexane

MF: C_8H_{16}



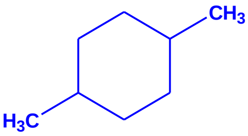
1,2-Dimethyl-cyclohexane

C_8H_{16}



1,3-Dimethyl-cyclohexane

C_8H_{16}



1,4-Dimethyl-cyclohexane

C_8H_{16}

3.3 Stereoisomers: Stereoisomers are isomers that have same formula and connectivity but differ in the position of the atoms in space.

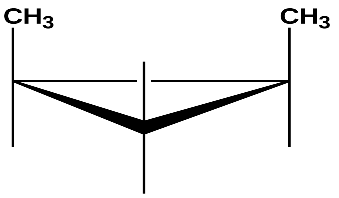
Stereoisomer can be divided into two categories configurational and conformational isomers.

3.4 Configurational isomers: Configurational isomers are divided into two types optical and geometrical isomers.

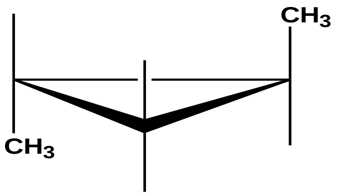
3.4a Geometrical or *cis-trans* isomers: Geometrical isomers are a type of stereoisomers resulting from difference in the special arrangement of the atoms or groups attached to the bonds around which rotation is largely restricted.

In Alicyclic compounds, the rigidity of atoms in rings to rotate completely about their bonds leads to ***cis- trans***- isomerism as shown in the next examples (Fig. 3.2).

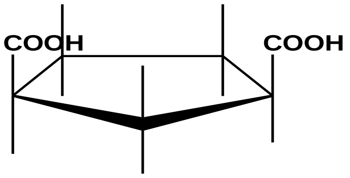
Ex: *cis- trans*- isomers of 1,2-dimethylcyclopropane, cyclopentane-1,3-dicarboxylic acid and cyclopentane-1,2-diol. The ***cis***- isomer has both methyls on the same side of the ring; the ***trans-*** isomer has them on opposite sides.



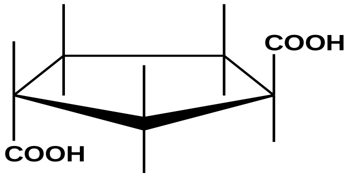
cis-1,2-dimethylcyclopropane



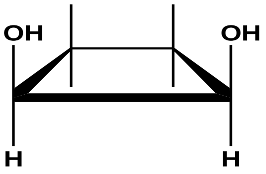
trans-1,2-dimethylcyclopropane



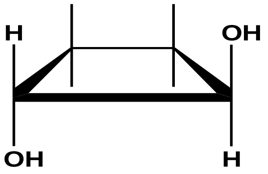
cis-cyclopentane
-1,3-dicarboxylic acid



trans-cyclopentane
-1,3-dicarboxylic acid



cis-cyclobutan-1,2-diol



trans-cyclobutan-1,2-diol

Fig. 3.2

3.4b Optical isomers:

Optical isomers are isomers that resulting from presence of one or more chiral centers within a molecule.

- **Optical Activity:** The ability of some compounds to rotate plane polarized light.
- **Chirality:**

Chirality refers to objects which are related as non–superimposable mirror images.

❖ Chiral carbon atom:

Chiral carbon atom is a carbon atom attached to four different atoms or groups.

Optical isomers can be divided into two general categories:

I- Enantiomers:

Enantiomers are stereoisomeric pair have the same chemical and physical properties but differ in the rotation of plane polarized light, one of them is mirror image of the other, and both enantiomers are non- superimposable.

II- Diastereoisomers:

Diastereoisomers stereoisomers that are not mirror images.

III- Racemic mixture:

Racemic mixture is an equimolar mixture (1:1) of two enantiomers.

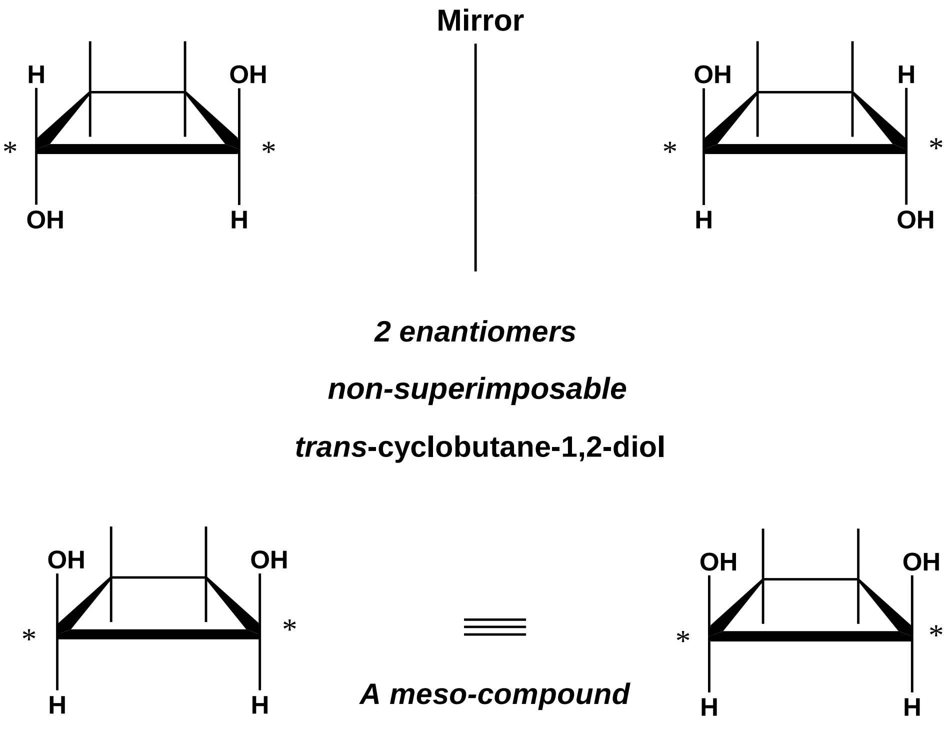
IV- Meso-form:

The Meso-form is optically inactive compound with at least 2 stereocenters that is achiral due to the presence of a plane of symmetry, and is superimposable.

V- Molecules with **n** different chiral centers exist in $\mathbf{2^n}$ enantiomeric forms, and number ($\mathbf{2^{n-1}}$) of racemic mixtures.

An example, if we examine models of ***cis***- and ***trans***-cyclobutane-1,2-diol, it can be found two types of isomerism, geometrical and optical isomerism.

The ***trans***-isomer exists in two optically active enantiomers, whereas, the ***cis***-isomer has a plane of symmetry and is therefore optically inactive Meso-form.



2 enantiomers

non-superimposable

***trans*-cyclobutane-1,2-diol**

A meso-compound

superimposable

cis-cyclobutane-1,2-diol

*** - chiral carbon atom**

Fig. 3.3

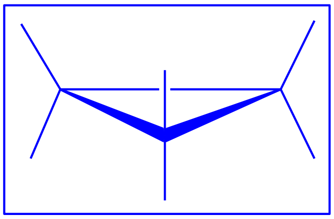
Unit 1

Lesson 4: Conformations of cycloalkanes

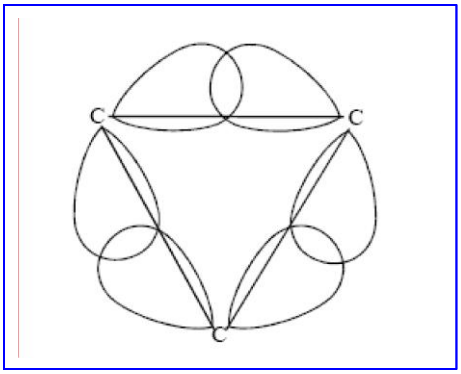
4.1 Geometrical shape of the rings

A- Cyclopropane: must be geometrically planar, three carbons into a plane. The hydrogen atoms in cyclopropane necessarily are eclipsed (Fig. 4.1).

On the other hand, according to the modern conceptions, the σ bonds in cyclopropane differ from ordinary σ bonds and their hybridization is different from ordinary *sp3* hybridization, in fact, it occupies an intermediate position between the ordinary σ- and π-bond. This bond is known as "**banana-(or bent) bond**" (Fig. 4.1). Now, the angle between the bonds in cyclopropane is 106^{O} instead of 60^{O} according to the classical conceptions, and the bond **H-C-H** angle is about ~ 120^{O}.



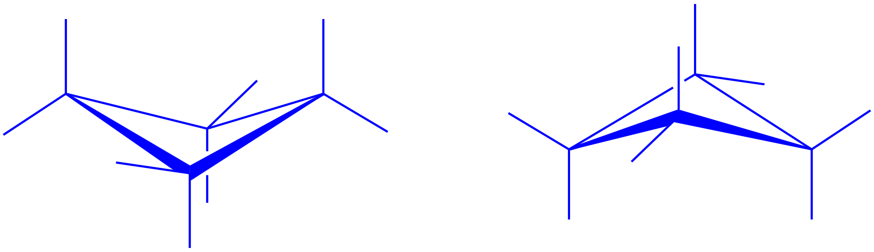
Propane molecule



Banana-bond of cyclopropane

Fig. 4.1

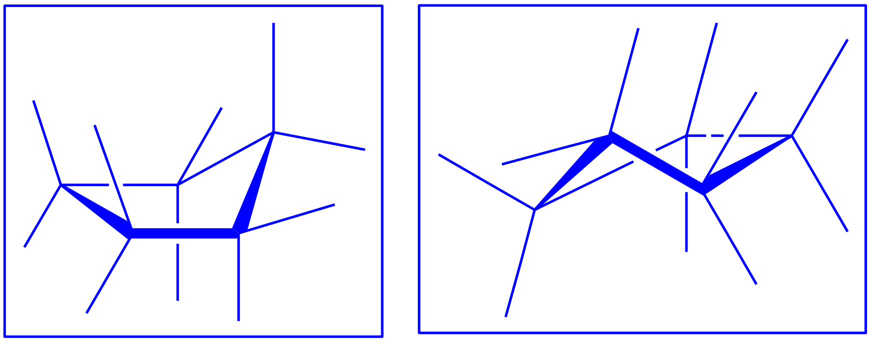
B- Cyclobutane: (Flat bond angles will be = 90^{O}) is puckered, even through the puckered causes more-strained bond angles (Fig. 4.2).



Puckered conformation of cyclobutane

Fig. 4.2

C- Cyclopentane has near-optimal bond angle ($109^{O}28`$) if it was flat, but cyclopentane also is slightly puckered, so that the hydrogen atoms attached to the ring carbons are staggered as in envelop and half-chair conformers. Envelope and half-chair are of similar stability and interconvert rapidly.(Fig. 4.3).

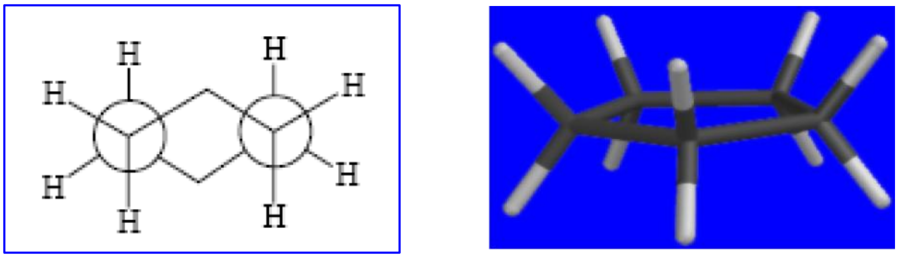


Envelop-form **Half chair-form**

Envelop-, and half-chair conformations of cyclopentane
Fig. 4.3

D- Cyclohexane

If the cyclohexane ring was flat, all the hydrogen atoms on the ring carbons would be eclipsed. So, the planar conformation destabilized by torsional strain, but in puckered conformation (Fig. 4.4) that all the hydrogen atoms are staggered and the energy of this puckered conformer is lower than the energy of flat cyclohexane, due to the more-favorable *sp3* bond angle and fewer hydrogen-hydrogen repulsions.



Puckered conformation of cyclohexane

The hydrogen atoms are staggered

Planar conformation of cyclohexane

The hydrogen atoms are eclipsed

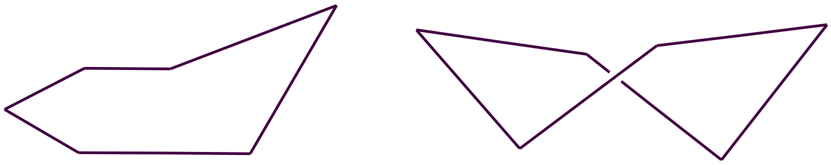
Fig. 4.4

4.2 Flexible conformers of cyclohexane

Cyclohexane is the most important of all the ring systems, it can be exists in a number of flexible forms in all of which angle strain is largely eliminated. These forms are known as chair, half-chair, boat, and twist-boat (Fig 4.5).

The chair-form of cyclohexane

The boat-form of cyclohexane

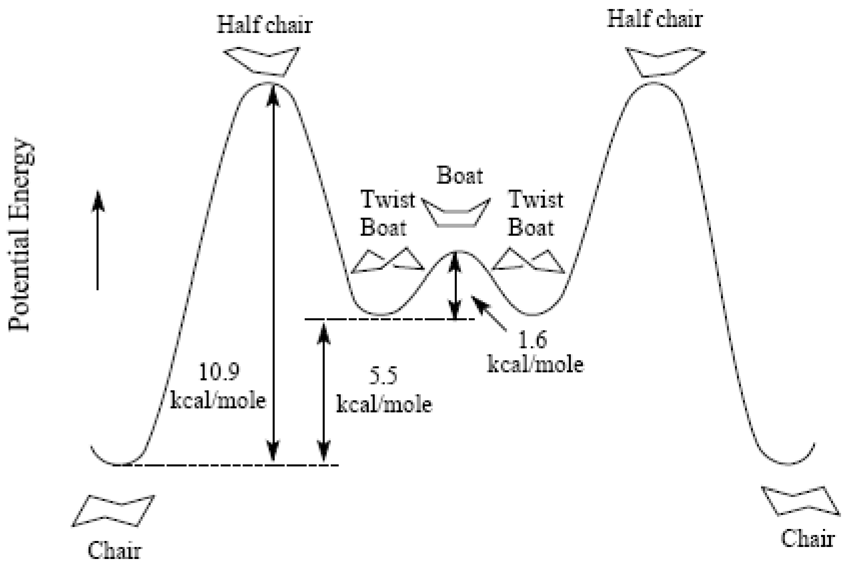


The half-chair form
of cyclohexane

The twist-boat form of
of cyclohexane

Fig. 4.5

The relative energies of the different forms of cyclohexane are shown in the following energy diagram (4.6).

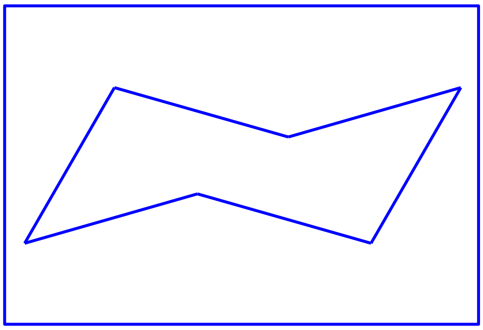


The energy diagram for the ring inversion of cyclohexane.

Diagram 4.6

From the above diagram, it can be concluding that:

1- The chair-form is the most stable conformation of cyclohexane (about 99.9% of cyclohexane molecules are in the chair-form at any time) (Fig. 4.7).



The chair-form of cyclohexane

Fig. 4.7

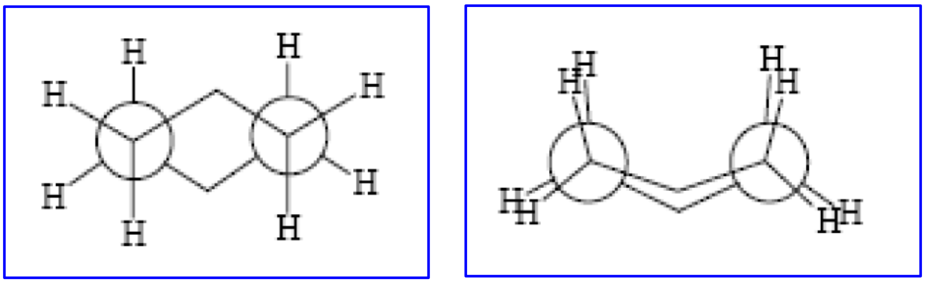
The stability of the chair-form is due to the following reasons:

(i) The chair-form is the less energy one.

(ii) The chair-form is free of angle stain (α), and torsional strain.

(iii) All hydrogen atoms in the chair-form are staggered in four of its carbon atoms as shown in (Fig. 4.8).

2- The boat-form of cyclohexane has eclipsed bonds in four of its carbon atoms, this eclipsing produces a significant amount of torsional. This torsional strain increases the energy of the boat-form and destabilizes it (Fig. 4.8).

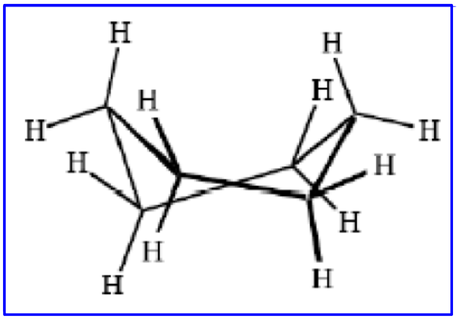


Newman projection of the chair-form

Newman projection of the boat-form

Fig. 4.8

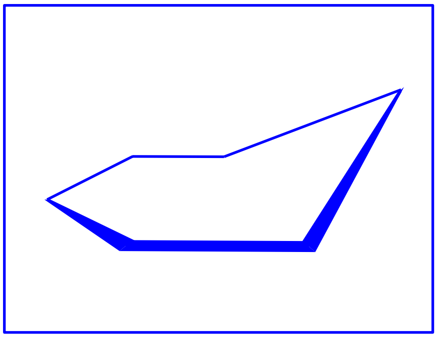
3- A third conformation of cyclohexane is the twist-boat (Fig. 4.9), there is a relieving in this form minimizes the torsional strain and make the twist-boat is lower in energy than the boat-conformation.



The twist-boat form of cyclohexane

Fig. 4.9

4- The last conformation is called half-chair, which has an almost-planar structure. So, it has the highest energy and the less stability (Fig. 4.10).

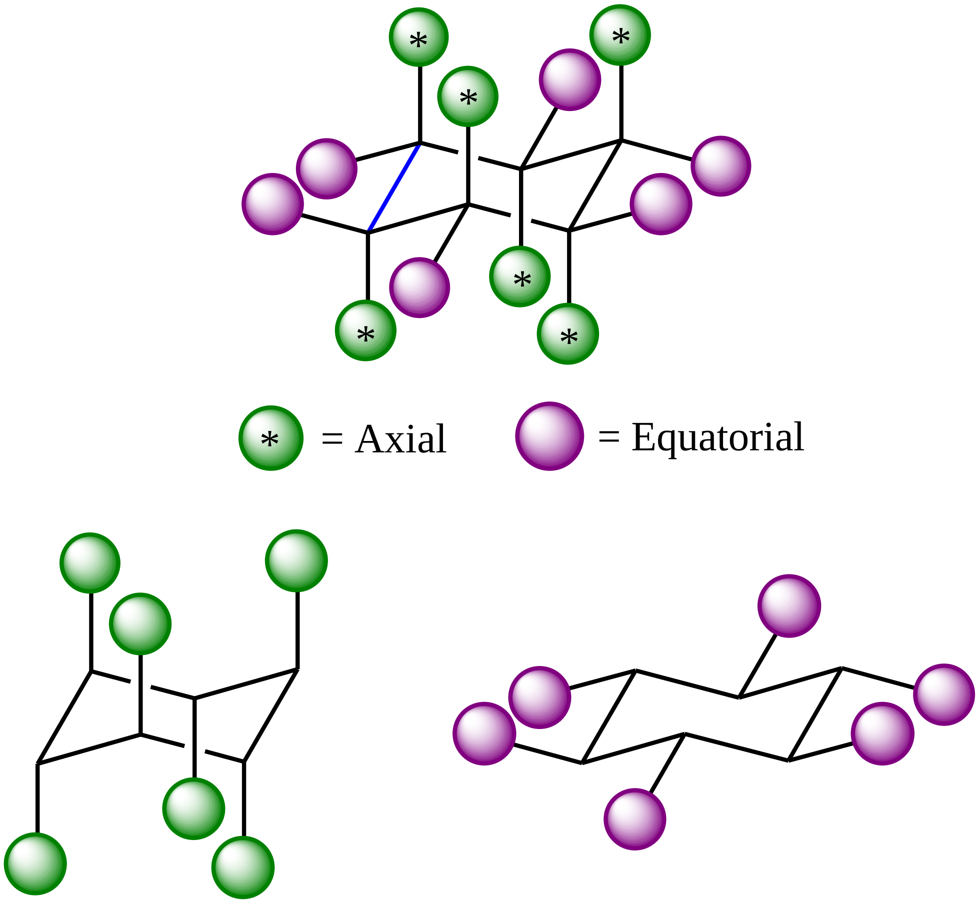


The half-chair form of cyclohexane

Fig. 4.10

4.3 Axial and equatorial hydrogens of cyclohexane

The chair conformation of cyclohexane has two distinct types of carbon—hydrogen bonds: **axial** and **equatorial**. Six of these bonds are **axial** and the other six **equatorial**, with one axial and one equatorial bond on each carbon (Fig. 4.11).



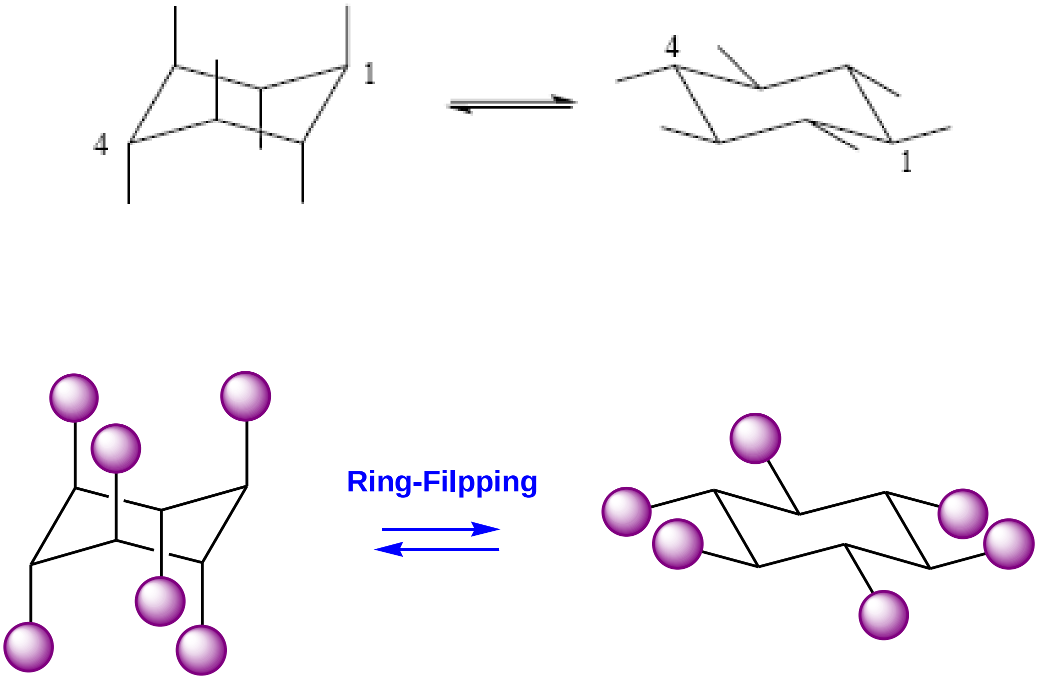
Axial hydrogens of cyclohexane

Equatorial hydrogens of cyclohexane

Fig. 4.11

4.4 Conformational inversion of cyclohexane

A ring flipping: is a chair-chair interconversion, one chair form of cyclohexane converts to another chair form of cyclohexane. In this process of ring flipping, the equatorial substituents become axial, and the axial substituents become equatorial (Fig. 4.12).



Axial hydrogens of cyclohexane   Euatorial hydrogens of cyclohexane

Fig. 4.12

Activities:

Try to draw well each puckered conformer of the cycloalkanes in this lesson.

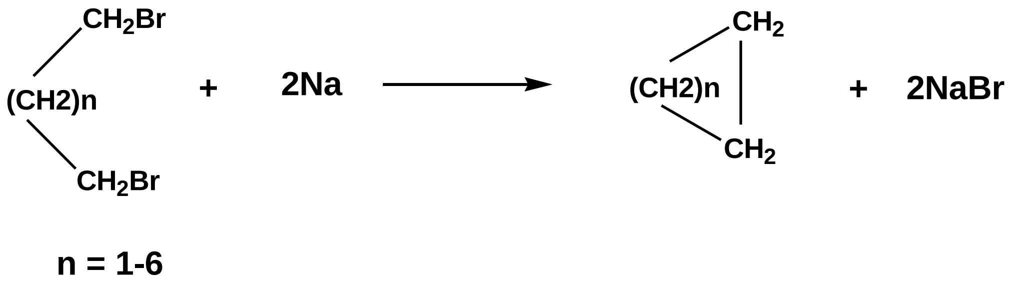
Unit 2

Lesson 5: General methods for the preparation of alicyclic compounds

Many methods have been introduced to prepare various-sized rings as follows:

1. Freund method (1882):

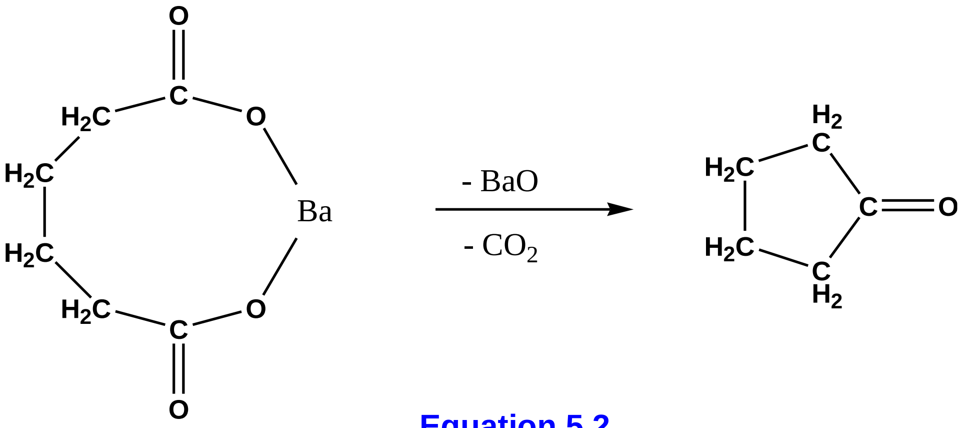
Treatment of an alkyl dihalide with sodium or zinc gives the corresponding cycloalkane (Equation 5.1).



Equation 5.1

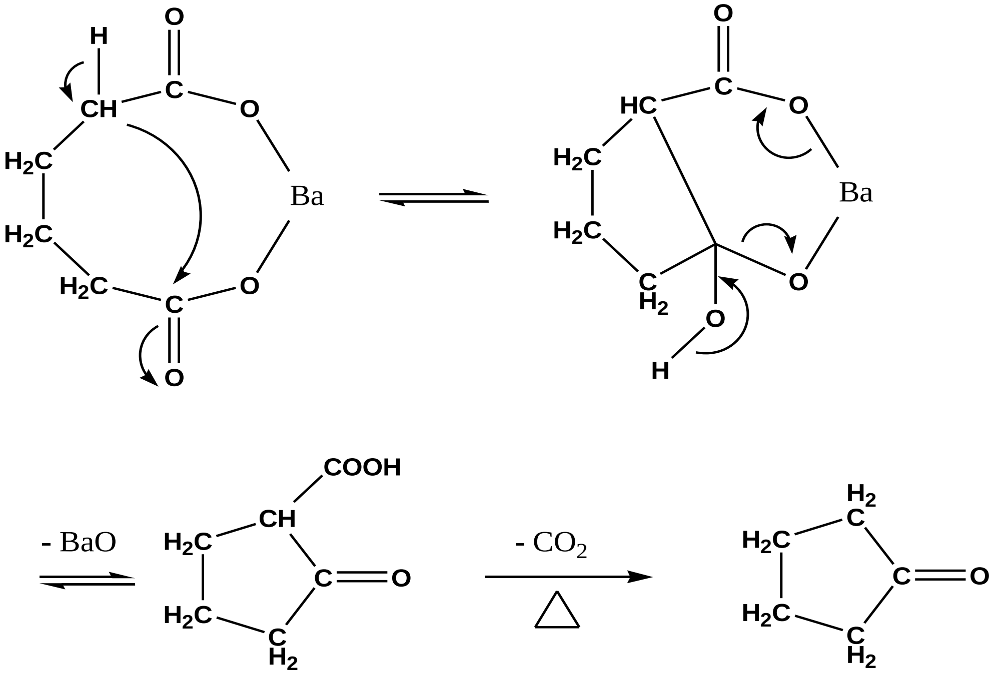
2. Pyrolysis of the salts of dibasic acid:

A cyclic ketone is formed, when the calcium or barium salts of a dicarboxylic acid is distilled, e.g., barium adipate gives cyclopentanone (Equation 5.2).



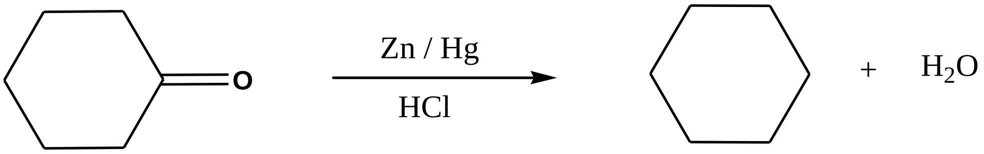
Equation 5.2

The reaction mechanism;



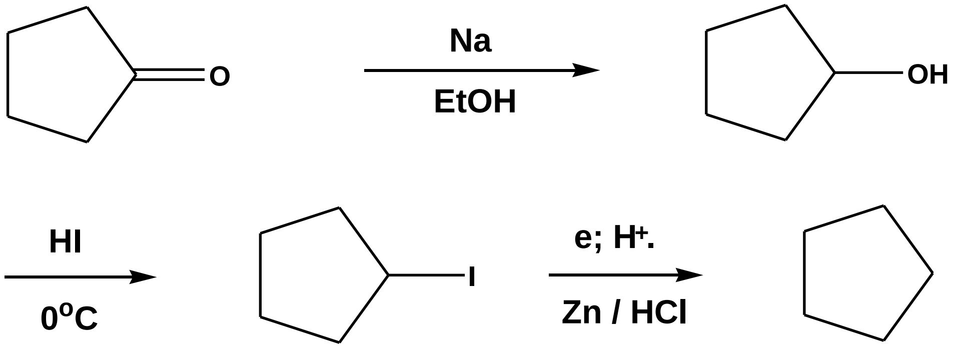
3. Reduction of cyclic ketones:

Cyclic ketones may be converted into the corresponding cycloalkanes by means of the **Clemmensen** reduction (Equation 5.3).

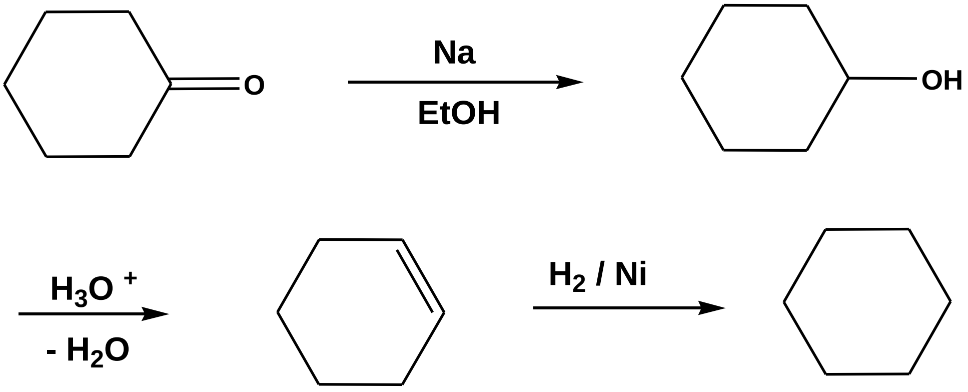


Equation 5.3

There are another two methods for this conversion as follows (Equations 5.4 and 5.5):



Equation 5.4



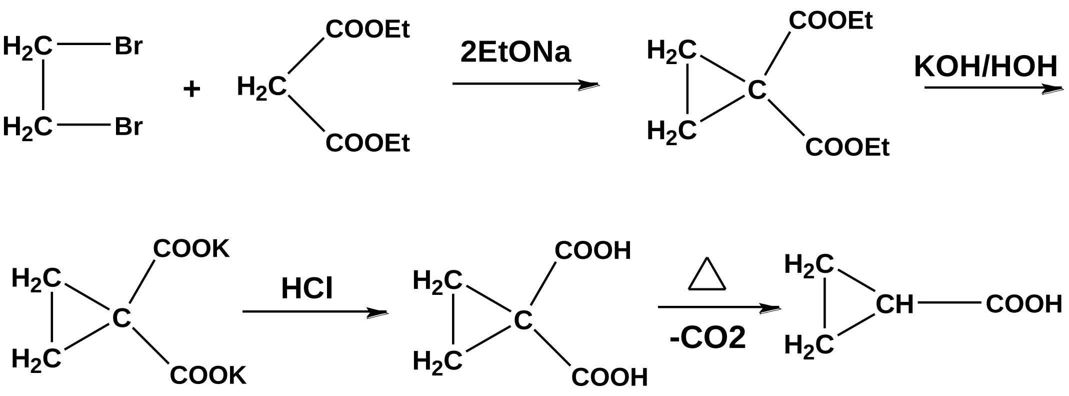
Equation 5.5

4. Perkin's methods (1883):

Condensation of certain alkyl dihalide (**$Br(CH_2)_nBr$; n= 2-5**) with either malonic ester or ethylacetoacetate in presence of sodium ethoxide gives the corresponding cyclic ester, which upon hydrolysis followed by decarboxylation turns to the cycloalkane derivative.

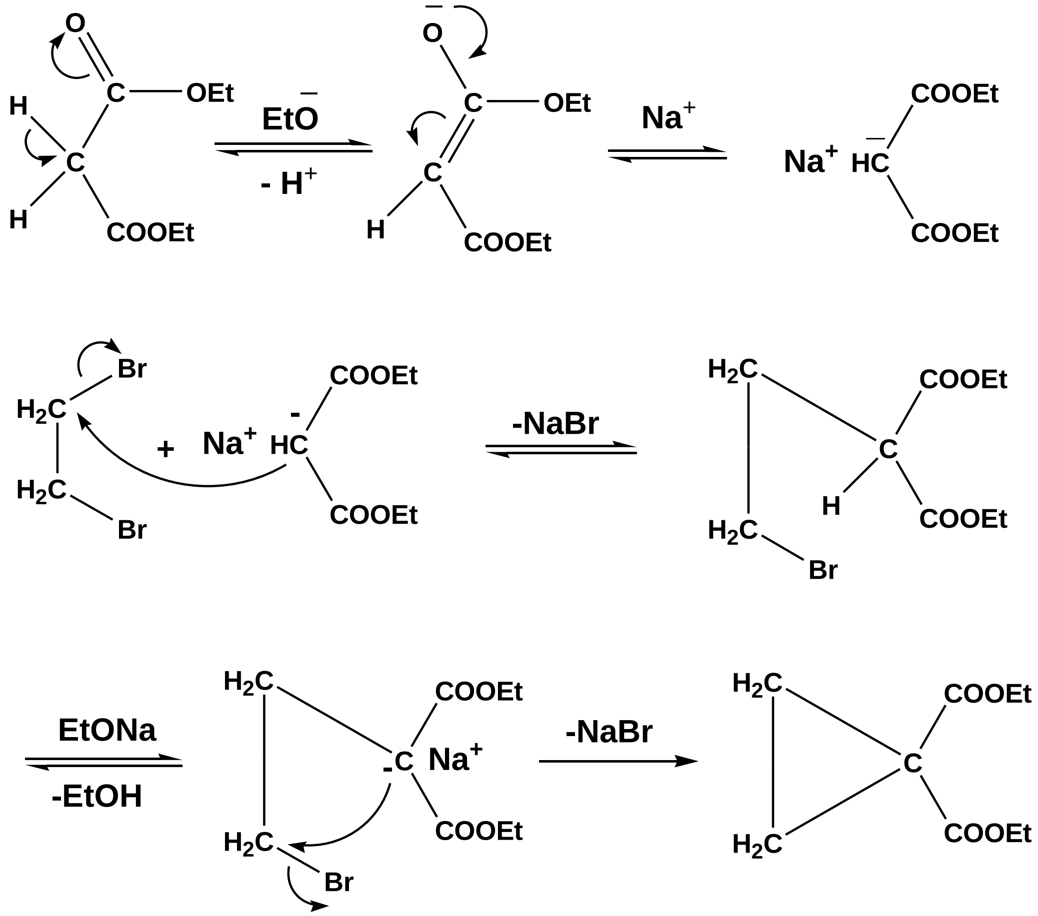
I- Condensation with malonic ester:

One molecule of malonic ester condenses with an alkyl dihalide in presence of two molecules of sodium ethoxide to form cycloalkane-dicarboxylic ester, which may be converted into the monocarboxylic acid by hydrolysis then decarboxylation (Equations 5.6).



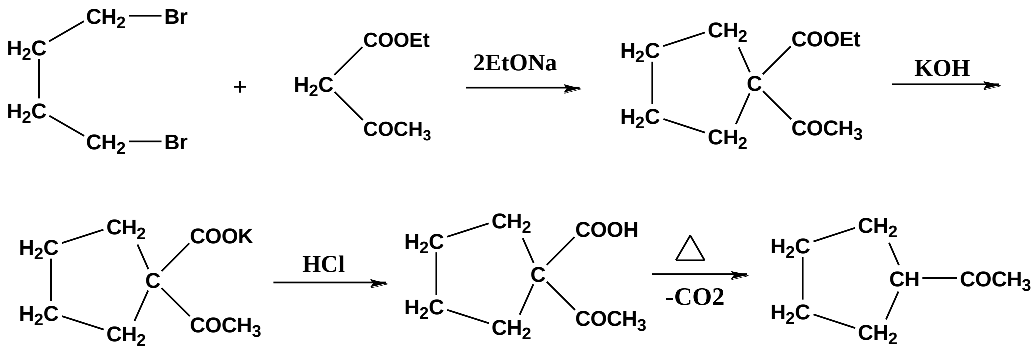
Equation 5.6

The reaction mechanism;



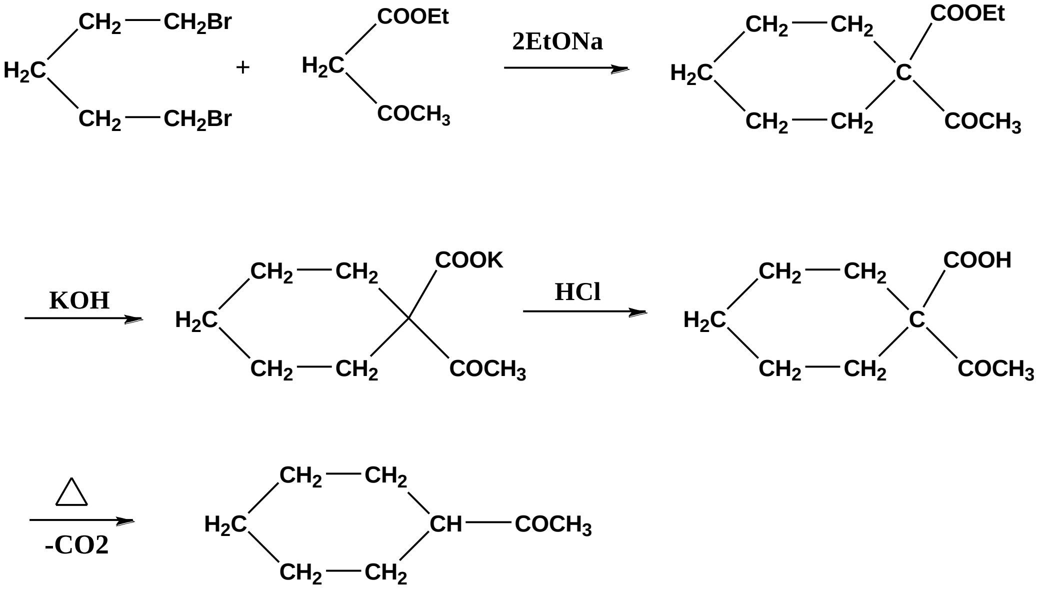
I- Condensation with ethylacetoacetate:

On treatment of ethylacetoacetate with appropriate alkyldihalide; three, five, six and seven-membered rings are obtained ((Equations 5.7 and 5.8).



cyclopentylmethylketone

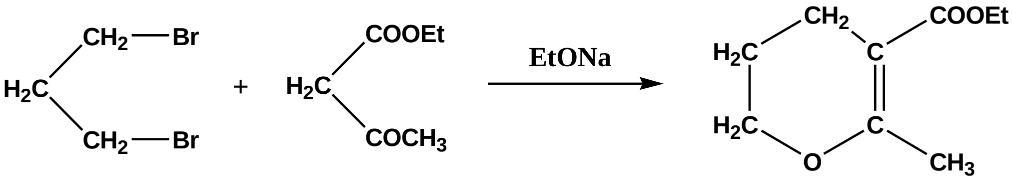
Equation 5.7



cyclohexylmethylketone

Equation 5.8

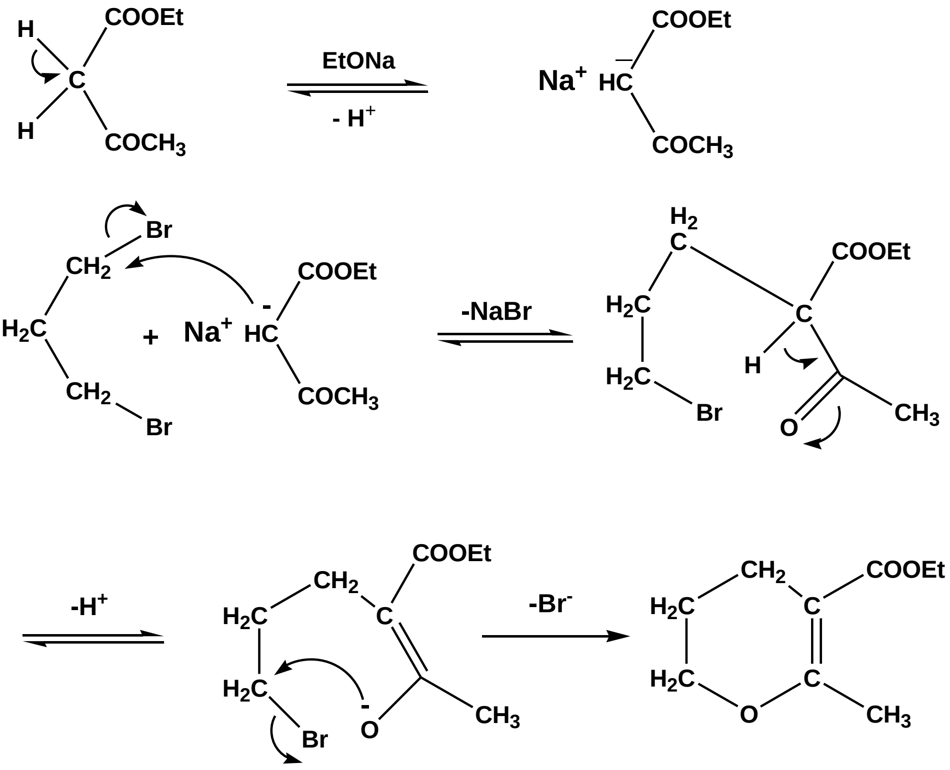
All attempts to prepare a four-membered ring result in the formation of a dihydropyran derivative (Equations 5.9).



2-methyl-5,6-dihydro-4*H*-pyran-3-ethylcarboxylate

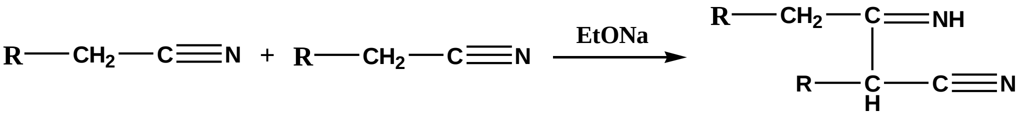
Equation 5.9

The reaction mechanism;



5. Ziegler-Thorpe reaction:

Thorpe nitrile reaction is a base catalyzed condensation of two nitrile molecules to yield a **β-iminonitrile** (Equation 5.10).

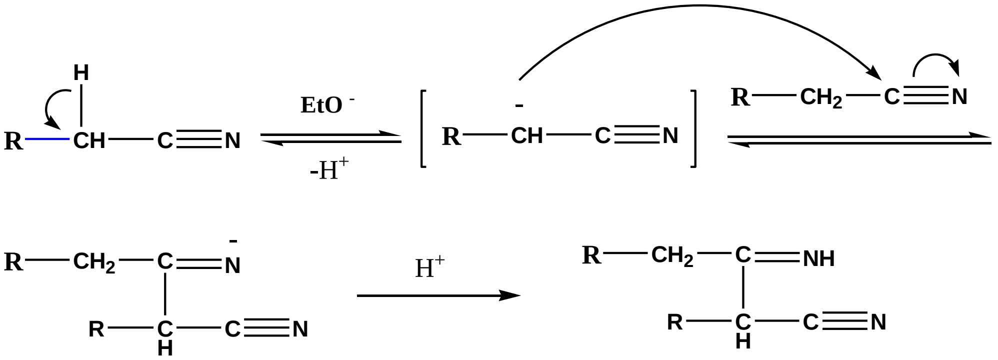


β – iminonitrile

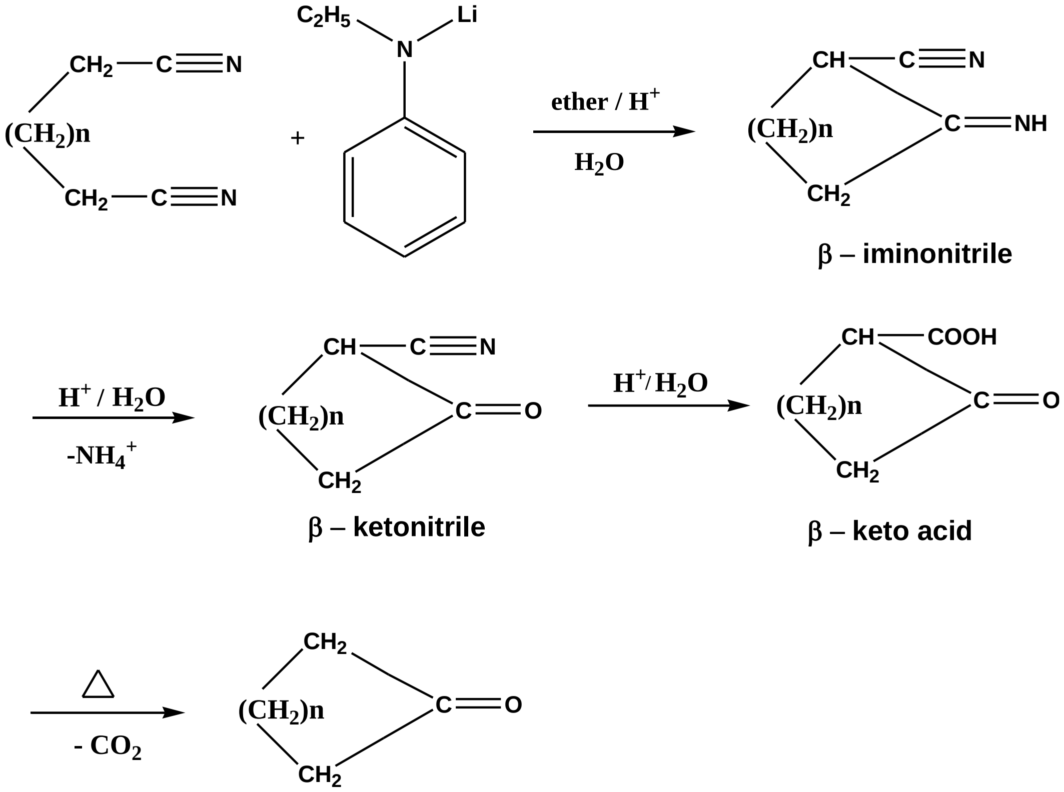
Equation 5.10

The Mechanism of this reaction shown as follows:

The reaction Mechanism;



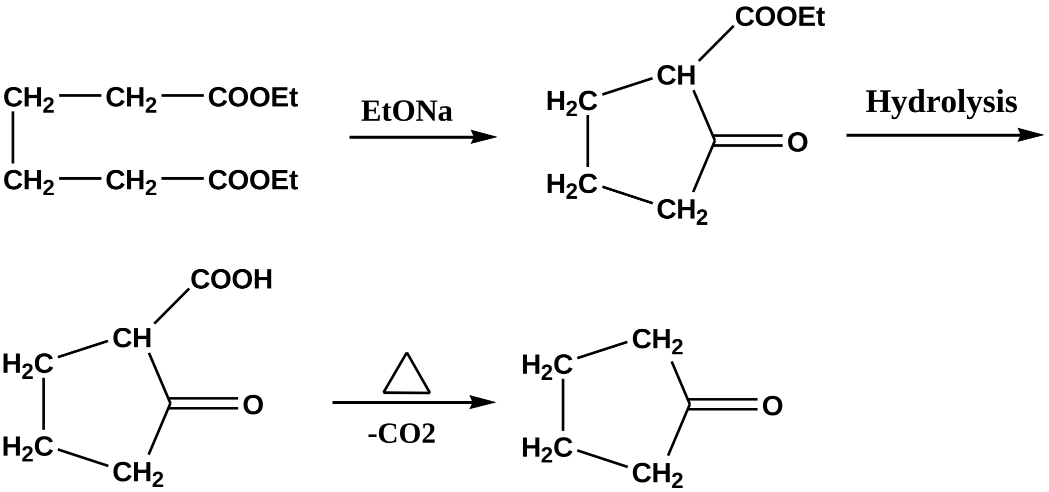
Ziegler used **Thorpe** reaction to yield a **cyclic iminonitrile** using Lithium n-ethylaniline as a basic catalyst, then the product hydrolyzed with aqueous acid to yield the **cyclic ketonitrile**. Boiling the later with aqueous acid converts the nitrile group to a carboxylic acid to yield **β-ketoacid**, which on decarboxylation gives the **cyclic ketone** (Equation 5.11).



Equation 5.11

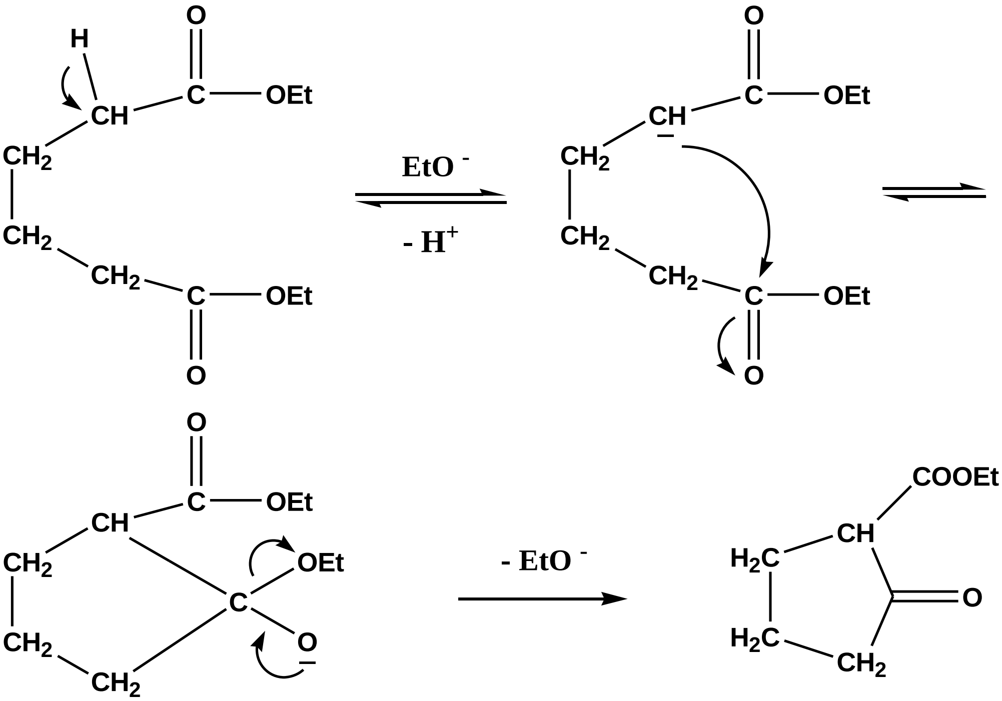
6. Dieckmann condensation:

This reaction is an intramolecular Claisen condensation, many cycloalkanes (five-, six- and seven-membered rings) can be obtained by treating the esters of adipic, pimelic or suberic acids with sodium ethoxide (Equation 6.1).

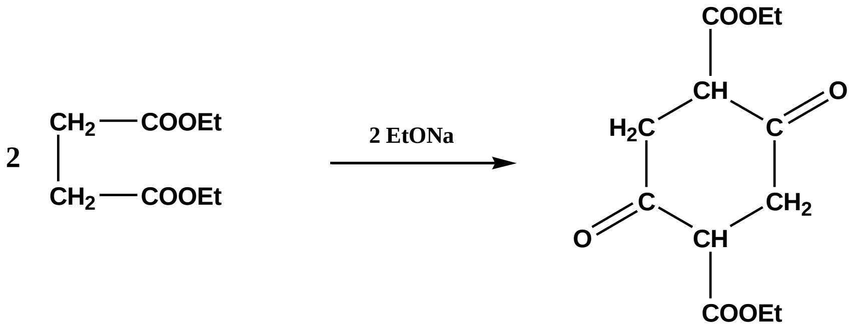


Equation 6.1

The reaction mechanism;



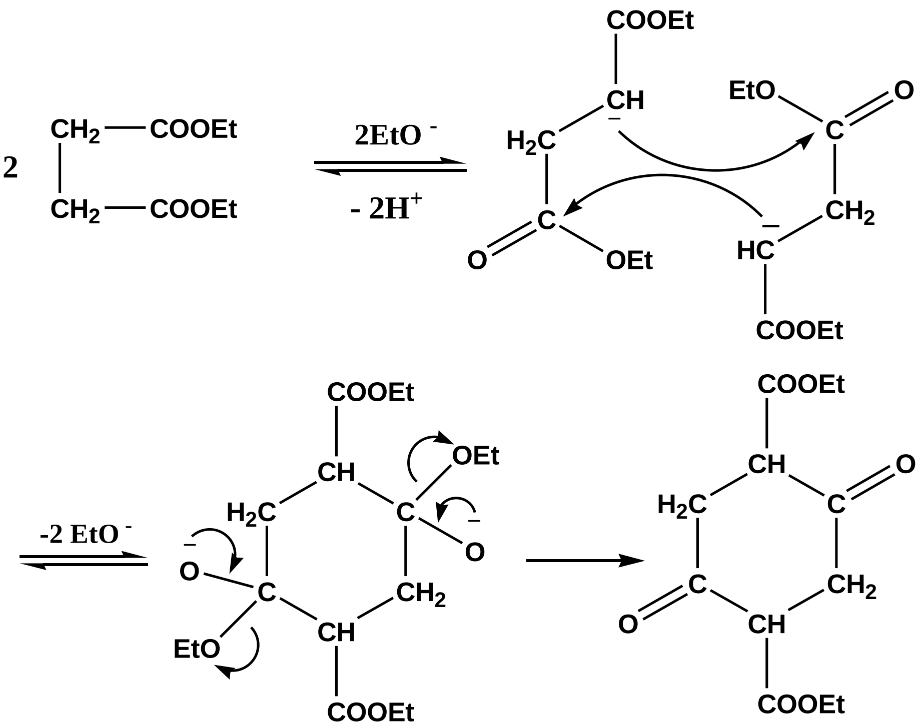
Esters lower than adipic ester may form cyclic products through the intermolecular condensation and cyclization, e. g., treatment of ethyl succinate in presence of sodium ethoxide forms succino-succinic ester (cycohexane-2,5-dione-1,4-carboxylic ester) (Equation 6.2).



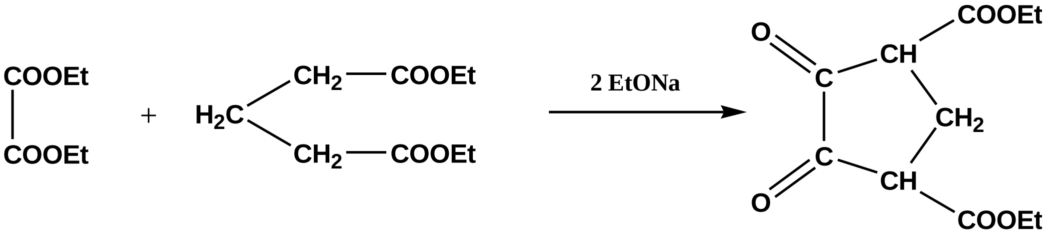
succino-succinic ester

Equation 6.2

The reaction mechanism;



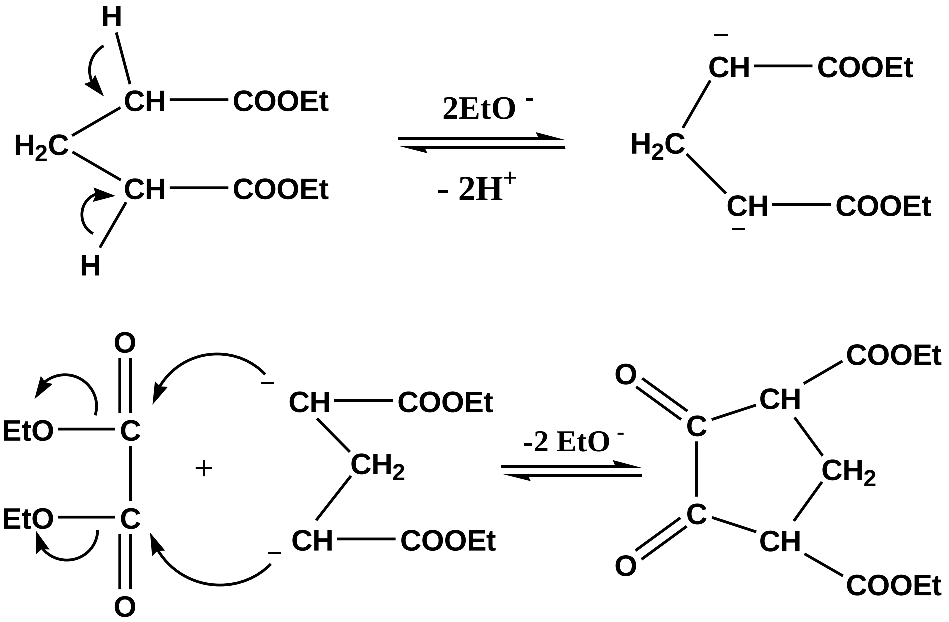
Also, five-membered ring cycloalkanes may be obtained through the intermolecular condensation between two different esters, such as, ethyl oxalate and ethyl glutarate (Equation 6.3).



cyclopentane-4,5-dione-1,3-diethylcarboxylate

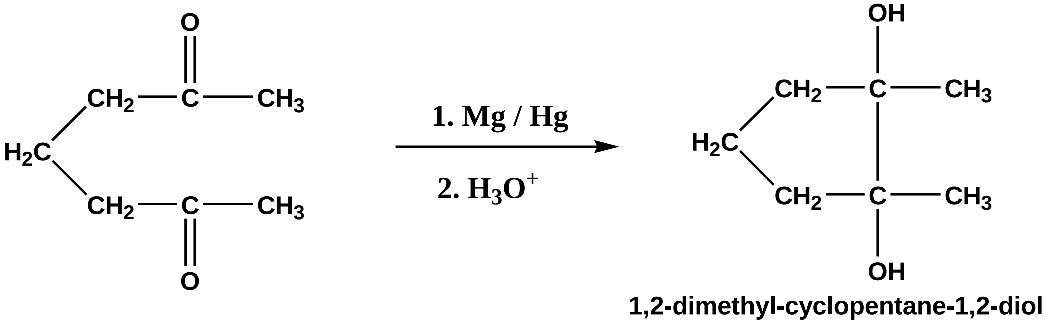
Equation 6.3

The reaction mechanism;



7. Reduction of diketones:

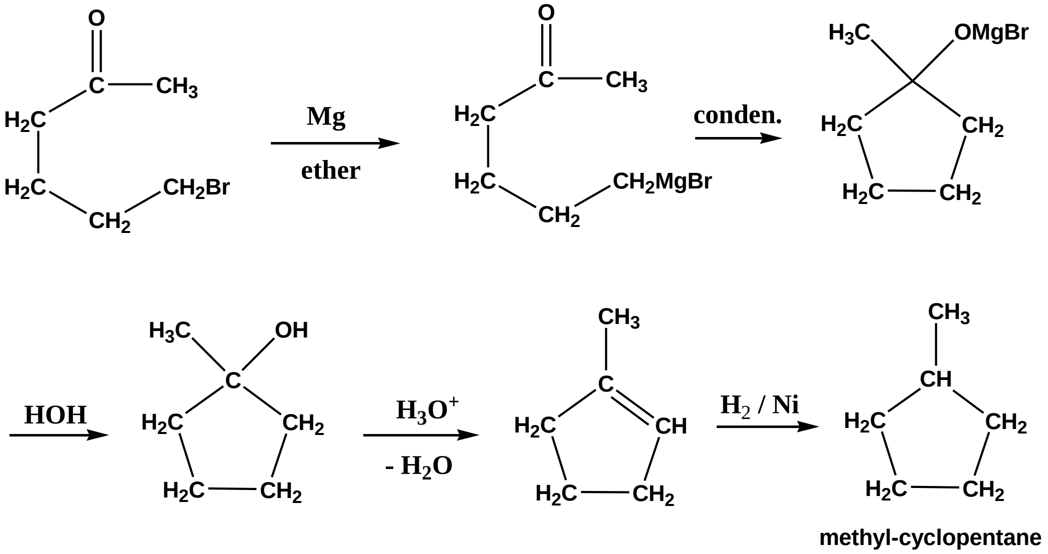
Five- or six-membered ring can be obtained through an intramolecular cyclization of certain diketones with magnesium amalgam, e. g., reduction of heptane-2,6-dione to form 1,2-dimethylcyclopentane-1,2-diol (Equation 6.4).



Equation 6.4

8. The Grignard method:

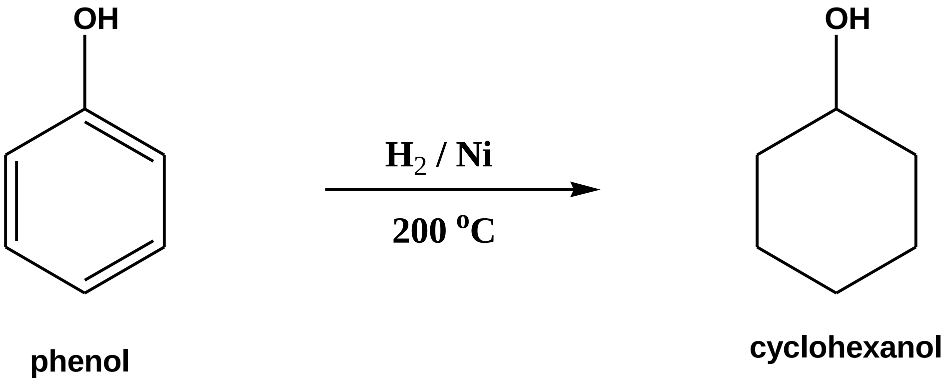
Certain halogen compounds react with magnesium which condenses internally to give cycloalkane derivatives, e. g., 6-bromo-2-hexanone reacts with **Mg** to give 1-methylcyclopentanol, which up on hydrolysis then reduction gives methylcyclopentane (Equation 6.5).



Equation 5.6

9. Reduction of benzene and its derivatives:

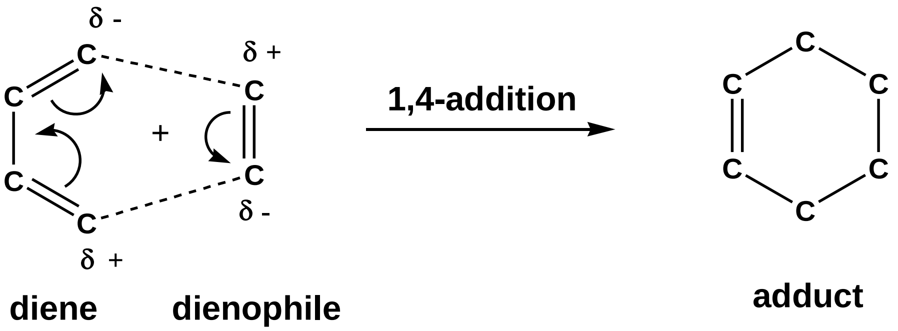
Catalytic reduction under pressure using nickel converted benzene or its derivatives into the corresponding six-membered cycloalkanes (Equation 6.6).



Equation 6.6

10. Diels-Alder reaction (Cyclo-addition reactions):

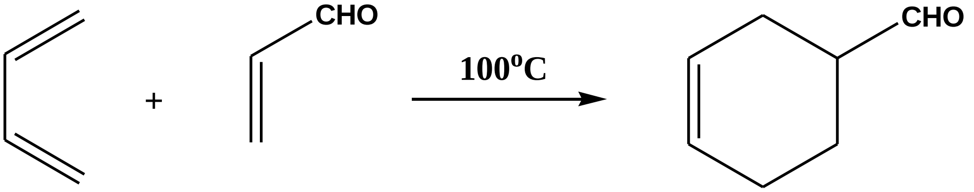
Diels-Alder reaction is an addition reaction between the diene (a compound containing conjugated double bonds) and the dienophile (unsaturated hydrocarbon) to yield a product known as the adduct. The adduct is usually a six-membered ring, the addition taking place in the 1,4-positions. In general terms, this reaction may be written as the following (Equation 6.7).



Equation 6.7

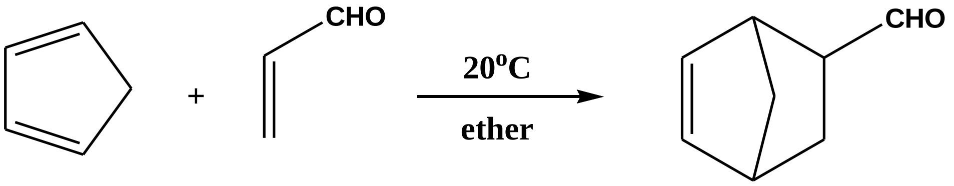
The diene may be of various types: acyclic, cyclic, semicyclic, bicyclic,

aromatic hydrocarbon with at least three linear benzene rings and certain heterocyclic compounds, also the dienophile may be: acyclic or cyclic. Some examples are in the following (Equations 6.8- 6.13).



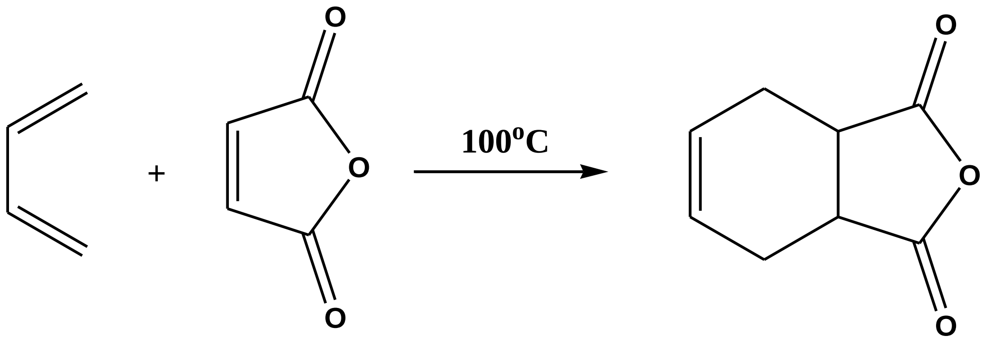
3-cyclohexene-carbaldehyde

Equation 6.8



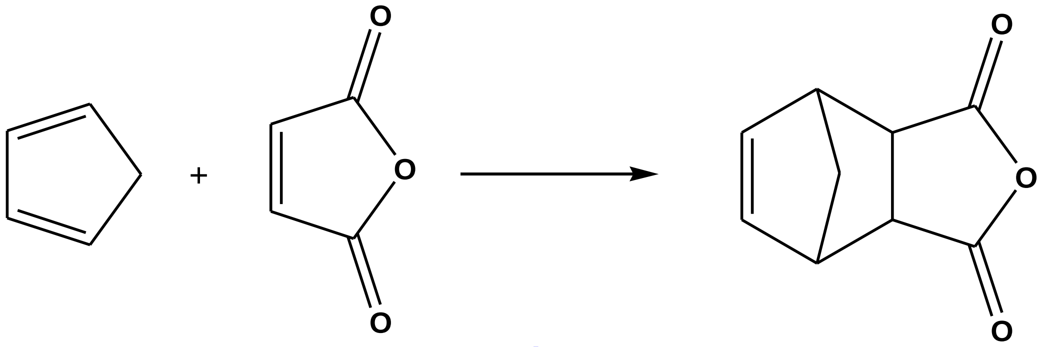
bicyclo[2.2.1]hept-5-ene-2-carbaldehyde

Equation 6.9

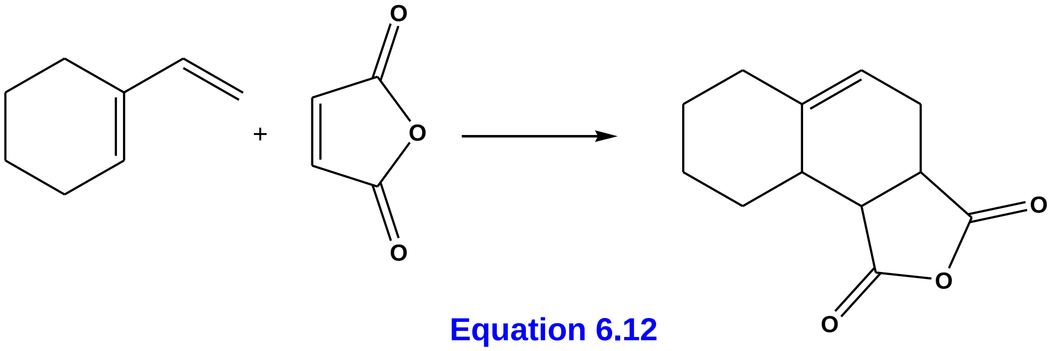


tetrahydrophthalic anhydride

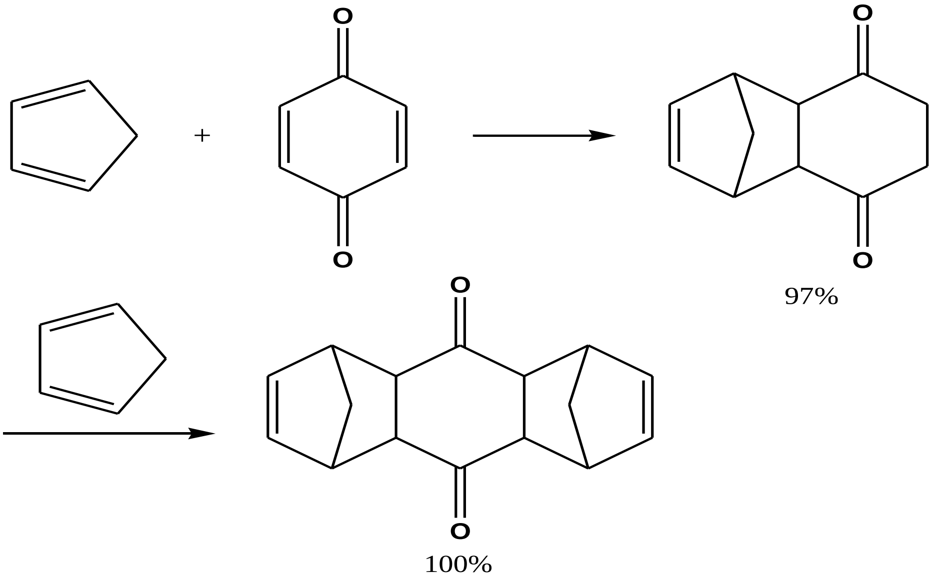
Equation 6.10



Equation 6.11

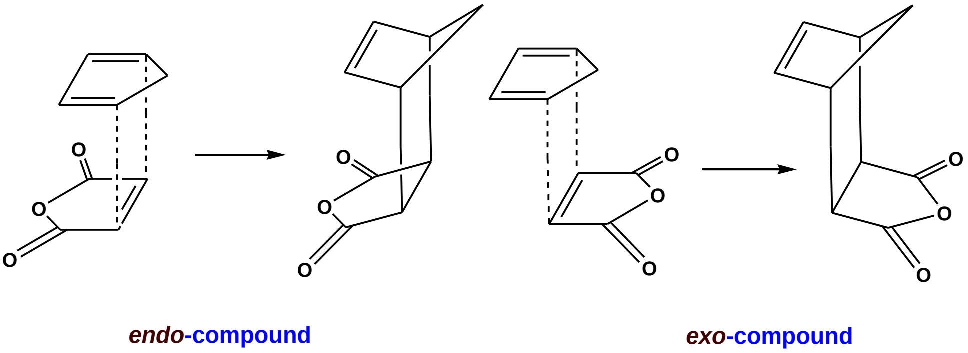


Equation 6.12



Equation 6.13

When the diene is cyclic, there are two *cis*-addition types, one giving the *endo*-compound and the other the *exo*-compound. The *endo*-compound is usually obtained exclusively due to the *endo*-compound is kinetically controlled, while the *exo*-compound is thermodynamically controlled. So, raising the temperature of the reaction favors the formation of the *exo*-compound (Fig. 6.14).



cis-addition

Fig. 6.14

Unit 3

Lesson 6: Cyclopropane and its derivatives

6.1 Physical properties of cyclopropane: b.p.= -34^{o}C. It is used as a general anaesthetic in surgical operations. Also, cyclopropane is explusive and its explosions with oxygen are more powerful, so cyclopropane is dangerous to handle and manufacture.

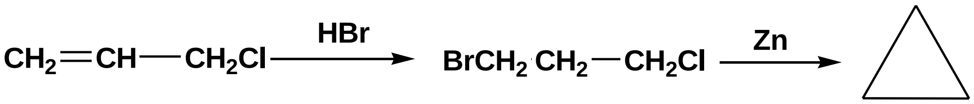
6.2 Chemical properties:

Several methods have been introduced to prepare cyclopropane and its derivatives as follows:

I- Methods of preparation:

1. Gustavson method:

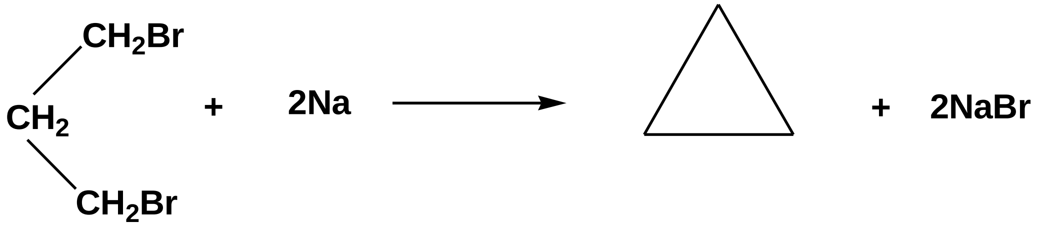
Cyclopropane is produced on an industrial scale by the action of zinc on 1,3-chlorobromo-propane, which prepared by addition of HBr to allylchloride (Equation 6.1).



Equation 6.1

2. Freund method:

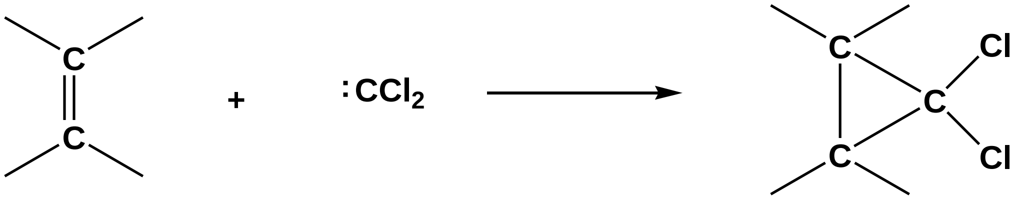
Treatment of 1,3-dibromopropane with metallic sodium gives the cyclopropane (Equation 6.2).



Equation 6.2

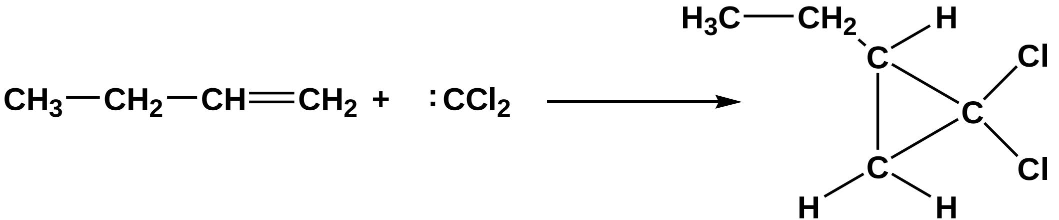
3. Action of carbenes on unsaturated compounds:

Addition reactions of carbenes to alkenes lead to the formation of the cyclopropanes. In general, this reaction may be written as follows (Equation 6.3).



Equation 6.3

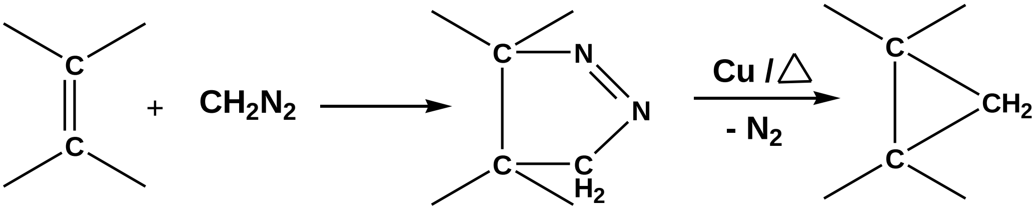
For example, (Equation 6.4).



Equation 6.4

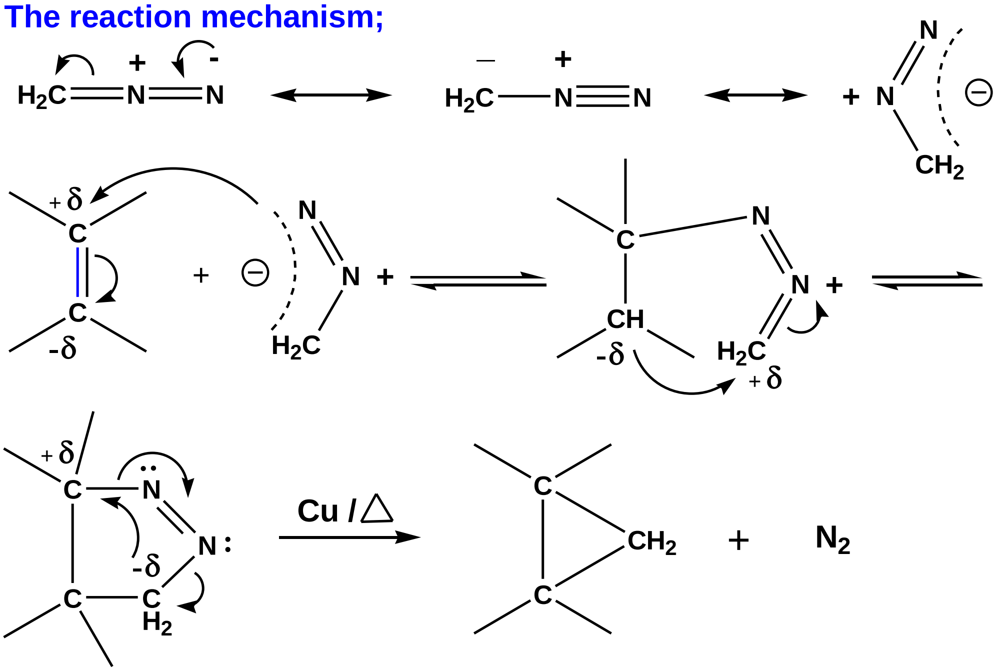
4. Buchner and Curtius reaction:

Addition of diazomethane to the double bonds affords the pyrazole ring, which upon heating with copper decomposed to yield the cyclopropane derivatives (Equation 6.5).



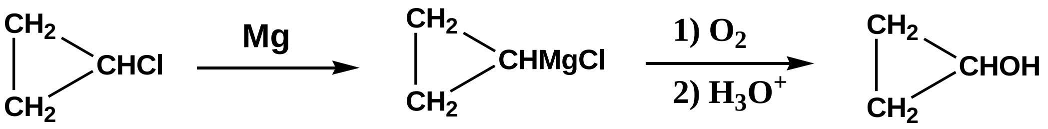
Equation 6.5

The reaction mechanism;



5. Synthesis of cyclopropanol:

Cyclopropanol has been prepared in a crude form as shown in (Equation 6.6).

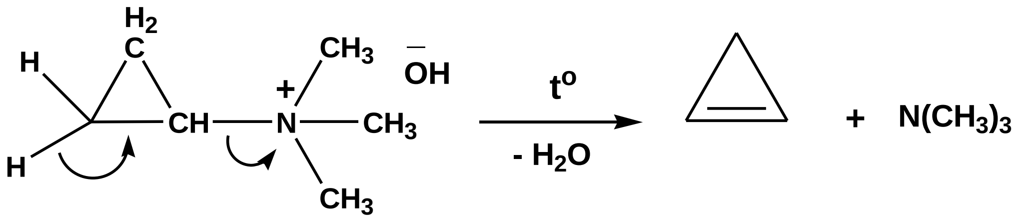


Equation 6.6

6. Synthesis of cyclopropenes:

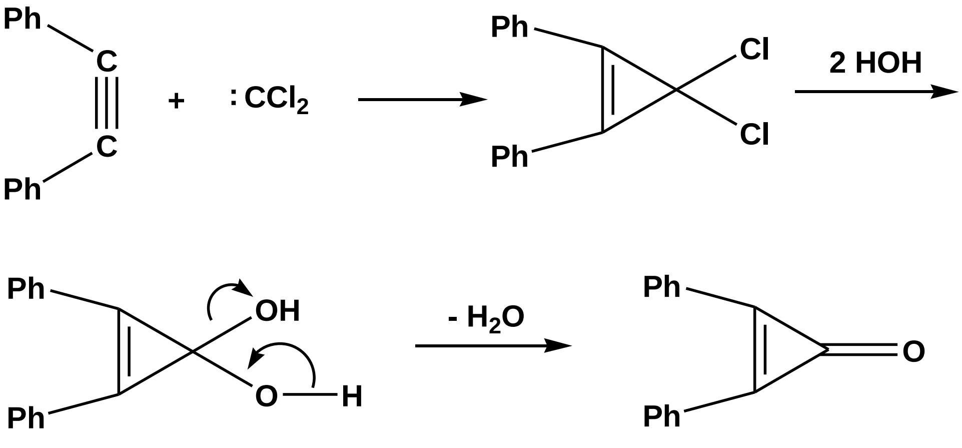
Two methods described the preparation of cyclopropene and cyclopropenenone as follows:

i- Decomposition of the cyclopropyltrimethylammonium hydroxide (Equation 6.7).



Equation 6.7

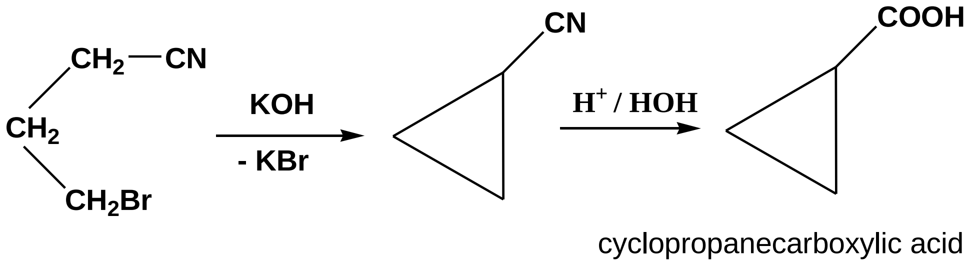
ii- Action of carbenes on acetylenes (Equation 6.8).



Equation 6.8

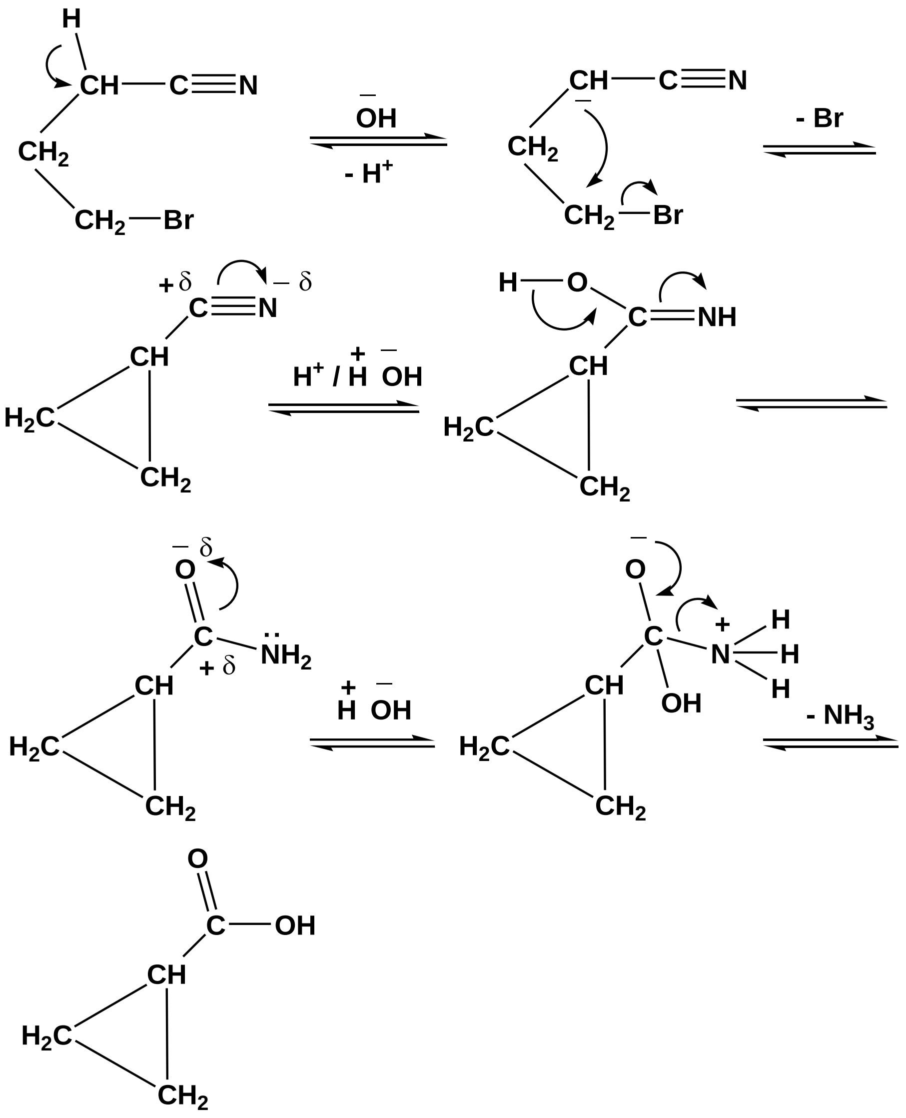
7. Synthesis of cyclopropanecarboxylic acid:

Cyclopropanecarboxylic acid has been prepared by the action of potassium hydroxide on 4-bromo-butyronitrile followed by hydrolysis of cyclopropanecarbonitrile (Equation 6.9).



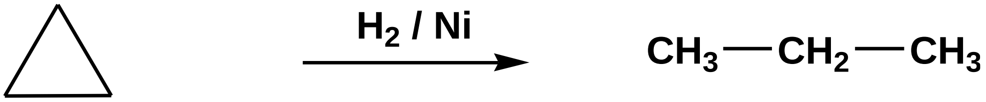
Equation 6.9

Mechanism;



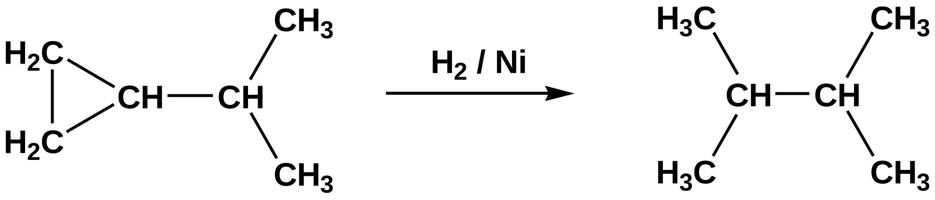
II- Chemical reactions of cyclopropane and its derivatives:

1. Hydrogenation: cyclopropane turns to propane when hydrogenated over nickel (Equation 6.10).



Equation 6.10

Hydrogenation of isopropylcyclopropane affords 2,3-dimethylbutane (Equation 6.11).



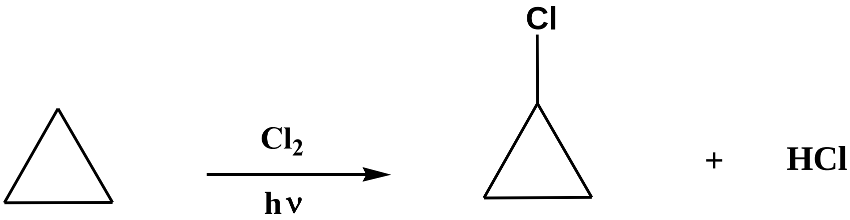
2,3-dimethyl-butane

Equation 6.11

2. Halogenation: Bromination of the cyclopropane affords 1,3-dibromocyclopropane (Equation 6.12).

Equation 6.12

Chlorination of cyclopropane takes place a replacement of hydrogen (Equation 6.13).

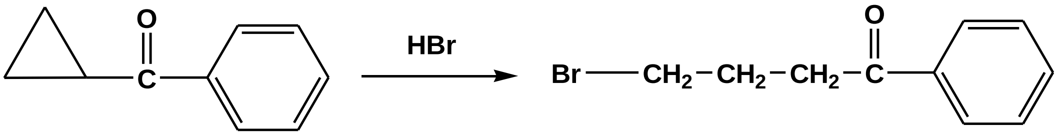


Equation 6.13

3. Hydrohalogenation: Hydrogen bromide reacts with cyclopropane to yield the bromopropane (Equation 6.14).

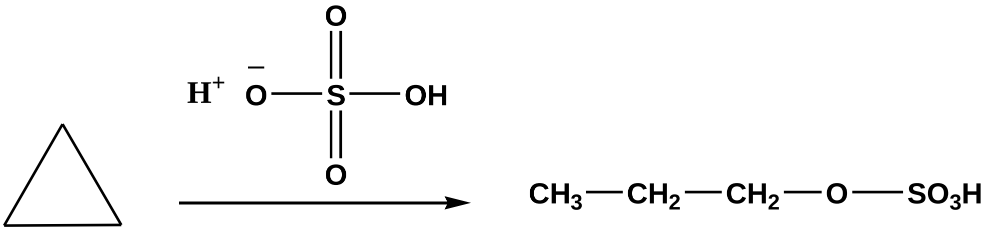
Equation 6.14

Action of hydrogen bromide to benzoylcyclopropane proceeds contrary to Markonikov's rule (Equation 6.15).



Equation 6.15

4. Action of strong mineral acids: Cyclopropane reacts with sulphuric acid to give sulphuric acid monopropyl ester (Equation 6.16).



Equation 6.16

Unit 3

Lesson 7: Cyclobutane and its derivatives

7.1 Physical properties of cyclobutane: C_4H_8, b.p.= 12.5^oC, with a molecular mass of 56.107g/mol, is a four carbon alkane in which all the carbon atoms are arranged cyclically. Cyclobutane is a gas and commercially available as a liquefied gas.

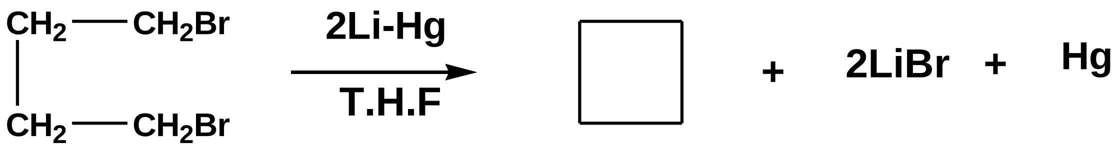
7.2 Chemical properties:

Several methods have been introduced to prepare cyclobutane and its derivatives as follows:

I- Methods of preparation:

1. Connor and Wilson reaction (1967):

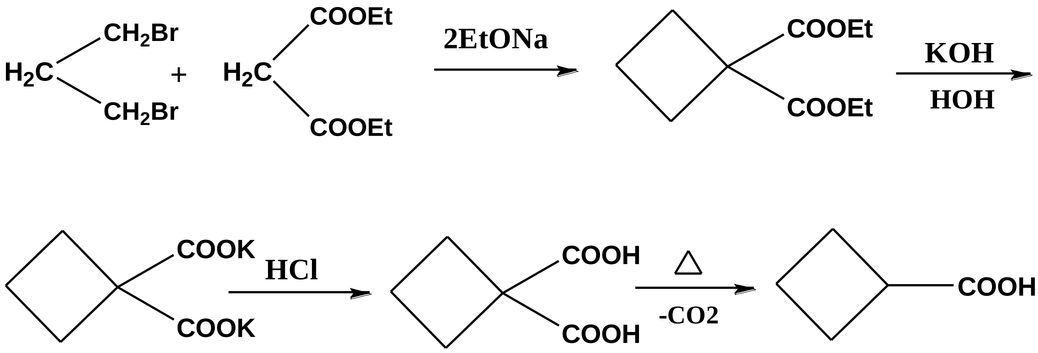
When 1,4-dibromobutane reacted with lithium amalgam in tetrahydrofuran, cyclobutane in a good yield was obtained (Equation 7.1).



Equation 7.1

2- Perkin's reaction:

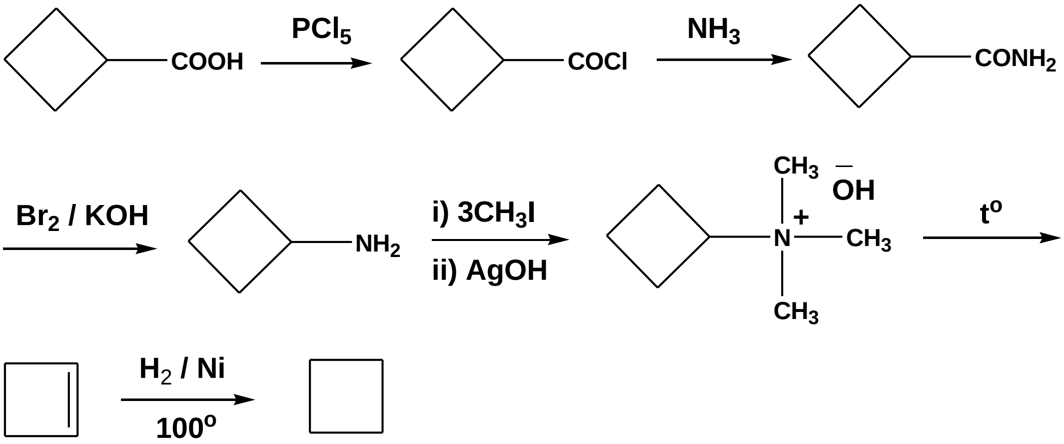
1,3-dibromobutane reacts with diethyl malonate in presence of sodium ethoxide to give cyclobutane dicarboxylic esters, which converts to cyclobutanecarboxylic acid (Equation 7.2).



Equation 7.2

3- From cyclobutanecarboxylic acid:

Attempts to decarboxylate of cyclobutanecarboxylic acid lead to opening of the ring, but it may be converting into cyclobutane by the following routs (Equation 7.3).



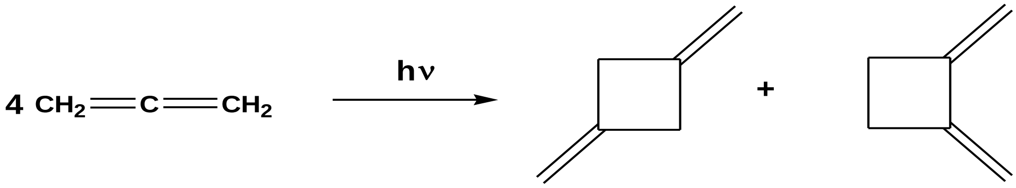
Equation 7.3

4- By photochemical reactions:

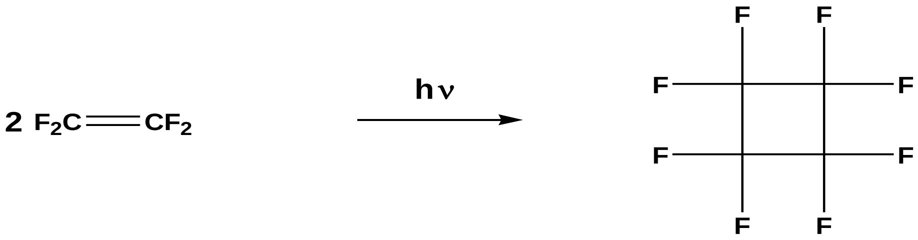
Cyclobutane or its derivatives can be prepared photochemically according to the following methods:

a- Dimerization of allenes or perfluoro olefins:

Photolysis of allenes or perfluoro olefins leads to formation of cyclobutane derivatives (Equations 7.4 and 7.5).

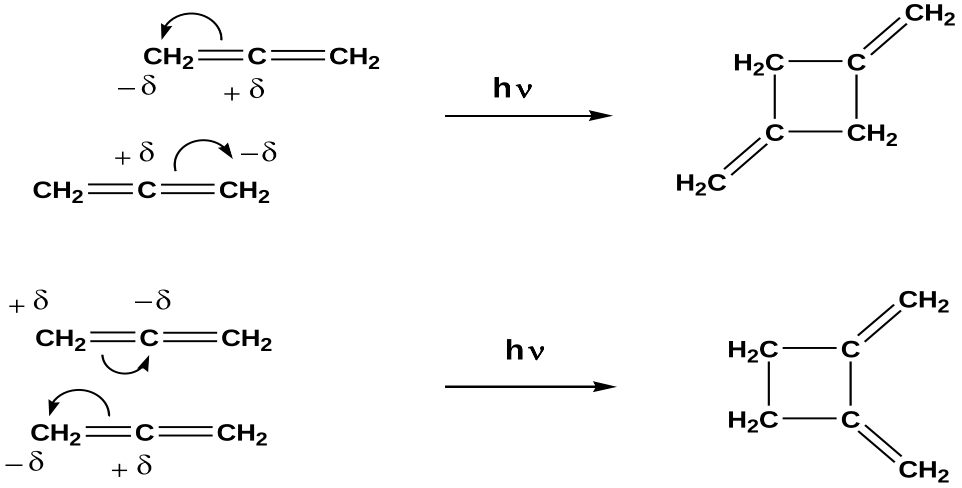


Equation 7.4



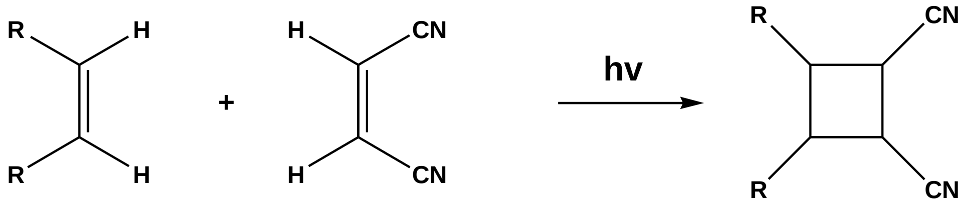
Equation 7.5

The reaction Mechanism;

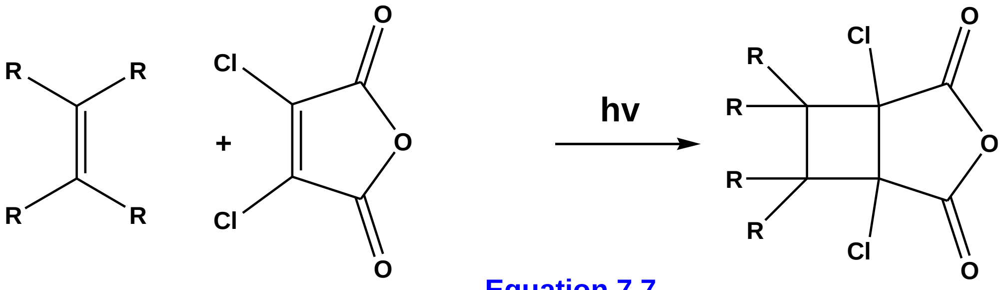


b- Olefin- Olefin addition:

Under the action of irradiated light, olefins such as maleic anhydride and some other dienophiles are capable to adding on to olefin to form 4-membered rings (Equations 7.6 and 7.7).



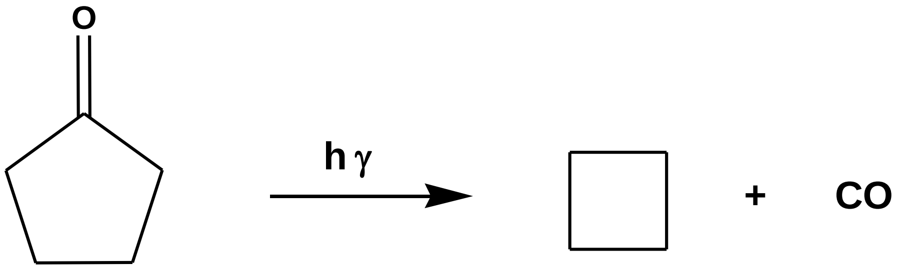
Equation 7.6



Equation 7.7

c- Proteolysis of cyclopentanone:

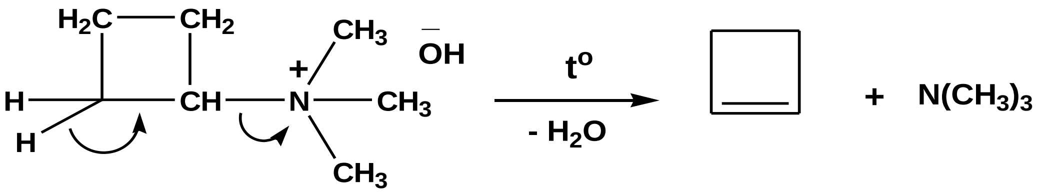
cyclobutane and carbon monoxide are the products of the proteolysis of cyclopentanone (Equation 7.8).



Equation 7.8

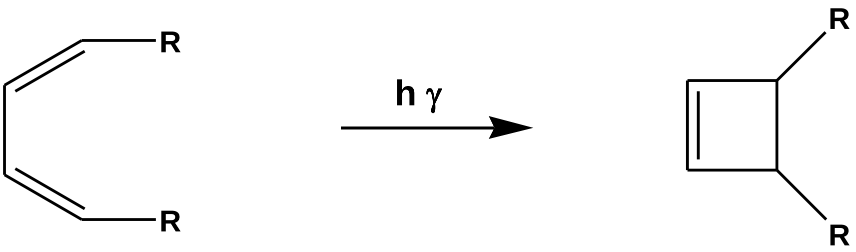
5- Preparation of cyclobutenes:

Decomposition of cyclobutyl trimethyl ammonium hydroxide gives the cyclobutene (Equation 7.9).



Equation 7.9

Irradiation of 1,3-dienes by ultraviolet rays affords cyclobutene derivatives (Equation 7.10).

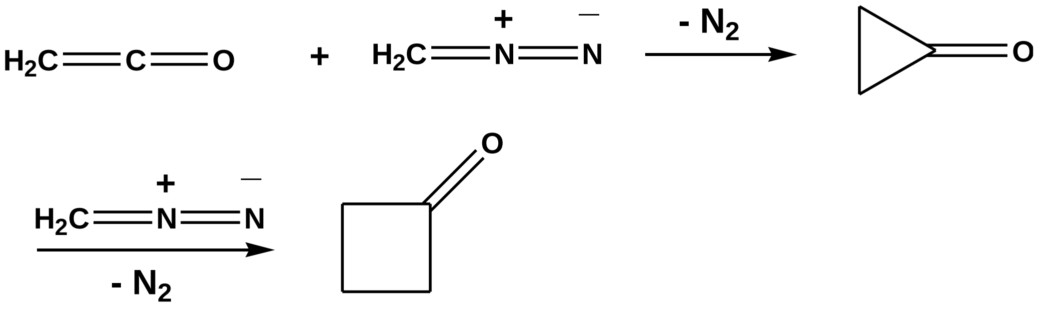


Equation 7.10

6- Carbonyl compounds of cyclobutane:

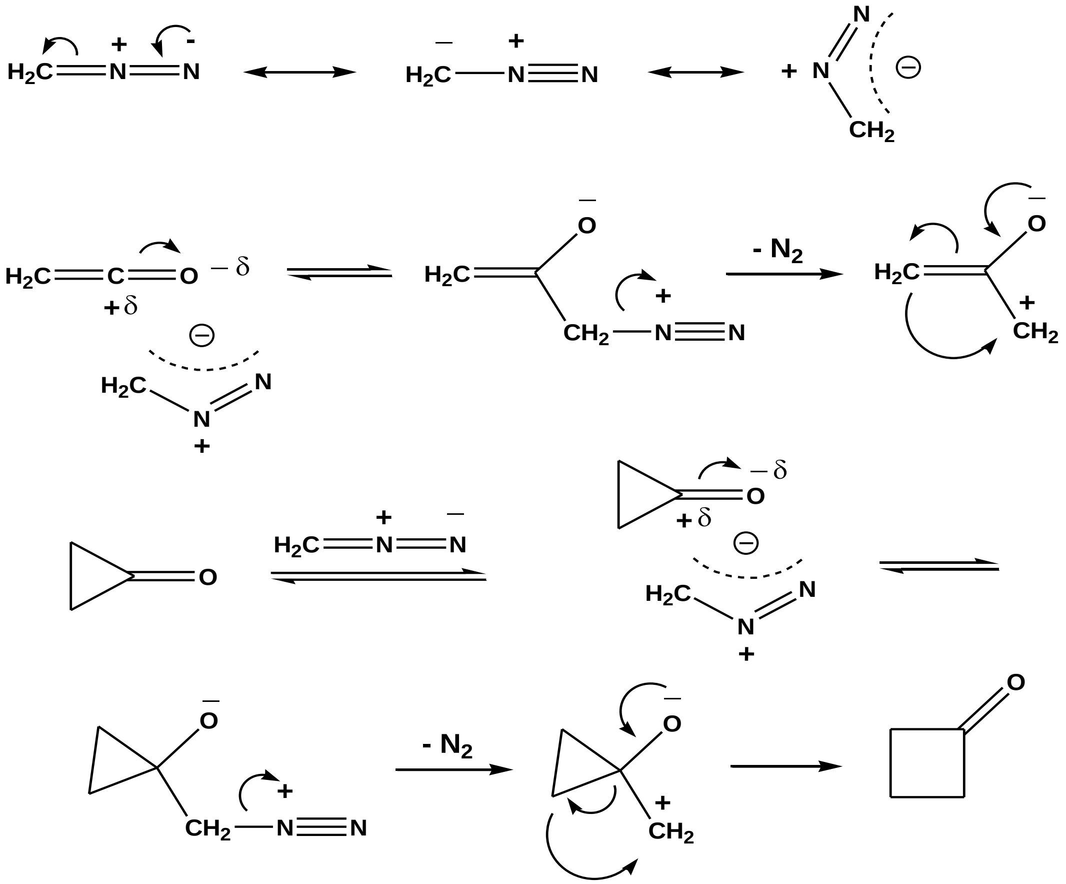
a- Cyclobutanone:

When diazomethane reacted with ketene, cyclobutanone was obtained through the stage of formation of cyclopropanone (Equation 7.11).



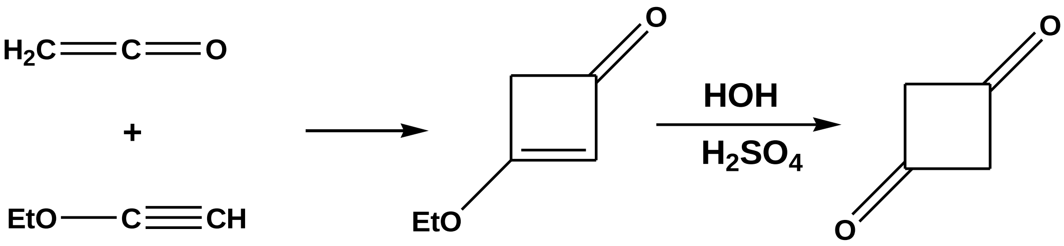
Equation 7.11

The reaction mechanism;

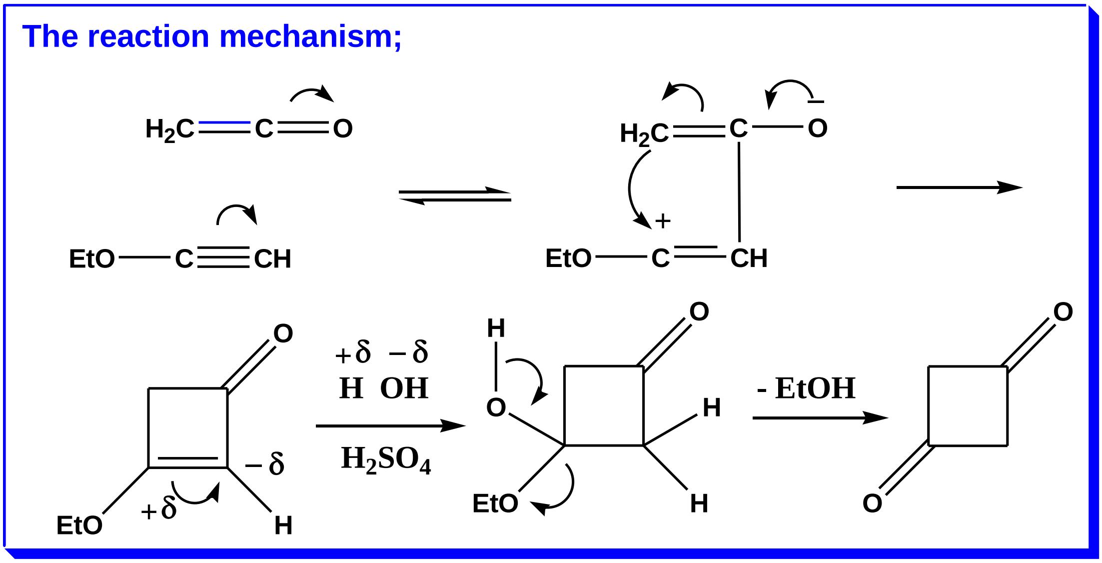


b- Cyclobutanedione:

Cyclobutane-1,3-dione was obtained as follows (Equation 7.12).

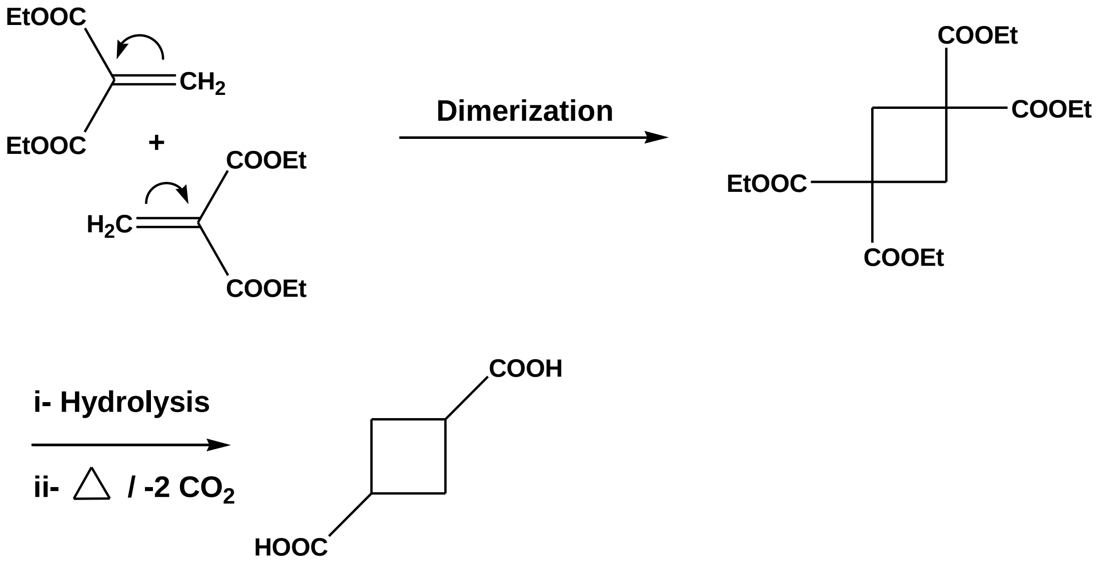


Equation 7.12



7- Cyclobutanecarboxylic acids:

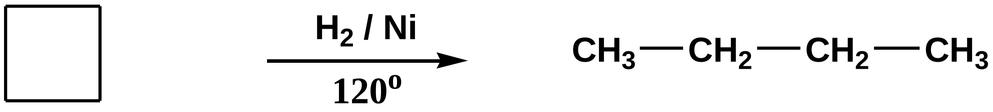
Cyclobutane-1,3-dicarboxylic acid as an example was prepared by the dimerization of 2-methylene-malonic acid diethyl ester (Equation 7.13).



Equation 7.13

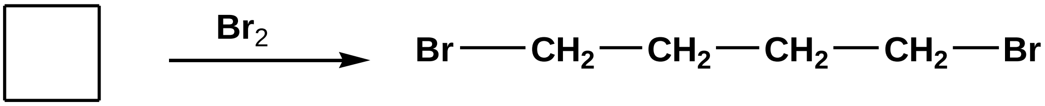
II- Chemical reactions of cyclobutane and its derivatives:

1- Hydrogenation: cyclobutane converted to butane under the action of hydrogen over nickel at 120° (Equation 7.14).



Equation 7.14

2- Halogenation: Bromination of the cyclobutane gives 1,4-dibromobutane (Equation 7.15).

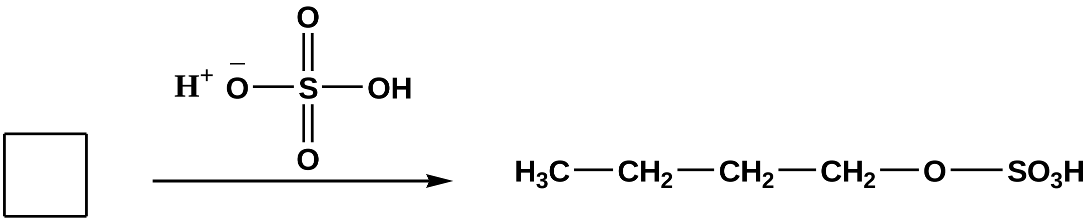


Equation 7.15

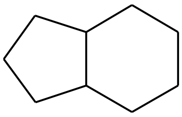
3- Hydrohalogenation: Cyclobutane reacts with hydrogen bromide to give the bromobutane (Equation 7.16).

Equation 7.16

5. **Action of strong mineral acids:** When sulphuric acid reacts with cyclobutane, sulphuric acid monobutyl ester was obtained (Equation 7.17).



Equation 7.17



Unit 4

Lesson 8: Cyclopentane and its derivatives

8.1 Physical properties of cyclopentane: C_5H_{10}, cyclopentane is a gas with bp. 49.5 ^oC and its molecular mass 70.1 g/mol. Petroleum contains a great variety of hydrocarbons, Markonikove and Ogloblin succeeded in isolating cyclopentane from petroleum, where the major proportion of naphthenes consists of cyclopentane and its homologues.

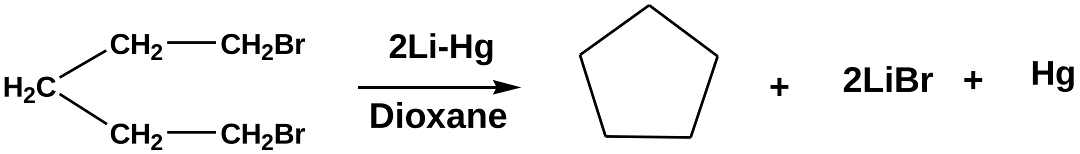
8.2 Chemical properties:

Several methods for the preparation of cyclopentane and its derivatives have been introduced as follows:

I- Methods of preparation:

1. Connor and Wilson reaction:

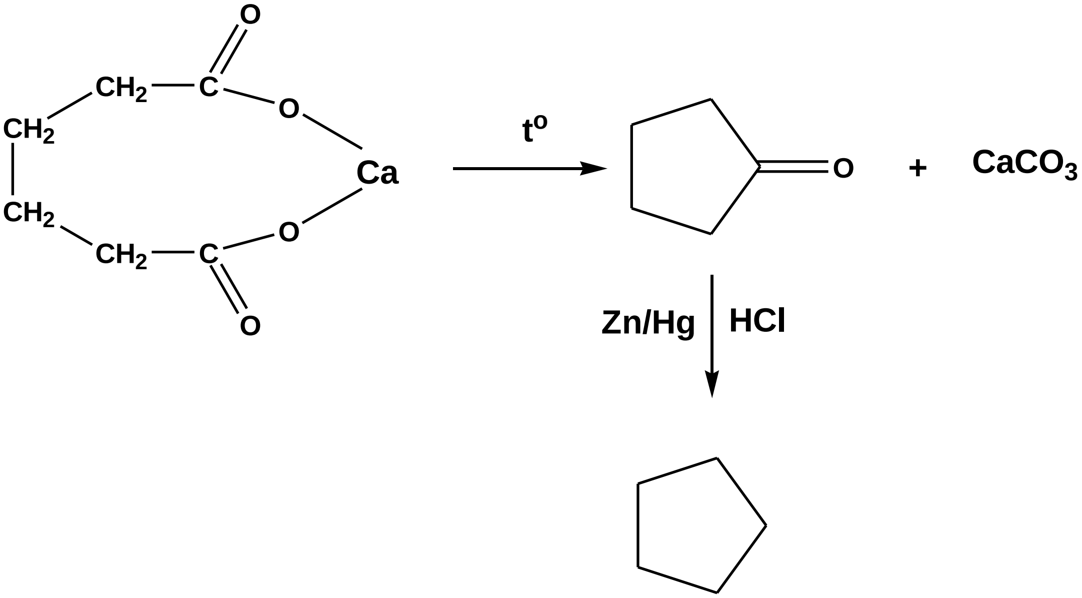
Action of lithium amalgam on a dioxane solution of 1,5-dibromopentane can give cyclopentane in 75% yield (Equation 8.1).



Equation 8.1

2. Pyrolysis of calcium salt of adipic acid:

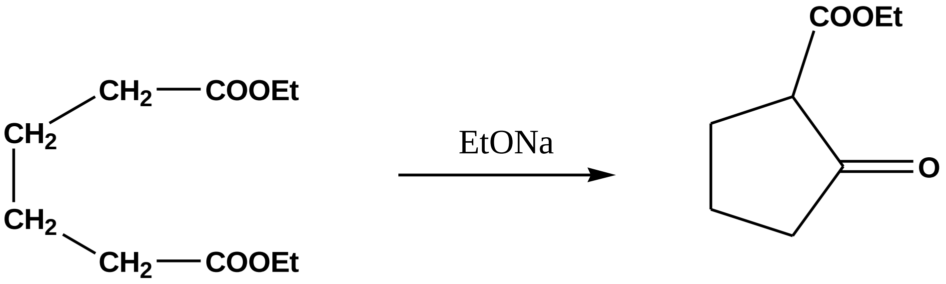
This method can be used to synthesize cyclopentanone with good yield under pyrolysis of the calcium adipate. Cyclopentanone may be converted into cyclopentane by means of the Clemmenson reduction (Equation 8.2).



Equation 8.2

3. Dieckmann condensation:

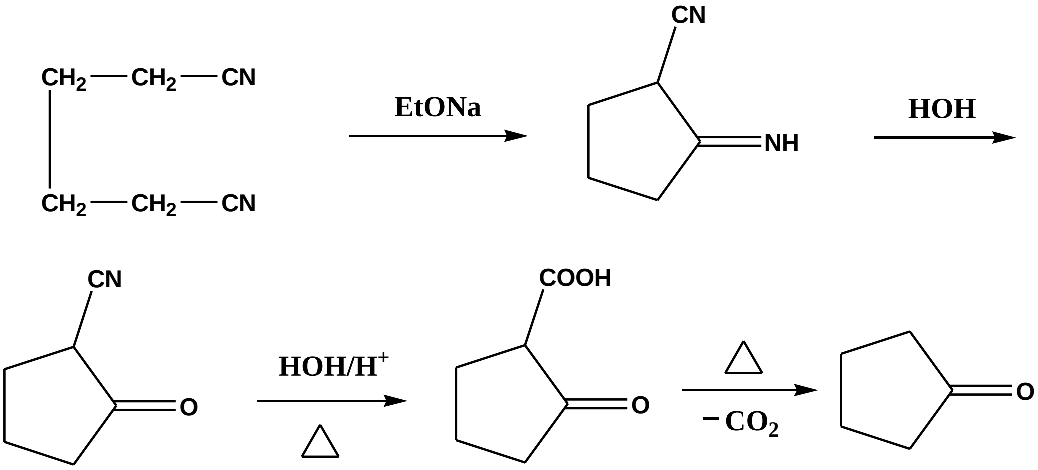
Treatment of diethyl adipate with excess of sodium ethoxide can give 2-cyclopentanonecarboxylic acid ethyl ester (Equation 8.3).



Equation 8.3

4. Ziegler-Thorpe reaction:

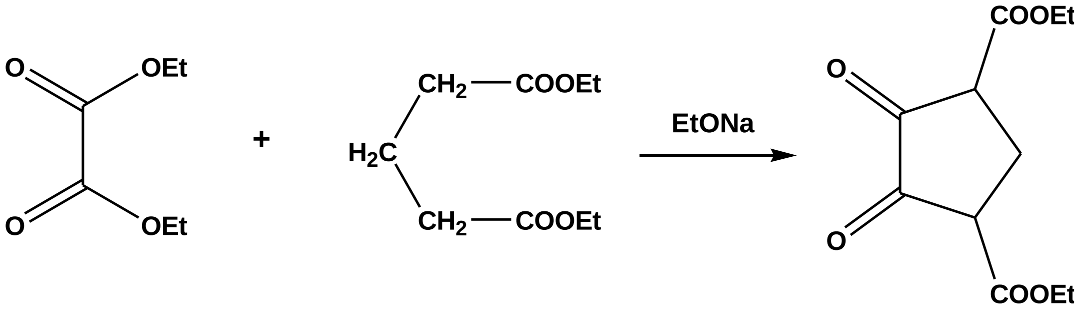
Condensation of hexanedinitrile in presence of sodium ethoxide gives 2-cyclopentanonecarbonitrile, which up-on hydrolysis affords 2-cyclopentanonecarboxylic acid. Decarboxylation of the later gives cyclopentanone (Equation 8.4).



Equation 8.4

5. Condensation of oxalic ester with glutatric ester:

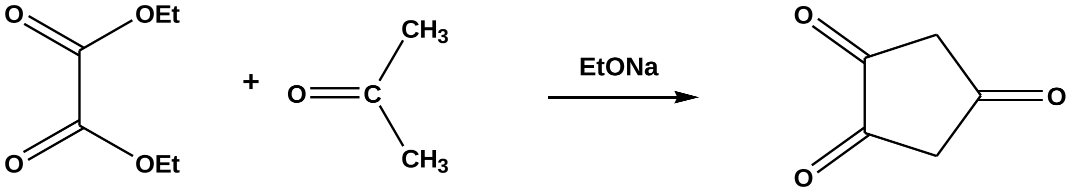
Treatment of ethyl oxalate with ethyl glutrate in presence of sodium ethoxide gives cyclopentan-4,5-dione-1,3-dicarboxylic acid diethyl ester (Equation 8.5).



Equation 8.5

6. Condensation of oxalic ester with acetone:

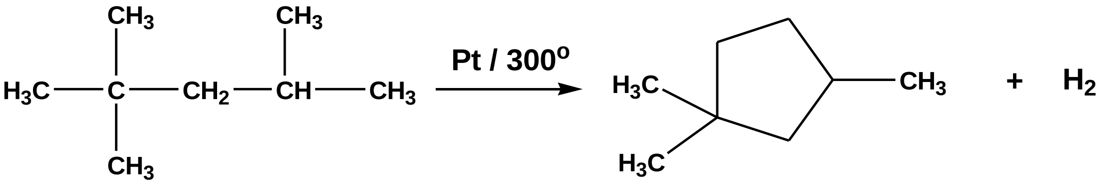
Treatment of acetone with ethyl oxalate in presence of sodium ethoxide gives cyclopentane-1,2,4-trione (Equation 8.6).



Equation 8.6

7. Dehydrocyclization of hydrocarbon chains:

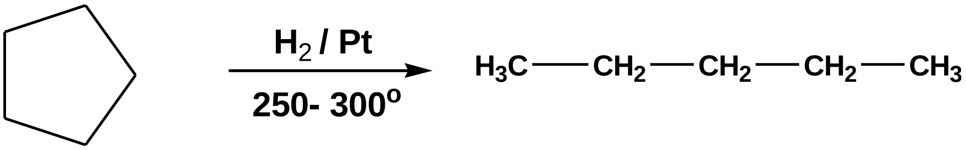
When a five carbon atoms chain contains a quaternary carbon atom is passed over a platinium catalyst at 300 ^oC, cyclopentane derivative was obtained (Equation 8.7).



Equation 8.7

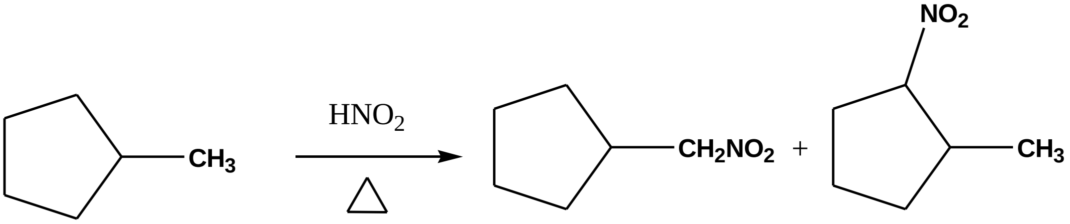
II- Chemical reactions of cyclopentane and its derivatives:

1. Hydrogenation: cyclopentane undergoes hydrogenation over platinium at 250-300 °C to form pentane (Equation 8.8).



Equation 8.8

2. Nitration: cyclopentane and its derivatives can be nitrated, e. g., nitration of methylcyclopentane yields two products (Equation 9.9).

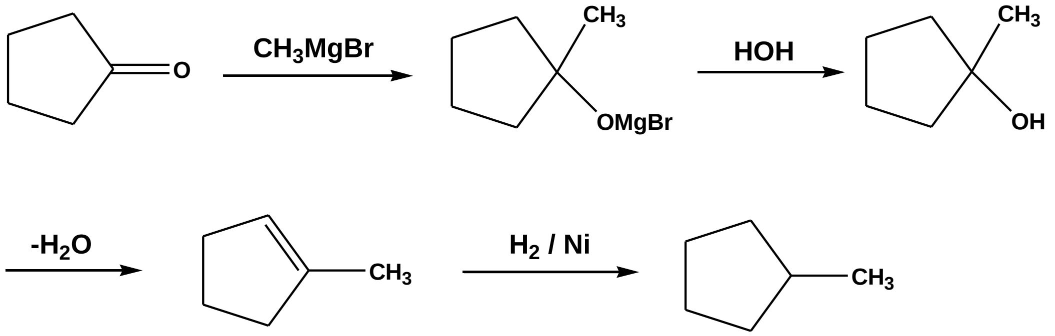


Equation 8.9

3. Cyclopentanone:

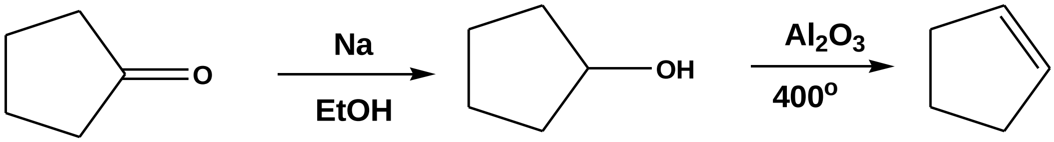
a- Grignard reaction: treatment of cyclopentanone with Grignard reagent (CH_3MgBr) followed by hydrolysis gives 1-

methyl-cyclopentanol. The later lose a molecule of water to give 1-methyl-cyclopentene, which on hydrogenation gives methylcyclopentane (Equation 8.10).



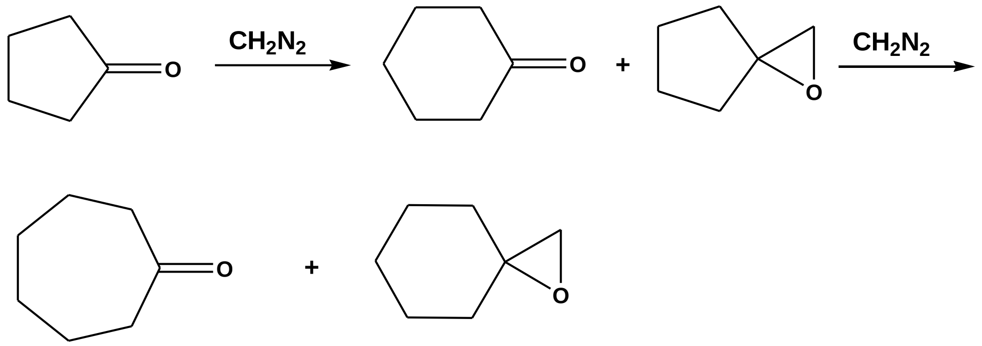
Equation 8.10

b- Reduction of cyclopentanone: With sodium in alcohol gives cyclopentanol, which up-on heating to 400 °C in presence of **Al_2O_3** lose a molecule of water to give cyclopentene (Equation 8.11).



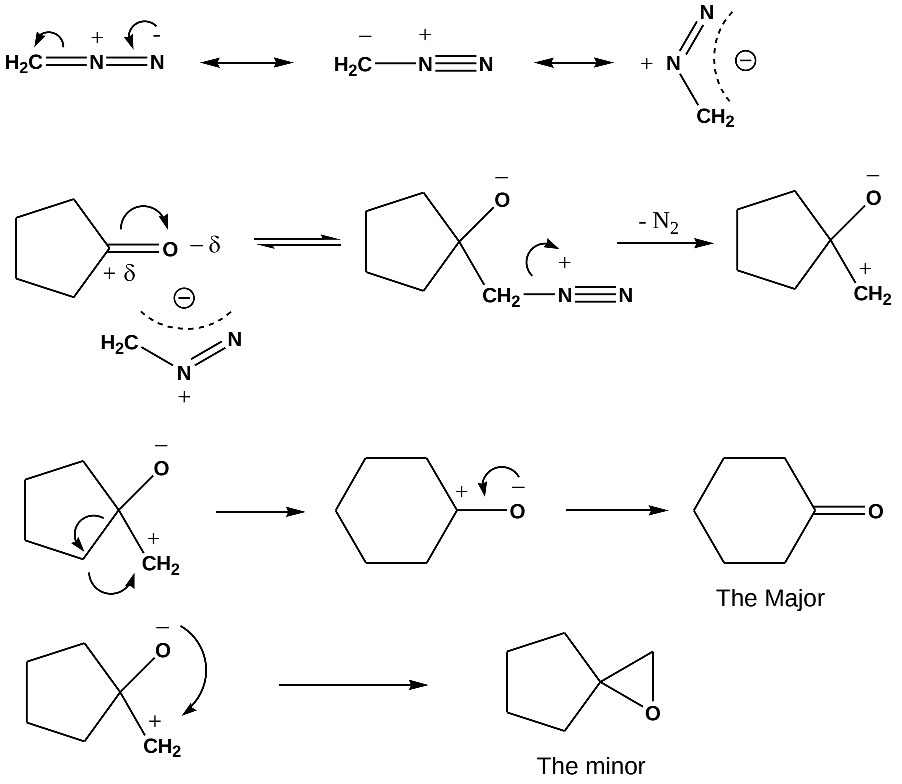
Equation 8.11

c- Treatment of cyclopentanone with diazomethane: undergoes ring expansion to form cyclohexanone, which reacts with diazomethane to form cycloheptanone and 1-oxa-spiro[2,5]octane (Equation 8.12).



Equation 8.12

The reaction mechanism;



4. Cyclopentadiene:

Cyclopentadiene is found in the crude benzene that is obtained from coal-tar.

The hydrogen atoms of methylene group are very reactive, e. g., treatment of cyclopentadiene with sodium gives sodium cyclopentadienide as shown in following figure (8.13);

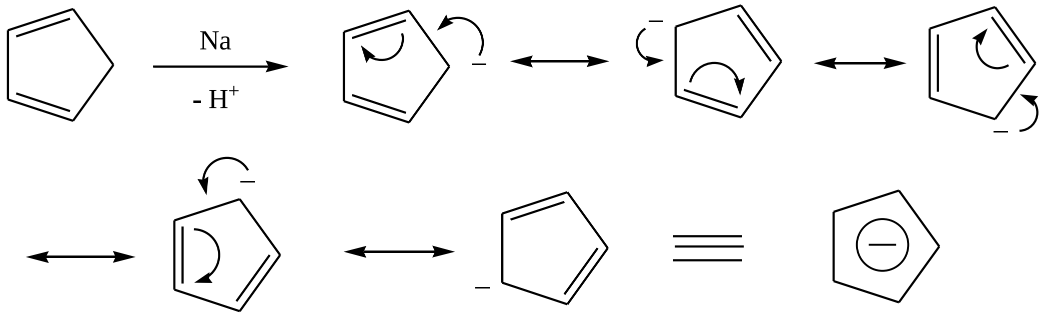
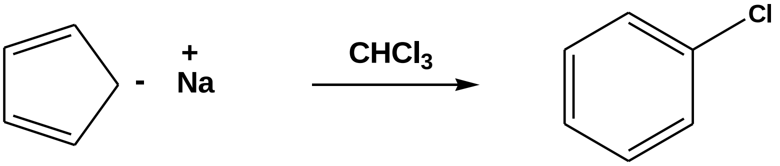


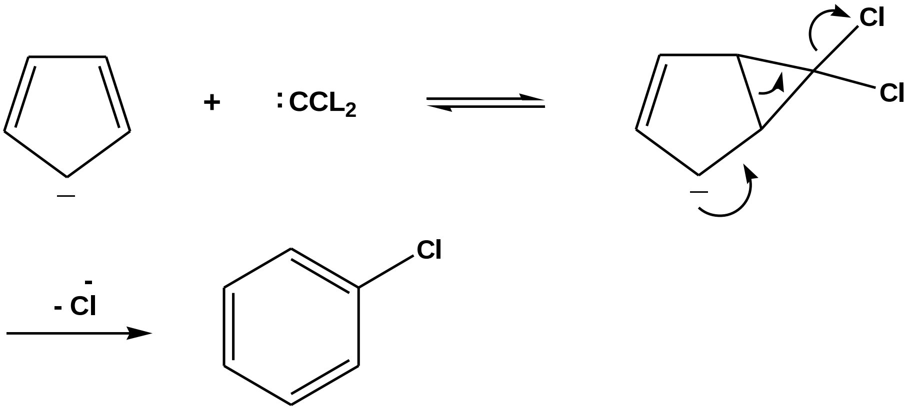
Figure 8.13

a- Cyclopentadienyl sodium: reacts with chloroform to give chlorobenzene (Equation 8.14).

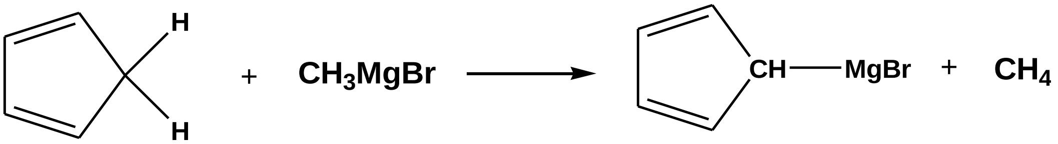


Equation 8.14

The reaction mechanism;

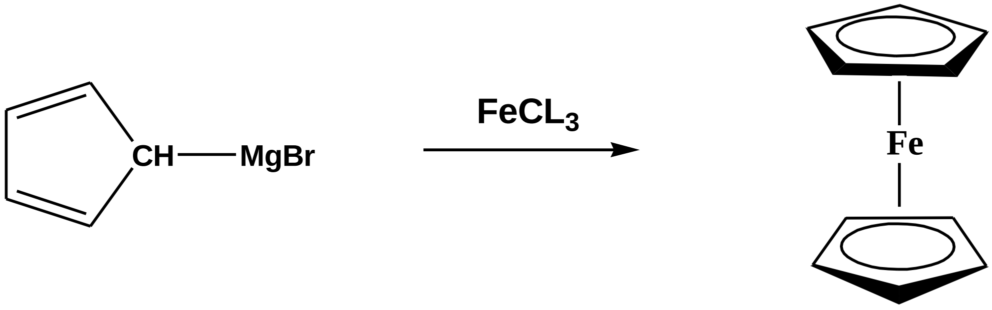


b- Grignard reaction: cyclopentadiene reacts with Grignard reagents to form cyclopentadienyl magnesium halide and the corresponding hydrocarbon (Equation 8.15).



Equation 8.15

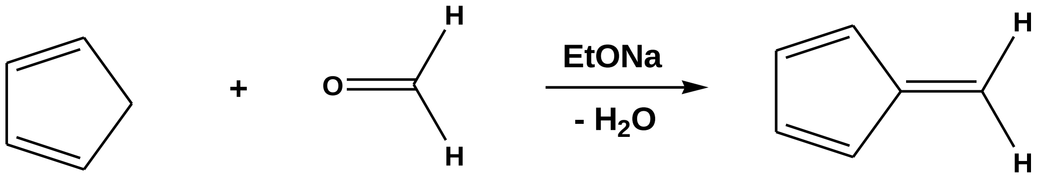
When cyclopentadienyl magnesium bromide reacts with ferric chloride, dicyclopentadienyl iron was isolated. This iron (Fe II) complex was named *ferrocene* by Woodward *et al* (Equation 8.16).



Ferrocene

Equation 8.16

c- Condensation reactions: cyclopenta-1,3-diene condenses with aldehydes or ketones in presence of sodium ethoxide to afford *fluvenes* (Equation 8.17).



Equation 8.17

d- Dimerization: cyclopentadiene dimerizes into dicyclopentadiene, which regenerates the monomer on heating (Equation 8.18).

Equation 8.18

Unit 4

Lesson 9: Cyclohexane and its derivatives

9.1 Physical properties of cyclohexane: C_6H_{12}, cyclohexane is a colorless liquid. It is a cyclic alkane that melts at 6°C and boils at 81°C. It is insoluble in water. Cyclohexane is found naturally to some extent in petroleum and is widely used as a solvent and in making certain compounds used in the preparation of nylon.

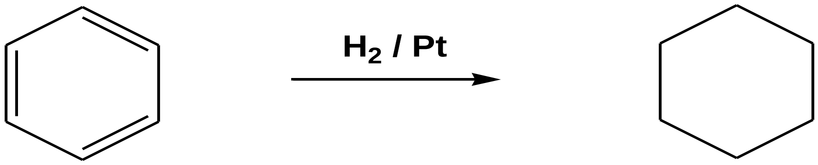
9.2 Chemical properties:

Many methods for the preparation of cyclohexane and its derivatives have been introduced as follows:

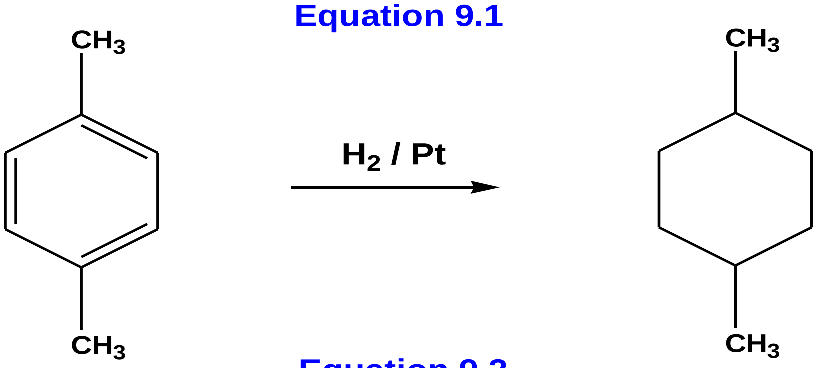
I- Methods of preparation:

1. Hydrogenation of benzene and its derivatives:

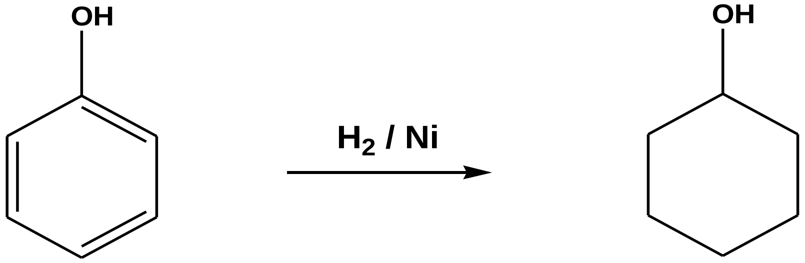
Cyclohexane is prepared commercially by catalytic hydrogenation of benzene. Certain derivatives of cyclohexane are mainly prepared by catalytic hydrogenation of certain aromatic compounds over platinum or nickel (Equations 9.1-9.4).



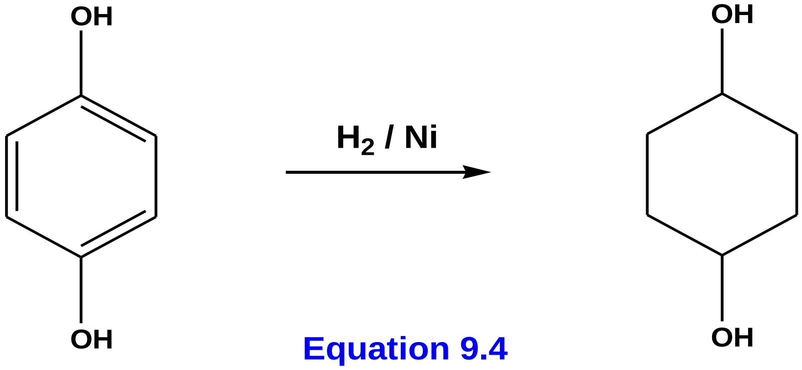
Equation 9.1



Equation 9.2



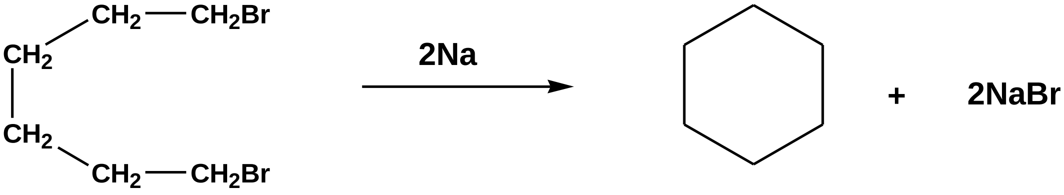
Equation 9.3



Equation 9.4

2- Freund reaction:

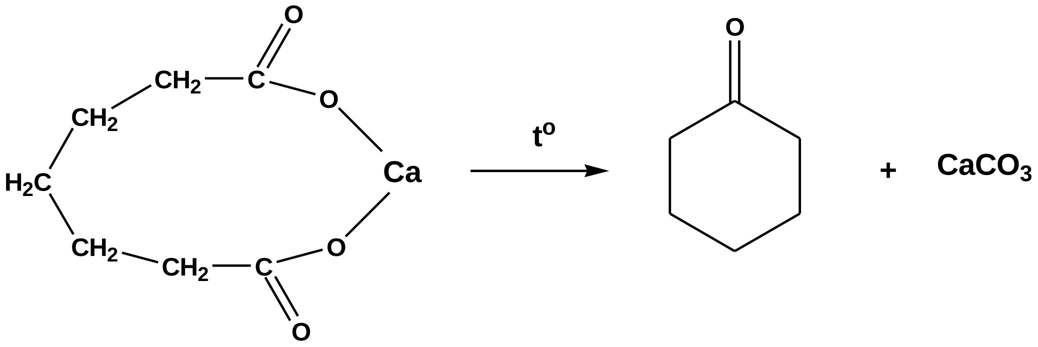
Treatment of 1,6-dibromohexane with a metal like sodium or zinc gives cyclohexane (Equation 9.5).



Equation 9.5

3. Pyrolysis of calcium salt of pimelic acid:

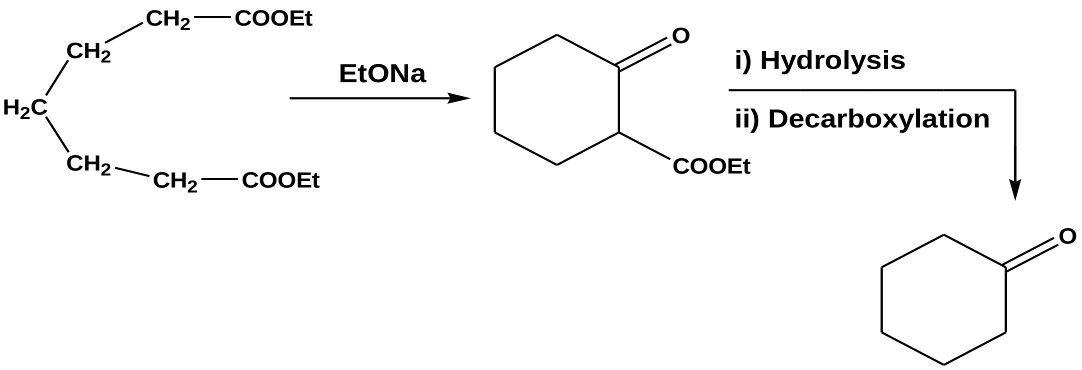
Cyclohexanone can be obtained under the pyrolysis of calcium pimelate (Equation 9.6).



Equation 9.6

4. Dieckmann condensation:

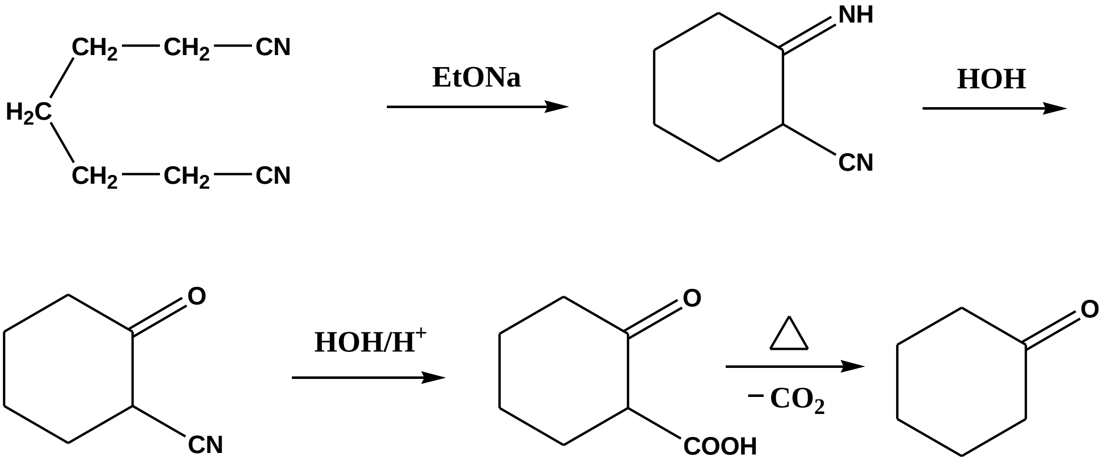
Treatment of diethyl pimelate with sodium ethoxide can give 2-cyclohexanonecarboxylic acid ethyl ester, which upon hydrolysis and decarboxylation turns to cyclohexanone (Equation 9.7).



Equation 9.7

5. Ziegler-Thorpe reaction:

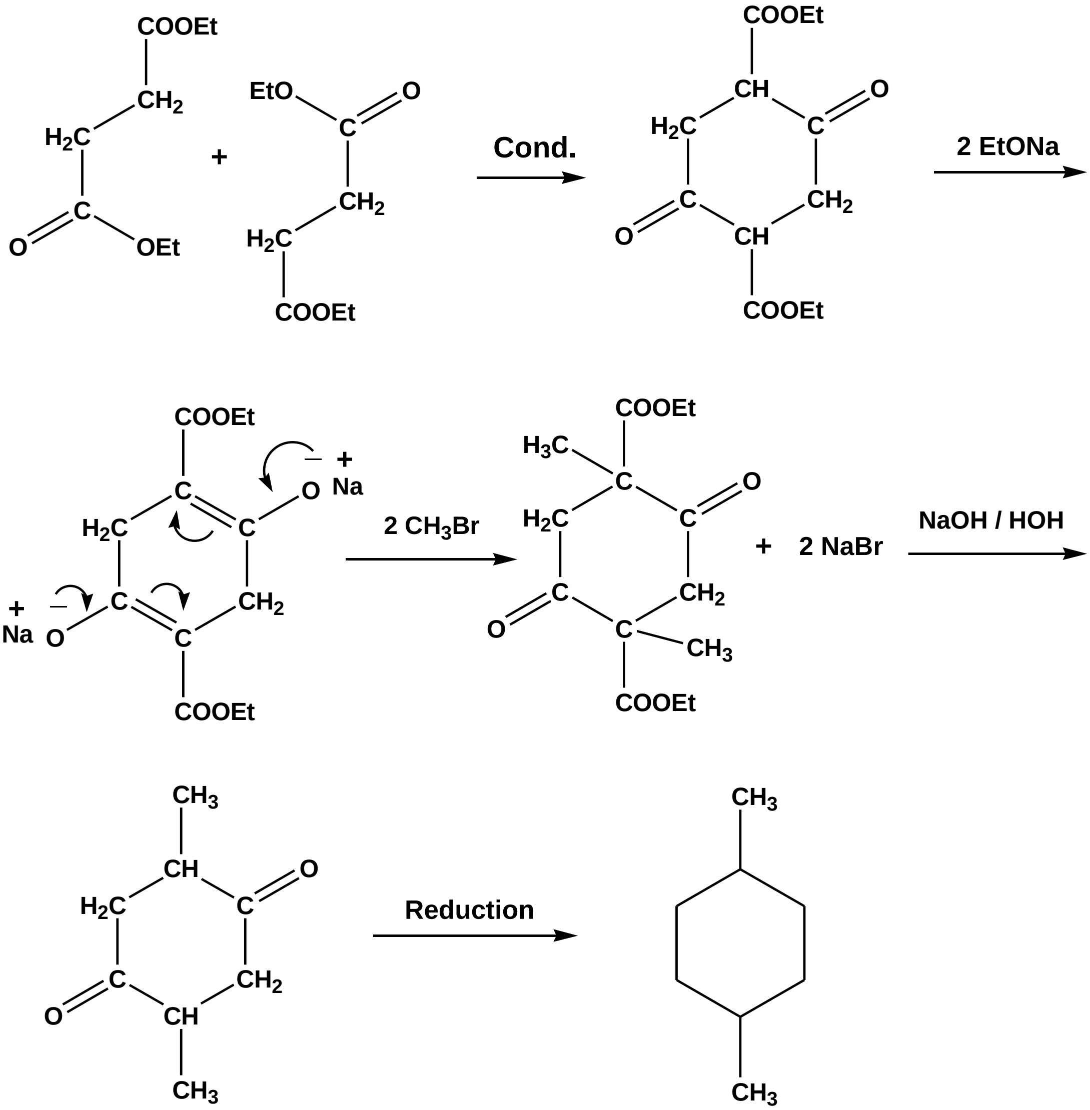
When heptanedinitrile treated with sodium ethoxide followed by hydrolysis affords 2-cyclohexanonecarbonitrile. After hydrolysis and decarboxylation of the later, cyclohexanone was obtained (Equation 9.8).



Equation 9.8

6. Ester condensation of succinic ester:

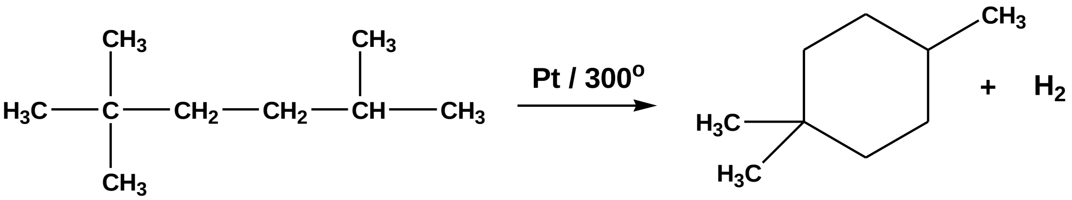
Condensation of two molecules of diethylsuccinate in presence of sodium ethoxide gives succinosuccinic ester. The sodium salt of the later was treated with alkyl halide followed by saponification and then finally Clemmenson reduction to afford 1,4-disubstituted-cyclohexane (Equation 9.9).



Equation 9.9

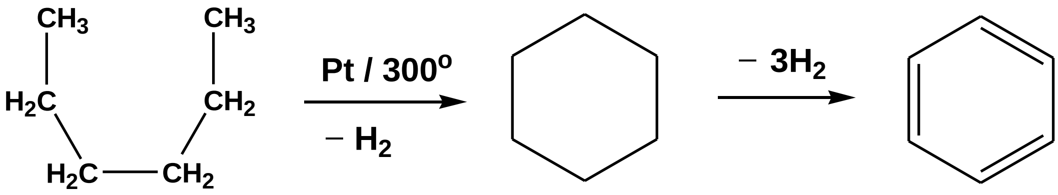
7. Dehydrocyclization of hydrocarbon chains:

When a six carbon atoms chain with a quaternary carbon atom is passed over a platinium catalyst at 300 °C, a six-membered ring was obtained (Equation 9.10).



Equation 9.10

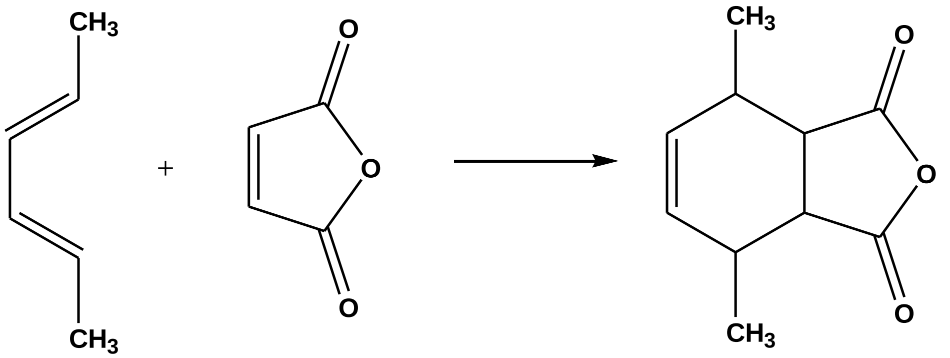
Absence of a quaternary carbon atom in the carbon chain makes the produced cyclohexane dehydrogenated to benzene (Equation 9.11).



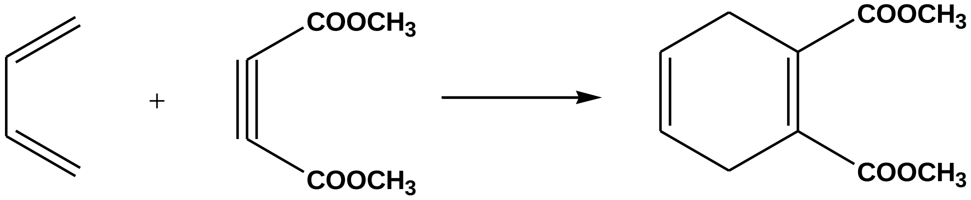
Equation 9.11

8. Diels-Alder reaction:

Six-membered rings with unsaturated bonds can be prepared by Diels-Alder reaction (Equations 9.12 and 9.13).



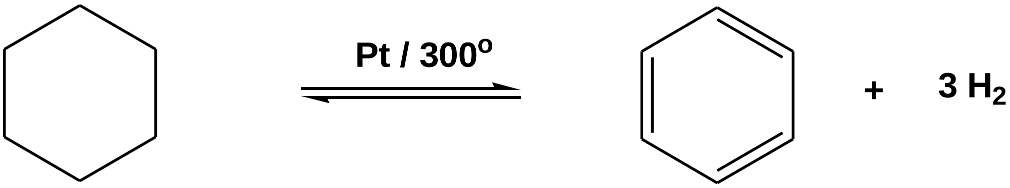
Equation 9.12



Equation 9.13

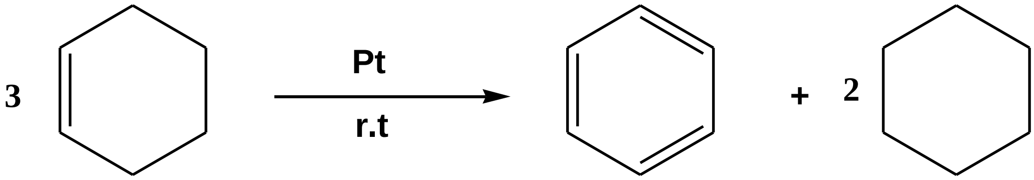
II- Chemical reactions of cyclohexane and its derivatives:

1. Deydrogenation reactions: In absence of hydrogen, cyclohexane can be dehydrogenated to benzene over platinum at about 300°C (Equation 9.14).



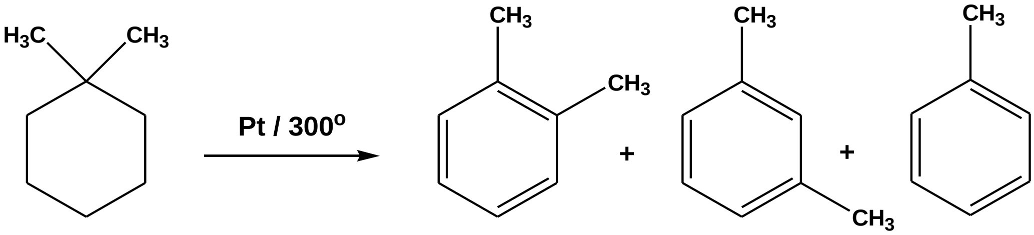
Equation 9.14

In the presence of platinum as a catalyst, cyclohexene even at room temperature disproportionate to benzene and cyclohexane as a result of an exothermic reaction (Equation 9.15).



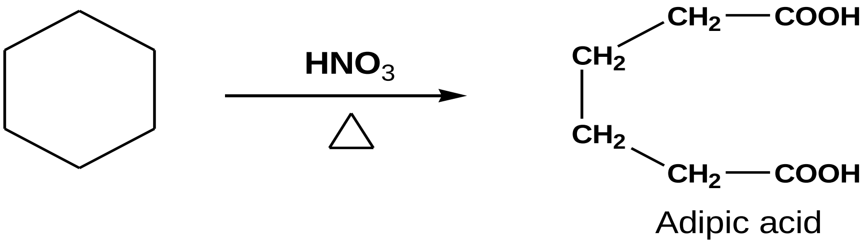
Equation 9.15

Dehydrogenation of 1,1-dimethylcyclohexane gives a mixture of *ortho*- and *meta*-xylenes, toluene and methane, where the dehydrogenation is accompanied by isomerization and elimination of one of the alkyl groups (Equation 9.16).



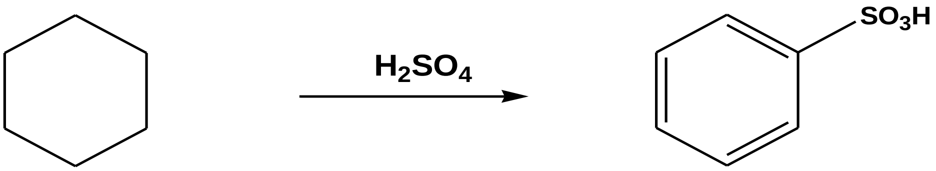
Equation 9.16

2. Nitration: in hot concentrated nitric acid, cyclohexane can be oxidized to adipic acid (Equation 9.17).



Equation 9.17

3. Sulphonation: fuming sulphuric acid converts cyclohexane into benzenesulphonic acid (Equation 9.18).

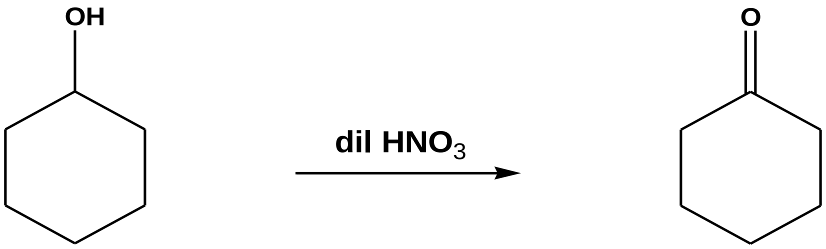


Benzenesulphonic acid

Equation 9.18

4. Cyclohexanol:

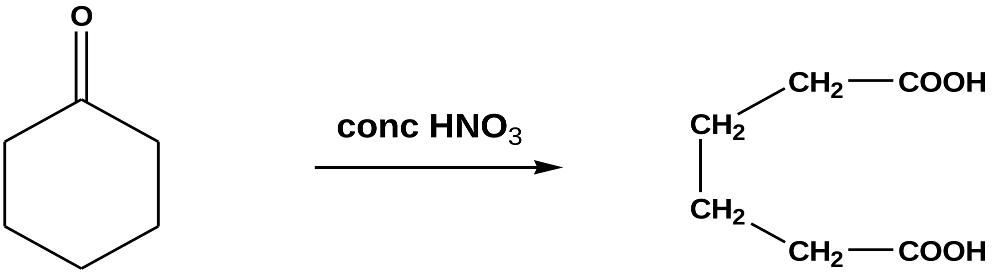
Cyclohexanol is converted by oxidation with dilute nitric acid into cyclohexanone (Equation 9.19).



Equation 9.19

5. Cyclohexanone:

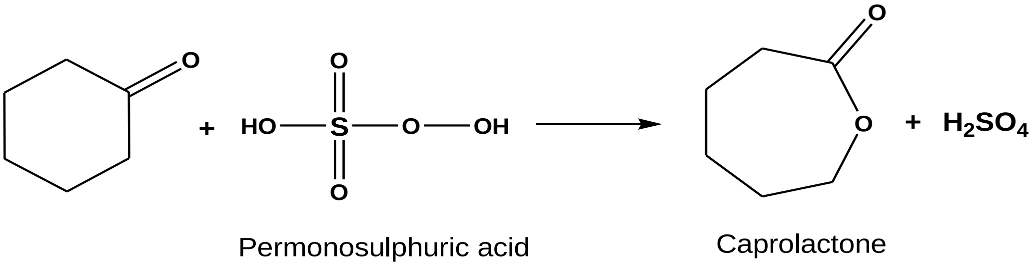
a- Oxidation with nitric acid: The vigorous oxidation of cyclohexanone with *conc* nitric acid produces adipic acid (Equation 9.20).



Adipic acid

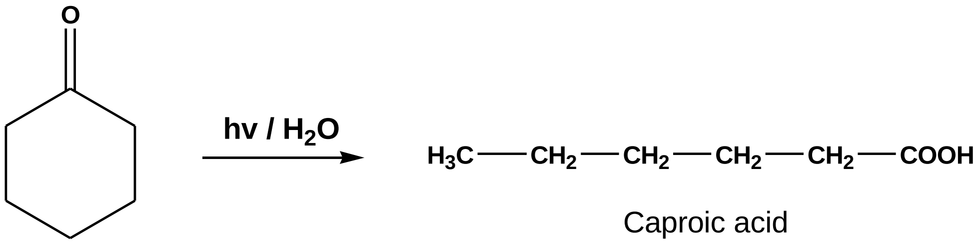
Equation 9.20

b- Oxidation with Caro's acid: cyclohexanone oxidized by Caro's acid (Permonosulphuric acid) to give the caprolactone (Oxepan-2-one) (Equation 9.21).



Equation 9.21

c- The influence of light: cyclohexanone is opened and gives caproic acid under the influence of light in presence of water (Equation 9.22).



Equation 9.22

Unit 4

Lesson 10: Cycloheptane and its derivatives

10.1 Physical properties of cycloheptane: C_7H_{14}, It is a cyclic alkane that melts at -12°C and boils at 118°C. Cycloheptane is found naturally in petroleum.

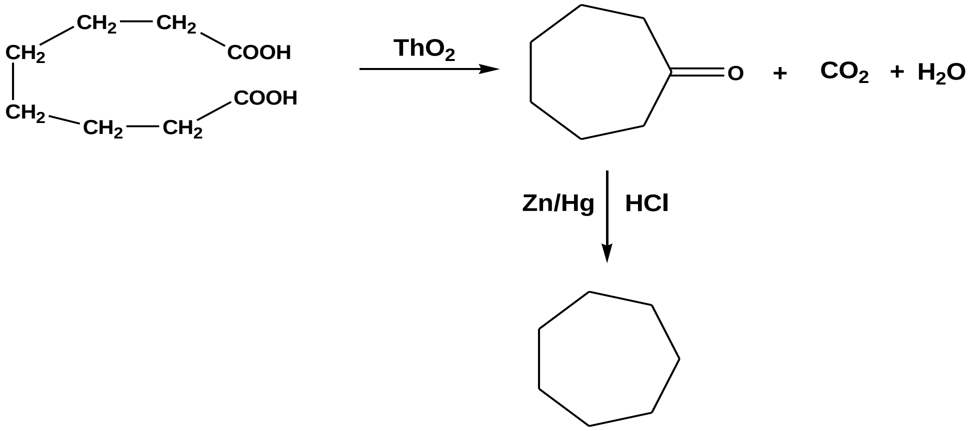
10.2 Chemical properties:

I- Methods of preparation:

The following methods are suitable for preparation of cycloheptane and its derivatives as follows:

1. Pyrolysis of dibasic acids:

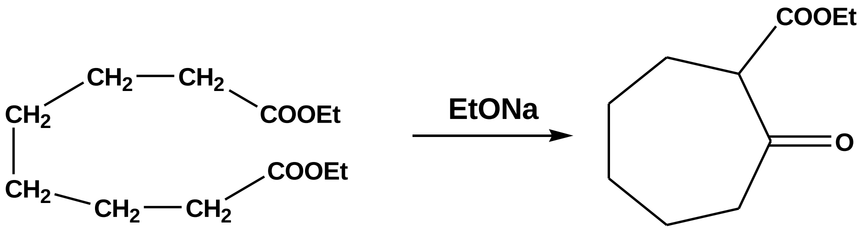
Pyrolysis of suberic acid over **ThO_2** gives cycloheptanone, which turns to cycloheptane by Clemmenson reduction (Equation 10.1).



Equation 10.1

2. Dieckmann condensation:

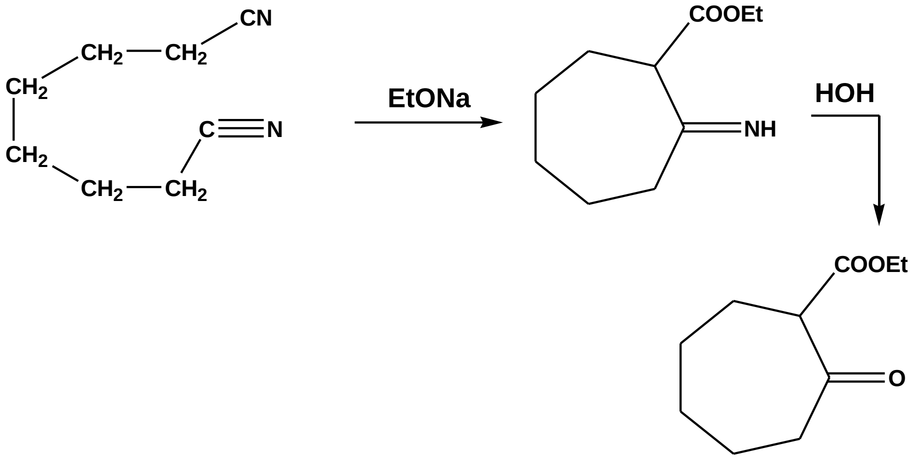
Ester condensation of octanedioic acid diethyl ester in a basic medium (sodium ethoxide) affords 2-cycloheptanonecarboxylic acid ethyl ester (Equation 10.2).



Equation 10.2

3. Thorpe reaction:

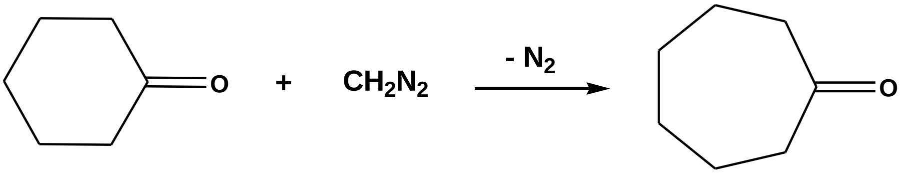
Condensation of octanedinitrile in presence of sodium ethoxide followed by hydrolysis affords 2-cycloheptanonecarbonitrile (Equation 10.3).



Equation 10.3

4. Action of diazomethane:

Suberone (cycloheptanone) can be prepared by the action of diazomethane on cyclohexanone in light, which an extension of six-membered ring to seven-membered one occurred (show the mechanism of this reaction in page (86)) (Equation 10.4).



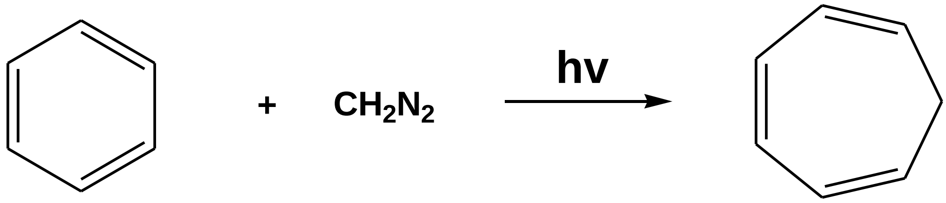
Equation 10.4

5. Synthesis of tropilidene:

Tropilidene (1,3,5-cycloheptatriene) may be prepared by two methods as follows:

a- Ring expansion of benzene:

Pyrolysis of diazomethane in presence of benzene undergoes ring expansion to give the tropilidene ring (Equation 10.5).

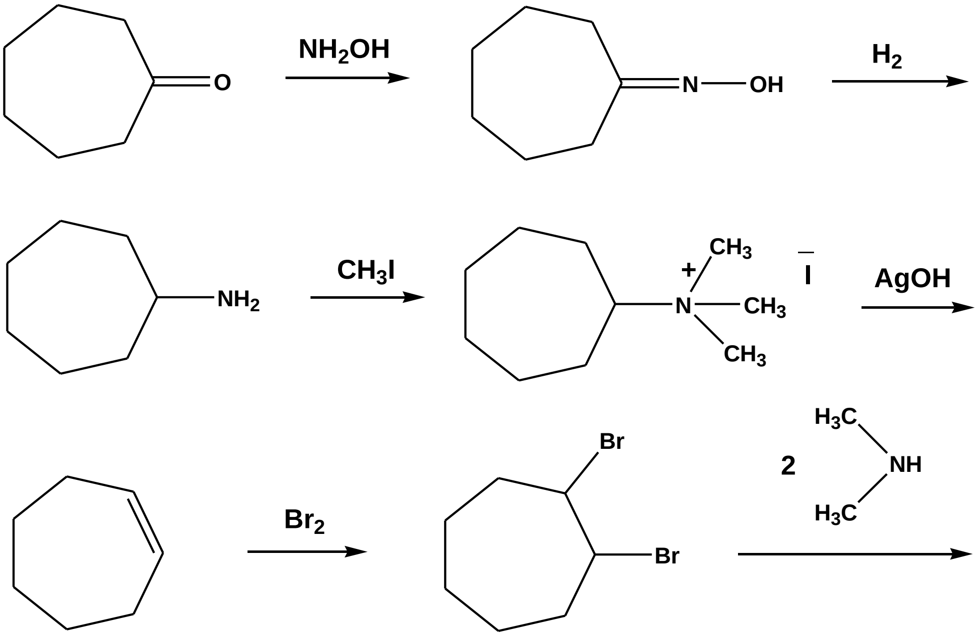


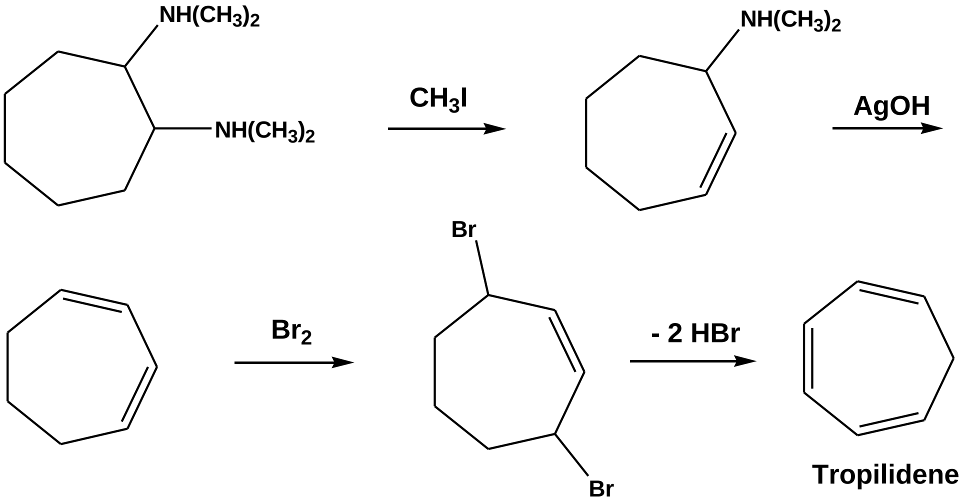
Tropilidene

Equation 10.5

b- From cycloheptanone:

Willstattler used cycloheptanone as starting material to prepare tropilidene according to the following (Scheme 10.6):





Scheme 10.6

Unit 4

Lesson 11: Alicyclic compounds with two or more Rings

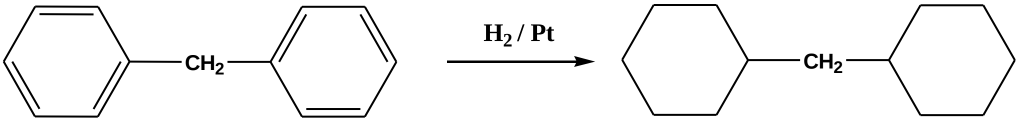
11.1 Bicyclic compounds with isolated rings.

❖ Methods of preparation:

The following methods are suitable for the preparation of this type of alicyclic compounds:

1- Hydrogenation:

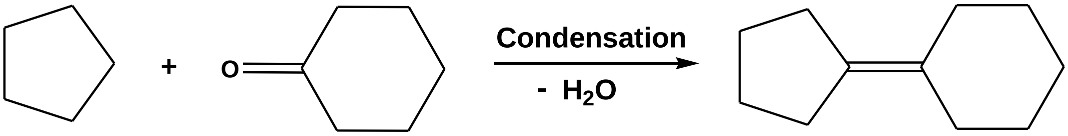
In presence of platinum as a catalyst, hydrogenation of certain aromatic compounds gave the corresponding bicyclic rings (Equation 11.1).



Equation 11.1

2- Condensation of cyclic aldehydes or ketones:

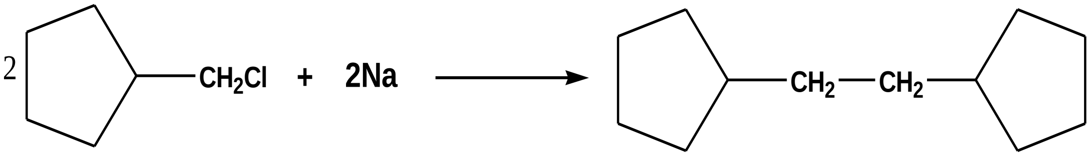
Cyclohexanone and cyclopentane may be condenses to give the cyclopentylidene-cyclohexane (Equation 11.2).



Equation 11.2

3- Wurtz reaction:

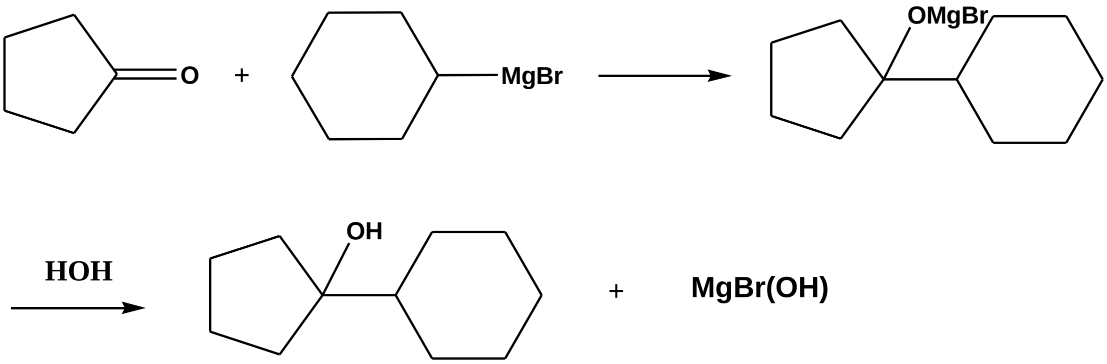
According to Wurtz reaction, the treatment of the chloromethyl-cyclopentane with sodium metal can give 1,2-dicyclopentyl-ethane (Equation 11.3).



Equation 11.3

4- By using organomagnesium compounds:

When cyclohexyl magnesium bromide treated with cyclopentanone, 1-cyclohexyl-cyclopentanol was obtained (Equation 11.4).

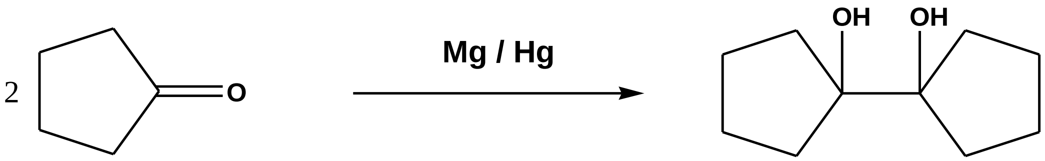


1-cyclohexyl-cyclopentanol

Equation 11.4

5- Reduction of cyclic ketones:

Cyclopentanone can be reduced by magnesium amalgam to give bicyclopentyl-1,1`-diol (Equation 11.5).



bicyclopentyl-1,1'-diol

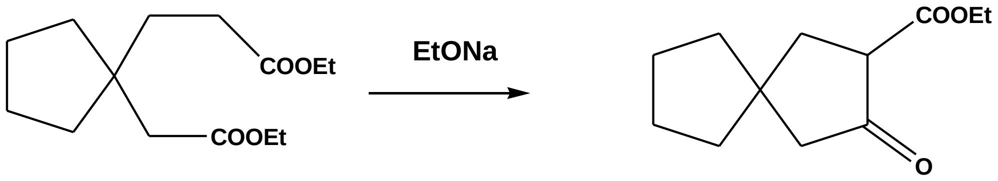
Equation 11.5

11.2 Spirans

Spirans are bicyclic structures in which two rings systems share one carbon atom.

Spirans can be prepared by ordinary methods of cyclization as the following examples:

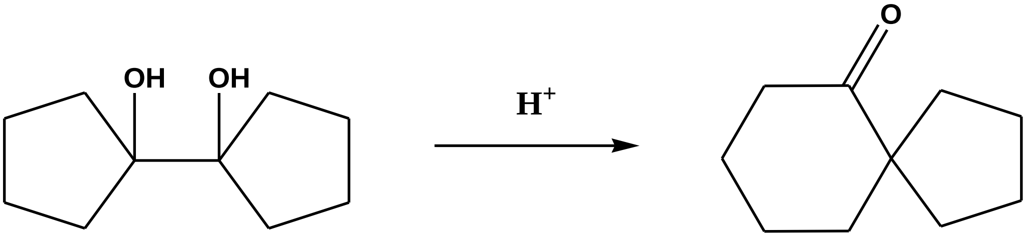
Example 1: (Equation 11.6).



3-Oxo-spiro[4.4]nonane-2-carboxylic acid ethyl ester

Equation 11.6

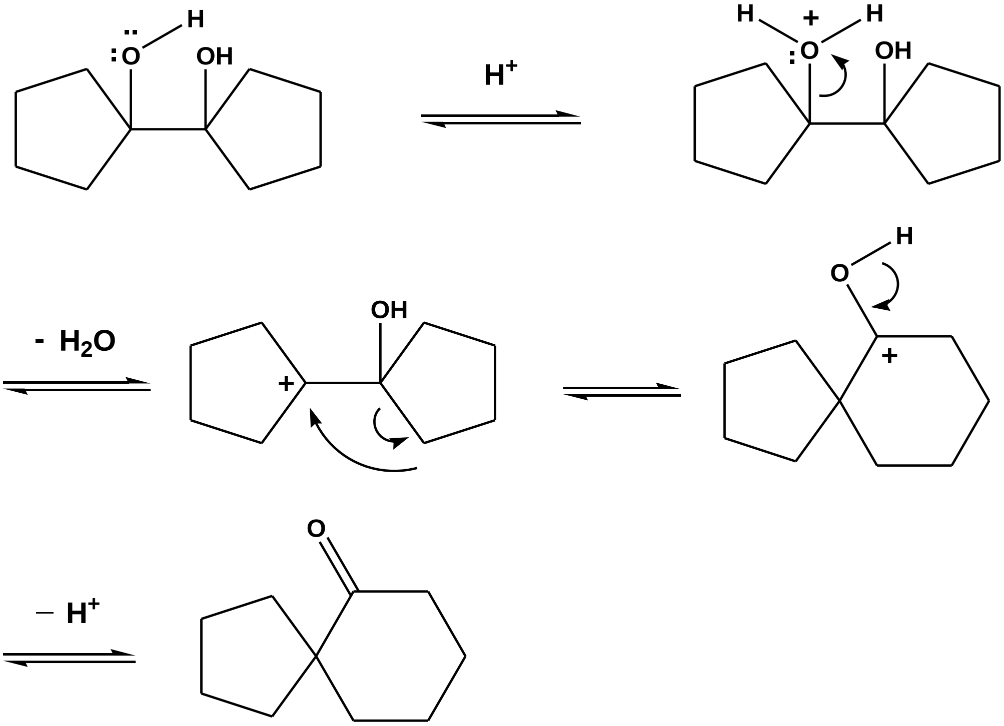
Example 2: Extension of the rings of certain bicyclic compounds (Equation 11.7).



Spiro[4.5]decan-6-one

Equation 11.7

The reaction mechanism;



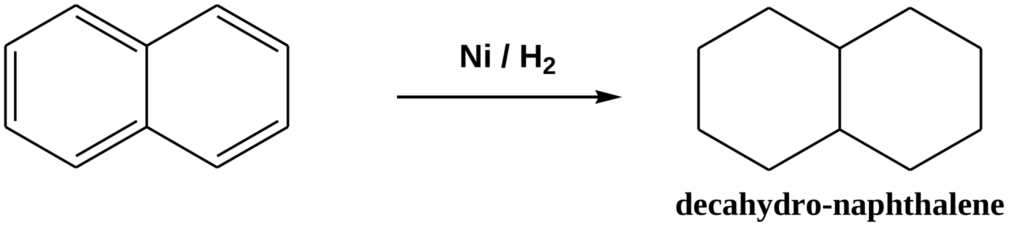
11.3 Alicyclic compounds with fused rings

❖ **Methods of synthesis:**

There are many methods used for the preparation of alicyclic fused-ring compounds as follows:

1- Catalytic hydrogenation of condensed aromatic system:

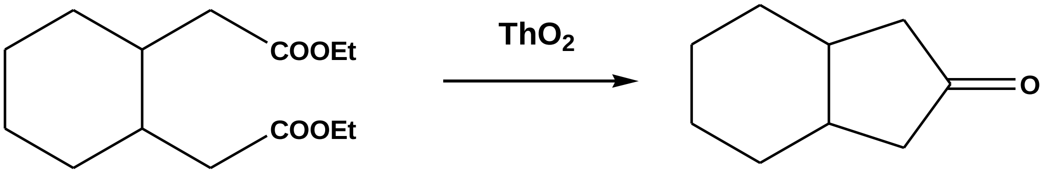
Catalytic hydrogenation of naphthalene, anthracene or phananthrene can give fused rings (Equation 11.8).



Equation 11.8

2- Cyclization of a compound containing one ring:

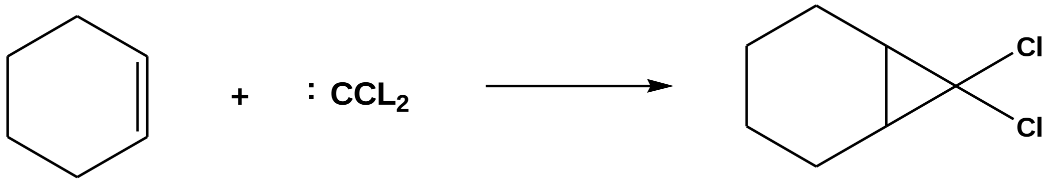
Treatment of 1,2-diethoxycarbonylmethyl-cyclohexane with thorium oxide (**ThO_2**) gives octahydro-inden-2-one (Equation 11.9).



Equation 11.9

3- Addition of carbenes to unsaturated monocyclic compounds:

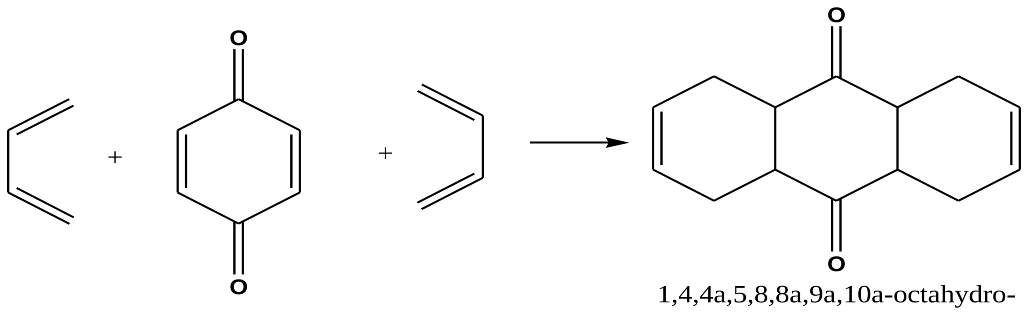
Cyclohexene reacts with carbenes to give bicyclo[4.1.0]heptane (Equation 11.10).



Equation 11.10

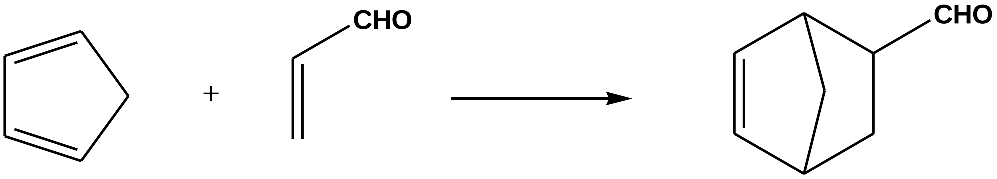
4- Diels-Alder reaction:

Diene reacts with dienophile to give the adduct as follows (Equations 11.11 – 11.13).



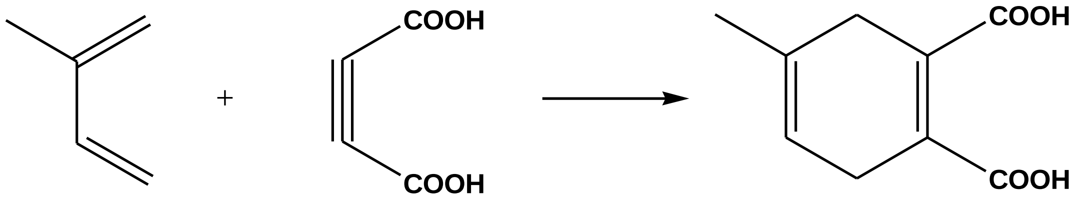
1,4,4a,5,8,8a,9a,10a-octahydro-
anthraquinone

Equation 11.11



bicyclo[2.2.1]hept-5-ene-2-carbaldehyde

Equation 11.12



4-methyl-cyclohexa-1,4-diene
-1,2-dicarboxylic acid

Equation 11.13

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PETROLEUM CHEMISTRY,
NATURAL GAS and
PETROCHEMICALS INDUSTRIES

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Contents:

History of Petroleum

Where Does Petroleum Occur

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Inorganic Theory

A number of scientists adhere to the concept that inorganic oil and gas have originated in the earth's interior as a result of chemical reactions between hydrogen and carbon under conditions of high temperature and high pressures in the absence of organic matter.

Organic Theory

The organic theory of the origin of oil – the most accepted theory- maintains that the hydrogen and carbon source for petroleum was organic material from decaying plants and animals forming and accumulating in oceanic sediment. The acceptance of the organic theory of the origin of petroleum dictates that the search for oil be directed to areas underlying by thick sections of sedimentary rock.

At the present time most authorities favor the organic approach. Their principal reasons are the followings:

-1 No inorganic theory can account for the necessary quantities of carbon and hydrogen needed to form large petroleum deposits. The abundance of plant and animal life present in sediments is a sufficient source.

-2 Many crude oil contain –porphyrins- and nearly all contain nitrogen. The presence of these materials strongly suggests organic origin as they are present in all organic matter. Also porphyrins of vegetable origin have been found to be more plentiful than those of animal origin.

3 -Petroleum rotates the plane of polarized light. This property is restricted primarily to organic materials known as optical isomers and further suggests organic matter as the source of petroleum.

Formation of Petroleum

The complete process of alteration whereby organic materials are transformed into petroleum is not known. The main factor, which prohibits complete laboratory verification of the theory, is the inability to reproduce the million or so years, during which the process occurs. The role of "anerobic" bacteria in promoting this alteration may be considerable. The evidence from studies of oil fields has led most geologists to the following general conclusions.:

1- Petroleum originates from organic material, primarily vegetable, which has been altered by heat, bacterial action, pressure and other agents overlying periods of time.

2-Conditions favoring petroleum formation are found only in sedimentary rocks.

3-The principal sediments generally considered as probable source rocks are shales and limestones that were originally mud under saline water.

In shallow, stagnant water basins host of blue green algae, arthropodal and planktonic organisms develop. On dying, they fall to the bottom of bodies of water along with the dust of plants and entrained fine mineral substances, and form soft, sometimes rather thick layers of organic ooze, or sapropel. The strata of sapropel and humus sediments gradually accumulate at the bottom of water basins. In these strata, the reactions of hydrolysis of fat may take place depending on the pressure, temperature, amount of oxygen and salinity of water.

These reactions yield fatty acids, glycerin, and other products, which then transform into hydrocarbons (methane, napthene and aromatic types) and oxygen compounds (ketones). All these compounds dissolve in fatty acids to give a homogeneous tar like mass that remains at the bottom together with mineral matter (sand, clay) and is gradually covered with mineral sediments. Such a tar like accumulation can be called primary oil (protopetroleum). The conversion of organic matter into oil in a reducing medium involves chemical reactions, which tend to raise the carbon and hydrogen content and to decrease the oxygen content.

It is now believed that combination of factors is necessary to transform primary organic matter into oil, such as elevated temperatures and pressures, the activity of bacteria and the action of radioactive substances.

Petroleum , also known as **crude oil** and **oil**, is a naturally occurring, yellowish-black liquid found in geological formations beneath the Earth's surface. It is commonly refined into various types of fuels. Components of petroleum are separated using a technique called fractional distillation, i.e., separation of a liquid mixture into fractions differing in boiling point by means of distillation, typically using a fractionating column. It consists of naturally occurring hydrocarbons of various molecular weights and may contain miscellaneous organic compounds.

The name petroleum covers both naturally occurring unprocessed crude oil and petroleum products that are made up of refined crude oil. A fossil fuel, petroleum is formed when large quantities of dead organisms, mostly zooplankton and algae, are buried underneath sedimentary rock and subjected to both intense heat and pressure.

Petroleum is a mixture of naturally occurring hydrocarbons that may exist in the solid, liquid or gaseous states, depending upon the conditions of pressure and temperature to which it is subjected.

Virtually all petroleum is produced from the reservoir in either liquid or gaseous form, and commonly, these materials are referred to as either crude oil or natural gas, depending upon the state of the hydrocarbon mixture.

Crude Oil Composition

Petroleum consist of approximately .12-16 wt % hydrogen and 84-87 wt % of carbon. Traces of oxygen, sulphur, nitrogen and helium may be found as impurities in crude oil. Crude oils obtained from different oil reservoirs have widely different characteristics. Some are black, heavy, and thick like tar, and others are brown or nearly clear with low viscosity and low specific gravity. However, nearly all crude oils have elemental analyses within the limits given below.

Elemental Analysis of Typical Crude Oils
Element % by wt
Carbon 84 – 87 , Hydrogen 11 – 14
,Sulphur 0.06 – 2.0 , Nitrogen 0.1 – 2.0 ,
Oxygen 0.1 – 2.0

Typical crude oil fractions
Crude Fractions Boiling point, °F Chemical composition Use
=Hydrocarbon gas C1 – C4 Natural gas, bottled fuel gas
=Petroleum ether To 160 C5 – C6 Solvent, paint thinner, cleaner
Gasoline 160 – 400 C7 – C8 Motor fuel, solvent=
Kerosene 400 – 575 C10 – C16 Illuminating oil, diesel fuel, jet fuel=

=Light gas oil 575 – 850 C16 – C30
Lubricating oil, mineral oil, cracking=
stock
Heavy gas oil 850 – 1100 , C30 – C50 Lubricating oil, bunker fuel=
Residue 1200+ C80+=
=Tars, asphalts, wood preservatives, roofing compounds

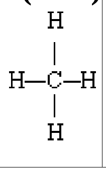
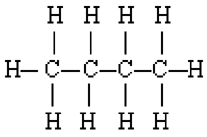
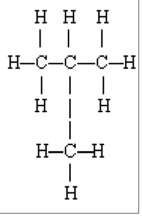
Composition of Crude Oil

- **Aliphatic Hydro carbons (Gases, Light HCS, Medium HCS, Heavy HCS)**
- **Aromatics**
- **Naphtha**
- **Sulfur content**
- **Oxygen, and Nitrogen content**

Paraffins.

The paraffinic series of hydrocarbon compounds found in crude oil have the general formula C_nH_{2n+2} and can be either straight chains (normal) or branched chains (isomers) of carbon atoms. The lighter, straight-chain paraffin molecules are found in gases and paraffin waxes. Examples of straight-chain molecules are methane, ethane, propane, and butane (gases containing from one to four carbon atoms), and pentane and hexane (liquids with five to six carbon atoms). The branched-chain (isomer) paraffins are usually found in heavier fractions of crude oil and have higher octane numbers than normal paraffins. These compounds are saturated hydrocarbons, with all carbon bonds satisfied, that is, the hydrocarbon chain carries the full complement of hydrogen atoms.

Typical Paraffins

Example of simplest HC molecule (CH_4):	**Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula (C_4H_{10}):**	**isobutane**
Methane (CH_4)  $\begin{array}{ccc} & H & \\ & \vert & \\ H- & C & -H \\ & \vert & \\ & H & \end{array}$	**Butane (C_4H_{10})**  $\begin{array}{cccccc} & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \\ & H & H & H & H & \end{array}$	 $\begin{array}{ccccc} & H & H & H & \\ & \vert & \vert & \vert & \\ H- & C- & C- & C & -H \\ & \vert & \vert & \vert & \\ & H & \vert & H & \\ & & \vert & & \\ & H- & C & -H & \\ & & \vert & & \\ & & H & & \end{array}$

Aromatics.

Aromaatics are unsaturated ring-type (cyclic) compounds which react readily because they have carbon atoms that are deficient in hydrogen. All aromatics have at least one benzene ring (a single-ring compound characterized by three double bonds alternating with three single bonds between six carbon atoms) as part of their molecular structure. Naphthalenes are fused double-ring aromatic compounds. The most complex aromatics, polynuclears (three or more fused aromatic rings), are found in heavier fractions of crude oil.

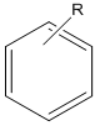
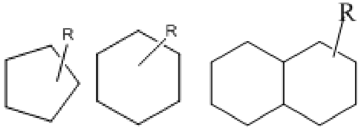
Naphthenes.

Naphthenes are saturated hydrocarbon groupings with the general formula C_nH_{2n}, arranged in the form of closed rings (cyclic) and found in all fractions of crude oil except the very lightest. Single-ring naphthenes (monocycloparaffins) with five and six carbon atoms predominate, with two-ring naphthenes (dicycloparaffins) found in the heavier ends of naphtha.

Other Hydrocarbons

Alkenes are mono-olefins with the general formula C_nH_{2n} and contain only one carbon-carbon double bond in the chain. The simplest alkene is ethylene, with two carbon atoms joined by a double bond and four hydrogen atoms. Olefins are usually formed by thermal and catalytic cracking and rarely occur naturally in unprocessed crude oil.

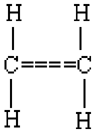
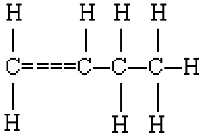
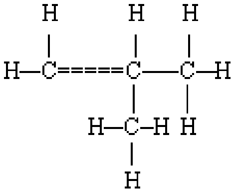
Typical Aromatics

Example of simple aromatic compound:	Examples of simple double-ring aromatic compound:
Benzene (C_6H_6) 	**Napthalene ($C_{10}H_8$)** 

Typical Naphthenes

	Examples of naphthene with same chemical formula (C_6H_{12}) but different molecular structure:

Typical Alkenes

Simplest Alkene (C_2H_4):	Typical Alkenes with the same chemical formula (C_4H_8) but different molecular structures:	
Ethylene (C_2H_4) 	**1-Butene (C_4H_8)** 	**Isobutene (C_4H_8)** 

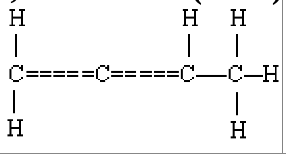
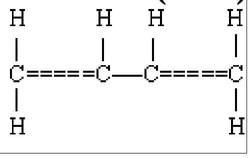
Dienes and Alkynes.

Dienes

Dienes also known as diolefins, have two carbon-carbon double bonds. The alkynes, another class of unsaturated hydrocarbons, have a carbon-carbon triple bond within the molecule. Both these series of hydrocarbons have the general formula C_nH_{2n-2}. Diolefins such as 1,2-butadiene and 1,3-butadiene, and alkynes such as acetylene, occur in C_5 and lighter fractions from cracking. The olefins, diolefins, and alkynes are said to be unsaturated because they contain less than the amount of hydrogen

necessary to saturate all the valences of the carbon atoms. These compounds are more reactive than paraffins or naphthenes and readily combine with other elements such as hydrogen, chlorine, and bromine.

Typical Diolefins and Alkynes

Simplest Alkyne (C_2H_2):	Typical Diolefins with the same chemical formula (C_4H_6) but different molecular structures:	
Acetylene (C_2H_2)	1,2-Butadiene (C_4H_6) 	1,3-Butadiene (C_4H_6) 

Nonhydrocarbons

Sulfur Compounds.

Sulfur may be present in crude oil as hydrogen sulfide (H_2S), as compounds (e.g. mercaptans, sulfides, disulfides, thiophenes, etc.) or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans. Moreover, the corrosive sulfur compounds have an obnoxious odor.

Thiols, RSH

Sulfides RSR. Polysulfides R(S)nR n=1,2,3…

Pyrophoric iron sulfide results from the corrosive action of sulfur compounds on the iron and steel used in refinery process equipment, piping, and tanks. The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide. Catalytic hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams. Sweetening processes either remove the obnoxious sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans.

Oxygen Compounds.

Oxygen compounds such as phenols, ketones, and carboxylic acids occur in crude oils in varying amounts.

Nitrogen Compounds.

Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as nonbasic compounds that may also include trace metals such as copper, vanadium, and/or nickel. Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

Trace Metals.

Metals, including nickel, iron, and vanadium are often found in crude oils in small quantities and are removed during the refining process. Burning

heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts.

Salts.

Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine). These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH_4Cl), which causes fouling and corrosion.

Carbon Dioxide.

Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

Naphthenic Acids.

Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 450° F when the acid value of the crude

characterization properties

Numerous important feed and product characterization properties in refinery engineering include

1- API gravity 2- Watson Characterization factor

3- Viscosity 4- Sulfur content 5- Pour point

6- Flash and fire point 8- ASTM distillation curve 7- Octane number

API gravity (Density)

API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 ^oF, the API gravity is expressed as $^oAPI = 141.5/\text{specific gravity} - 131.5$ where specific gravity is measured at 60 ^oF.

According to the above expression, 10 ^oAPI gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter NPTEL .

Crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality. 3.4.2 Watson characterization factor The Watson characterization factor is usually expressed as K = (TB)1/3/specific gravity Where TB is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized. Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5. Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.

SULFUR CONTENT: Since crude oil is obtained from petroleum reservoirs, sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process.

This indicates that large quantities of inorganic sulphur needs to be removed from the fuel. Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide.

A typical refinery consists of good number of hydrotreaters to achieve the desired separation. The hydrotreaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved NPTEL using the crude distillation . The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium.

Important characterization properties

Numerous important feed and product characterization properties in refinery engineering include

1-API gravity 2-Viscosity 3-Sulfur content 4-True boiling point (TBP) curve

5-Pour point 6-Flash and fire point 7-Octane number

Viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 oF and 210 oF. Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit.

Flash and fire point : Are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.

Pour point

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will ceases to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a NPTEL desired range and this is achieved by blending appropriate amounts of lighter intermediate products.

Octane number

Though irrelevant to the crude oil stream, the octane number is an important property for many intermediate streams that undergo blending later on to produce automotive gasoline, diesel etc. Typically gasoline tends to knock the engines. The knocking tendency of the gasoline is defined in terms of the maximum compression ratio of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa. However, for comparative purpose, still one needs to have a pure component whose compression ratio is known for knocking. Iso-octane is eventually considered as the barometer for octane number comparison. While iso-octane was given an octane number of 100, n-heptane is given a scale of 0. Therefore, the octane number of a fuel is equivalent to a mixture of a iso-octane and n-heptane that provides the same compression ratio in a fuel engine. Thus an octane number of 80 indicates that the fuel is equivalent to the performance characteristics in a fuel engine fed with 80 vol % of isooctane and 20 % of n-heptane. Octane numbers are very relevant in the reforming, isomerisation and alkylation processes of the refining industry. These processes enable the successful reactive transformations to yield long side chain paraffins and aromatics that possess higher octane numbers than the feed constituents which do not consist of higher quantities of constituents possessing straight chain paraffins and non-aromatics (naphthenes). is above a certain level.

Sulfur content

Sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 –5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process. Strict and tighter legislations enforce the production of various consumer petroleum products with low quantities of sulphur (in the range of ppm).

Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide. A typical refinery consists of good number of hydrotreaters to achieve the desired separation. The hydrotreaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved

PETROLEUM HYDROCARBONS

Petroleum hydrocarbons themselves are diverse mixtures of chemical components. Site characterization as well as risk assessment is best accomplished with insight on site-specific contaminant compositions.

The components of petroleum and petroleum products number in the tens of thousands. They range in molecular weight from methane to very large uncharacterized components with molecular weight in the thousands.

Overall, the components of these mixtures have only two common properties: They are derived from petroleum and they contain hydrocarbon functional groups (C-H).

The more common functional categories of compounds found in petroleum products are n-alkanes, branched alkanes, cycloalkanes, and aromatic compounds. In certain mixtures there are other functional categories present (alkenes, mercaptans, porphorins, etc.)

Added chemicals such as petroleum oxygenates (MBTE, et al.) are sometimes included.

The “Petroleum Products and Petroleum Hydrocarbons Measurements” chart on the previous page illustrates boiling point (actually, vapor pressure) distribution ranges for some petroleum products. The “X” axis is calibrated using normal alkane standards ranging from methane (C1) to dotricontane (C32). Volatility decreases to the right.
Also included on this chart are applicable ranges for certain analytical methods frequently used in testing petroleum hydrocarbons levels.

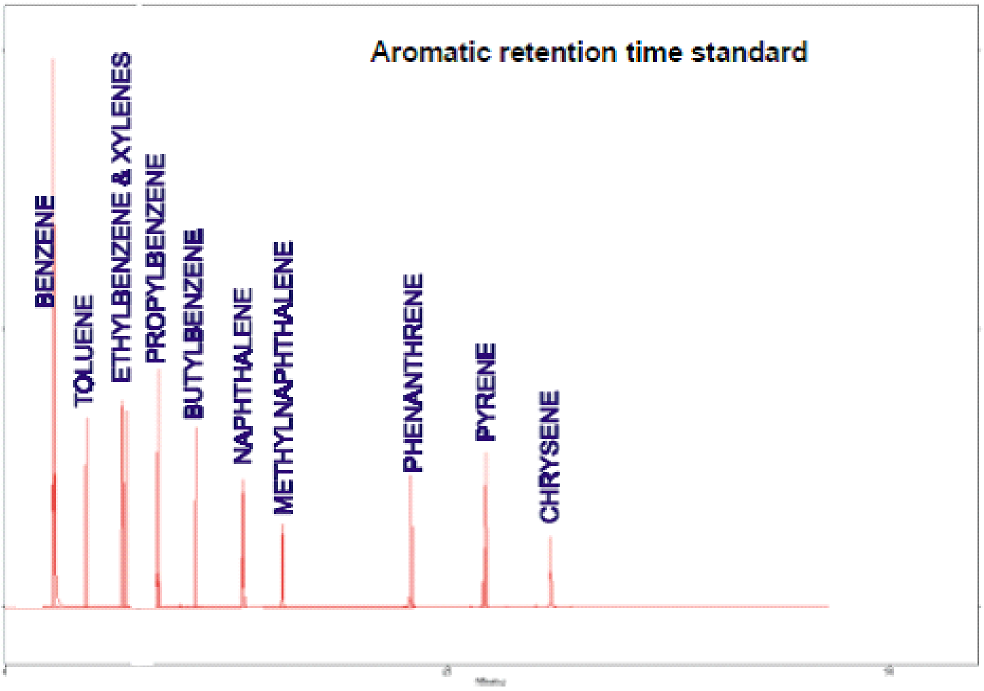
This presentation builds upon the general concepts in the chart using petroleum hydrocarbon fingerprints obtained using gas chromatography.

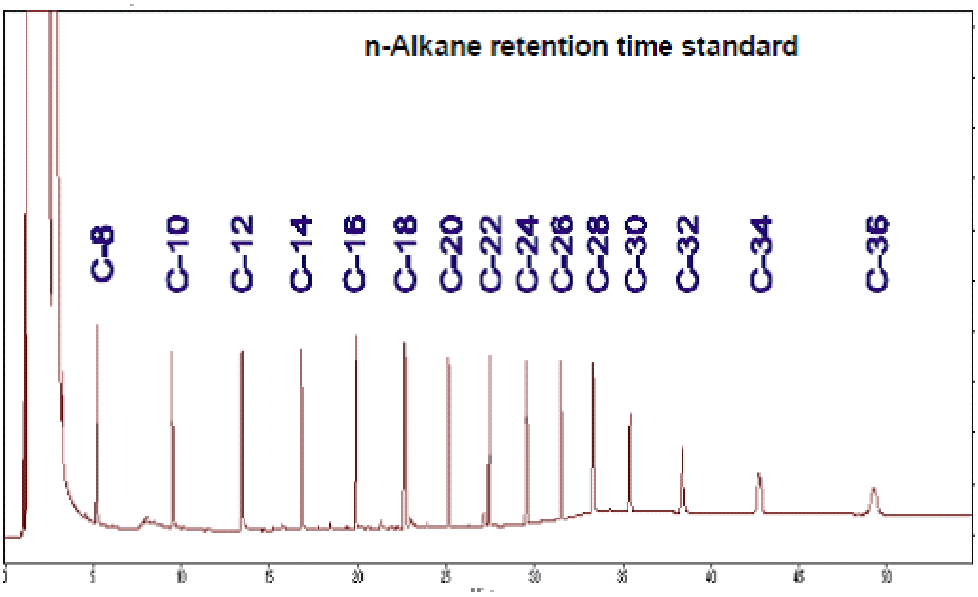
Gas Chromatographic Profiling of Petroleum Hydrocarbons

Gas chromatography is a technique for separating and detecting components of mixtures. In obtaining component profiles for petroleum hydrocarbons the gas chromatograph is configured to separate components based on component vapor pressures over a range extending from butane (n-C_4H_{10}) to dotricontane (n-$C_{32}H_{66}$). This window includes products from gasoline through paraffin wax.

The “X” axis is calibrated using hydrocarbons of known vapor pressure. The “Y” axis is a component concentration axis. The peaks are individual compounds or mixes of compounds with the same volatility.

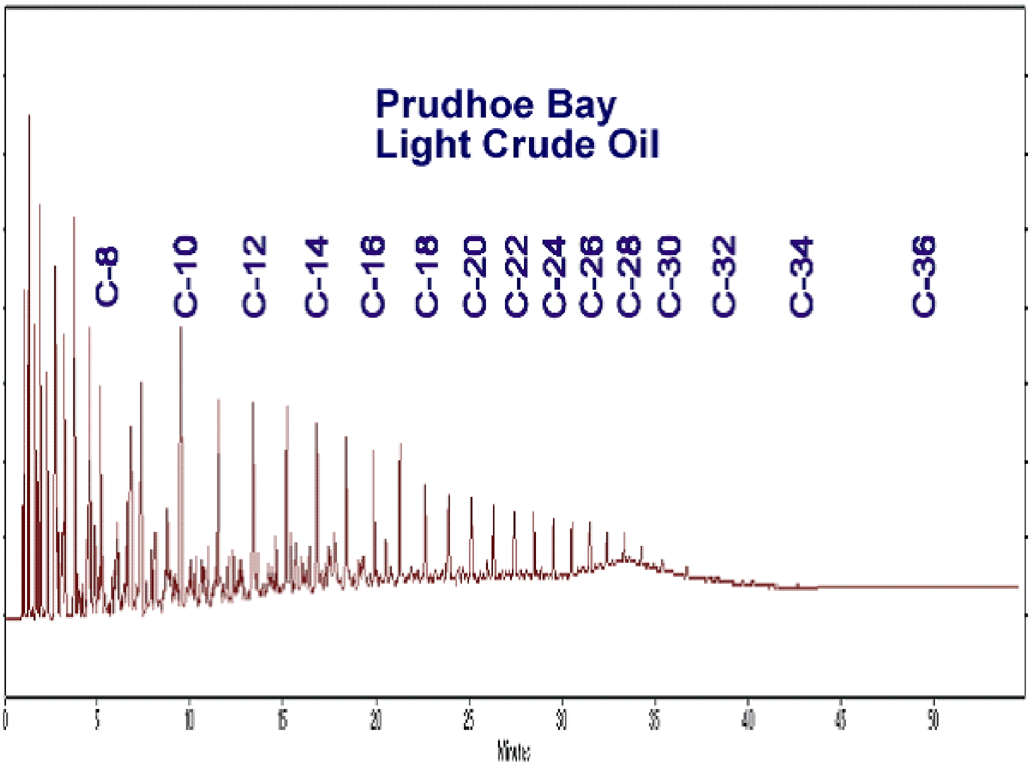
The conditions used to obtain the pictured retention time standard profiles were used for all chromatograms in this presentation unless otherwise noted. This enabenables direct comparison of





Crude Oil and Petroleum Product Production

Crude oil is the raw material used by refineries in manufacturing petroleum products. The composition of crude oil varies considerably from source to source. Some crudes, like the Prudhoe Bay Light Crude pictured, contain a considerable amount of low and medium weight hydrocarbons. Others are very heavy, tar-like materials. The refinery adapts its process to manufacture as much gasoline (the product with the highest commercial demand) as possible from a given crude. Diesel fuel/No. 2 heating oil is second in demand. Hundreds of other products are manufactured from crude oil including jet fuel/kerosene, lubricants, asphalt, coke, petrochemical feedstocks, LPG, etc.



Straight-run distillates

The fundamental refinery process is distillation of the crude into low-boiling, medium-boiling, high-boiling and residual fractions. These fractions are used directly in some cases and are called straight-run distillates. Heating fuel (No. 2) is usually a straight-run distillate.

Blended products

To maximize gasoline production, medium and high weight fractions are converted to low weight materials in a process called cracking/reforming. The resulting “reformate” is blended with low weight straight-run distillate. Additives are included such as gasoline oxygenates to improve performance. Straight-run distillates are also blended to achieve specifications and improve yields for various fuel oils.

Further refined products

Additional processing yields highly refined products like lubricating oils, waxes, chemical feedstocks, etc. Diesel fuels are essentially No. 2 fuels with added processing to remove sulfur and waxes.

Gasoline

Gasoline is a low-weight, high-volatility blended product. Benzene and alkyl-substituted benzenes are predominant components. Addition of volatile oxygenated organics such as t-butyl methyl ether improve combustion efficiency of the product. These oxygenates are more water soluble than other components in the blend and migrate more rapidly in the environment.

Gasolines from different sources and of varying grades have very similar component profiles.

Diesel Fuel

Diesel fuel and oil are usually straight-run distillates with the same gross component profile. They have the same manufacturing specification except diesel fuel is lower in sulfur (and sometimes wax) content. The predominant peaks are n-alkanes. The majority of the remaining components are alkyl-substituted aromatics and branched and cyclic aliphatics.

Fuel oils also have similar component profiles but the distributions are shifted to the higher boiling component end of the range. Sometimes these heavier fuels are straight-run distillates, but frequently they are blends of distillates with residuum (the nonvolatile bottoms of the distillation process) and cracked residuum. “Bunker C” is primarily a residuum based product.

Other Petroleum Hydrocarbons

- Motor oil is a refined formulation of mostly high-weight branched and cyclic alkanes. Additives include rust inhibitors, viscosity modifiers, detergents, and synthetic lubricants.
- Paraffin wax is almost entirely n-alkanes.
- Mineral spirits is primarily low weight mixed aliphatics and aromatics
- Kerosene (No. 1 fuel oil) and mineral spirits are straight-run distillates

Evaluation and Measuring Petroleum Hydrocarbons

- Physical properties
- Sulfur content % determination
- Elemental analysis C,H,S, %
- Spectral measurements :

IR. UV.Gravimetric,Gas Chromatograph, GCMS,
H1nmr, and C13 NMR

Infrared spectrometer is a device which measures a sample’s transparency to the range of frequencies in the infrared band of the electromagnetic spectrum. The instrument provides a plot of radiation absorbed vs radiation frequency called an infrared spectrum. A sample infrared spectrum is presented below.

The character of a sample’s infrared spectrum (the frequencies at which radiation is absorbed and the intensities of those absorbances) is a function of the types and abundances of chemical bonds present in the sample. For example, the C=O in ethers produces an absorbance at ca. 1740 cm-1 and the C-H bond in hydrocarbons produces an absorbance ca. 3000 cm-1. Infrared analysis of TPH uses the absorbance at 3000 cm-1 to measure the presence of hydrocarbons, then assumes they are all petroleum based materials. The method involves:

Extracting the sample with a solvent that has no C-H functionality of its own. The solvent chosen is trichlorotrifluoroethane (Freon(TM)).

Measuring the extract's absorbance at 3000 cm-1 and calculating the hydrocarbon concentration using a calibration graph prepared from arbitrary hydrocarbon standards. There are limitations to this method:

Only a concentration value results from the analysis - a number related to the sample extract's opacity at the invisible frequency of 3000 cm-1. No insight as to what is being measured is provided.

Volatile components are lost in extraction. Weathered products and products with high weight components have limited solubility in Freon(TM).

Gravimetric Method.

There are basically two gravimetric EPA methods. These include EPA 413.1 for oil and grease and EPA 1664A for silica gel n-hexane extractable material (also regarded as total petroleum hydrocarbons).

They both involve solvent extraction, evaporation, and weighing to a constant weight but the oil and grease method does not differentiate the polar organic matter from the petroleum hydrocarbon portion [74]. EPA 1664A was developed to replace EPA 413.1 that uses Freon 113 (a Class I ozonedepleting substance) as its extracting solvent. The new method performs extraction with n-hexane which is more environmentally friendly but flammable and could determine total petroleum hydrocarbon concentration in the same procedure for the oil and grease analysis

A procedure begins with adjustment of the aqueous sample pH to a value less than 2 with either H2SO4 or HCl. The sample is then extracted with n-hexane using LLE (or SPE) method and the organic portion is filtered through a funnel containing anhydrous Na2SO4, after which the solvent is distilled off from the flask at 85◦ C in a water bath. The flask is then dried and weighed to constant weight for the estimation of the oil and grease concentration [75]. For the TPHC determination, the oil and grease in the flask is dissolved in fresh portion of n-hexane. A suitable amount of silica gel is added to remove the polar substances (e.g., fats, dyes, oils, waxes, and some heavier organic molecules from animals and plants origin) in the extract and the mixture is stirred using a magnetic stirrer, filtered, and gravimetrically determined as nonpolar material (NPM), also known as silica gel treated n-hexane extractable material

Other gravimetric methods reported for solid samples involved the addition of 3 g KOH (to enhance the extraction of the humic substances) and 100 cm3 methanol to about 100 g air-dried samples prior to the Soxhlet extraction process. The subsequent steps involving gravimetric measurement of the polar and nonpolar compounds are as discussed above.

Gas Chromatography

"Non-Halogenated Organics Using GC/FID" was specifically developed to take care of volatile and semivolatile organics separately as gasoline range organics (GRO) in the boiling point range of 60◦ C–170◦ C (C6–C10) and diesel range organics (DRO) in range of 170◦ C–430◦ C (C10 to C28).The method has the ability to provide some necessary information on the product type unlike the gravimetric and IR methods . The volatile samples are usually introduced into the gas chromatograph (GC) by purge and trap method. The aliphatic and aromatic fractions are analyzed separately on the gas chromatograph using a flame ionization detector (GC-FID) which is mostly preferred for its relative sensitivity and selectivity for hydrocarbons.

The aliphatic and aromatic fractions are usually divided into carbon number ranges (GRO and DRO) on the basis of the PAH and n-alkane markers, respectively . Unfractionated extract can also be quantified as the oil and grease, yielding a concentration greater than the sum of the aliphatic and aromatic fractions

Total hydrocarbons are sometimes measured with FID while the aromatic fraction is determined with a photoionization detector (PID). The aliphatic fraction is therefore estimated by subtracting the aromatic from the total hydrocarbon result

Ultraviolet Fluorescence Spectrophotometry.

Ultraviolet fluorescence (UVF) spectrophotometry is a fast and valuable screening method for TPHC analysis in the environmental samples. It involves solvent extraction and optical measurement of the hydrocarbon molecules using an ultraviolet fluorescence spectrometer. It is always used in the field for aqueous samples without solvent extraction . The aromatic hydrocarbons fluoresce when their π- bonds are excited by ultraviolet light and the hydrocarbon concentration in the sample extracts is measured using a fluorometer .

Gas Chromatograph (GC) Separation of Hydrocarbons

Saturated and Unsaturated Aliphatic Hydrocarbon Compounds

- -C_1–C_5 hydrocarbon compounds

50 m $A1_2O_3$/KCl Plot column

40 (1 min)−200° at 10°/min or 60–200° at 3°/min.

30 to 50 m GS-Q column or Poraplot Q column

35–100° at 10°/min. 100° (5 min); 100–200° at 10°/min, or 40 (2 min)–115° at 10°/min.

2) -C_4 hydrocarbon isomers

Picric acid column on Carbopak C, 30–100° at 2°/min.

3) C_4–C_{12} hydrocarbon compounds

4) -C_5–C_{100} hydrocarbon compounds

. 5)- Low-Boiling Aromatic Hydrocarbon Compounds

Benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene .Benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, butylbenzene, styrene, *o*, *m*-, and *p*-diethylbenzenes.

6)- Polynuclear Aromatic Hydrocarbon Compounds

7) -Naphthalene, acenaphthane, acenaphthene, fluorene, phenanthrene,* anthracene,*fluoranthene, pyrene, benzanthracene, benzophenanthrene, and benzpyrene .

8)- Phenanthrene, anthracene, and other polynuclear aromatic compounds.

9)-Gasoline

Gasoline contains more than 250 components of a mixture of C_4–C_{12}hydrocarbons, which varies in concentration from batch to batch. Some of these components are: *iso*butane, *n*-butane, *iso*pentane, *n*-pentane, 2,3-dimethylbutane, 3-methylpentane, *n*-hexane, 2,4-dimethylpentane, benzene, 2-methylhexane, 3-methylhexane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2,5-dimethylhexane, 2,4-dimethylhexane, toluene, 2,3-dimethylhexane, ethylbenzene, methylethylbenzenes, *m*-, *p*-, and *o*-xylene, trimethylbenzenes, naphthalene, methylnaphthalenes, and dimethylnaphthalenes

Mass Spectra of Hydrocarbon Compounds

n-Alkanes

The molecular ions decrease in intensity with increasing chain length but are still detectable at C_{40}. In contrast to branched alkanes, the loss of a methyl group is not favored for *n*-alkanes. Usually the first fragment ion below the molecular ion is at mass M – 29. Compounds of C_4 and higher show a base peak at *m/z* 43 or 57. Alkanesyield a series of peaks

Diesel Range Organics (DRO) and Gasoline Range Organics (GRO)

Diesel Range Organics (DRO) and Gasoline Range Organics (GRO) are two gas chromatographic methods for measuring hydrocarbon contamination.

The GRO analysis utilizes a purge & trap sample introduction technique for transferring components from the sample to the Gas chromatograph (GC), and low weight, high volatility components are well recovered.

The DRO analysis utilizes an ultrasonic extraction in sample preparation.
The analysis of pre-extracted, non-halogenated organic compounds (specifically polynuclear aromatic hydrocarbons) is described.

Both methods provide usable chromatographic profiles for interpreting the nature of site-specific contamination. Use these methods in scouting for petroleum hydrocarbon contamination during site assessments and monitoring of remediation processes.

Volatile Petroleum Hydrocarbons (VPH)

The VPH method uses a purge & trap for GC sample introduction. Chromatograms are obtained using two detectors, and FID and a PID. The PID is non-selective for alkanes and the chromatogram is considered to be primarily an aromatic profile. The FID gives a total hydrocarbon profile.

The chromatographic profile for the PID is used to quantify individual target aromatic hydrocarbons as well as C_9 to C_{10} aromatics. The FID chromatogram is integrated over two ranges to obtain C_5 to C_8 aliphatics and C_9 to C_{12} aliphatics. Target aromatics are subtracted from the ranges to prevent considering these compounds twice.

VPH Profiles for a Gasoline Sample

In this chart, a real-world sample (fresh gasoline) is subjected to the VPH analysis.

The range for the C_9 to C_{10} aromatics analysis begins as specified in the method at 1,2,4trimethylbenzene. Certain C_9 aromatics may not be included in this range

A **crude oil desalter**

A **desalter** : is a process unit in an oil refinery that removes salt from the crude oil. The salt is dissolved in the water in the crude oil, not in the crude oil itself.

The desalting is usually the first process in crude oil refining. The salt content after the desalter is usually measured in PTB - pounds of salt per thousand barrels of crude oil.

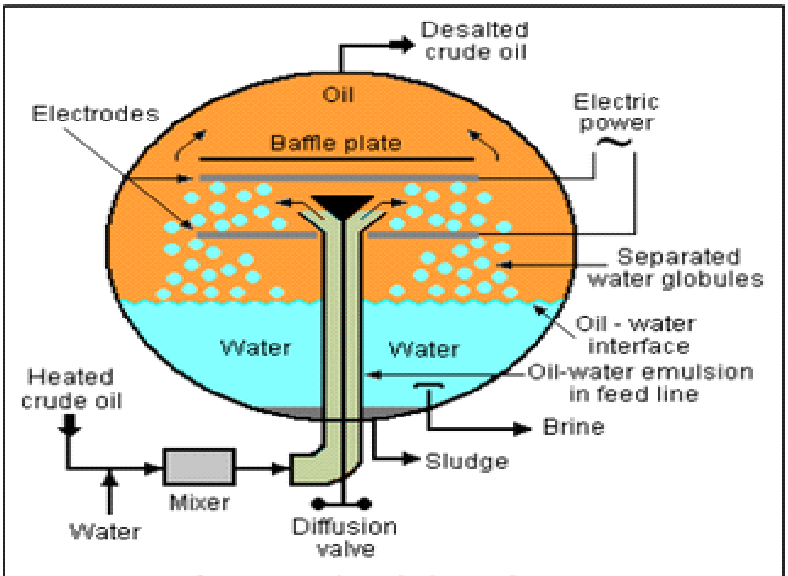
The salts that are most frequently present in crude oil are calcium, sodium and magnesium chlorides. If these compounds are not removed from the oil several problems arise in the refining process. The high temperatures that occur downstream in the process could cause water hydrolysis, which in turn allows the formation of corrosive hydrochloric acid. Sand, silts and salt cause deposits and foul heat exchangers or result in plugging. The need to supply heat to vaporize water reduces crude pre-heat capacity. Sodium, arsenic and other metals can poison catalysts. By removing the suspended solids, they are not carried into the burner and eventually flue gas, where they would cause problems with environmental compliance such as flue gas opacity norms.

Crude oil to be desalted is heated to a temperature of 100-150 °C and mixed with 4-10% fresh water, which dilutes the salt. The mixture is then pumped into a settling tank where the salt water separates from the oil and is drawn off. An electrostatic field is applied by electrodes in the settling tank, inducing polarization of the water droplets floating in the larger volume of oil. This results in the water droplets clumping together and settling to the bottom of the tank.

Desalting is a water-washing operation performed initially at the production field and thereafter at the refinery site for additional crude oil cleanup, where the salt and water content specifications are even more rigid because of their negative effect in the downstream processes due to scale formation, corrosion, and catalyst deactivation.

Desalting involves mixing heated crude oil with washing water, using a mixing valve or static mixers to ensure a proper contact between the crude oil and the water, and then passing it to a separating vessel, where a proper separation between the aqueous and organic phases is achieved.

The process starts by mixing the raw crude oil with an appropriate amount of washing water also known as dilution water. The washing water as a volume percent of the crude oil processed could oscillate between 3 and 10%, depending on the API gravity of the crude oil – the heavier the crude oil, the more the water required . Demulsifiers are added to the crude oil in this process step.



Cross - sectional view of Electrostatic crude oil desalter

The salts that are most frequently present in crude oil are calcium, sodium and magnesium chlorides. If these compounds are not removed from the oil several problems arise in the refining process. The high temperatures that occur downstream in the process could cause water hydrolysis, which in turn allows the formation of corrosive hydrochloric acid. Sand, silts and salt cause deposits and foul heat exchangers or result in plugging. The need to supply heat to vaporize water reduces crude pre-heat capacity. Sodium, arsenic and other metals can poison catalysts. By removing the suspended solids, they are not carried into the burner and eventually flue gas, where they would cause problems with environmental compliance such as flue gas opacity norms.

:Desalter is a device used in petroleum refineries to remove 1inorganic salts, water and sediment from the incoming petroleum crude oil feedstock before it is refined. This article focuses on the use of 1electrostatic desalters to produce a dehydrated, desalted crude oil with a low sediment content. Almost all refineries now use electrostatic desalters. However, there may still be a few refineries employing the older, less efficient method that utilizes chemicals and settling tanks.

Removal of the salts, water and sediment is necessary to avoid excessive fouling of equipment as well as corrosion from the generation of 1hydrochloric acid (HCl) by the 1hydrolysis of the chloride salts present in the incoming crude oil, in particular 1magnesium chloride ($MgCl_2$) and 1calcium chloride ($CaCl_2$). Any salts that are not removed represent a source of metals that can "poison expensive catalysts used in various petroleum refinery processes.

Contaminants in crude oil as received by refineries

The amount of water, salts and sediment in the crude oil as received at petroleum refineries varies widely with the source of the crude oil, the prior processing of the crude oil at the source sites and with the mode of transporting the crude oil from its source to the refineries.

Typically, the raw crude oil produced by oil wells drilled into underground petroleum oil reservoirs is accompanied by 1brine (i.e.,water containing inorganic chloride salts). The amount of chloride salts in the brine may be as high as 20 % by weight. Some of that brine is 1emulsified with the crude oil. The salts present in raw crude oil may be in the form of crystals dispersed in the oil and some of the salts are dissolved in the brine in their ionized form.

The salts present in petroleum crude oils are mainly chlorides with following approximate breakdown:

75 weight percent 1Sodium chloride (NaCl)

15 weight percent Magnesium chloride ($MgCl_2$)

10 weight percent Calcium chloride ($CaCl_2$)

The sediment present in petroleum crude oils include 1clay, 1rust, 1iron sulfide (FeS), 1asphaltenes and various other water-insoluble particles.

Such oilfield processing typically involves washing the oil with water to remove salts, some heating, use of demulsifying chemicals and simple settling vessels and tanks. In some cases, the oilfield processing includes electrostatic desalting as well. In general, the oilfield processing facilities strive to remove enough water, sediment and salts so that the transported crude oil contains less that 1 to 2 % by volume of sediment and water (BS&W) and less than 10 to 20 pounds of salts per 1000 barrels (PTB) of clean, water-free crude oil (which is equivalent to a salt content of 34 to 68 ppm by weight). Nevertheless, the crude oils as received at petroleum refineries have a salt content that ranges from a PTB of 10 to 300 (34 to 1,020 ppm by weight), based on spot samples of many different crude oils as delivered to refineries.[1][7] Transportation by sea-going crude oil tankers is vulnerable to salt water pickup by the crude oil cargo.

Crude oil also contains trace elements such as vanadium (V), nickel (Ni), copper (Cu), cadmium (Cd), lead (Pb) and arsenic (As), all of which can cause problems in some of the various processing units in the petroleum refineries. They may be present in the form of oil-soluble 1organo-metallic compounds or as water-soluble salts.

Description of petroleum refinery electrostatic desalters

The crude oil distillation unit (CDU) is the first processing unit in virtually all petroleum refineries. The CDU distills the incoming crude oil into various fractions of different boiling ranges, each of which are then processed further in the other refinery processing units. Figure 1 below is a schematic flow diagram of a typical CDU and, as can be seen, the desalter (colored red for clarity) is typically installed in the 1heat exchange train that heats the incoming crude oil before it flows through a 1fired heater and into the distillation tower. The desalter is usually located at the point where the incoming crude oil has been heated to about 100 to 150 °C. The optimum desalter temperature varies somewhat with the crude oil source.

At that point, wash water is injected and mixed into the continuous flow of crude oil and the resulting oil-water emulsion then continuously enters the electrostatic desalter. The rate of wash water required is about 4 to 10 % by volume of the crude oil rate. The optimum wash water rate varies with the API gravity of the crude oil and with the desalter temperature.

Externally viewed, the typical electrostatic desalter is a horizontal, cylindrical vessel A cross-sectional end-view of the of the desalter's interior

. The oil-water emulsion that enters from the bottom of the desalter through the feed line is a thorough mixture of two non-miscible liquids consisting of a continuous phase (the crude oil) and a dispersed phase (water in the form of very small droplets with dimensions ranging from 1 to 10 micrometres).

Asphaltenes and finely divided sediment solids are adsorbed on the oil-water interface and stabilize the emulsion. Thus the degree of difficulty involved in 1coalescing the droplets into large globules which can be settled and removed is related to the presence of asphaltenes, sediments and other water-insoluble contaminants.

An electrical system connected to the 1electrodes within the desalter generates an 1electrostatic field at potentials ranging from about 6,000 volts to about 20,000 volts that induce 1dipole attractive forces between neighboring droplets of water.

In other words, the electrostatic field results in each droplet having a positive charge on one side and a negative charge on the other which cause the droplets to 1coalesce because of the attractive force generated by the opposite charges on neighboring droplets. The resulting larger water droplets (globules), along with water-insoluble solids, then settle to the bottom of the desalter. The settled water is continuously withdrawn from the desalter from a point somewhat above the desalter bottom (see Figure 2) and is referred to as a brine because it contains the inorganic salts that originally entered the desalter with the water in the crude oil. The settled sediment at the bottom of desalter is withdrawn as a sludge at intermittent intervals as needed to prevent solids from entering the settled water withdrawal outlet.

Desalting and Distillation

Although distillation is usually known as the first process in petroleum refineries, in many cases, desalting should take place before distillation (Figure 3.1). Salt dissolved in water (brine) enters the crude stream as a contaminant during the production or transportation of oil to refineries. If salt is not removed from crude oil, serious damage can result, especially in the heater tubes, due to corrosion caused by the presence of Cl. Salt in crude oil also causes reduction in heat transfer rates in heat exchangers and furnaces.

The three stages of desalting are:

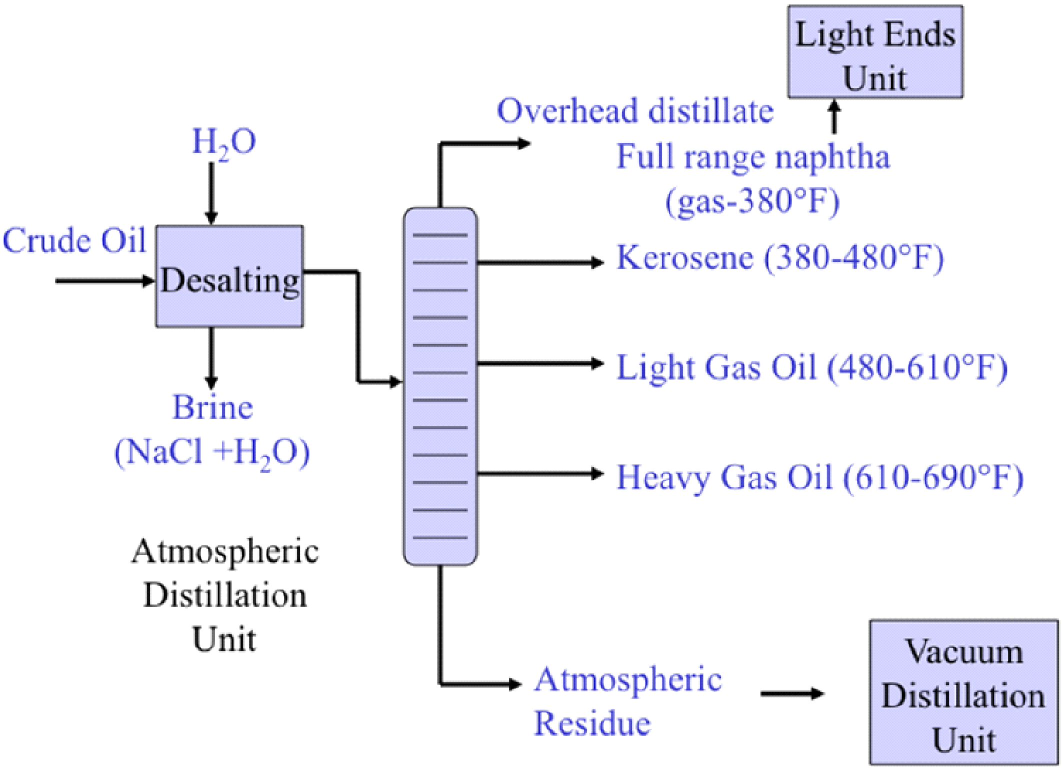
- **Adding dilution water to crude;**
- **Mixing dilution water with crude by a mixer;**
- **Dehydration of crude in a settling tank to separate crude and sediment and water (S&W).**

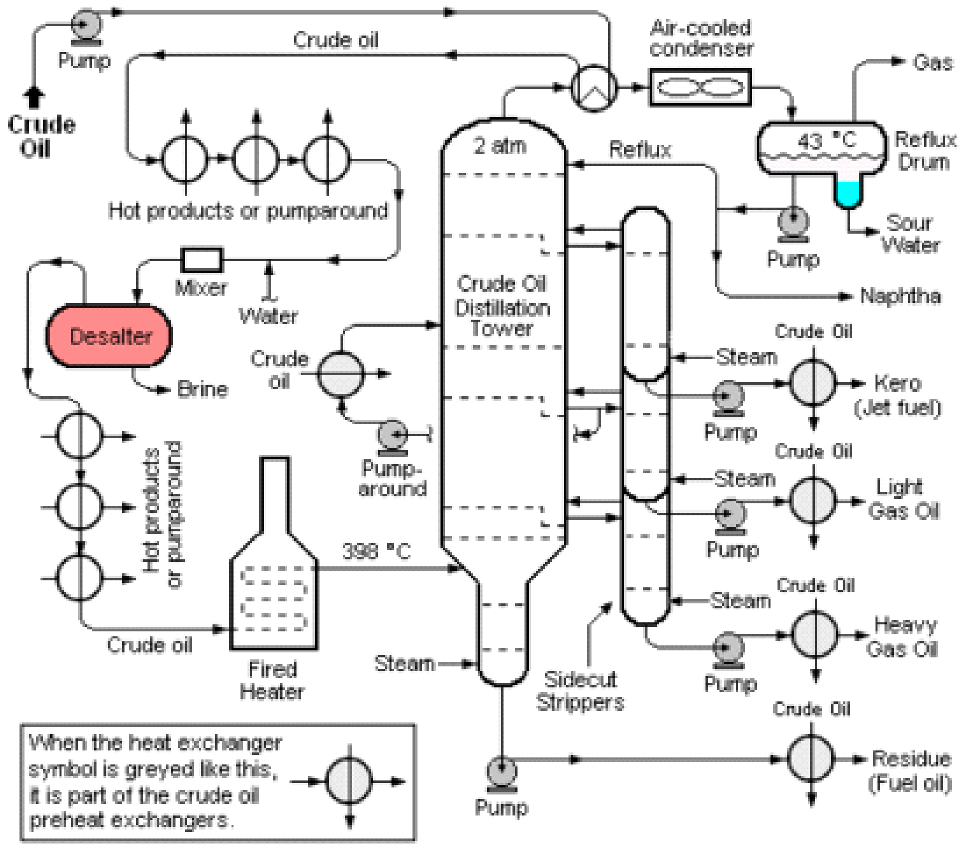
Desalting and fractional distillation of crude oil.

Desalting can be performed in a single-stage or two-stage units. Amount of water wash and temperature of the mixing process depend mainly on the crude API gravity

Distillation separates hydrocarbon compounds into distillate fractions based on their boiling points or volatility. More volatile compounds (with low boiling points) tend to vaporize more readily than heavy compounds, and this forms the basis of separation through distillation. In a distillation column, light components are removed from the top of the column, and the heavier part of the mixture appears in the bottom. For a crude that is a mixture of thousands of hydrocarbons, some very light compounds such as ethane and propane only appear in the top product, while extremely heavy and non-volatile compounds such as asphalts only appear in the bottom.

Figure 2 shows a simple diagram of atmospheric and vacuum distillation units and the fractional separation of the crude oil into different boiling fractions with the indicated boiling ranges. The lightest compounds found in crude oil come out from the top of the distillation column (referred to as overhead distillate, or full-range naphtha) and are sent to the Light Ends Unit (LEU) for further separation into LPG and naphtha, as discussed later. The side streams separated in the atmospheric distillation column give fractions that include the “straight-run” products called kerosene, and light and heavy gas oils. The residue from the atmospheric distillation column generates two side streams, light and heavy vacuum gas oils, and vacuum residue from the bottom. All of these distillation products are subjected to subsequent processing to produce light and middle distillate fuels and non-fuel products, as described in the following sections starting with LEU.


Light Ends Unit
Overhead distillate
Full range naphtha (gas-380°F)
H_2O
Crude Oil
Desalting
Kerosene (380-480°F)
Light Gas Oil (480-610°F)
Brine
(NaCl +H_2O)
Heavy Gas Oil (610-690°F)
Atmospheric Distillation Unit
Atmospheric Residue
Vacuum Distillation Unit


Pump
Crude oil
Air-cooled condenser
Gas
Crude Oil
2 atm
Reflux
43 °C
Reflux Drum
Hot products or pumparound
Sour Water
Pump
Mixer
Water
Naphtha
Crude Oil Distillation Tower
Desalter
Crude oil
Steam
Kero (Jet fuel)
Brine
Pump
Pump-around
Crude Oil
Hot products or pumparound
Steam
Light Gas Oil
Pump
398 °C
Crude Oil
Steam
Heavy Gas Oil
Crude oil
Fired Heater
Steam
Sidecut Strippers
Pump
Crude Oil
When the heat exchanger symbol is greyed like this, it is part of the crude oil preheat exchangers.
Residue (Fuel oil)
Pump

The desalter depicted in Figure 2 and described above is referred to as a *single-stage* desalter and represents but one of many available configurations, including configurations such as:

1-Flowing the crude oil through two stages in series and recycling part of the brine from the second stage for use as wash water to the first stage.

2-Flowing the crude oil through two stages in series with no recycle of brine from the second stage.

3-Using multiple electrostatic fields in a single vessel so as to create, in effect, two or three stages of desalting within that single vessel.

Desalter wash water

Many of the refining processes in a petroleum refinery produce 1wastewater streams (commonly referred to as *sour waters*) which contain dissolved 1hydrogen sulfide (H_2S) and ammonia (NH_3) gases in the form ionic 1ammonium hydrosulfide (NH_4HS). Usually, refineries collect all of their sour waters and use 1steam distillation towers (called 1sour water strippers) to strip virtually all of the hydrogen sulfide and somewhat less of the ammonia from aggregated sour waters.[3] The striped sour water is then recycled for reuse as desalter wash water, augmented by fresh water if needed.

Some of the refinery sour water streams contain also contain 1phenols[9] which are not easily stripped out. Thus, the stripped sour water used as desalter wash water contains phenols which are preferentially absorbed by the crude oil and will subsequently become part of the naphtha and kerosene fractions distilled from the crude oil .

Desalter performance

When a desalter has been well-designed and well-operated, it will achieve an average of 85 to 95% removal of inorganic salts from the crude oil and the water content of the desalted crude oil will be less than 0.2 volume percent of the crude oil.

Petroleum Refining Operations

- **Introduction.**

  Petroleum refineries change crude oil into petroleum products for use as fuels for transportation, heating, paving roads, and generating electricity and as feedstocks for making chemicals.

  Petroleum refining begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups. The resultant products are directly related to the characteristics of the crude processed. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes as discussed in this chapter. These converted products are then subjected to various treatment and separation processes such as extraction, hydrotreating, and sweetening to remove undesirable constituents and improve product quality. Integrated refineries incorporate fractionation, conversion, treatment, and blending operations and may also include petrochemical processing.

Refining Operations.

Petroleum refining processes and operations can be separated into five basic areas:

- **Fractionation (distillation) : is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."**
- **Conversion processes : change the size and/or structure of hydrocarbon molecules. These processes include:**

  A) Decomposition (dividing) by thermal and catalytic cracking;

  B) Unification (combining) through:

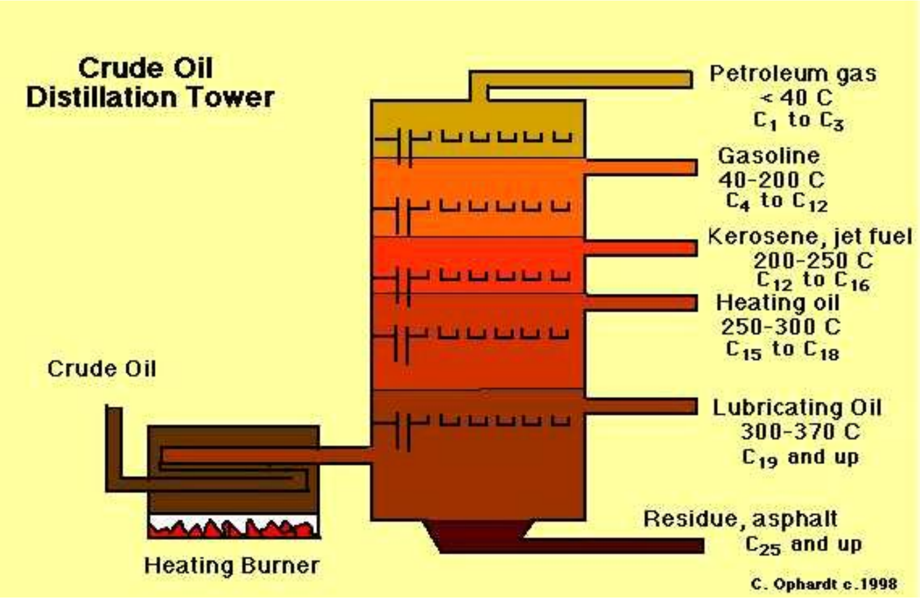
  i) Alkylation and ii) Polymerization

  iii) Isomerization and

  iv)Catalytic reforming.

- **Treatment processes :are intended to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include :**
- **Removal or separation of aromatics and naphthenes as well as impurities and undesirable contaminants.**
- **Treatment may involve chemical or physical separation such as dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.**
- **Formulating and Blending is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.**

- **Other Refining Operations include:**
  - **Light-ends recovery; sour-water stripping; solid waste and wastewater treatment; process-water treatment and cooling; storage and handling; product movement; hydrogen production; acid and tail-gas treatment; and sulfur recovery.**
  - **Auxiliary operations and facilities include: steam and power generation; process and fire water systems; flares and relief systems; furnaces and heaters; pumps and valves; supply of steam, air, nitrogen, and other plant gases; alarms and sensors; noise and pollution controls; sampling, testing, and inspecting; and laboratory, control room, maintenance, and administrative facilities.**



Refinery Processes Tower

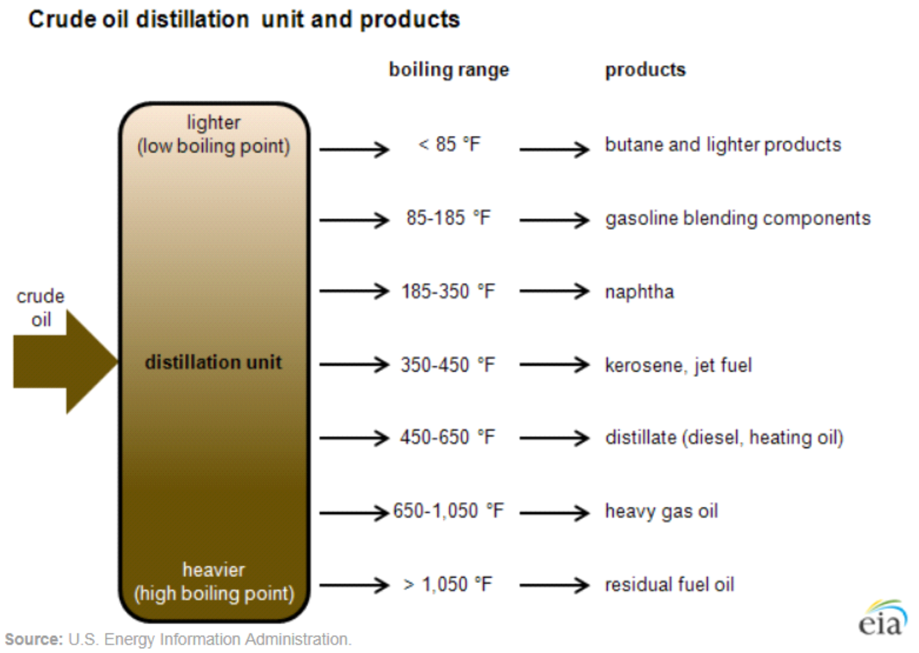
Crude Oil Distillation (Fractionation)

- **Description.**

  Industrial distillation is typically performed in large, vertical cylindrical columns known as "distillation or fractionation towers" or "distillation columns" with **diameters ranging from about 0.65 to 6 meters (2 to 20 ft) and heights ranging from about 6 to 60 meters (20 to 197 ft) or more.**

  The distillation towers have liquid outlets at intervals up the column which allow for the withdrawal of different fractions or products having different boiling points or boiling ranges. By increasing the temperature of the product inside the columns, the different products are separated. The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (those with the highest boiling point) exit from the bottom of the column.

  The first step in the refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in atmospheric and vacuum towers. The main fractions or "cuts" obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.


Crude oil distillation unit and products

Source: U.S. Energy Information Administration.

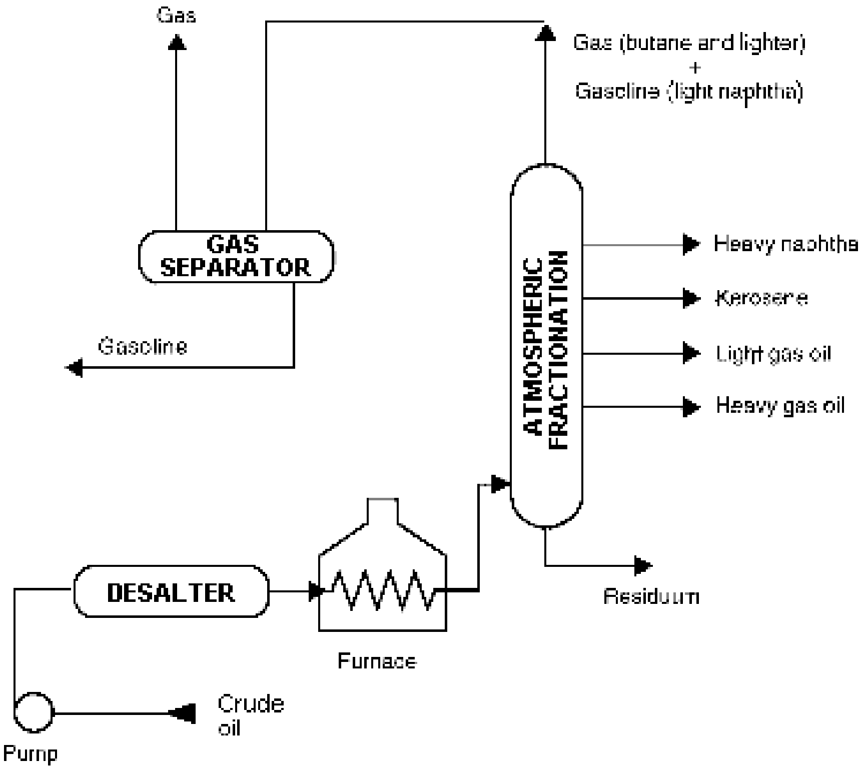
Atmospheric Distillation Tower •

- At the refinery, the desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater where it is fed into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 650° to 700° F (heating crude oil above these temperatures may cause undesirable thermal cracking). All but the heaviest fractions flash into vapor. As the hot vapor rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.
- The fractionating tower, a steel cylinder about 120 feet high, contains horizontal steel trays for separating and collecting the liquids. At each tray, vapors from below enter perforations and bubble caps. They permit the vapors to bubble through the liquid on the tray, causing some condensation at the temperature of that tray. An overflow pipe drains the condensed liquids from each tray back to the tray below, where the higher temperature causes re-evaporation. The evaporation, condensing, and scrubbing operation is repeated many times until the desired degree of product purity is reached. Then side streams from certain trays are taken off to obtain the desired fractions. Products ranging from uncondensed fixed gases at the top to heavy fuel oils at the bottom can be taken continuously from a fractionating tower. Steam is often used in towers to lower the vapor pressure and create a partial vacuum. The distillation process separates the major constituents of crude oil into so-called straight-run products. Sometimes crude oil is "topped" by distilling off only the lighter fractions, leaving a heavy residue that is often distilled further under high vacuum.

3-Atmospheric Distillation Process

Typical products...To	Process	From	Feedstock
Gases...Atmospheric distillation tower Naphthas...Reforming or treating Kerosene or distillates...Treating Gas oil...Catalytic cracking Residual...vacuum tower or visbreaker	Separation	Desalting	Crude

Atmospheric Distillation



Vacuum Distillation

In order to further distill the residuum or topped crude from the atmospheric tower at higher temperatures, reduced pressure is required to prevent thermal cracking. The process takes place in one or more vacuum distillation towers.

The principles of vacuum distillation resemble those of fractional distillation and, except that larger-diameter columns are used to maintain comparable vapor velocities at the reduced pressures, the equipment is also similar.

The internal designs of some vacuum towers are different from atmospheric towers in that random packing and demister pads are used instead of trays. A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane deasphalting.

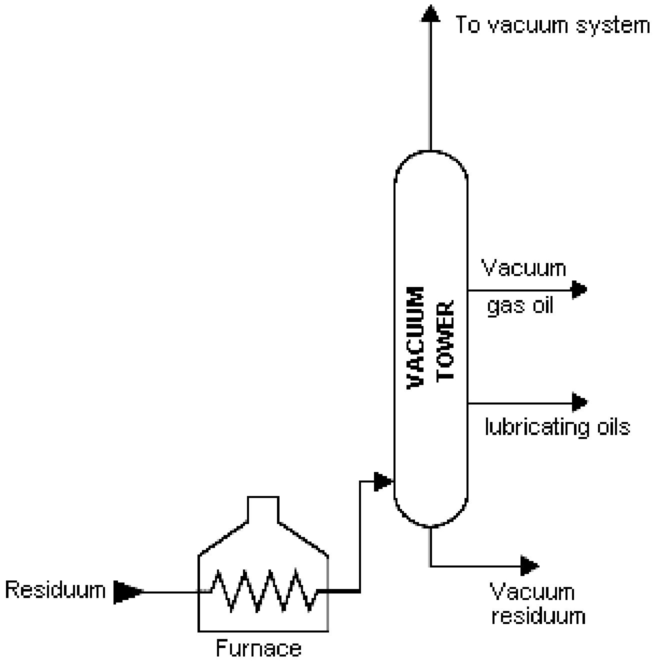
A second-phase tower operating at lower vacuum may distill surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for deasphalting. Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum.

Other Distillation Towers (Columns).

Within refineries there are numerous other, smaller distillation towers called columns, designed to separate specific and unique products. Columns all work on the same principles as the towers described above. For example, a depropanizer is a small column designed to separate propane and lighter gases from butane and heavier components. Another larger column is used to separate ethyl benzene and xylene. Small "bubble" towers called strippers use steam to remove trace amounts of light products from heavier product streams.

Vacuum Distillation Process

Gas oils...Catalytic cracker Lubricants...Hydrotreating or solvent Residual...Deasphalter, visbreaker, or coker	Separation	Atmospheric tower	Residuals



Vacuum Distillation unit

Solvent Extraction and Dewaxing

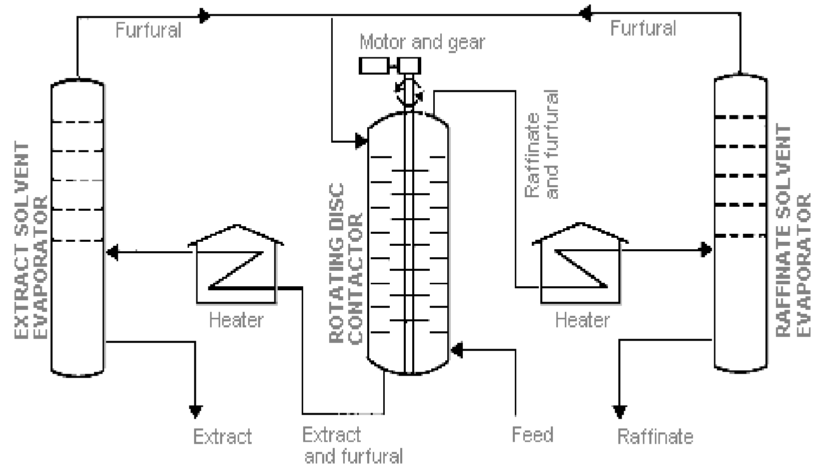
- **Description.**

  Solvent treating is a widely used method of refining lubricating oils as well as a host of other refinery stocks. Since distillation (fractionation) separates petroleum products into groups only by their boiling-point ranges, impurities may remain. These include organic compounds containing sulfur, nitrogen, and oxygen; inorganic salts and dissolved metals; and soluble salts that were present in the crude feedstock.

  In addition, kerosene and distillates may have trace amounts of aromatics and naphthenes, and lubricating oil base-stocks may contain wax. Solvent refining processes including solvent extraction and solvent dewaxing usually remove these undesirables at intermediate refining stages or just before sending the product to storage.

- Solvent Extraction
  - The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks. The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation. The feedstock is first dried and then treated using a continuous countercurrent solvent treatment operation. In one type of process, the feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product. In another process, selected solvents are added to cause impurities to precipitate out of the product. In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces.
  - The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing. Electric precipitation may be used for separation of inorganic compounds. The solvent is then regenerated to be used again in the process.
  - The most widely used extraction solvents are phenol, furfural, and cresylic acid. Other solvents less frequently used are liquid sulfur dioxide, nitrobenzene, and 2,2'-dichloroethyl ether. The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirement

Aromatics Extraction



4-Solvent Dewaxing.

Solvent dewaxing is used to remove wax from either distillate or residual basestocks at any stage in the refining process. There are several processes in use for solvent dewaxing, but all have the same general steps, which are:

(1) Mixing the feedstock with a solvent,

(2) Precipitating the wax from the mixture by freezing,

(3) Recovering the solvent from the wax and dewaxed oil for recycling by distillation and steam stripping. Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent. Other solvents that are sometimes used include benzene, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and sulfur dioxide. In addition, there is a catalytic process used as an alternate to solvent dewaxing.

The process of crude oil refining

Refinery operations are very complicated, but the basic functions of the refinery can be broken down into three categories of chemical processes:

1-Distillation involves the separation of materials based on differences in their volatility. This is the first and most basic step in the refining process, and is the precursor to cracking and reforming.

2-Cracking involves breaking up heavy molecules into lighter (and more valuable) hydrocarbons.

3-Reforming involves changing the chemical nature of hydrocarbons to achieve desired physical properties (and also to increase the market value of those chemicals).

Cracking

What is cracking?

1-Cracking involves the decomposition of heavier hydrocarbon feedstocks to lighter hydrocarbon feed stocks.

2- Cracking can be carried out to any hydrocarbon feedstock but it is usually applied for vacuum gas oil (VGO)

3- Cracking can be with or without a catalyst.

4-When cracking is carried out without a catalyst higher operating temperatures and pressures are required. This is called as thermal cracking. This was the principle of the old generation refineries. Now a days, cracking is usually carried out using a catalyst.

- The catalyst enabled the reduction in operating pressure and temperature drastically.

Cracking chemistry

What is cracking?

1-Long chain paraffins converted to olefins and olefins

2- Straight chain paraffins converted to branched paraffins

3-Alkylated aromatics converted to aromatics and paraffins

4-Ring compounds converted to alkylated aromatics

5-Dehydrogenation of naphthenes to aromatics and hydrogen
6-Undesired reaction: Coke formation due to excess cracking
7- Cracking is an endothermic reaction

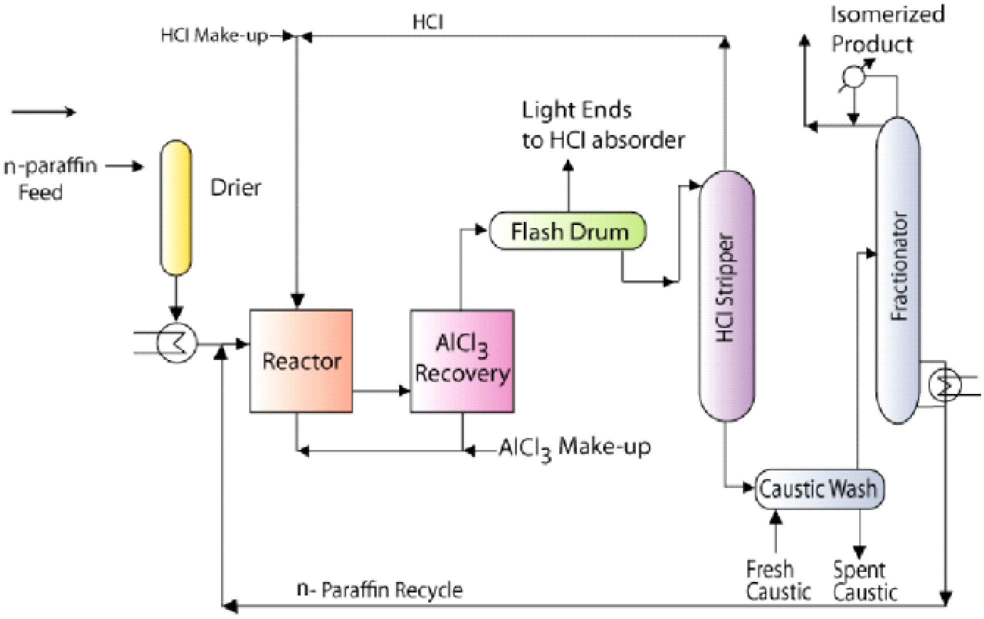
Cracking Chemistry

1- Paraffin isomerisation takes place
2-Naphthene isomerisation also takes place to produce cycloalkanes
3-Cyclo alkanes undergo dehydrogenation to generate aromatics
4-Dehydrocyclization takes places to convert side chained alkanes to cyclo alkanes and hydrogen
5-In summary lower octane number feeds are converted to high octane products
6-The reformate thus produced has high octane and aromatics (benzene, toluene and xylene) content.

Process technology

1-The feed is mixed with recycled hydrogen
2-Subsequently, it is heated before sending to reactor
3- Since the reactions are highly endothermic, several combinations of reactor + heaters are used.
4-The products from the final reactor are cooled. Often this is carried out with heat recovery principle in which heat is recovered using the fresh feed to the first reactor.
5-After this, the product mixture enters a phase separator which separates the hydrogen gas stream from the liquid stream.
6-The liquid stream from the phase separator is sent to a debutanizer distillation column that separates butanes and lower alkanes from the reformate product.
7-The hydrogen produced in the phase separator is compressed and sent back to the first reactor.
8-Excess hydrogen generated in the reactions is taken out as a bleed stream
9- Catalyst regeneration (not shown in the flow sheet) needs to be carried out to

regain catalyst activity.



Typically cracking involves the thermal or catalytic decomposition of petroleum fractions having huge quantities of higher molecular weight compounds. Since heat is required, typically cracking reactions are carried. Cracking facilitates initiation, propagation and termination reactions amongst the hydrocarbon themselves

Catalyst

- Acid treated silica-alumina was used as catalyst.
- 20 - 80 mesh size catalysts used for FCCR and 3 – 4 mm pellets used for MBRs
- During operation, poisoning occurs with Fe, Ni, Vd and Cu

Therefore, in principle cracking generates lighter hydrocarbons constituting paraffins, olefins and aromatics. In other words, high boiling low octane number feed stocks are converted to low boiling high octane number products.

There are TWO types of cracking

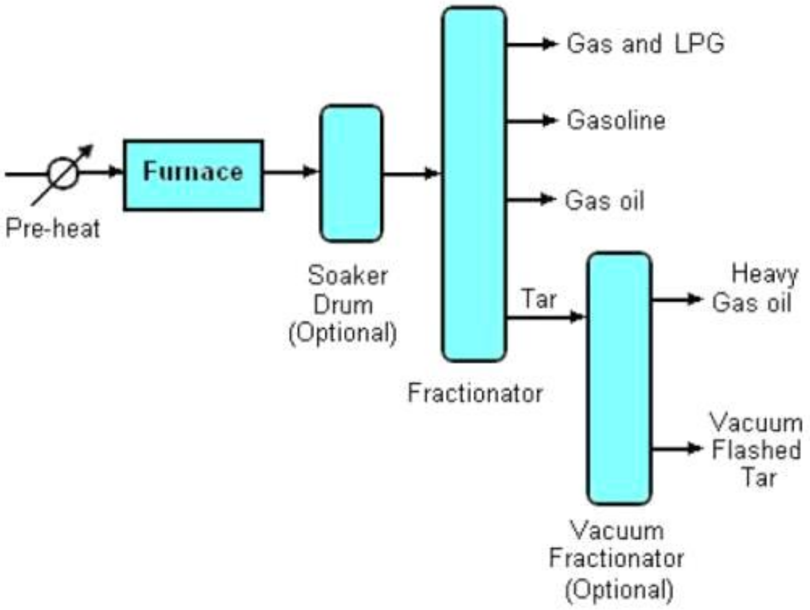
1-THERMAL CRACKING

2- CATALYTIC CRACKING

1-**Thermal Cracking**

(typically in the range of 450°C to 750°C)

and pressures (up to about 70 atmospheres)



Thermal cracking or simply cracking is a process of breaking down the larger and heavier nonvolatile molecules of hydrocarbons (primarily crude oil) into smaller and lighter molecules by application of heat at high temperatures and pressures in the presence of a catalyst. This process is sometimes also called pyrolysis of oil. This process helps in extracting the lighter petroleum fractions such as gasoline and diesel fuel.

Thermal cracking processes is a heat distillate fuels and heavy oils under pressure and very high temperatures until they crack and divide into smaller molecules, and it does not require the addition of a catalyst. As the temperature and residence time are increased, the primary products undergo further reaction to produce various secondary products and so on, with the ultimate products being formed at extreme temperature of approximately 1000 °C.

Description

- Because the simple distillation of crude oil produces amounts and types of products that are not consistent with those required by the marketplace, subsequent refinery processes change the product mix by altering the molecular structure of the hydrocarbons. One of the ways of accomplishing this change is through "cracking," a process that breaks or cracks the heavier, higher boiling-point petroleum fractions into more valuable products such as gasoline, fuel oil, and gas oils. The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking.
- Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics. However, this method produced large amounts of solid, unwanted coke. This early process has evolved into the following

applications of thermal cracking: visbreaking, steam cracking, and coking.

The term thermal cracking applies to the decomposition of petroleum constituents that is induced by elevated temperatures (>350 ^{0}c) whereby the higher molecular weight constituents of petroleum are converted to lower molecular weight products.

Cracking reactions involve carbon-carbon bond rupture and are thermodynamically favored at high temperature.

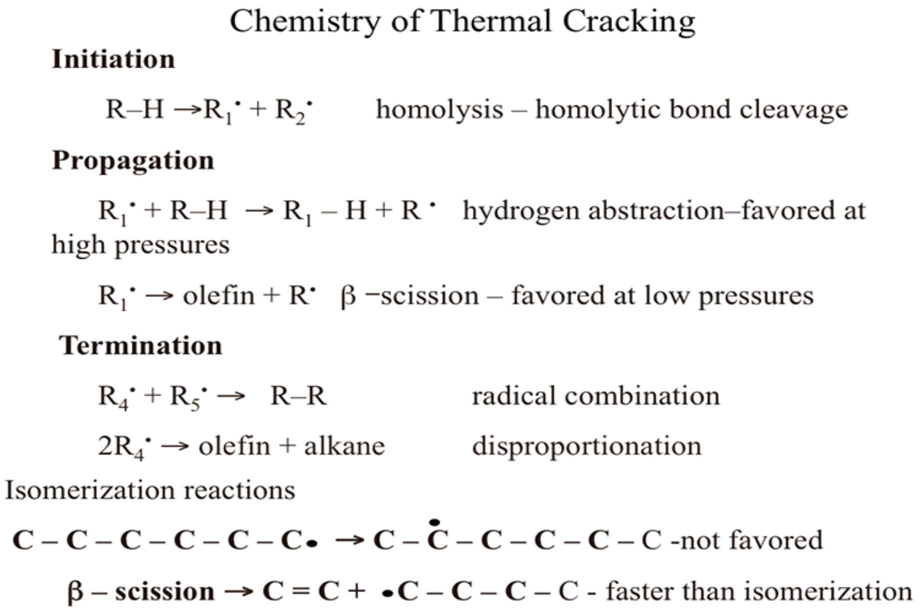
Chemistry of Thermal Cracking

Thermal cracking produces shorter straight chain alkanes from longer straight chains found in gas oils or other crude oil fractions. Free radicals (reactive species with unpaired electrons, but no electronic charge) are the active species that govern thermal cracking reactions. Because of the free radical chemistry, thermal cracking of gas oil would produce gasoline with relatively low octane numbers, as will be discussed later in this section

The three steps of free radical chain reactions as initiation, propagation, and termination. In the figure, R-H represents a paraffin chain which can be expanded such as (H_3-$(CH_2)_n$ – H) where n represents the number of carbon atoms in the alkane. In other words, R represents a radical with an unpaired electron that becomes an alkane (R-H) when combined with a hydrogen atom. A Hydrogen atom with one proton and one electron is the simplest radical.

The free radical chain reaction starts with breaking the weakest C-C bond in the reactant alkane (R-H) to form two free radicals R_1 and R_2, each with one unpaired electron resulting from the homolysis of the C-C bond (initiation). Once formed by the initiation step, each free radical can go through two different propagation reactions:

- Hydrogen abstraction
- Beta (β) scission



Chemistry of Thermal Cracking

Initiation

$R–H \rightarrow R_1^{\bullet} + R_2^{\bullet}$ homolysis – homolytic bond cleavage

Propagation

$R_1^{\bullet} + R–H \rightarrow R_1 – H + R^{\bullet}$ hydrogen abstraction–favored at high pressures

$R_1^{\bullet} \rightarrow$ olefin + $R^{\bullet}$ β –scission – favored at low pressures

Termination

$R_4^{\bullet} + R_5^{\bullet} \rightarrow R–R$ radical combination

$2R_4^{\bullet} \rightarrow$ olefin + alkane disproportionation

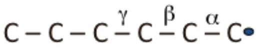
Isomerization reactions

$\mathbf{C – C – C – C – C – C^{\bullet}} \rightarrow \mathbf{C –} \overset{\bullet}{\mathbf{C}} – \mathbf{C – C – C –} C$ -not favored

β – scission $\rightarrow$ **C = C +** $\bullet$**C – C – C –** C - faster than isomerization

Free radical chain reactions.

In a hydrogen abstraction reaction, for example, the radical R_1 removes (abstracts) a hydrogen atom from an alkane (R-H) to produce a shorter chain alkane product (R_1-H) and a new radical R (hydrogen abstraction), thus propagating the free radical chain. Alternatively, the radical $R_{1,}$ (or R_2) can go through a β scission reaction to produce an olefin (ethylene) as a product, and a radical R to propagate the chain. The β scission refers to the breaking of covalent bond in the β position relative to the position of the unpaired electron as shown below:



$$C – C – C \overset{\gamma}{–} C \overset{\beta}{–} C \overset{\alpha}{–} C^{\bullet}$$

The β scission

Note that the initiation step produces two free radicals, the propagation step produces a reaction product and one radical to continue the chain. The last step in the chain reaction, the termination step, removes two radicals to produce one or two stable compounds depending on the termination reaction, The principal end result of the free radical chain reactions in thermal cracking is to produce from long chain alkanes shorter-chain alkanes, light olefins, and some aromatic compounds. One important feature of free radical reactions is that isomerization reactions, e.g., shifting of the unpaired electron site from an edge atom of a molecule to the interior atoms, are not favored reactions. In other words, isomerization reactions take place at a slower rate than other propagation reactions, e.g., β scission reaction.

The critical importance of this observation is that the thermal cracking reactions produce shorter straight-chain alkanes and olefins without any significant formation of branched-chain (or iso-alkanes). This is the reason why catalytic cracking processes have virtually replaced thermal cracking processes to produce high octane number gasoline, as will be discussed in the next section on catalytic cracking.

However, certain products may interact with one another to yield products having higher molecular weights than the constituents of the original feedstock. Some of the products are expelled from the system as, say, gases, gasoline-range materials, kerosene-range materials, and the various intermediates that produce other products such as coke. Materials that have boiling ranges higher than gasoline and kerosene may (depending upon the refining options) be recycled in the cracking equipment until conversion is complete. Two general types of reaction occur during cracking:

1. The decomposition of large molecules into small molecules (primary reactions):

$$CH_3CH_2CH_2CH_3 \sim CH_4 + CH_3CH = CH_2$$

butane methane propene

CH3CH2CH2CH3 -----C2H6+ CH2=CH2

butane ethane ethylene

2. Reactions by which some of the primary products interact to form higher molecular weight materials (secondary reactions). Thermal cracking of petroleum is a free radical chain reaction and it is their mode of reaction of the free radicals that actually determines the product distribution. Free radical reacts with a hydrocarbon by abstracting a hydrogen atom to produce a stable end product and a new free radical. The prevailing reaction conditions and those reaction sequences that are thermodynamically favored determine the product distribution.

CH2 = CH2 + CH2 = CH2 -----CH3 CH2 CH=CH2+ coke + other products

- Thermal cracking of petroleum is a free radical chain reaction and it is their mode of reaction of the free radicals that actually determines the product distribution. Free radical reacts with a hydrocarbon by abstracting a hydrogen atom to produce a stable end product and a new free radical. The prevailing reaction conditions and those reaction sequences that are thermodynamically favored determine the product distribution.

Visbreaking Process

Visbreaking, a mild form of thermal cracking, significantly lowers the viscosity of heavy crude-oil residue without affecting the boiling point range. Residual from the atmospheric distillation tower is heated (800°-950° F) at atmospheric pressure and mildly cracked in a heater.

It is then quenched with cool gas oil to control overcracking, and flashed in a distillation tower.

1- Middle distillates may also be produced, depending on product demand. The thermally cracked residue tar, which accumulates in the bottom of the fractionation tower, is vacuum flashed in a stripper and the distillate recycled.

2-Steam Cracking Process. Steam cracking is a petrochemical process sometimes used in refineries to produce olefinic raw materials (e.g., ethylene) from various feedstock for petrochemicals manufacture. The feedstock range from ethane to vacuum gas oil, with heavier feeds giving higher yields of by-products such as naphtha. The most common feeds are ethane, butane, and naphtha. Steam cracking is carried out at temperatures of 1,500°-1,600° F, and at pressures slightly above atmospheric. Naphtha produced from steam cracking contains benzene, which is extracted prior to hydrotreating. Residual from steam cracking is sometimes blended into heavy fuels.

- **Coking Processes.**

  Coking is a severe method of thermal cracking used to upgrade heavy residuals into lighter products or distillates. Coking produces straight-run gasoline (coker naphtha) and various middle-distillate fractions used as catalytic cracking feedstock. The process so completely reduces hydrogen that the residue is a form of carbon called "coke." The two most common processes are delayed coking and continuous (contact or fluid) coking. Three typical types of coke are obtained (sponge coke, honeycomb coke, and needle coke) depending upon the reaction mechanism, time, temperature, and the crude feedstock

  - **Delayed Coking.** In delayed coking the heated charge (typically residuum from atmospheric distillation towers) is transferred to large coke drums which provide the long residence time needed to allow the cracking reactions to proceed to completion.

    1-Initially the heavy feedstock is fed to a furnace which heats the residuum to high **temperatures (900°-950° F) at low pressures (25-30 psi)** and is designed and controlled to prevent premature coking in the heater tubes. The mixture is passed from the heater to one or more coker drums where the hot material is held approximately 24 hours (delayed) at pressures of 25-75 psi, until it cracks into lighter products.

    2-Vapors from the drums are returned to a fractionator where gas, naphtha, and gas oils are separated out. The heavier hydrocarbons produced in the fractionator are recycled through the furnace.

    3-After the coke reaches a predetermined level in one drum, the flow is diverted to another drum to maintain continuous operation. The full drum is steamed to strip out uncracked hydrocarbons, cooled by water injection, and decoked by mechanical or hydraulic methods. The coke is mechanically removed by an auger rising from the bottom of the drum. Hydraulic decoking consists of fracturing the coke bed with high-pressure water ejected from a rotating cutter.

  - **Continuous Coking.** Continuous (contact or fluid) coking is a moving-bed process that operates at temperatures higher than delayed coking. In continuous coking, thermal cracking occurs by using heat transferred from hot, recycled coke particles to feedstock in a radial mixer, called a reactor, at a pressure of 50 psi. Gases and vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The reacted coke enters a surge drum and is lifted to a feeder and classifier where the larger coke particles are removed as product. The remaining coke is dropped into the preheater for recycling with feedstock. Coking occurs both in the reactor and in the surge drum. The process is automatic in that there is a continuous flow of coke and feedstock.

2- **Catalytic Cracking**

- Initial processes temperature (400-550 ^{0}C)

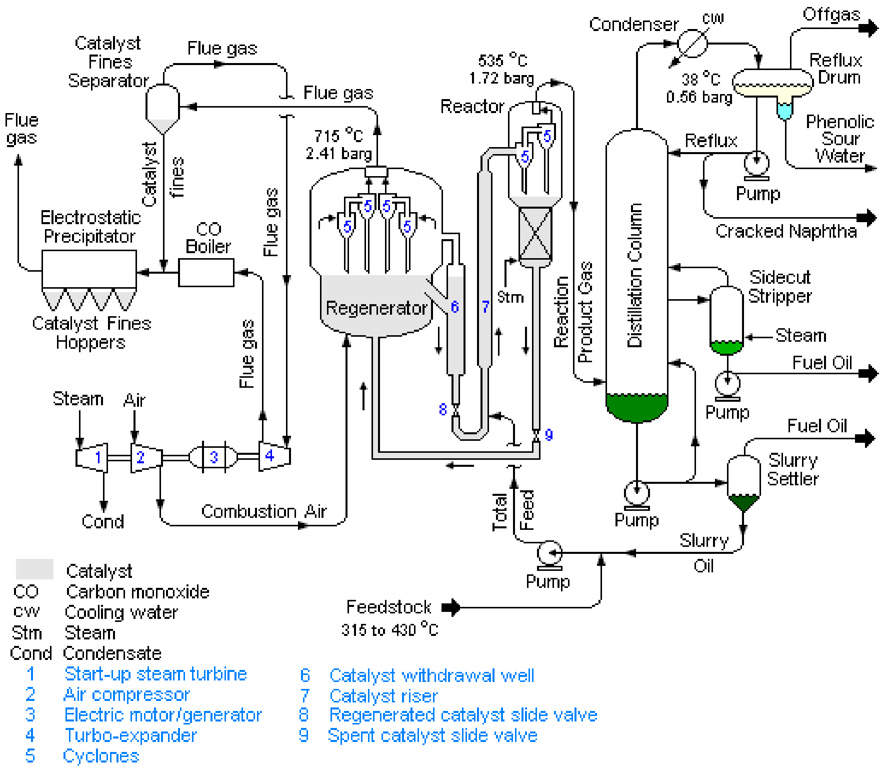
and a pressure of about 2.41 bar, (200 to 600 or higher)

- With air at a temperature of about 715 °C and a pressure of about 2.41 bar,

catalytic cracking is a process that uses a variation of the continuously moving catalyst bed in a method designed to obtain high yields of high-octane gasoline and from reduced crude charge.

Deep Catalytic Cracking is a new fluid catalytic cracking process using a new catalyst for heavy feed stocks to give light olefins. The yield of olefins depends greatly on the type of feedstock. Paraffenic feeds give the lightest propylene yield of 23 wt % and 6.9 wt% isobutylene .
In catalytic cracking process the catalyst is regenerated by burning off the deposited coke with air at a temperature of about 715 °C and a pressure of about 2.41 bar,

Catalytic cracking process takes place in the presence of a catalyst. The catalyst promotes breaking of the large molecules in a certain way that maximizes the yield of gasoline. Cat cracking produces a full range of hydrocarbons, from methane to residue.



In catalytic cracking process the catalyst is regenerated by burning off the deposited coke with air at a temperature of about 715 °C and a pressure of about 2.41 bar,

The hot catalyst (at about 715 °C) leaves the regenerator into a catalyst withdrawal

The feed to the cat cracker is typically gas oil or naphtha. The trend in the design of modern cracking units is the ability to include the residuum as a part of the cracker feed. The residue produced by the catalytic cracker is recycled back into the feed stream. This recycling of the residue is called “recycling to extinction”.

Catalytic cracking consists of three major processes:

1-Reaction 2-Regeneration 3-Fractionation

In the reaction step, the hydrocarbon feed is contacted by the catalyst at a high temperature (400-550 ^{0}C) An initial boiling point of 340 °C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher .and the cracking reaction takes place.

All of the cracking reactions take place in the catalyst riser within a period of 2–4 seconds. The hydrocarbon vapors the powdered catalyst and the mixture of hydrocarbon vapors and catalyst flows up to enter the *reactor* at a temperature of about 535 °C and a pressure of about 1.72 bar.

The catalyst is renewed by burning off the coke deposits from the catalyst surface during regeneration. The cracked hydrocarbons are separated using fractionating processes.

There are three basic types of catalytic crackers:

1-Fluid bed 2-Moving bed 3-Fixed bed

The mostly, catalytic cracker is in the form of beads or pellets. In the form of finely divided powder. And within air or hydrocarbon vapor it behaves like a fluid and can be moved through pipes and valves.

The equipment consists of a series of reactor vessels containing the catalyst bed. Some of these reactors will be on-line producing cracked hydrocarbons while others will be off-line having the catalyst regenerated.

Fluid Catalytic Cracking

The catalytic cracking processes units consist of three units :

1-The reaction chamber in which the hot feed is mixed with the catalyst and the cracking reactions take place
2-The regenerator in which the catalyst is regenerated by burning the coke produced in the reactor from its surface

3-The fractionator where the cracked hydrocarbons are separated into useful

products.

Catalyst

Platinum base catalysts are used :

$AlCl_3$ is used as a promoter for the catalyst .

During reaction, part of the $AlCl_3$ gets converted to HCl Therefore, completely dry conditions shall be maintained to avoid catalyst deactivation and corrosion. .

Catalytic reaction takes place in the presence of hydrogen to suppress coke formation.

Light naphtha and hydrogen (make up) are totally dried and sent to an isomerisation reactor after pre-heating the feed mixture in a heat exchanger

A) Reaction operating conditions: 150 – 200 °C and 17 – 28 barg

B) Typical conversions: 75 – 80 % for pentanes.

C) After reaction, AlCl3 is recovered from the product using condensation or distillation

D) The basic principle for AlCl3 recovery is that at the reactor operating conditions, the AlCl3 is in volatile conditions and is soluble in hydrocarbons

E) After AlCl3 is recovered from the product, it is sent back to the reactor along with the make- up AlCl3

F) Eventually, the product enters a flash drum where bulkly light ends along with little quantities of HCl are separated from the liquid product.

G) The light ends recovered from the flash drum are sent to aHCl absorber where HCl is absorbed into caustic solution to generate the light end gases.

H) The light end gases can be further used for other processes in the refinery.

I) The bottom product then enters aHCl stripper where most of the HCl is stripped from the isomerisation product rich stream. The HCl is recycled back to the reactor to ensure good catalyst activity. Make-up HCl is added to account for losses

J) Subsequently, caustic wash is carried out to remove any trace quantities of HCl

K) The isoermized product rich stream is then sent to a fractionators that separates the isomerized product from the unreacted feed.

L) The unreacted feed from the fractionators is sent back to the reactor.

Catalytic Cracking

Cracking Reaction Conditions:

Temperature:	520 - 550°C
Pressure:	2 - 3 atm
Cat/Oil:	4.5 - 6
Contact Time:	2 - 6 sec.
Conversion:	70 - 80%

Increased temperature results in increased conversion, but decreased yield of gasoline-range hydrocarbon products, due to secondary cracking to smaller products.

Catalyst Regenerator Conditions:

Temperature:	650 - 760°C
Pressure:	~3 atm

Chemistry of Catalytic cracking

Secondary reactions occurring after the initial cracking steps are important in determining the final product composition. These include the following:

6. Hydrogen transfer:

$$\text{Naphthene} + \text{olefin} \longrightarrow \text{aromatic} + \text{paraffin} \tag{8}$$

$$\text{Aromatic coke precursor} + \text{olefin} \longrightarrow \text{coke} + \text{paraffin} \tag{9}$$

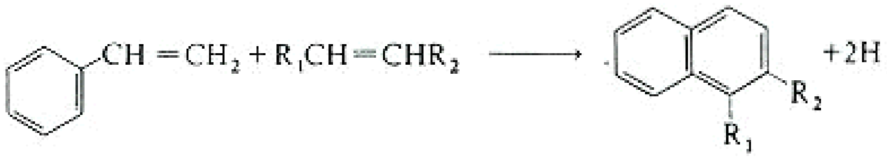
7. Isomerization:

$$\text{Olefin} \longrightarrow \text{isoolefin} \tag{10}$$

8. Alkyl-group transfer:

$$C_6H_4(CH_3)_2 + C_6H_6 \longrightarrow C_6H_5(CH_3) + C_6H_5(CH_3) \tag{11}$$

9. Condensation reactions:



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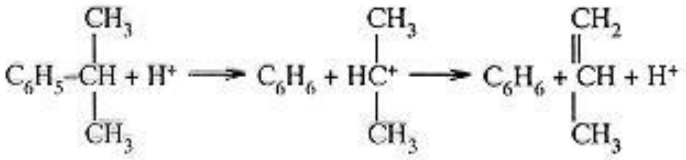
10. Disproportionation of low-molecular-weight olefins:

$$2H_2C{=}CHCH_2CH_3 \longrightarrow H_2C{=}CHCH_3 + H_2C{=}CHCH_2CH_2CH_3 \tag{13}$$

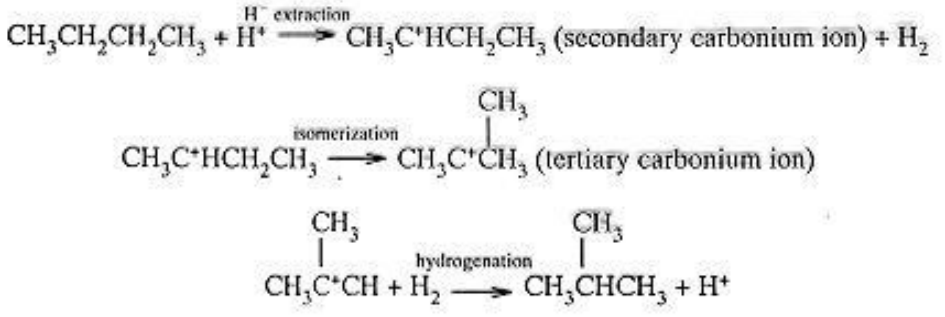
Selected proposed mechanisms of other important reactions in FCC are as follows:

Acid-catalyzed dealkylation and alkene formation



$$C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} + H^+ \longrightarrow C_6H_6 + \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HC^+}} \longrightarrow C_6H_6 + \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{CH}} + H^+$$

Acid-catalyzed isomerism:

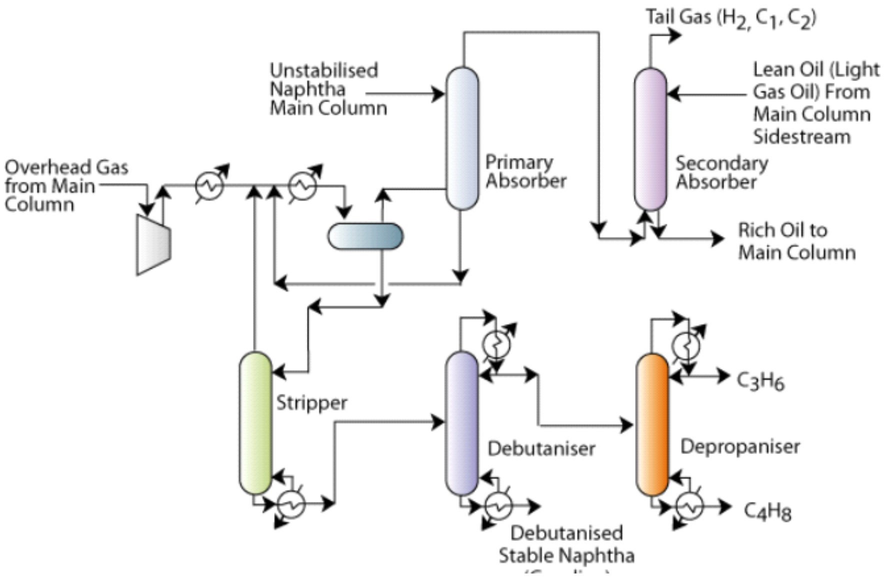


$$CH_3CH_2CH_2CH_3 + H^+ \xrightarrow{H^-\text{ extraction}} CH_3C^+HCH_2CH_3\ \text{(secondary carbonium ion)} + H_2$$

$$CH_3C^+HCH_2CH_3 \xrightarrow{\text{isomerization}} CH_3\overset{\overset{CH_3}{|}}{C^+}CH_3\ \text{(tertiary carbonium ion)}$$

$$CH_3\overset{\overset{CH_3}{|}}{C^+}CH + H_2 \xrightarrow{\text{hydrogenation}} CH_3\overset{\overset{CH_3}{|}}{C}HCH_3 + H^+$$

Catalytic Cracking : Overview



Description

- Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock.

- Catalytic cracking is similar to thermal cracking except that catalysts facilitate the conversion of the heavier molecules into lighter products. Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking. Typical temperatures are from 850°-950° F at much lower pressures of 10-20 psi. The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudites.
- There are three basic functions in the catalytic cracking process:
    - Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons;
    - Regeneration: Catalyst is reactivated by burning off coke; and
    - Fractionation: Cracked hydrocarbon stream is separated into various products.
- The three types of catalytic cracking processes are fluid catalytic cracking (FCC), moving-bed catalytic cracking, and Thermofor catalytic cracking (TCC). The catalytic cracking process is very flexible, and operating parameters can be adjusted to meet changing product demand. In addition to cracking, catalytic activities include dehydrogenation, hydrogenation, and isomerization.

Fluid Catalytic Cracking

- **Description**
    - The most common process is FCC, in which the oil is cracked in the presence of a finely divided catalyst which is maintained in an aerated or fluidized state by the oil vapors. The fluid cracker consists of acatalyst section and a fractionating section that operate together as an integrated processing unit. The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit. The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media.
    - A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor. The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°- 1,000°F) by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10-30 psi.
    - In the more modern FCC units, all cracking takes place in the riser. The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for the cyclones. This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones. The resultant product stream (cracked product) is then charged to a

fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser.

- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process. Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

2-Moving Bed Catalytic Cracking.

The moving-bed catalytic cracking process is similar to the FCC process. The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator. The regenerator and hopper are isolated from the reactor by steam seals. The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas.

3-Thermofor Catalytic Cracking.

In a typical thermofor catalytic cracking unit, the preheated feedstock flows by gravity through the catalytic reactor bed. The vapors are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue gas from regeneration is sent to a carbon-monoxide boiler for heat recovery.

Hydrocracking

- **Description**
  - Hydrocracking is a two-stage process combining catalytic cracking and hydrogenation, wherein heavier feedstocks are cracked in the presence of hydrogen to produce more desirable products. The process employs high pressure, high temperature, a catalyst, and hydrogen. Hydrocracking is used for feedstocks that are difficult to process by either catalytic cracking or reforming, since these feedstocks are characterized usually by a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.
  - The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking.

Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts. When the feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. Another important role of hydrogen in the hydrocracking process is to reduce tar formation and prevent buildup of coke on the catalyst. Hydrogenation also serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.

- Hydrocracking produces relatively large amounts of isobutane for alkylation feedstock. Hydrocracking also performs isomerization for pour-point control and smoke-point control, both of which are important in high-quality jet fuel.

Hydrocracking Process

In the first stage, preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulfur and nitrogen compounds to hydrogen sulfide and ammonia. Limited hydrocracking also occurs.

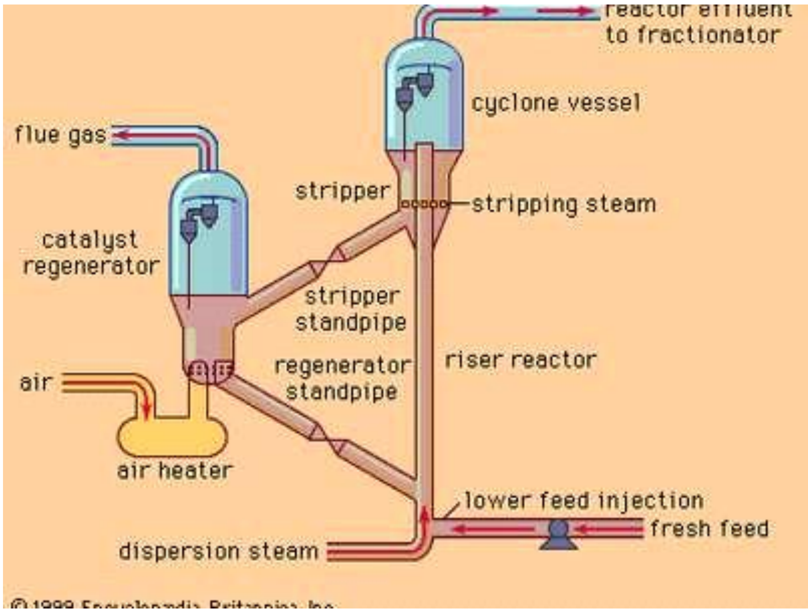
After the hydrocarbon leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator. The hydrogen is recycled to the feedstock. The liquid is charged to a fractionator. Depending on the products desired (gasoline components, jet fuel, and gas oil), the fractionator is run to cut out some portion of the first stage reactor outturn. Kerosene-range material can be taken as a separate side-draw product or included in the fractionator bottoms with the gas oil.

The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Like the outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator.

Thermal reforming processes

Thermal reforming employed temperatures of 510–565 °C (950–1,050 °F) at moderate pressures—about 40 bars (4 MPa), or 600 psi—to obtain gasolines (petrols) with octane numbers of 70 to 80 from heavy naphthas with octane numbers of less…

As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha and then enters a fractional distillation tower where the heavy products are separated. The remainder of the reformed material leaves the top of the tower and is separated into gases and reformate. The reformate has a high octane number due to cracking of the longer-chain paraffins into higher-octane olefins.



The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (about 1%). The amount and quality of gasoline, known as reformate, is very dependent on the temperature. As a rule, the higher the reforming temperature, the higher the octane number, but the lower the yield of reformate.

Catalytic Reforming

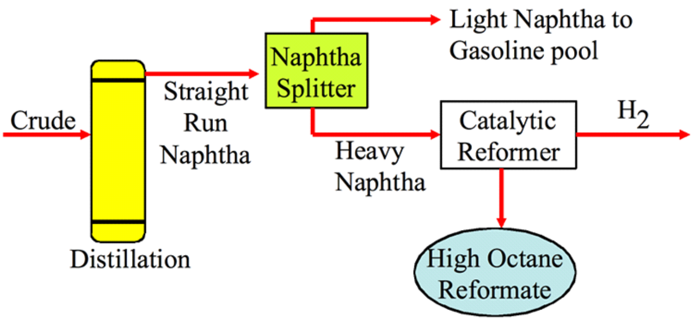
The reaction conditions

Temperature: 495 to 525 °C

pressures of about : 5 to 45 atm.

Catalysts contain platinum or rhenium on a silica or silica-alumina

Fresh catalyst is chlorided (chlorinated) prior to use.



catalytic reforming process in a refinery.

Chemistry of Catalytic Reforming

The general categories of the desired reactions in catalytic reforming are identified in list below, along with the catalysts used in the process.

Considering that the main purpose of the process is to increase the octane number of heavy naphtha, conversion of naphthenes to aromatics and isomerization of n-paraffins to iso-paraffins are the most important reactions of interest. Under the right reaction conditions, aromatics in the feed, or those produced by dehydrogenation naphthenes should remain unchanged.

The reforming reactions produce large quantities of hydrogen, and one should remember that the dehydrogenation catalysts used in reforming can also catalyze hydrogenation and hydrocracking of aromatics during catalytic reforming. It is, therefore, important to keep these side reactions to a minimum by controlling the reactor conditions such as temperature and hydrogen pressure, as discussed in more detail later in this section.

The catalysts used in reforming contains platinum (Pt), palladium (Pd), or, in some processes, bimetallic formulations of Pt with Iridium or Rhenium supported on alumina (Al_2O_3).

Catalytic Reforming Reactions and Catalysts

Reactions of Interest

- naphthenes → aromatics
- paraffins are isomerized
- aromatics are unchanged

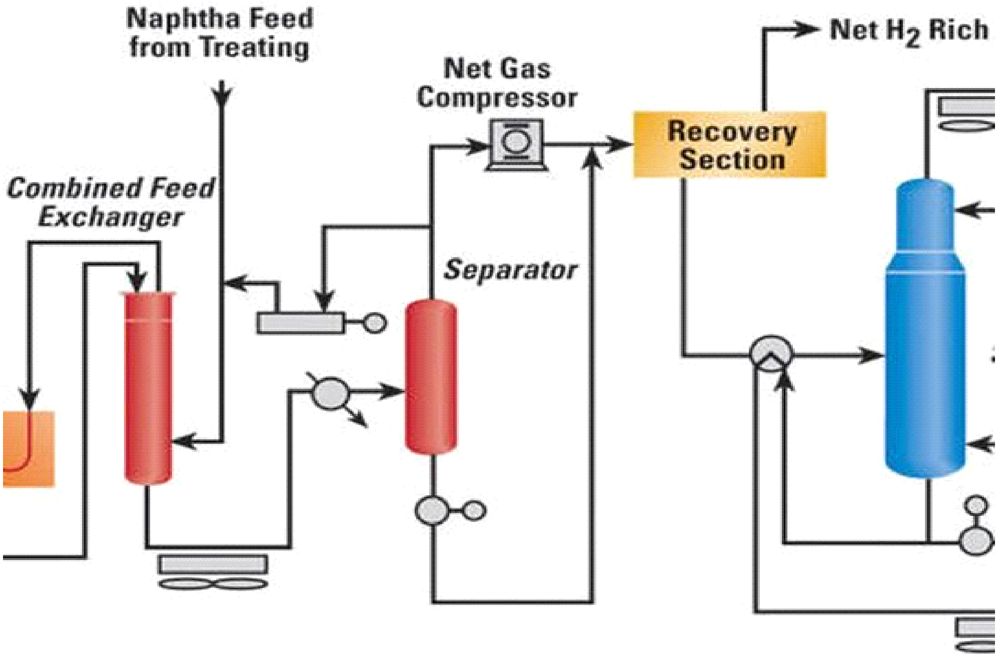
Catalysts Used

Platinum catalyst on metal oxide support (platforming)

$Pt/Al2O_3$

Bimetallic – Iridium or Rhenium

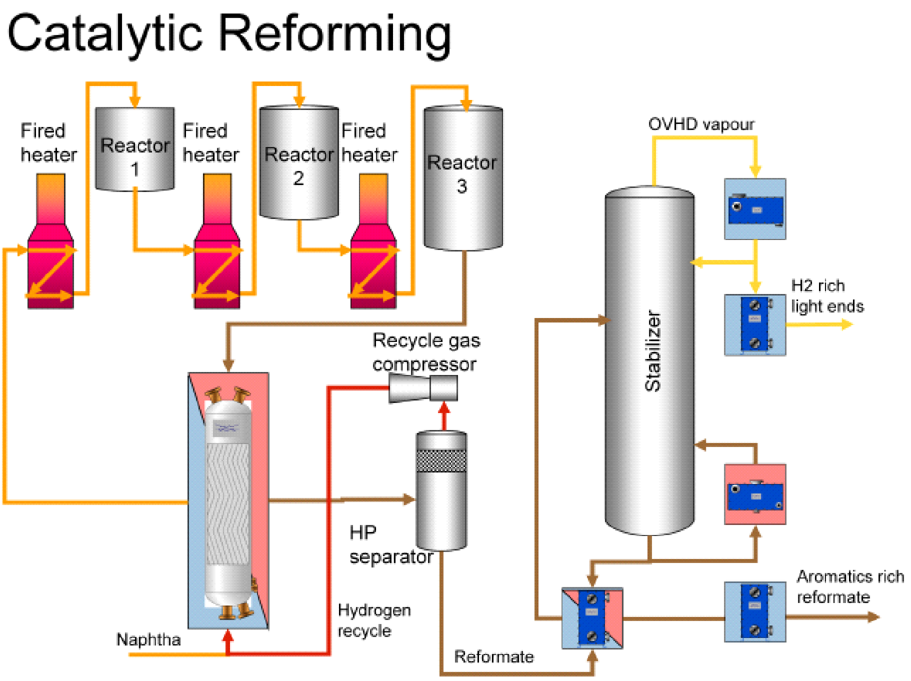
$Pt\text{-}Re/Al2O_3$



Platforming Process in egypt

Description

Catalytic reforming converts low-octane, straight-run naphtha fractions, particularly heavy naphtha that is rich in naphthenes, into a high-octane, low-sulfur reformate, which is a major blending product for gasoline



Most reforming catalysts contain platinum as the active metal supported on alumina, and some may contain additional metals such as rhenium and tin in bi- or tri-metallic catalyst formulations.

In most cases, the naphtha feedstock needs to be hydrotreated before reforming to protect the platinum catalyst from poisoning by sulfur or nitrogen species. With the more stringent requirements on benzene and the total aromatics limit for gasoline, the amount of reformate that can be used in gasoline blending has been limited, but the function of catalytic reforming as the only internal source of hydrogen continues to be important for refineries.

- Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called reformates. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously.
- Depending on the properties of the naphtha feedstock (as measured by the paraffin, olefin, naphthene, and aromatic content) and catalysts used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Hydrogen, a significant by-product, is separated from the reformate for recycling and use in other processes.
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- There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and Thermofor catalytic reforming. In the platforming process, the first step is preparation of the naphtha feed to remove impurities from the naphtha and reduce catalyst degradation. The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst. The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling. The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer). It makes a bottom product called reformate; butanes and lighter go overhead and are sent to the saturated gas plant.
- Some catalytic reformers operate at low pressure (50-200 psi), and others operate at high pressures (up to 1,000 psi). Some catalytic reforming systems continuously regenerate the catalyst in other systems. One reactor at a time is taken off-stream for catalyst

regeneration, and some facilities regenerate all of the reactors during turnarounds

Catalytic reforming is a process whereby light petroleum distillates (naphthas) are contacted with a platinum-containing catalyst at elevated temperatures and hydrogen pressures ranging from 345 to 3,450 kPa (50–500 psig) for the purpose of raising the octane number of the hydrocarbon feed stream. The low octane, paraffin-rich naphtha feed is converted to a high-octane liquid product that is rich in aromatic compounds. Hydrogen and other light hydrocarbons are also produced as reaction by-products. In addition to the use of reformate as a blending component of motor fuels, it is also a primary source of aromatics used in the petrochemical industry

Catalytic reforming is a chemical process used to convert petroleum refinery naphthas distilled from crude oil (typically having low octane ratings) into high-octane liquid products called reformates, which are premium blending stocks for high-octane gasoline. The process converts low-octane .linear hydrocarbons (paraffins) into branched alkanes (isoparaffins) and cyclic naphthenes, which are then partially dehydrogenated to produce high-octane aromatic hydrocarbons. The dehydrogenation also produces significant amounts of byproduct hydrogen gas, which is fed into other refinery processes such as hydrocracking. A side reaction is hydrogenolysis, which produces light hydrocarbons of lower value, such as methane, ethane, propane and butanes.

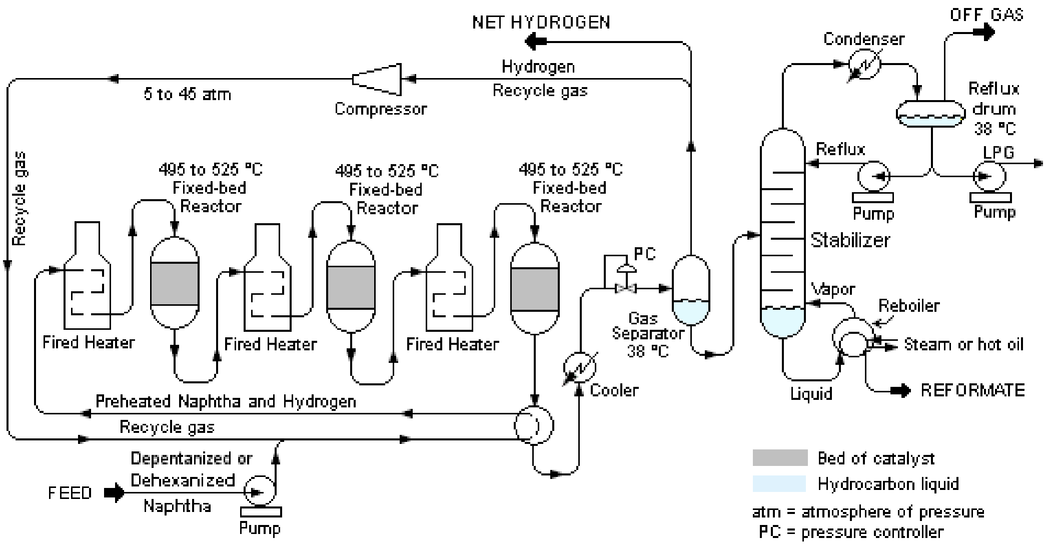
In addition to a gasoline blending stock, reformate is the main source of aromatic bulk chemicals such as benzene, toluene, xylene and ethylbenzene which have diverse uses, most importantly as raw materials for conversion into plastics. However, the benzene content of reformate makes it carcinogenic, which has led to governmental regulations effectively requiring further processing to reduce its benzene content.

The naphtha from the crude oil distillation is often further distilled to produce a "light" naphtha containing most (but not all) of the hydrocarbons with 6 or fewer carbon atoms and a "heavy" naphtha containing most (but not all) of the hydrocarbons with more than 6 carbon atoms. The heavy naphtha has an initial boiling point of about 140 to 150 °C and a final boiling point of about 190 to 205 °C. The naphthas derived from the distillation of crude oils are referred to as "straight-run" naphthas.

On reforming reactions, the carbon number of the reactants remains unchanged, except for hydrocracking reactions which break down the hydrocarbon molecule into molecules with fewer carbon atoms.

The hydrocracking of paraffins is the only one of the above four major reforming reactions that consumes hydrogen. The isomerization of normal paraffins does not consume or produce hydrogen.

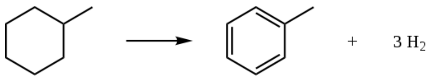
However, independently of the crude oil used in the refinery, all catalysts require a maximum final boiling point of the naphtha feedstock of 180 °C.



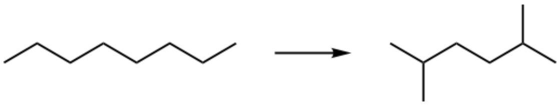
Schematic diagram of a typical semi-regenerative catalytic reformer unit in a petroleum refinery

The four major catalytic reforming reactions are:

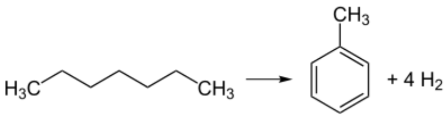
1: The dehydrogenation of naphthenes to convert them into aromatics as exemplified in the conversion methylcyclohexane (a naphthene) to toluene (an aromatic), as shown below:



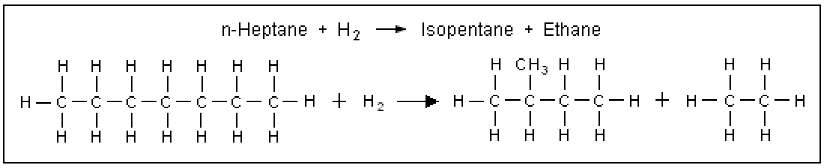
2: The isomerization of normal paraffins to isoparaffins as exemplified in the conversion of normal octane to 2,5-Dimethylhexane (an isoparaffin), as shown below:



3: The dehydrogenation and aromatization of paraffins to aromatics (commonly called dehydrocyclization) as exemplified in the conversion of normal heptane to toluene, as shown below:



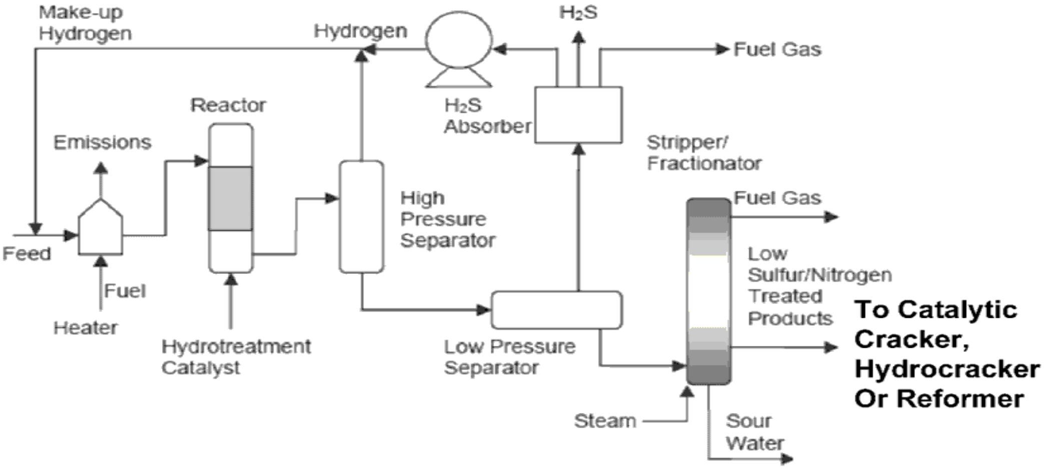
4: The hydrocracking of paraffins into smaller molecules as exemplified by the cracking of normal heptane into isopentane and ethane, as shown below:



REF; 1- Peter R. Pujadó and Mark Moser ., ./---Handbook of Petroleum Processing pp 217-237

Catalytic hydrotreatment can be used as a pretreatment step to protect catalysts from crude oil contaminants such as heteroatom (S, N, O) compounds, as well as metals (mainly Ni, V). Hydrotreatment is also used as a major finishing process in a petroleum refinery. Shifting to the side stream products from the distillation column, kerosene and light gas oil fractions can be hydrotreated to remove the heteroatoms to produce the final products of jet fuel, and diesel fuel, catalysts used for hydrotreating are Co and Mo compounds supported on alumina (Al_2O_3). Jet fuel consists of C_{10} to C_{15} hydrocarbons, and diesel fuel consists of C_{15} to C_{20} hydrocarbons.

Catalytic hydrotreating



Catalytic Hydrotreating Unit Flow Diagram (2007)

Description.

Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product. Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils. In addition, hydrotreating converts olefins and aromatics to saturated compounds.

1-Catalytic Hydrodesulfurization Process.

Hydrotreating for sulfur removal is called hydrodesulfurization. In a typical catalytic hydrodesulfurization unit, the **feedstock is deaerated and mixed with hydrogen, preheated in a fired heater (600°-800° F) and then charged under pressure (up to 1,000 psi) through a fixed-bed catalytic reactor**.

In the reactor, the sulfur and nitrogen compounds in the feedstock are converted into H_2S and NH_3. The reaction products leave the reactor and after cooling to a low temperature enter a liquid/gas separator. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure gas stream rich in H_2S is sent to a gas treating unit where H_2S is removed. The clean gas is then suitable as fuel for the refinery furnaces. The liquid stream is the product from hydrotreating and is normally sent to a stripping column for removal of H_2S and other undesirable components. In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulfurized products are blended or used as catalytic reforming feedstock.

Other Hydrotreating Processes •

- Hydrotreating processes differ depending upon the feedstock available and catalysts used. Hydrotreating can be used to improve the burning characteristics of distillates such as kerosene. Hydrotreatment of a kerosene fraction can convert aromatics into naphthenes, which are cleaner-burning compounds.
- Lube-oil hydrotreating uses catalytic treatment of the oil with hydrogen to improve product quality. The objectives in mild lube hydrotreating include saturation of olefins and improvements in color, odor, and acid nature of the oil. Mild lube hydrotreating also may be used following solvent processing.

  Operating temperatures are usually below 600° F and operating pressures below 800 psi. Severe lube hydrotreating, at temperatures in the 600°-750° F range and hydrogen pressures up to 3,000 psi, is capable of saturating aromatic rings, along with sulfur and nitrogen removal, to impart specific properties not achieved at mild conditions.
- Hydrotreating also can be employed to improve the quality of pyrolysis gasoline (pygas), a by-product from the manufacture of ethylene. Traditionally, the outlet for pygas has been motor gasoline blending, a suitable route in view of its high octane number. However, only small portions can be blended untreated owing to the unacceptable odor, color, and gum-forming tendencies of this material. The quality of pygas, which is high in diolefin content, can be satisfactorily improved by hydrotreating, whereby conversion of diolefins into mono-olefins provides an acceptable product for motor gas blending.

Isomerization

- **Description**
  - Isomerization converts n-butane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number. The straight-chain paraffins are converted to their branched-chain counterparts whose component atoms are the same but are arranged in a different geometric structure. Isomerization is important for the conversion of n-butane into isobutane, to provide additional feedstock for alkylation units, and the conversion of normal pentanes and hexanes into higher branched isomers for gasoline blending. Isomerization is similar to catalytic reforming in that the hydrocarbon molecules are rearranged, but unlike catalytic reforming, isomerization just converts normal paraffins to isoparaffins
  - There are two distinct isomerization processes, butane (C_4) and pentane/hexane (C_5/C_6). Butane isomerization produces feedstock for alkylation. Aluminum chloride catalyst plus hydrogen chloride are universally used for the low-temperature processes. Platinum or another metal catalyst is used for the higher-temperature processes. In a typical low-temperature process, the feed to the isomerization plant is n-butane or mixed butanes mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 230°-340° F and 200-300 psi. Hydrogen is flashed off in a high-pressure separator and the hydrogen chloride removed in a stripper column. The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product.

c-Pentane / hexane isomerization increases the octane number of the light gasoline components n-pentane and n-hexane, which are found in abundance in straight-run gasoline. In a typical C_5/C_6 isomerization process, dried and desulfurized feedstock is mixed with a small amount of organic chloride and recycled hydrogen, and then heated to reactor temperature. It is then passed over supported-metal catalyst in the first reactor where benzene and olefins are hydrogenated. The feed next goes to the isomerization reactor where the paraffins are catalytically isomerized to isoparaffins. The reactor effluent is then cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle hydrogen-gas stream. The isomerate is washed (caustic and water), acid stripped, and stabilized before going to storage.

Polymerization

Description

- Polymerization in the petroleum industry is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks. Polymerization combines two or more identical olefin molecules to form a single molecule with the same elements in the same proportions as the original molecules. Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures.

- The olefin feedstock is pretreated to remove sulfur and other undesirable compounds. In the catalytic process the feedstock is either passed over a solid phosphoric acid catalyst or comes in contact with liquid phosphoric acid, where an exothermic polymeric reaction occurs. This reaction requires cooling water and the injection of cold feedstock into the reactor to control temperatures between 300° and 450° F at pressures from 200 psi to 1,200 psi. The reaction products leaving the reactor are sent to stabilization and/or fractionator systems to separate saturated and unreacted gases from the polymer gasoline product.

  NOTE: In the petroleum industry, polymerization is used to indicate the production of gasoline components, hence the term "polymer" gasoline. Furthermore, it is not essential that only one type of monomer be involved. If unlike olefin molecules are combined, the process is referred to as "copolymerization." Polymerization in the true sense of the word is normally prevented, and all attempts are made to terminate the reaction at the dimer or trimer (three monomers joined together) stage. However, in the petrochemical section of a refinery, polymerization, which results in the production of, for instance, polyethylene, is allowed to proceed until materials of the required high molecular weight have been produced.

Alkylation

- **Description.** Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with isobutene in the presence of a catalyst, either sulfuric acid or hydrofluoric acid. The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons. Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning. The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.

Sulfuric Acid Alkylation Process

In cascade type sulfuric acid (H_2SO_4) alkylation units, the feedstock (propylene, butylene, amylene, and fresh isobutane) enters the reactor and contacts the concentrated sulfuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion). The reactor is divided into zones, with olefins fed through distributors to each zone, and the sulfuric acid and isobutanes flowing over baffles from zone to zone.

The reactor effluent is separated into hydrocarbon and acid phases in a settler, and the acid is returned to the reactor. The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized. The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock. The isobutane is recycled to the feed.

Hydrofluoric Acid Alkylation Process.

Their two common types of hydrofluoric acid alkylation processes in use.:

In the olefin and isobutane are dried and fed to a combination reactor/settler system. Upon leaving the reaction zone, the reactor effluent flows to a settler (separating vessel) where the acid separates from the hydrocarbons. The acid layer at the bottom of the separating vessel is recycled. The top layer of hydrocarbons (hydrocarbon phase), consisting of propane, normal butane, alkylate, and excess (recycle) isobutane, is charged to the main fractionator, the bottom product of which is motor alkylate. The main fractionator overhead, consisting mainly of propane, isobutane, and HF, goes to a depropanizer. Propane with trace amount of HF goes to an HF stripper for HF removal and is then catalytically defluorinated, treated, and sent to storage. Isobutane is withdrawn from the main fractionator and recycled to the reactor/settler, and alkylate from the bottom of the main fractionator is sent to product blending.

The process uses two reactors with separate settlers. Half of the dried feedstock is charged to the first reactor, along with recycle and makeup isobutane. The reactor effluent then goes to its settler, where the acid is recycled and the hydrocarbon charged to the second reactor. The other half of the feedstock also goes to the second reactor, with the settler acid being recycled and the hydrocarbons charged to the main fractionator. Subsequent processing is similar to the Phillips process. Overhead from the main fractionator goes to a depropanizer. Isobutane is recycled to the reaction zone and alkylate is sent to product blending.

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Sweetening and Treating Processes

Desulphurization of jet fuel, diesel oil, heavy residue and commercial furnace oil is carried out through extraction with aqueous solutions of sodium chloride, barium chloride, sodium hydroxide, mercury chloride, arsenic trioxide, potassium iodide, lead acetate, calcium hydroxide, zinc chloride, aluminum chloride, hydrochloric acid and sulphuric acid. Among the solutions used, $HgCl_2$ and $Ca(OH)_2$ were found to be the most efficient for the removal of sulphur compounds from the fractions understudy at 40 °C temperature and 30 min of shaking time. The total sulphur depletion of 60 % and 58 % has been achieved in case of jet fuel oil, 71 % and 62 % in case of diesel oil, 68 % and 67 % in case of heavy residue and 67 % and 69 %in case of commercial furnace oil with 10% $HgCl_2$ and 5% $Ca(OH)_2$ aqueous solutions, respectively.

Desulphurization of Kerosene oil

In case of kerosene oil, the highest desulphurization yields achieved are 60.11 %, 53.65 %, 58.36 and 59.61 % with $HgCl_2$(10 %), HC1 (IN), Ca(OH) (5 %) and NaOH (10 %), respectively. In case of extraction with aqueous solutions of NaCl (10 %), $BaCl_2$ (10 %), AsO_3 (5 %), KI (10 %), Pb-acetate (10 %), $ZnCl_2$ (10 %), $A1C1_3$ (10 %) and H_2SO_4 (IN), desulphurization performance is exhibited by attaining the yields of 37.95 %, 15.66 %, 15.29 %, 20.49 %, 49.7 %, 48.25 %, 12.37 % and 35.91 %, respectively.

In case of kerosene oil, the sulphur compounds mostly prevailing include mercpatans, sulphides, disulphides and thiophenes[23]. NaOH is extensively used in a variety of sweetening processes like caustic treatment, Merox process, chelate sweetening, inhibitor sweetening etc. which shows that NaOH has greater affinity for the sulphur compounds in the petroleum fractions. This is probably due to the acidic character of the certain sulphur compounds like mercaptans, which readily distributes from the oil phase in to the alkaline layer of NaOH and converts to sulphides

Desulphurization of Diesel oil

In case of diesel oil, the highest desulphurization yields of 64.95, 71.74, 59.83, 62.21 and 65.21 %are achieved with aqueous solutions of $HgCl_2$(10 %), HCl (IN), Ca $(OH)_2$(5 %), NaOH (10 %) and AsO_3 (5 %), respectively. On the other hand, relatively poor desulphurization yields of 35.80, 31.30, 43.77, 40.28, 52.89, 30.69 and 38.78 % are attained with the solutions of NaCl (10 %), $BaCl_2$ (10 %), KI (10 %), Pb-acetate (10 %), $ZnCl_2$(10 %), $A1C1_3$(10 %) and H_2SO_4 (1N), respectively

The HCl solution is also found effective for desulphurization of heavy residue, which may be explained on the fact that the chloride salts of the heavier sulphur compounds are formed during the extraction process, which distribute in the polar acidic layer of the acid solution and hence easily extracted. The high desulphurization efficiency of arsenic oxide solution can be attributed to high reactivity of arsenic towards sulphur compounds, .

Desulphurization of Heavy residue

The sulphur compounds present in the heavy residue are mostly high molecular weight sulphides and aromatic hetero cyclic sulphur compounds particularly thiophene, benzothiophene and dibenzothiophene. The percentage of aromatic sulphur heterocycles is higher than the aliphatic sulphides and marcaptans. The extraction of these compounds is relatively difficult than mercaptans.

Description

Treating is a means by which contaminants such as organic compounds containing sulfur, nitrogen, and oxygen; dissolved metals and inorganic salts; and soluble salts dissolved in emulsified water are removed from petroleum fractions or streams. Petroleum refiners have a choice of several different treating processes, but the primary purpose of the majority of them is the elimination of unwanted sulfur compounds. A variety of intermediate and finished products, including middle distillates, gasoline, kerosene, jet fuel, and sour gases are dried and sweetened. Sweetening, a major refinery treatment of gasoline, treats sulfur compounds (hydrogen sulfide, thiophene and mercaptan) to improve color, odor, and oxidation stability. Sweetening also reduces concentrations of carbon dioxide.

Treating can be accomplished at an intermediate stage in the refining process, or just before sending the finished product to storage. Choices of a treating method depend on the nature of the petroleum fractions, amount and type of impurities in the fractions to be treated, the extent to which the process removes the impurities, and end-product specifications. Treating materials include acids, solvents, alkalis, oxidizing, and adsorption agents.

Acid, Caustic, or Clay Treating.

- Sulfuric acid is the most commonly used acid treating process. Sulfuric acid treating results in partial or complete removal of unsaturated hydrocarbons, sulfur, nitrogen, and oxygen compounds, and resinous and asphaltic compounds. It is used to improve the odor, color, stability, carbon residue, and other properties of the oil. Clay/lime treatment of acid-refined oil removes traces of asphaltic materials and other compounds improving product color, odor, and stability. Caustic treating with sodium (or potassium) hydroxide is used to improve odor and color by removing organic acids (naphthenic acids, phenols) and sulfur compounds (mercaptans, H_2S) by a caustic wash. By combining caustic soda solution with various solubility promoters (e.g., methyl alcohol and cresols), up to 99% of all mercaptans as well as oxygen and nitrogen compounds can be dissolved from petroleum fractions.

Drying and Sweetening.

Feedstocks from various refinery units are sent to gas treating plants where butanes and butenes are removed for use as alkylation feedstock, heavier components are sent to gasoline blending, propane is recovered for LPG, and propylene is removed for use in petrochemicals. Some mercaptans are removed by water-soluble chemicals that react with the mercaptans. Caustic liquid (sodium hydroxide), amine compounds (diethanolamine) or fixed-bed catalyst sweetening also may be used. Drying is accomplished by the use of water absorption or adsorption agents to remove water from the products. Some processes simultaneously dry and sweeten by adsorption on molecular sieves.

Sulfur Recovery

Sulfur recovery converts hydrogen sulfide in sour gases and hydrocarbon streams to elemental sulfur. The most widely used recovery system is the Claus process, which uses both thermal and catalytic-conversion reactions. A typical process produces elemental sulfur by burning hydrogen sulfide under controlled conditions. Knockout pots are used to remove water and hydrocarbons from feed gas streams. The gases are then exposed to a catalyst to recover additional sulfur. Sulfur vapor from burning and conversion is condensed and recovered.

Hydrogen Sulfide Scrubbing.

Hydrogen sulfide scrubbing is a common treating process in which the hydrocarbon feedstock is first scrubbed to prevent catalyst poisoning. Depending on the feedstock and the nature of contaminants, desulfurization methods vary from ambient temperature-activated charcoal absorption to high-temperature catalytic hydrogenation followed by zinc oxide treating.

Asphalt Production

Description

Asphalt is a portion of the residual fraction that remains after primary distillation operations. It is further processed to impart characteristics required by its final use. In vacuum distillation, generally used to produce road-tar asphalt, the residual is heated to about 750° F and charged to a column where vacuum is applied to prevent cracking.

Asphalt for roofing materials is produced by air blowing. Residual is heated in a pipe still almost to its flash point and charged to a blowing tower where hot air is injected for a predetermined time. The dehydrogenization of the asphalt forms hydrogen sulfide, and the oxidation creates sulfur dioxide. Steam, used to blanket the top of the tower to entrain the various contaminants, is then passed through a scrubber to condense the hydrocarbons.

A third process used to produce asphalt is solvent deasphalting. In this extraction process, which uses propane (or hexane) as a solvent, heavy oil fractions are separated to produce heavy lubricating oil, catalytic cracking feedstock, and asphalt. Feedstock and liquid propane are pumped to an extraction tower at precisely controlled mixtures, temperatures (150°-250° F), and pressures of 350-600 psi. Separation occurs in a rotating disc contactor, based on differences in solubility. The products are then evaporated and steam stripped to recover the propane, which is recycled. Deasphalting also removes some sulfur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.

Deasphfaling processes

As the first step in deasphalting, residue (feedstock) is mixed with four to eight times volume of liquid propane. Heavier residua require a higher solvent to residue (S/R) ratio for effective separation of asphalt. Following the precipitation of asphalt, DAO and asphalt are separated, and each stream is purified and flashed to recover and recycle the propane solvent,

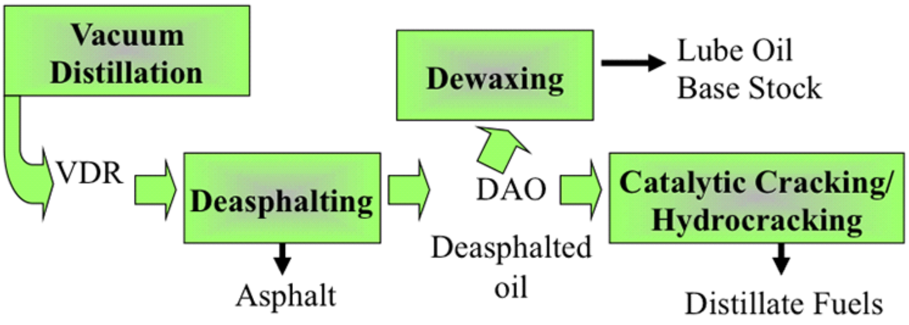
Direct hydro-desulfurization followed by hydrocracking of crude oil heavy cuts and vacuum residues is one of the best methods of heavy residue upgrading in refining industry. But, problem emerges when metal and asphaltene contents of residue are high. In fact, the presence of these compounds adversely influences the activities of the hydro-desulfurization and hydrocracking catalysts.

The solvent deasphalting process (SDA) which is based on liquid–liquid extraction by using paraffinic solvents (C4–C7) is one of the most efficient approaches to reduce metal and asphaltene contents of heavy oil cuts before sending them to hydro-desulfurization and hydrocracking units. A number of deasphalting process parameters are to be considered, amongst which the DAO process yield and the levels of demetalization and deasphalting could be noted. The important factors

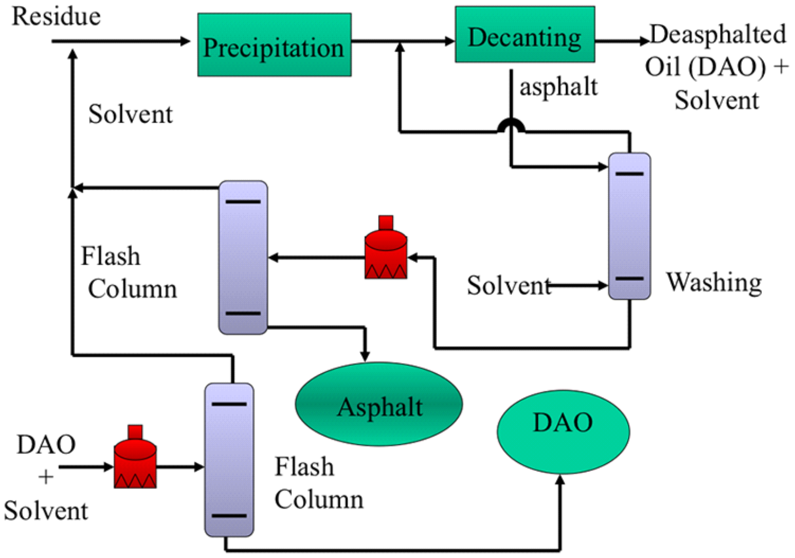
influencing the mentioned parameters are solvent composition and ratio of the solvent to the feed temperature, pressure and the type of extractor equipment ,

Increasing the solvents molecular weight increases the yield of recovered DAO by allowing more of the heavier, more – resinous components of the feed stock to remain in the DAO. At the same time however, the quality of the DAO decreases because these heavier materials have higher contaminant levels. Consequently, proper solvent selection involves balancing increased product yield and decreased product quality. The precipitation increases substantially as the solvent/feed ratio increases

up to 10 folds. Beyond this value, precipitation increases by very small amounts



Deasphalting and dewaxing processes in a petroleum refinery.



Simplified Flow Diagram of a Deasphalting Process

The four unit operations of deasphalting illustrated in the process flow diagram are:

- Flocculation (& precipitation) of asphaltenes
- Asphalt decanting - separation
- Asphalt washing - to remove entrained oil
- Solvent recovery and recycle

A **-deasphalter** is a unit in a crude oil refinery or bitumen upgrader that separates asphalt from crude oil or bitumen. The deasphalter unit is usually placed after the vacuum distillation tower. It is usually a solvent deasphalter unit, (SDA). The (SDA) separates the asphalt from the feedstock because light hydrocarbons will dissolve aliphatic compounds but not asphaltenes. The output from the de-asphalter unit is de-asphalted oil ("DAO") and asphalt.

deasphalted oil DAO from propane de-asphalting has the highest quality but lowest yield, whereas using pentane may double or triple the yield from a heavy feed, but at the expense of contamination by metals and carbon residues that shorten the life of downstream cracking catalysts. If the solvent is butane the unit will be referred to as a 1butane de-asphalter ("BDA") and if the solvent is propane, it will be called a 1propane de-asphalter ("PDA") unit. Pentane and hexane were also used as a solvent.

Hydrogen Production

Description

High-purity hydrogen (95%-99%) is required for hydrodesulfurization, hydrogenation, hydrocracking, and petrochemical processes. Hydrogen, produced as a by-product of refinery processes (principally hydrogen recovery from catalytic reformer product gases), often is not enough to meet the total refinery requirements, necessitating the manufacturing of additional hydrogen or obtaining supply from external sources.

In steam-methane reforming, desulfurized gases are mixed with superheated steam (1,100°-1,600° F) and reformed in tubes containing a nickel base catalyst. The reformed gas, which consists of steam, hydrogen, carbon monoxide, and carbon dioxide, is cooled and passed through converters containing an iron catalyst where the carbon monoxide reacts with steam to form carbon dioxide and more hydrogen. The carbon dioxide is removed by amine washing. Any remaining carbon monoxide in the product stream is converted to methane.

Steam-naphtha reforming is a continuous process for the production of hydrogen from liquid hydrocarbons and is, in fact, similar to steam-methane reforming. A variety of naphthas in the gasoline boiling range may be employed, including fuel containing up to 35% aromatics. Following pretreatment to remove sulfur compounds, the feedstock is mixed with steam and taken to the reforming furnace (1,250°-1,500° F) where hydrogen is produced.

Lubricant, Wax, and Grease Manufactoring Processes

Description. Lubricating oils and waxes are refined from the residual fractions of atmospheric and vacuum distillation. The primary objective of the various lubricating oil refinery processes is to remove asphalts, sulfonated aromatics, and paraffinic and isoparaffinic waxes from residual fractions. reduced crude from the vacuum unit is deasphalted and combined with straight-run lubricating oil feedstock, preheated, and solvent-extracted (usually with phenol or furfural) to produce raffinate.

2-Wax Manufacturing Process.

Raffinate from the extraction unit contains a considerable amount of wax that must be removed by solvent extraction and crystallization. The raffinate is mixed with a solvent (propane) and precooled in heat exchangers. The crystallization temperature is attained by the evaporation of propane in the chiller and filter feed tanks. The wax is continuously removed by filters and cold solvent-washed to recover retained oil. The solvent is recovered from the oil by flashing and steam stripping. The wax is then heated with hot solvent, chilled, filtered, and given a final wash to remove all oil.

3-Lubricating Oil Process.

The dewaxed raffinate is blended with other distillate fractions and further treated for viscosity index, color, stability, carbon residue, sulfur, additive response, and oxidation stability in extremely selective extraction processes using solvents (furfural, phenol, etc.). In a typical phenol unit, the raffinate is mixed with phenol in the treating section at temperatures below 400° F. Phenol is then separated from the treated oil and recycled. The treated lube-oil base stocks are then mixed and/or compounded with additives to meet the required physical and chemical characteristics of motor oils, industrial lubricants, and metal working oils.

3-Grease Compounding.

Grease is made by blending metallic soaps (salts of long chained fatty acids) and additives into a lubricating oil medium at temperatures of 400°-600° F. Grease may be either batch-produced or continuously compounded. The characteristics of the grease depend to a great extent on the metallic element (calcium, sodium, aluminum, lithium, etc.) in the soap and the additives used.

Hydrocracking

Used primarily for cracking gas-oil that contains high percentages of polynuclear aromatics, to give gasoline, diesel fuel, or jet fuel. Conventional catalytic cracking of such compounds is not as selective, producing large amounts of low M.W. hydrocarbon products.

Hydrocracking catalysts require both an acidic component (for cracking reactions) and a metallic component (for hydrogenation reactions):

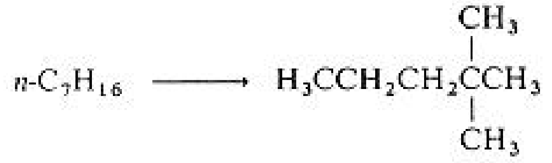
Acidic Component:	SiO_2-Al_2O_3, zeolites
Metallic Component:	Co, Mo, Ni, or W yield lubricating oils and middle or heavy distillate fuels. Pt or Pd yield gasoline or diesel and jet fuels.

Reaction Conditions:

Temperature:	300 - 425°C
Pressure:	100 - 170 atm
Reactor:	Fixed bed (little coking, compared to FCC, because of high H_2 pressure)

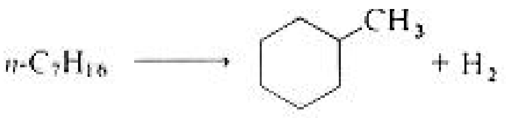
REFORMING REACTIONS

Paraffins. Typical virgin petroleum naphthas and many refinery charge stocks contain 15 to 75 percent straight-chain paraffins with a typical research octane number less than 50. The paraffins can be isomerized to branched-chain molecules, e.g.,



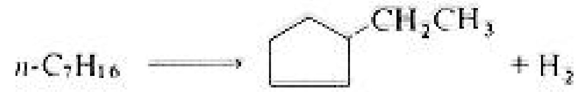
$$n\text{-}C_7H_{16} \longrightarrow H_3CCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3 \tag{1}$$

They can also undergo dehydrocyclization to give cycloparaffins:



(2)

or

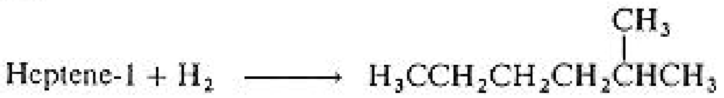


(3)

Paraffins can also undergo hydrocracking:

$$n\text{-}C_9H_{20} + H_2 \longrightarrow n\text{-}C_5H_{12} + n\text{-}C_4H_{10} \tag{4}$$

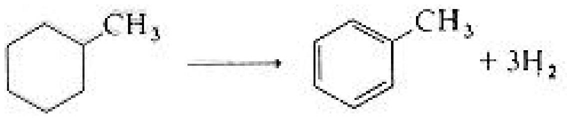
Olefins. Olefins are usually not present in straight-run naphthas but may be present in other refinery charge stocks. They are undesirable in high concentrations and are usually hydrogenated. They can also be hydroisomerized to give isoparaffins:



$$\text{Heptene-1} + H_2 \longrightarrow H_3CCH_2CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3 \tag{5}$$

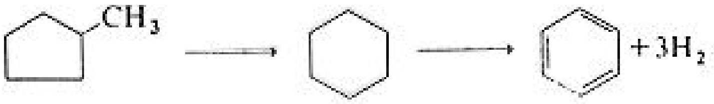
They can also undergo cyclization.

Naphthenes. Typical feeds contain from 18 to 50 percent naphthenes as cyclopentanes and cyclohexanes. Often there are more cyclopentanes than cyclohexanes. The cyclohexanes can be dehydrogenated to give aromatics, e.g.,



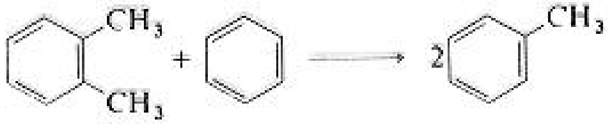
(6)

Cyclopentanes can be hydroisomerized to give cyclohexanes with subsequent dehydrogenation to give aromatics:



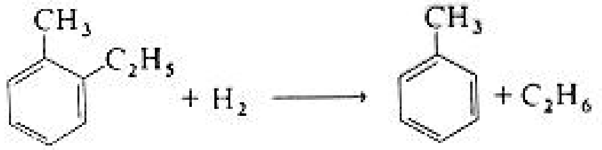
(7)

Unsaturated cyclic hydrocarbons. Some of these are present in charge stocks, and others are generated in the reactor. Reaction of substituted aromatics can occur as follows:



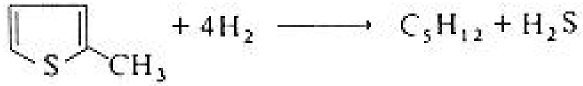
(8)

Aromatics can also experience hydrodealkylation:



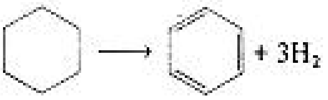
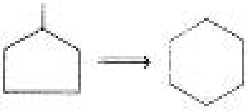
(9)

Species containing S or N can undergo hydrodesulfurization and hydrodenitrogenation, respectively, as discussed in Chap. 5:



(10)

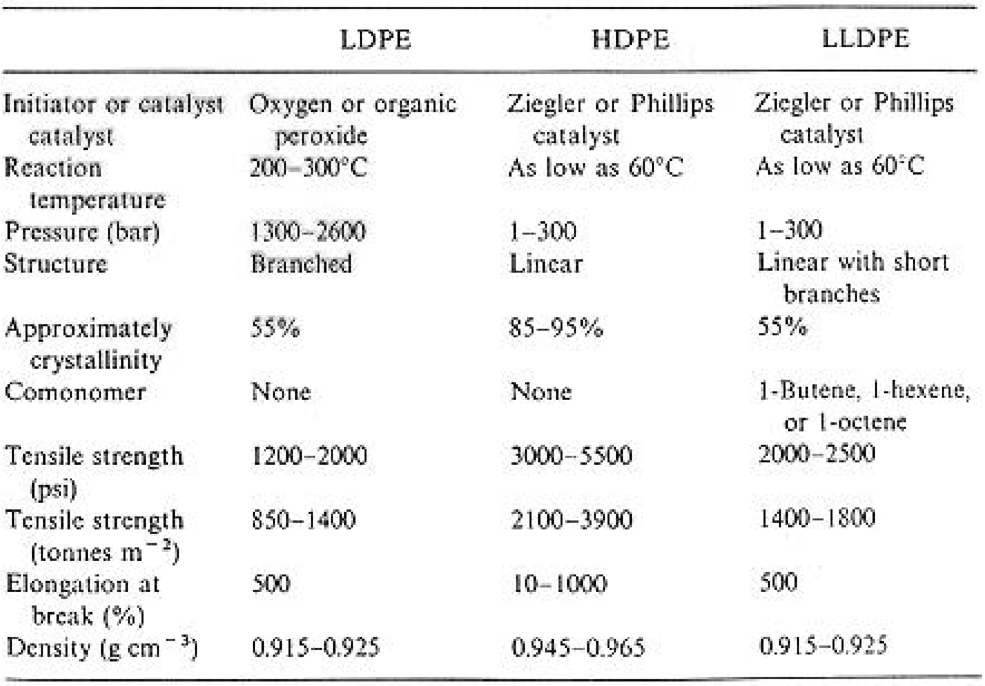
TABLE 9.3 Representative Catalytic Reforming Reactions

Reaction	K	ΔH, kJ/mol
1. Dehydrogenation of naphthenes to aromatics 	6×10^5	+221
2. Dehydrogenation of paraffins to olefins $C_6H_{14} \longrightarrow C_6H_{12} + H_2$	$\sim 4 \times 10^{-2}$	~+130
3. Isomerization of alkyl cyclopentanes 	8.6×10^{-2}	−15.9
4. Isomerization of *n*-paraffins to isoparaffins $n\text{-}C_6H_{14} \longrightarrow \text{iso-}C_6H_{14}$	~1	~5
5. Dehydrocyclization of paraffins to aromatics $n\text{-}C_6H_{14} \longrightarrow C_6H_6 + 4H_2$		
6. Hydrocracking of paraffins $C_6H_{14} + H_2 \longrightarrow$ olefins and paraffins		

SOURCE: Edmonds (1975).

Polymers from Ethylene

TABLE 3.1 Properties of Polyethylenes



	LDPE	HDPE	LLDPE
Initiator or catalyst catalyst	Oxygen or organic peroxide	Ziegler or Phillips catalyst	Ziegler or Phillips catalyst
Reaction temperature	200–300°C	As low as 60°C	As low as 60°C
Pressure (bar)	1300–2600	1–300	1–300
Structure	Branched	Linear	Linear with short branches
Approximately crystallinity	55%	85–95%	55%
Comonomer	None	None	1-Butene, 1-hexene, or 1-octene
Tensile strength (psi)	1200–2000	3000–5500	2000–2500
Tensile strength (tonnes m^{-2})	850–1400	2100–3900	1400–1800
Elongation at break (%)	500	10–1000	500
Density (g cm^{-3})	0.915–0.925	0.945–0.965	0.915–0.925

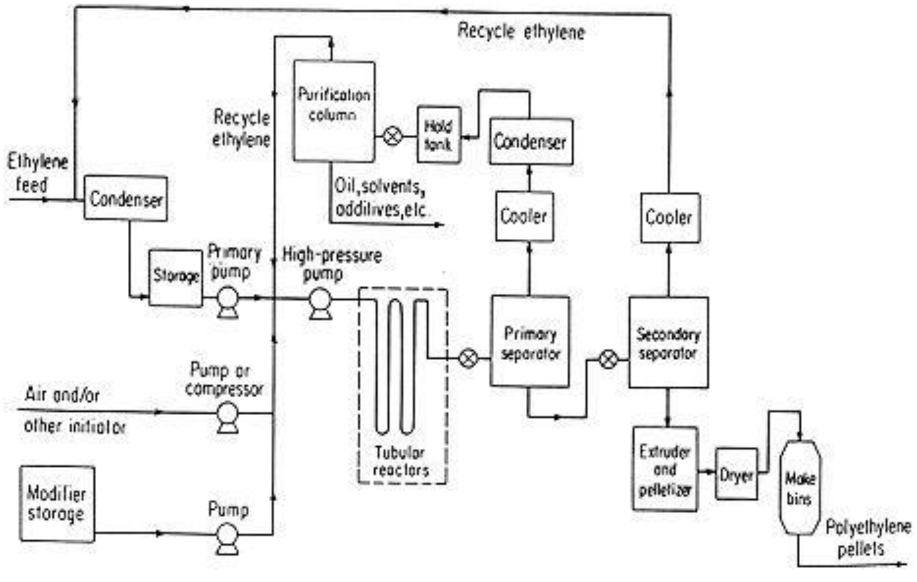


FIG. 1 High-pressure process for production of low-density polyethylene. (From Ref. 15 with permission of Krieger Publishing Co.)

Polymerization mechanism

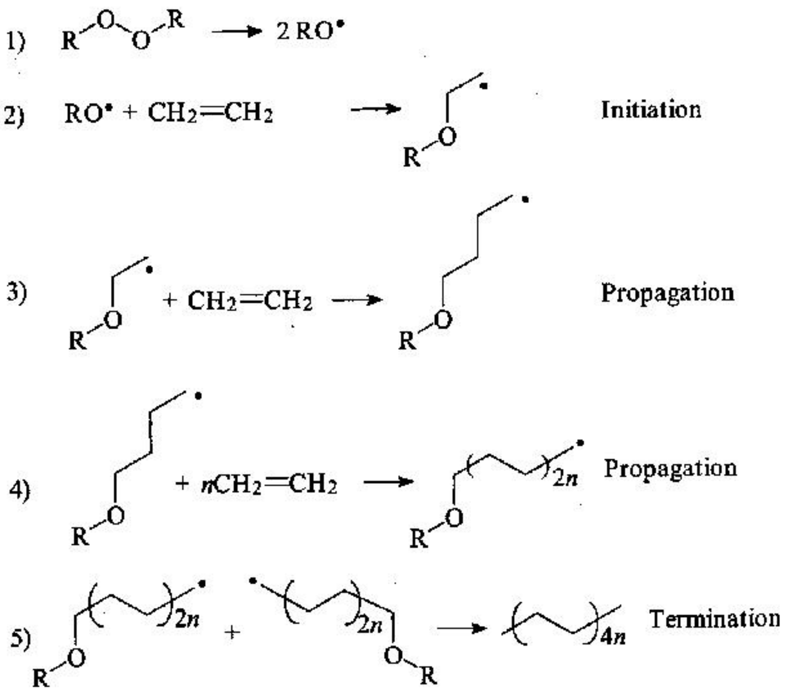


Fig. 2.2 Free radical chain mechanism for polymerization of ethylene.

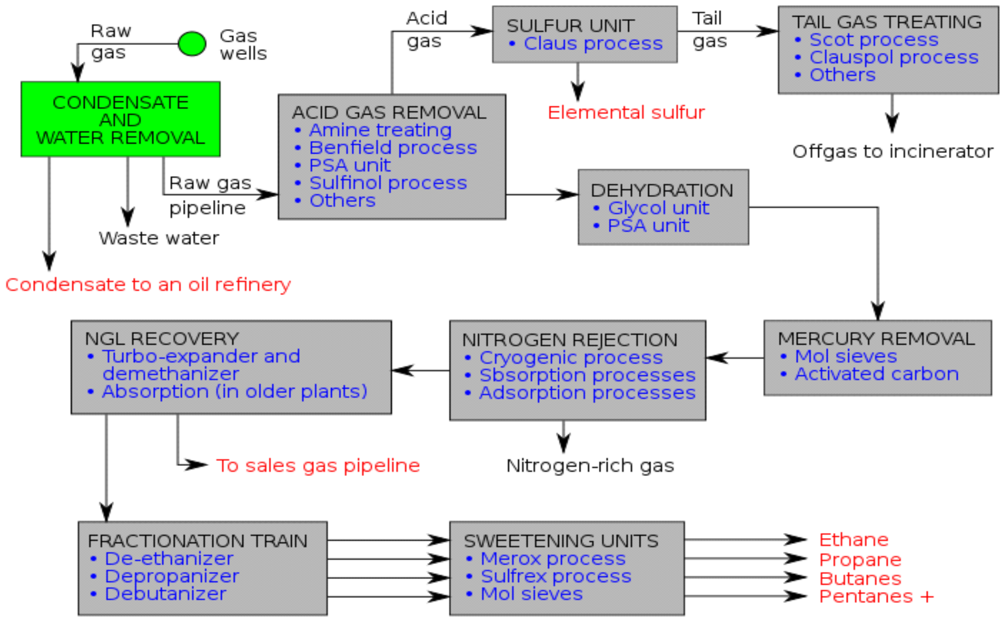
Natural Gas Processing

Natural gas, as it is used by consumers, is much different from the natural gas that is brought from underground up to the wellhead. Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users.

The natural gas used by consumers is composed almost entirely of methane. However, natural gas found at the wellhead, although still composed primarily of methane, is by no means as pure.

Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells. Natural gas that comes from oil wells is typically termed ‘associated gas’. This gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Natural gas from gas and condensate wells, in which there is little or no crude oil, is termed ‘nonassociated gas’. Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate. Whatever the source of the natural gas, once separated from crude oil (if present) it commonly exists in mixtures with other hydrocarbons; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds

Natural gas processing



Separating all of the various hydrocarbons and fluids from the pure natural gas, to produce what is known as ‘pipeline quality’ dry natural gas. Major transportation pipelines usually impose restrictions on the make-up of the natural gas that is allowed into the pipeline. That means that before the natural gas can be transported it must be purified. While the ethane, propane, butane, and pentanes must be removed from natural gas, this does not mean that they are all ‘waste products’.

The following are some of the unusual impurities that may require additional removal steps in gas treating.

- **• Elemental sulphur 2-• Mercury, Hg**
- **3-• Heavy hydrocarbons C8+**
- **• Ammonia**
- **5-• COS, CS_2, RSH, mercaptans, and solids such as FeS**

In fact, associated hydrocarbons, known as ‘natural gas liquids’ (NGLs) can be very valuable by-products of natural gas processing. NGLs include ethane, propane, butane, iso-butane, and natural gasoline. These NGLs are sold separately and have a variety of different uses; including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy.

While some of the needed processing can be accomplished at or near the wellhead (field processing), the complete processing of natural gas takes place at a processing plant, usually located in a natural gas producing region. The extracted natural gas is transported to these processing plants through a network of gathering pipelines, which are small-diameter, low pressure pipe

In addition to processing done at the wellhead and at centralized processing plants, some final processing is also sometimes accomplished at ‘straddle extraction plants’. These plants are located on major pipeline systems. Although the natural gas that arrives at these straddle extraction plants is already of pipeline quality, in certain instances there still exist small quantities of NGLs, which are extracted at the straddle plants.

The actual practice of processing natural gas to pipeline dry gas quality levels can be quite complex, but usually involves four main processes to remove the various impurities:

- Oil and Condensate Removal
- Water Removal
- Separation of Natural Gas Liquids
- Sulfur and Carbon Dioxide Removal

Scroll down, or click on the links above to be transported to a particular section.

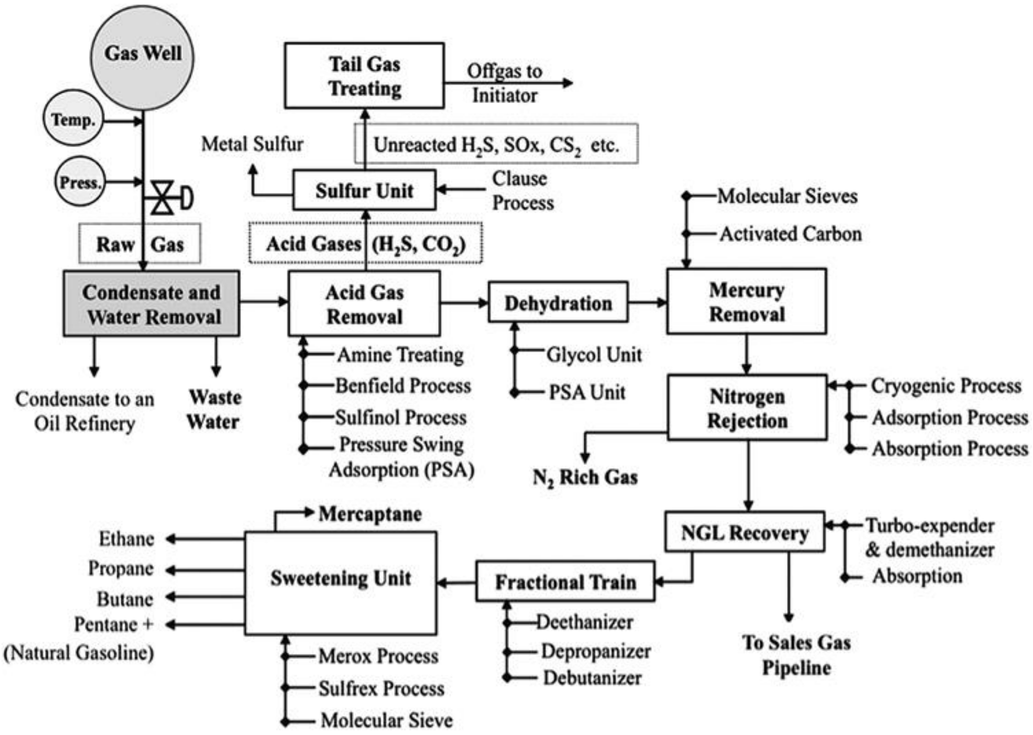
In addition to the four processes above, heaters and scrubbers are installed, usually at or near the wellhead. The scrubbers serve primarily to remove sand and other large-particle impurities. The heaters ensure that the temperature of the gas does not drop too low. With natural gas that contains even low quantities of water, natural gas hydrates have a tendency to form when temperatures drop. These hydrates are solid or semi-solid compounds, resembling ice like crystals. Should these hydrates accumulate, they can impede the passage of natural gas through valves and gathering systems. To reduce the occurrence of hydrates, small natural gas-fired heating units are typically installed along the gathering pipe wherever it is likely that hydrates may form.

Among individual Natural Gases , ethane has the largest share of NGL field production, followed by propane. Together, they make up 90% of the NGL barrel. Ethane is largely used to produce ethylene, the monomer used to produce polyethylene, ethylene oxide, ethylbenzene and dichloromethane, which are raw materials for the production of a wide variety of everyday objects. Propane is the precursor of polypropylene, which is used to produce plastics, resins, rubbers and other materials. It is also used as a residential and commercial heating fuel, as a drying agent for crops, as a ripening agent for fruit.

n-Butane is used to produce butadiene, the key component in synthetic rubber. Butane is also used during winter as a fuel additive in motor gasoline. I-Butane is mainly used in refineries as feedstock for the alkylation process to produce alkylate. It is also used in refrigerators, as fuel, and as propellant in cooking spray and hairspray. Pentane is used as a blending fuel in refineries to make motor gasoline, as petrochemical feedstock and as diluent for heavy crudes.

Oil and Condensate Removal

In order to process and transport associated dissolved natural gas, it must be separated from the oil in which it is dissolved. This separation of natural gas from oil is most often done using equipment installed at or near the wellhead.



A generalized natural gas processing flow diagram

The actual process used to separate oil from natural gas, as well as the equipment that is used, can vary widely. Although dry pipeline quality natural gas is virtually identical across different geographic areas, raw natural gas from different regions may have different compositions and separation requirements. In many instances, natural gas is dissolved in oil underground primarily due to the pressure that the formation is under. When this natural gas and oil is produced, it is possible that it will separate on its own, simply due to decreased pressure; much like opening a can of soda pop allows the release of dissolved carbon dioxide. In these cases, separation of oil and gas is relatively easy, and the two hydrocarbons are sent separate ways for further processing. The most basic type of separator is known as a conventional separator. It consists of a simple closed tank, where the force of gravity serves to separate the heavier liquids like oil, and the lighter gases, like natural gas.

In certain instances, however, specialized equipment is necessary to separate oil and natural gas. An example of this type of equipment is the Low-Temperature Separator (LTX). This is most often used for wells producing high pressure gas along with light crude oil or condensate. These separators use pressure differentials to cool the wet natural gas and separate the oil and condensate. Wet gas enters the separator, being cooled slightly by a heat exchanger. The gas then travels through a high pressure liquid ‘knockout’, which serves to remove any liquids into a low-temperature separator. The gas then flows into this low-temperature separator through a choke mechanism, which expands the gas as it enters the separator. This rapid expansion of the gas allows for the lowering of the temperature in the separator. After liquid removal, the dry gas then travels back through the heat exchanger and is warmed by the incoming wet gas. By varying the pressure of the gas in various sections of the separator, it is possible to vary the temperature, which causes the oil and some water to be condensed out of the wet gas stream. This basic pressure-temperature **relationship can work in reverse as well, to extract gas from a liquid oil stream.**

Water Removal

In addition to separating oil and some condensate from the wet gas stream, it is necessary to remove most of the associated water. Most of the liquid, free water associated with extracted natural gas is removed by simple separation methods at or near the wellhead. However, the removal of the water vapor that exists in solution in natural gas requires a more complex treatment. This treatment consists of ‘dehydrating’ the natural gas, which usually involves one of two processes: either absorption, or adsorption.

Absorption occurs when the water vapor is taken out by a dehydrating agent. Adsorption occurs when the water vapor is condensed and collected on the surface.

Glycol Dehydration

An example of absorption dehydration is known as Glycol Dehydration. In this process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. Glycol, the principal agent in this process, has a chemical affinity for water. This means that, when in contact with a stream of natural gas that contains water, glycol will serve to ‘steal’ the water out of the gas stream. Essentially, glycol dehydration involves using a glycol solution, usually either diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in what is called the ‘contactor’. The glycol solution will absorb water from the wet gas. Once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The natural gas, having been stripped of most of its water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution. While water has a boiling point of 212 degrees Fahrenheit, glycol does not boil until 400 degrees Fahrenheit. This boiling point differential makes it relatively easy to remove water from the glycol solution, allowing it be reused in the dehydration process.

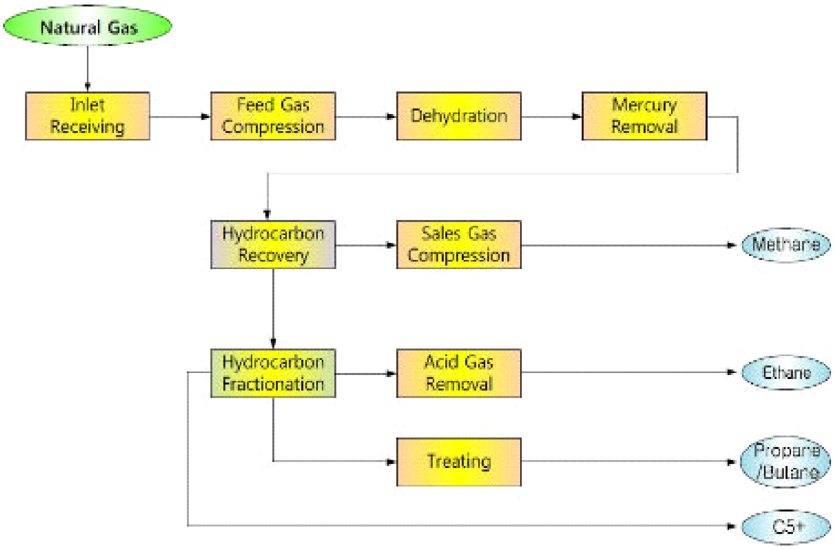
A new innovation in this process has been the addition of flash tank separator-condensers. As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In the past, this methane was simply vented out of the boiler. In addition to losing a portion of the natural gas that was extracted, this venting contributes to air pollution and the greenhouse effect. In order to decrease the amount of methane and other compounds that are lost, flash tank separator-condensers work to remove these compounds before the glycol solution reaches the boiler. Essentially, a flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbons to vaporize (‘flash’). The glycol solution then travels to the boiler, which may also be fitted with air or water cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. In practice, accordingly to these systems have been shown to recover 90 to 99 percent of methane that would otherwise be flared into the atmosphere.

Solid-Desiccant Dehydration

Solid-desiccant dehydration is the primary form of dehydrating natural gas using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower.

Solid-desiccant dehydrators are typically more effective than glycol dehydrators, and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To ‘regenerate’ the desiccant, a high-temperature heater is used to heat gas to a very high temperature. Passing this heated gas through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration.

Separation of Natural Gas Liquids



Separation of NG processes

Natural gas coming directly from a well contains many natural gas liquids that are commonly removed. In most instances, natural gas liquids (NGLs) have a higher value as separate products, and it is thus economical to remove them from the gas stream. The removal of natural gas liquids usually takes place in a relatively centralized processing plant, and uses techniques similar to those used to dehydrate natural gas.

There are two basic steps to the treatment of natural gas liquids in the natural gas stream. First, the liquids must be extracted from the natural gas. Second, these natural gas liquids must be separated themselves, down to their base components.

NGL Extraction

There are two principle techniques for removing NGLs from the natural gas stream: the absorption method and the cryogenic expander process. According to the Gas Processors Association, these two processes account for around 90 percent of total natural gas liquids production.

The Absorption Method

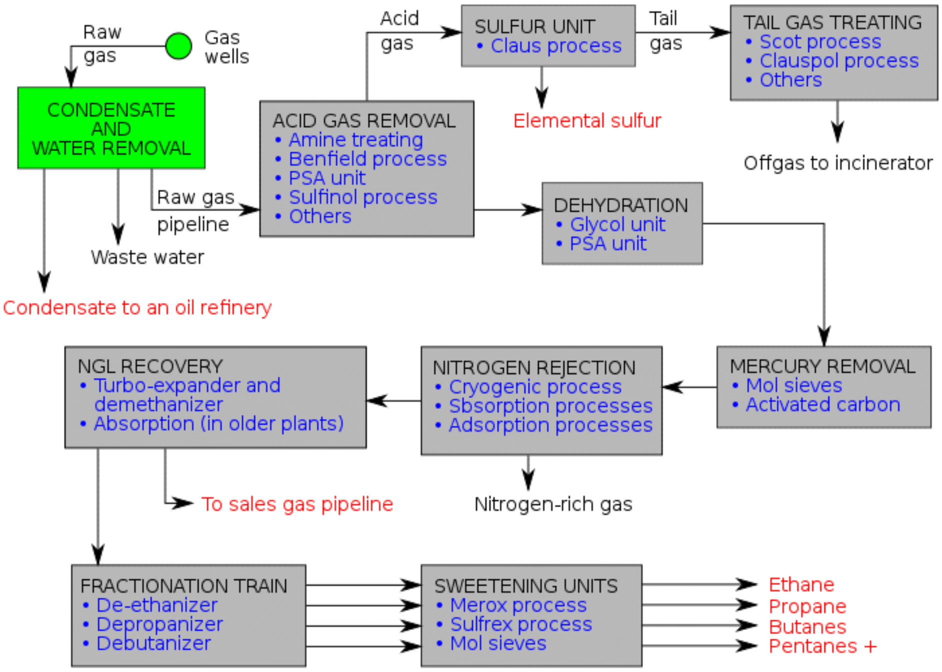
The absorption method of NGL extraction is very similar to using absorption for dehydration. The main difference is that, in NGL absorption, an absorbing oil is used as opposed to glycol. This absorbing oil has an ‘affinity’ for NGLs in much the same manner as glycol has an affinity for water. Before the oil has picked up any NGLs, it is termed ‘lean’ absorption oil. As the natural gas is passed through an absorption tower, it is brought into contact with the absorption oil which soaks up a high proportion of the NGLs. The ‘rich’ absorption oil, now containing NGLs, exits the absorption tower through the bottom. It is now a mixture of absorption oil, propane, butanes, pentanes, and other heavier hydrocarbons. The rich oil is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the

NGLs, but below that of the oil. This process allows for the recovery of around 75 percent of butanes, and 85 – 90 percent of pentanes and heavier molecules from the natural gas stream.

The basic absorption process above can be modified to improve its effectiveness, or to target the extraction of specific NGLs. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be upwards of 90 percent, and around 40 percent of ethane can be extracted from the natural gas stream. Extraction of the other, heavier NGLs can be close to 100 percent using this process.

The Cryogenic Expansion Process

Cryogenic processes are also used to extract NGLs from natural gas. While absorption methods can extract almost all of the heavier NGLs, the lighter hydrocarbons, such as ethane, are often more difficult to recover from the natural gas stream. In certain instances, it is economic to simply leave the lighter NGLs in the natural gas stream. However, if it is economic to extract ethane and other lighter hydrocarbons, cryogenic processes are required for high recovery rates. Essentially, cryogenic processes consist of dropping the temperature of the gas stream to around -120 degrees Fahrenheit.



Processes for separation of condensate gases and harmful impurities from natural gas

There are a number of different ways of chilling the gas to these temperatures, but one of the most effective is known as the turbo expander process. In this process, external refrigerants are used to cool the natural gas stream. Then, an expansion turbine is used to rapidly expand the chilled gases, which causes the temperature to drop significantly. This rapid temperature drop condenses ethane and other hydrocarbons in the gas stream, while maintaining methane in gaseous form. This process allows for the recovery of about 90 to 95 percent of the ethane originally in the gas stream. In addition, the expansion turbine is able to convert some of the energy released when the natural gas stream is expanded into recompressing the gaseous methane effluent, thus saving energy costs associated with extracting ethane.

The extraction of NGLs from the natural gas stream produces both cleaner, purer natural gas, as well as the valuable hydrocarbons that are the NGLs themselves.

Natural Gas Liquid Fractionation (NGL)

Once NGLs have been removed from the natural gas stream, they must be broken down into their base components to be useful. That is, the mixed stream of different NGLs must be separated out. The process used to accomplish this task is called fractionation. Fractionation works based on the different boiling points of the different hydrocarbons in the NGL stream. Essentially, fractionation occurs in stages consisting of the boiling off of hydrocarbons one by one. The name of a particular fractionator gives an idea as to its purpose, as it is conventionally named for the hydrocarbon that is boiled off. The entire fractionation process is broken down into steps, starting with the removal of the lighter NGLs from the stream. The particular fractionators are used in the following order:

- **Deethanizer** – this step separates the ethane from the NGL stream.
- **Depropanizer** – the next step separates the propane.
- **Debutanizer** – this step boils off the butanes, leaving the pentanes and heavier hydrocarbons in the NGL stream.
- **Butane Splitter or Deisobutanizer** – this step separates the iso and normal butanes.

By proceeding from the lightest hydrocarbons to the heaviest, it is possible to separate the different NGLs reasonably easily.

Sulfur and Carbon Dioxide Removal

Carbon dioxide (CO2) and hydrogen sulphide (H2S) are common impurities in natural gas. These impurities need to be removed to different levels to meet each client's specific process requirements.

Methods for removal of CO_2 and/or H2S from the gas is via:

- **amines, 2) physical solvents, 3) membranes or adsorbents**.

The choice of which technology to use depends on the levels of impurities to be removed.

In addition to water, oil, and NGL removal, one of the most important parts of gas processing involves the removal of sulfur and carbon dioxide. Natural gas from some wells contains significant amounts of sulfur and carbon dioxide. This natural gas, because of the rotten smell provided by its sulfur content, is commonly called 'sour gas'. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe. Sour gas can also be extremely corrosive.

The process for removing hydrogen sulfide from sour gas is commonly referred to as ‘sweetening’ the gas.

The primary process for sweetening sour natural gas is quite similar to the processes of glycol dehydration and NGL absorption. In this case, however, amine solutions are used to remove the hydrogen sulfide. The sour gas is run through a tower, which contains the amine solution. This solution has an affinity for sulfur, and absorbs it much like glycol absorbing water. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. Like the process for NGL extraction and glycol dehydration, the amine solution used can be regenerated (that is, the absorbed sulfur is removed), allowing it to be reused to treat more sour gas.

Although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponges to remove the sulfide and carbon dioxide.

In order to recover elemental sulfur from the gas processing plant, the sulfur containing discharge from a gas sweetening process must be further treated. The process used to recover sulfur is known as the Claus process, and involves using thermal and catalytic reactions to extract the elemental sulfur from the hydrogen sulfide solution.

Reactions of organic disulphides with sulphur are catalyzed by basic substances. Common catalysts are amines, which work only in the presence of H2S. As in the case of amines as solvents, formation of the hydrosulphide anion, HS–, is necessary before sulphur uptake can occur.

The overall chemistry can be summarized as follows.

Catalysis $\mathrm{H_2S + R1\,R2NH \rightarrow R_1R_2NH_2{+} + HS{-}}$

Sulphur uptake $\mathrm{HS{-} + RSSR \rightarrow RS{-} + RSSH}$

$\mathrm{RS{-} + S_8 \rightarrow RSS_8}$

$\mathrm{RSS_8{-} + RSSR \rightarrow RSS8SR + RS{-}}$

Overall $\mathrm{RSSR + xS_8 \rightarrow RSS8xSR}$

In all, the Claus process is usually able to recover 97 percent of the sulfur that has been removed from the natural gas stream. Since it is such a polluting and harmful substance, further filtering, incineration, and ‘tail gas’ clean up efforts ensure that well over 98 percent of the sulfur is recovered.

Gas processing is an instrumental piece of the natural gas value chain. It is instrumental in ensuring that the natural gas intended for use is as clean and pure as possible, making it the clean burning and environmentally sound energy choice. Once the natural gas has been fully processed, and is ready to be consumed, it must be transported from those areas that produce natural gas, to those areas that require it.

The removal of sulfurous compounds

Absorption methods (which fall intro three groups, depending on the way the acidic components of the gas react with the active component of the absorbent)

Chemical absorption (chemisorption) is based on the chemical reactions of hydrogen sulfide and carbon dioxide with the active components of the absorbents. Among other chemical absorbents, alcanolamines are widely used in the industry: MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), MDEA, DIPA (diisopropanolamine), as well as alkaline solutions, alkaline metal solutions (potassium carbonates, 25-30% K_2CO_3 or Na_2CO_3 solutions) and ferric hydroxide solution (Fe_2O_3). Chemical absorption is highly selective in relation to acidic components and assures highdegrees of H_2S and CO_2 removal from the gas. If amines are used, relatively minor quantities of sulfur-bearing organic compounds are removed.

Fine removal of such compounds is achieved by the use of alkali.

Physical adsorption involves the removal of acidic components and this is determined by the degree of solubility of the gas components in absorbents. Absorbents such as polyethylene glycol dimethyl ether (Selicsol®), methanol (Rectisol®), propylene carbonate (Fluor®), and various others are used. In contrast to chemisorption, physical absorption removes carbon oxysulfide, carbon bisulfide and mercaptans, as well as hydrogen sulfide and carbon dioxide.

Physicochemical absorption uses composite absorbents, that is to say a mixture of chemical and physical absorbents. Such absorbents have an intermediate capacity to dissolve the acidic components of gases. These absorbents enable the fine removal of not only hydrogen sulfide and carbon dioxide, but also of organosulfurous compounds. The most widely used absorbent in the industry is Sulfinol, a mixture of diisopropanolamine (30-45%), sulfolane (tetrahydrothiophene dioxide) (40-60%), and water (5-15%). Also, lately, Ukarsol, a domestic analogue of Ecosorb, has become increasingly popular. This absorbent makes it possible to selectively remove H2S in the presence of CO_2,

Removing of Organo sulfourus compounds from natural gas

High absorbing capacity; the conjunction of fine removal and deep dehydration (down to -70 ^{0}C). relatively high operating costs; 50%-50% adsorbtion/desorbtion operation cycle.

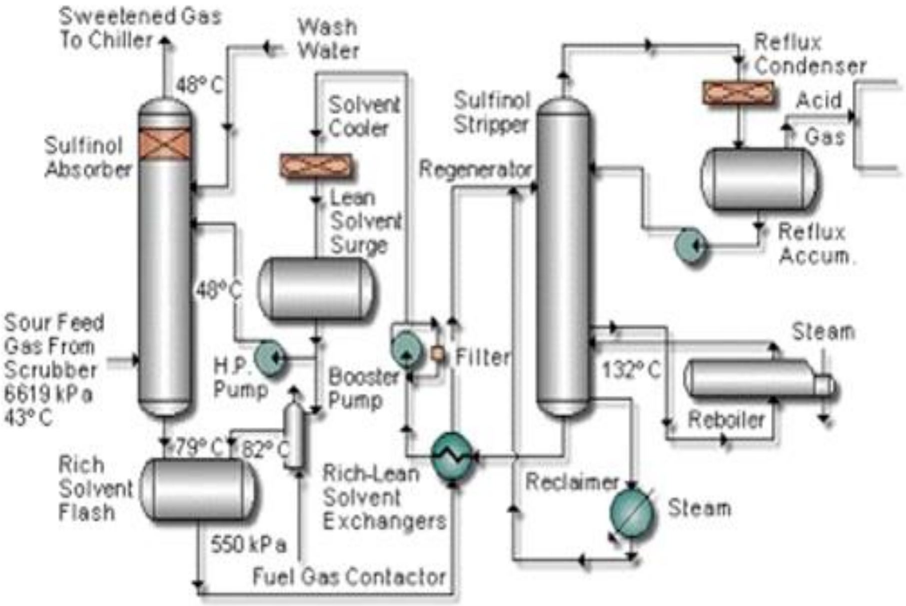
Catalytic methods are used when the gas contains impurities (e.g.

sulfides, disulfides, carbon oxide sulfide, carbon disulfide, thiophene) which cannot be efficiently removed by liquid absorbents or solid adsorbents. These are the following

:4- **Hydrogenation** into H_2S or sulfur-free compounds by hydrogen or water steam. The catalysts used are cobaltous oxide, nickel oxide, molybdenum on aluminum oxide.

5-H_2S Oxidation into elemental sulfur on active aluminum oxide or (via the Merox process) into disulfides.

In choosing a certain method for removing acidic components at the design stage, Premium Engineering takes into account a number of factors, for example the ecological standards and requirements for the disposal of sulfurous compounds; the type and concentration of impurities in sour (untreated) gas; gas purity, sour gas temperature and pressure, purified gas temperature and pressure, plant capacity, gas composition, etc.



Adsorption methods for gas purification are based on the selective removal of impurities by solid absorbents.

Heavy Hydrocarbon Removal

During phasing-in of new wells, feed gas is enriched with heavy hydrocarbons and oil. Hydro-carbon liquids are known to cause foaming in amine systems. It has been found that hydrocarbon liquid may reside in the piping; however, the liquid flow regime must be evaluated.

The first option is to drain these hydrocarbons from pipelines, for example by installing dip legs at different locations such as at the end of header, and between the final two branches.

Carbon filtration can be used upstream of the amine unit to further remove hydrocarbon molecules and other chemical contaminants which promote amine foaming.

Selective solvents have a capability of removing trace sulphur compounds, but hydrocarbon losses with the acid gas are high. Hydrocarbons have a higher solubility in physical solvent than in water; therefore, a higher physical solvent

concentration is likely to result in an increase in hydrocarbon content in the acid gas. There are other options that could be used for hydrocarbon removal, such as:

1- Using physical solvent for gas treating if applicable.

2- Draining the heavy hydrocarbons from pipelines upstream of the gas plant.

3-Providing a water wash scrubber (with a separation flash drum with sufficient residence time, the dissolved hydrocarbon can gravity-separate from the bulk solution) and using baffles and weirs.

- Providing a gas carbon filter upstream of multi-cyclone separator and coalescing filter.
- 5-Providing skimming facilities such as skimming pots for flash drums with sufficient residence time.

7- Using a molecular sieve bed downstream of the gas treating (molecular sieves could be designed with multi-beds for the dehydration, aromatic removal, and Hg removal, etc. in one package).

8- Adding one or two fractionation columns within gas treating for the removal of the remaining hydrocarbons, and to recover the C2-C4 and blend it back to the treated gas to maintain the required heating value.

9- If the amine-based solvent is applicable, some hydrocarbon removal could be achieved by minimizing the lean amine, running stripper at a lower pressure, and using low circulation rate.

10- If the sulphur recovery unit is located downstream of the gas plant, the heavy hydrocarbons and BTEX could be destroyed by designing a suitable burner to achieve 2,200°F (1,200°C) minimum.

11-If the acid gas feeding to the sulphur recovery unit has the low percent of H2S (lean gas), oxygen enrichment is recommended.

12-If the gas has retrograde properties close to its hydrocarbon dewpoints, it is of particular important minimize pressure losses. Drums could be equipped with proper hydrocarbon condensate withdrawal, such as skimming pots.

Petrochemical Industries

Petrochemicals (also known as **petroleum distillates**) are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels, such as coal or natural gas, or renewable sources such as corn, palm fruit or sugar cane.

The two most common petrochemical classes are olefins (including ethylene and propylene) and aromatics (including benzene, toluene and xylene isomers).

Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions. Chemical plants produce olefins by steam cracking of natural gas liquids like ethane and propane. Aromatics are produced by catalytic reforming of naphtha. Olefins and aromatics are the building-blocks for a wide range of materials such as solvents, detergents, and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels.

petrochemicals Production are divided into three groups

depending on their chemical structure:

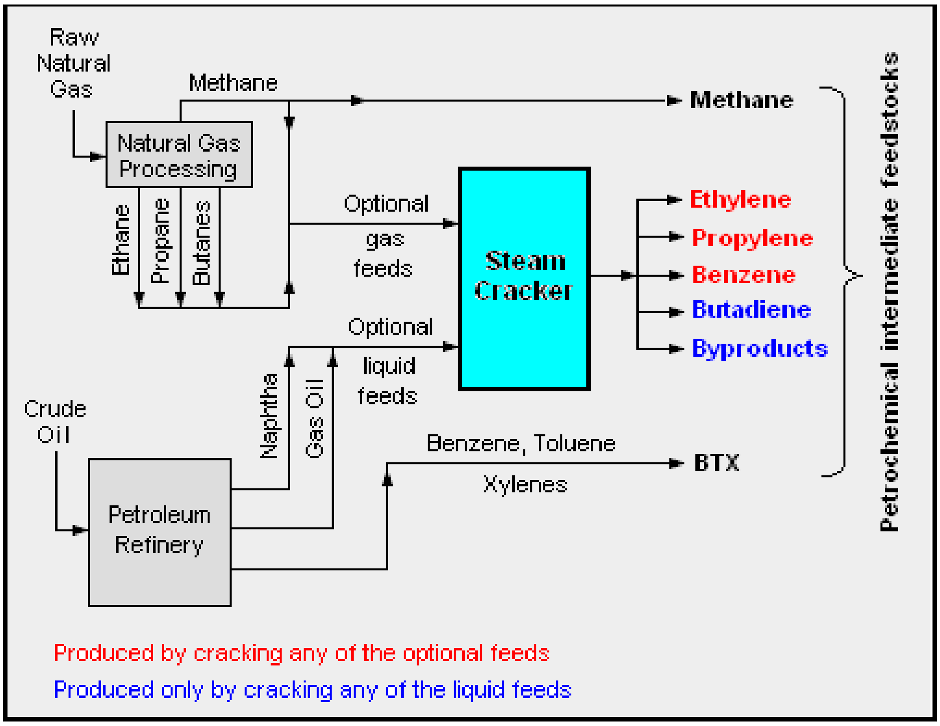
A) Olefins includes Ethene, Propene, Butenes and 13butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber.

B) Aromatics includes Benzene, toluene and xylenes, as a whole referred to as BTX and primarily obtained from petroleum refineries by extraction from the reformate produced in catalytic reformers using Naphtha obtained from petroleum refineries. Benzene is a raw material for dyes and synthetic detergents, and benzene and toluene for isocyanates MDI and TDI used in making polyurethanes. Manufacturers use xylenes to produce plastics and synthetic fibers.

C) Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate. Steam crackers are not to be confused with steam reforming plants used to produce hydrogen and ammonia.

- Methane, ethane, propane and butanes obtained primarily from natural gas processing plants.
- Methanol and formaldehyde.

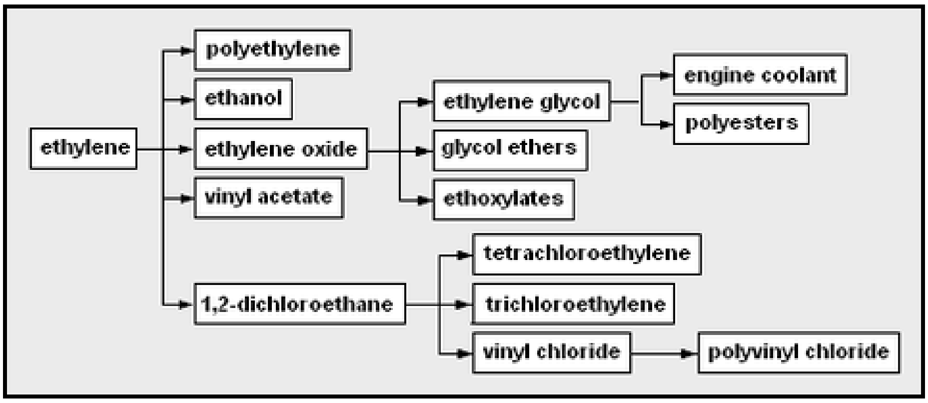
The adjacent diagram schematically depicts the major hydrocarbon sources and processes used in producing petrochemicals.[1][2][5][6]



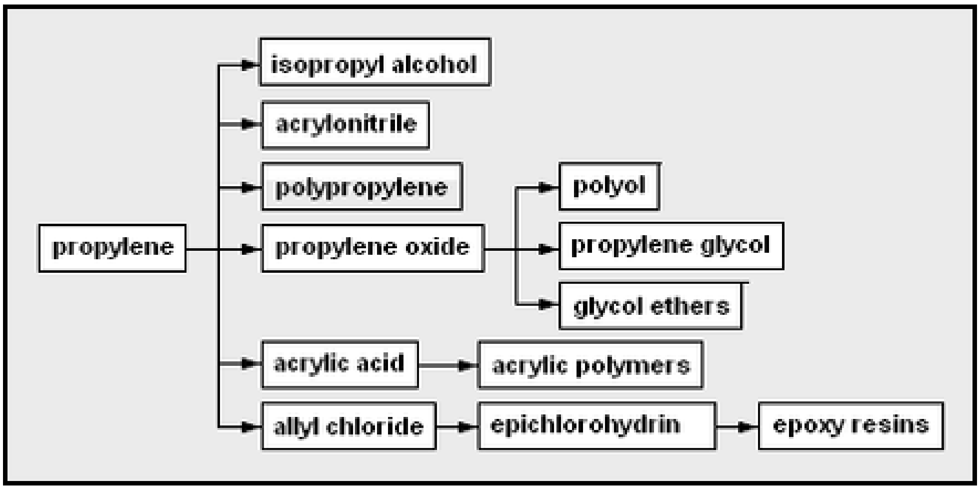
Petrochemical feedstock sources

Olefins

The following is a partial list of the major[according to whom?] commercial petrochemicals and their derivatives:



- Chemicals produced from ethylene
  - ethylene – the simplest olefin; used as a chemical feedstock and ripening stimulant
    - polyethylene – polymerized ethylene; LDPE, HDPE, LLDPE
    - ethanol – via ethylene hydration (chemical reaction adding water) of ethylene
    - ethylene oxide – via ethylene oxidation
      - ethylene glycol – via ethylene oxide hydration
        - engine coolant – ethylene glycol, water and inhibitor mixture
        - polyesters – any of several polymers with ester linkages in the main chain
      - glycol ethers – via glycol condescension
      - ethoxylates
    - vinyl acetate
    - 1,2-dichloroethane
      - trichloroethylene
      - tetrachloroethylene – also called perchloroethylene; used as a dry cleaning solvent and degreaser
      - vinyl chloride – monomer for polyvinyl chloride
        - polyvinyl chloride (PVC) – type of plastic used for piping, tubing, other things



Chemicals produced from propylene

propylene – used as a monomer and a chemical feedstock

isopropyl alcohol – 2-propanol; often used as a solvent or rubbing alcohol

acrylonitrile – useful as a monomer in forming Orlon, ABS

polypropylene – polymerized propylene

propylene oxide

polyether polyol – used in the production of polyurethanes

propylene glycol – used in engine coolant and aircraft deicer fluid

glycol ethers – from condensation of glycols

acrylic acid

acrylic polymers

allyl chloride –

epichlorohydrin – chloro-oxirane; used in epoxy resin formation

epoxy resins – a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine

Butene

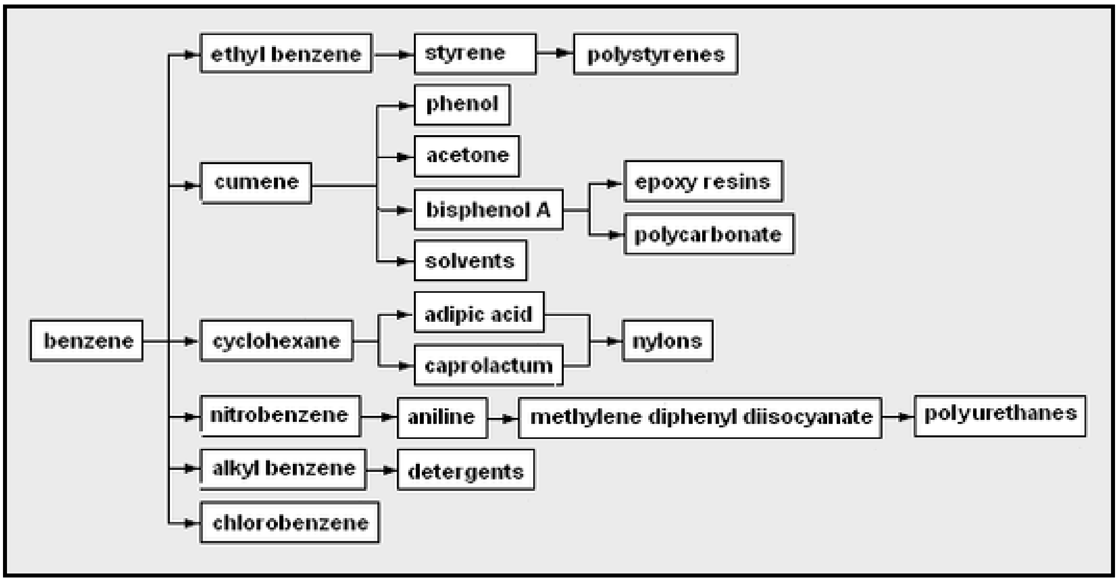
isomers of butylene – useful as monomers or co-monomers •

- isobutylene – feed for making methyl *tert*-butyl ether (MTBE) or monomer for copolymerization with a low percentage of isoprene to make butyl rubber

- 1,3-butadiene (or buta-1,3-diene) – a diene often used as a monomer or co-monomer for polymerization to elastomers such as polybutadiene, styrene-butadiene rubber, or a plastic such as acrylonitrile-butadiene-styrene (ABS)
  - synthetic rubbers – synthetic elastomers made of any one or more of several petrochemical (usually) monomers such as 1,3-butadiene, styrene, isobutylene, isoprene, chloroprene; elastomeric polymers are often made with a high percentage of conjugated diene monomers such as 1,3-butadiene, isoprene, or chloroprene

- higher olefins
    - polyolefins such poly-alpha-olefins, which are used as lubricants
    - alpha-olefins – used as monomers, co-monomers, and other chemical precursors. For example, a small amount of 11-hexene can be copolymerized with ethylene into a more flexible form of polyethylene.
    - other higher olefins
    - detergent alcohols

Aromatics

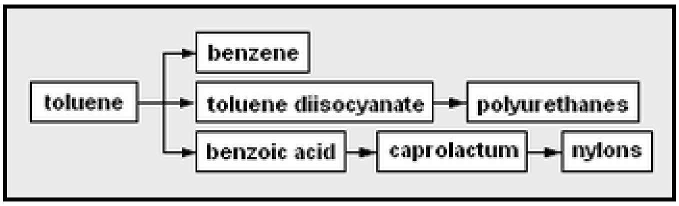


Chemicals produced from benzene

a. benzene – the simplest aromatic hydrocarbon

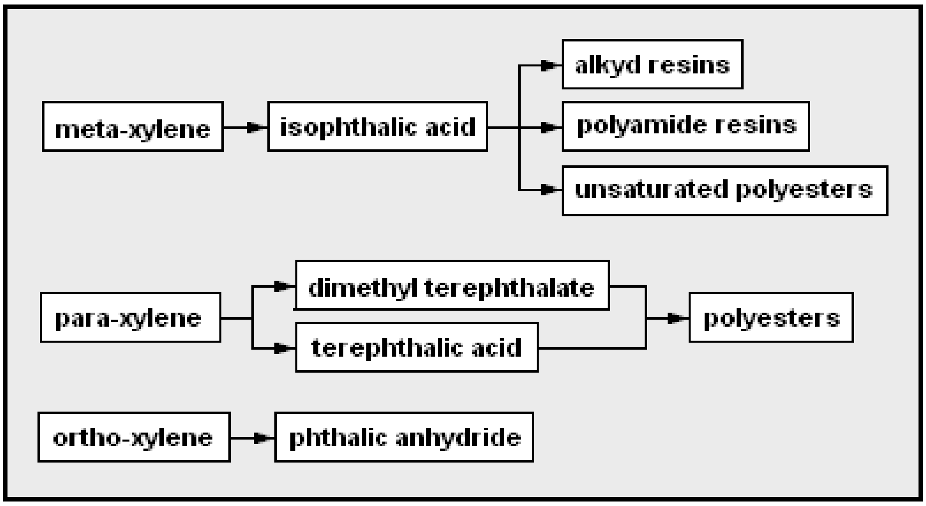
- ethylbenzene – made from benzene and ethylene
    - styrene made by dehydrogenation of ethylbenzene; used as a monomer
        - polystyrenes – polymers with styrene as a monomer
- cumene – isopropylbenzene; a feedstock in the cumene process
    - phenol – hydroxybenzene; often made by the cumene process
    - acetone – dimethyl ketone; also often made by the cumene process
    - bisphenol A – a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate
        - epoxy resins – a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine
        - polycarbonate – a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)

    - solvents – liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes
  - cyclohexane – a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent
    - adipic acid – a 6-carbon dicarboxylic acid, which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.
      - nylons – types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines
    - caprolactam – a 6-carbon cyclic amide
      - nylons – types of polyamides, some are from polymerizing caprolactam
  - nitrobenzene – can be made by single nitration of benzene
    - aniline – aminobenzene
      - methylene diphenyl diisocyanate (MDI) – used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
  - alkylbenzene – a general type of aromatic hydrocarbon, which can be used as a presursor for a sulfonate surfactant (detergent)
    - detergents – often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates
  - chlorobenzene



Chemicals produced from toluene

- toluene – methylbenzene; can be a solvent or precursor for other chemicals
  - benzene
  - toluene diisocyanate (TDI) – used as co-monomers with polyether polyols to form polyurethanes or with di- or polyamines to form polyureas polyurethanes
  - benzoic acid – carboxybenzene
    - caprolactam



Chemicals produced from xylenes

mixed xylenes – any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

ortho-xylene – both methyl groups can be oxidized to form (*ortho*-)phthalic acid

phthalic anhydride

para-xylene – both methyl groups can be oxidized to form terephthalic acid

dimethyl terephthalate – can be copolymerized to form certain polyesters

polyesters – although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.

purified terephthalic acid – often copolymerized to form polyethylene terephthalate

polyesters

meta-xylene

isophthalic acid

alkyd resins

Polyamide Resins

Unsaturated Polyesters

Fibers

List of petrochemicals

Chemicals	**Petroleum**	
		Basic **Feedstock**

		Benzene Butadiene Ethylene *p*-Xylene Propylene **Intermediates** 2-Ethylhexanol (2-EH) Acetic acid Acrylonitrile (AN) Ammonia Bis(2-ethylhexyl) phthalate (dioctyl phthalate) n-Butene Cyclohexane Dimethyl terephthalate (DMT) Dodecylbenzene Ethanol Ethanolamine Ethoxylate 1,2-Dichloroethane (ethylene dichloride or EDC) Ethylene glycol (EG) Ethylene oxide (EO) Formaldehyde Moulding Compound (FMC) n-Hexene Linear alkyl benzene (LAB) Methanol Methyl tert-butyl ether (MTBE) Phenol Propylene oxide Purified terephthalic acid (PTA) Styrene monomer (SM) Thermosetting Resin (Urea/Melamine) Vinyl acetate monomer (VAM) Vinyl chloride monomer (VCM) **Acrylic fibers** Acrylonitrile butadiene styrene (ABS) Acrylonitrile styrene (AS) Polybutadiene (PBR) Polyvinyl chloride (PVC) Polyethylene (PE) Polyethylene terephthalate (PET) Polyol Polypropylene (PP) Polystyrene (PS) Styrene 13butadiene (SBR) Acrylic-forma **The Primary Hydrocarbons**

Raw crude oil and natural gas are purified into a relatively small number of hydrocarbons (combinations of hydrogen and carbon). These are used directly in manufacturing and transportation or act as feedstock to make other chemicals.

- **Methane**: a greenhouse gas that can be used as fuel and is often included in rocket fuel
- **Ethylene:** used to make plastics and films, as well as detergents, synthetic lubricants, and styrenes (used to make protective packaging)
- **Propylene:** a colorless, odorless gas used for fuel and to make polypropylene, a versatile plastic polymer used to make products ranging from carpets to structural foam
- **Butanes**: hydrocarbon gases that are generally used for fuel and in industry
- **Butadiene:** used in the manufacture of synthetic rubbers
- **BTX (benzene, toluene, xylene**): benzene, toluene, and xylene are aromatic hydrocarbons. A major part of gasoline, benzene is also used to make nylon fibers which, in turn, are used to make clothing, packaging, and many other products

Medical uses

Petrochemicals play many roles in medicine because they are used to create resins, films, and plastics. Here are just a few examples:

- Phenol and Cumene are used to create a substance that is essential for manufacturing penicillin (an extremely important antibiotic) and aspirin.
- Petrochemical resins are used to purify drugs, thus cutting costs and speeding the manufacturing process.
- Resins made from petrochemicals are used in the manufacture of drugs including treatments for AIDS, arthritis, and cancer.
- Plastics and resins made with petrochemicals are used to make devices such as artificial limbs and skin.
- Plastics are used to make a huge range of medical equipment including bottles, disposable syringes, and much more.

Food

Petrochemicals are used to make most food preservatives that keep food fresh on the shelf or in a can. In addition, you'll find petrochemicals listed as ingredients in many chocolates and candies. Food colorings made with petrochemicals are used in a surprising number of products including chips, packaged foods, and canned or jarred foods.

Agriculture

More than a billion pounds of plastic, all made with petrochemicals, find use annually in U.S. agriculture. The chemicals are used to make everything from plastic sheeting and mulch to pesticides and fertilizers. Plastics are also used to make twine, silage, and tubing. Petroleum fuels are also used to transport foods (which are, of course, stored in plastic containers).

Household Products

Because it is used to make plastics, fibers, synthetic rubber, and films, petrochemicals are used in a bewildering array of household products. To name just a few:

Carpeting ,Crayons , Detergents , Dyes , Fertilizers , Milk jug , Pantyhose , Perfume ,Safety glass , Shampoo , Soft contact lenses , Wax

Questions and answers for students

- Hydrocarbons heavier than methane that is recovered from natural gas are referred as_____?
- Natural gas solid
- Paraffin
- Natural gas liquid
- Gasoline

The answer is C. Natural gas liquid

- In order to reduce corrosion problems and to prevent hydrate formation?
- Moisture must be removed
- Moisture must be added
- Crude oil must be removed
- Metal must be removed

The A. Moisture must be removed

- Alternation of molecular structure is important in order to
- Breaking of large hydrocarbon into smaller ones
- Convert more valuable hydrocarbon compound into valuable ones
- Convert less valuable hydrocarbon into valuable ones
- Convert less valuable hydrocarbon compound into less ones

		The answer is C. Convert less valuable hydrocarbon into valuable ones • In chemisorption, the is characterized by ______? • Removal of moisture • Corrosion • High capability of absorption large amount of acid gasses • Addition of water The answer is C. High capability of absorption large amount of acid gasses **Presence of aromatics in** (A) Diesel increases its cetane number (B) Kerosene increases its smoke point (C) Petrol increases its octane number (D) All (a), (b) and (c) Answer: Option C **The best method of determining sulphur in crude oil is by the __________ method.** (A) Kjeldahl (B) Dumas (C) Bomb calorimeter (D) Junkers calorimeter Answ . C **3. Which of the following is the most widely used cracking process in oil refineries?** (A) Dubbs process (B) T.C.C. moving bed process (C) Fluidised bed catalytic cracking process (D) Houdry's fixed bed proc Ans. C

4. Which of the following reactions is undesirable in the production of catalytically reformed gasoline?

(A) Dehydrogenation of Naphthene

(B) Dehydrogenation of lower paraffins

(C) Dehydrocyclization of higher paraffins

(D) Isomerization of paraffins

Ans B

5. Catalytic cracking compared to thermal cracking of residue of vacuum distillation of crude oil

(A) Gives higher yield of petrol

(B) Lower octane number of petrol

(C) Higher sulphur content in the product

(D) Higher gum forming material in petroleum

Ans: A

6. Pick out the wrong statement.

(A) A pale color of petroleum product indicates lower viscosity

(B) Color of petroleum products indicates the degree of refinement

(C) Lighter petroleum distillates are lighter in color than the heavier residual oils

(D) Fluorescence of oils helps to detect its adulteration

Ans: A

7. Which of the following is an additive used for improving the cetane number of diesel?

(A) Tetraethyl lead

(B) Tetramethyllead

(C) Ethyl nitrate or acetone

(D) None of these

Ans; A

8. Higher boiling fractions like atmospheric residue is distilled under vacuum at low temperature because at high temperature, there is a tendency of the predominance of

(A) Thermal cracking

(B) Gum formation

(C) Coking

(D) Discoloration

Ans: C

9. Octane number of gasoline produced by two stage fluidized catalytic cracking process is

(A) 80

(B) 87

(C) 92

(D) 97

Ans: D

10. Reforming converts

(A) Olefins into paraffins

(B) Naphthenes into aromatics

(C) Naphthenes into olefins

(D) Naphthenes into paraffin

Ans: B

11. Feedstock for polymerization is

(A) Naphtha

(B) Cracked gases rich in C_2 & C_4 olefins

(C) Low boiling aromatics

(D) None of these

Ans: B

12. Which of the following has the minimum °API gravity of all?

(A) Diesel

(B) Kerosene

(C) Petrol

(D) Furnace oil

Ans: D

13. Olefins are

(A) Saturated hydrocarbons

(B) Unsaturated cyclic compounds (hydrocarbons)

(C) Present in substantially good quantity in crude petroleum

(D) None of these

Ans: D

14. Natural gas recovered along with crude oil from oil wells is called wet natural gas which has a higher __________ compared to the dry natural gas.

(A) Unsaturated hydrocarbon content

(B) Calorific value

(C) Quantity of propane

(D) Quantity of butane

Ans: B

15. Which of the following processes is used for the production of petroleum coke?

(A) Stabilization

(B) Visbreaking

(C) Cracking

(D) Reforming

Ans: C

View All Answers

01. Answer: Option C 02. Answer: Option C 03. Answer: Option C 04. Answer: Option B 05. Answer: Option A 06. Answer: Option A 07. Answer: Option A 08. Answer: Option C 09. Answer: Option D 10. Answer: Option B 11. Answer: Option B 12. Answer: Option D 13. Answer: Option D 14. Answer: Option B 15. Answer: Option C

Multiple Choice Questions & Answers

Removal of water is done by ____________
a) Orsteds process
b) Kjeldahl’s process
c) Filtration
d) Cottrells process
View Answer
Answer: d
Explanation: Cottrells process is used to remove the water from the petroleum. kjeldahl’s process is used to know the percentage of nitrogen in the coal sample.

2. Crude oil is in the form of ____________
a) emulsion of oil and brine
b) emulsion of oil and impurities
c) emulsion of brine and impurities

d) emulsion of impurities and moisture
View Answer
Answer: a
Explanation: The crude oil is obtained from the earth’s crust which will be in the form of emulsion of oil and brine. It is very stable. When this emulsion is charged then water gets separated from the oil.

3. To remove sulphur compounds from petroleum, it is treated with ___________
a) copper nitrate
b) copper oxide
c) magnesium chloride
d) sodium chloride
View Answer
Answer: b
Explanation: The sulphur compounds can be removed by treating with copper oxide as the sulphur compounds are get converted into the insoluble copper sulphide.

4. The scales formed during the removal of harmful impurities can be removed by ___________
a) electrolysis
b) electroplating
c) electrotyping
d) dehydration
View Answer

The scales formed during the removal of harmful impurities can be removed by ___________
a) electrolysis
b) electroplating
c) electrotyping
d) dehydration
View Answer
Answer: d
Explanation: The corrosion is will be there if there is presence of magnesium chloride or sodium chloride salts in crude oil and forms scales. These scales can be removed by dehydration process.

5. During refining the petroleum, in fractional distillation, what is the temperature in still?
a) 800^{o}C
b) 400^{o}C
c) 300^{o}C
d) 100^{o}C
View Answer
Answer: b
Explanation: The crude oil is distilled and later it is sent into the

pre-heater or else it can be heated with steam, inside the still the temperature is about 400°C.

6. Which of the following fraction obtained on distillation used in dry cleaning?
a) petroleum ether
b) heavy oil
c) gas oil
d) naphtha
View Answer
Answer: d
Explanation: Naphtha is used for dry cleaning. It is also called as solvent spirit. Heavy oil is mainly used in producing gasoline by cracking method.

7. What is the catalyst used in catalytic polymerization?
a) Phosphoric acid
b) Al_2O_3
c) $Al_2(siO_3)_3$
d) Zirconium oxide
View Answer
8. Which of the following reactions indicates the Fischer-tropsch method?
a) $nC+H_{(2n+2)} \rightarrow C_nH_{(2n+2)}$
b) $nC+H_{2n} \rightarrow C_nH_{2n}$
c) $nCO+2nH_2 \rightarrow C_nH_2n+nH_2O$
d) $nC+H_{(2n-1)} \rightarrow C_nH_{(2n-1)}$
View Answer
9. What is the catalyst used in Bergius process?
a) nickel oleate
b) phosphoric acid
c) zirconium oxide
d) aluminum oxide
View Answer
Answer: a
Explanation: In Bergius process the catalyst used is Nickel oleate. In this process the low ash coal is finely powdered and turned into a paste using heavy oil and the catalyst is taken into temperature.

10. What is the pressure applied during hydrogenation of coal?
a) 200-280atm
b) 200-250atm
c) 300-380atm
d) 300-350atm
View Answer
11. The boiling range of un-condensed gas is ____________
a) < 300C
b) < 400C
c) > 500C

d) < 200C
View Answer
Answer: a

Explanation: The boiling range of un-condensed gas must be very low that is less than $30^{o}C$. As the gases are un-condensed they are ready to condense and become steam. So, a small amount of heat is sufficient to boil them.

12. Heavy oil on refractionation produces __________
a) Asphalt
b) diesel oil
c) grease
d) kerosene oil
View Answer
Answer: c

Explanation: Heavy oil on refractionation produces grease. It also produces lubricating oil, petroleum jelly, paraffin wax.

13. How much percentage of petrol is produced by the synthesis of coal?
a) 40%
b) 50%
c) 80%
d) 30%
View Answer
Answer: d

Explanation: 30% of petrol is produced from the synthesis of coal. Coal is mainly utilized in producing electricity and petrol.50% of petrol is produced form the process called cracking.

14. Which of the following can be used as a preservative for wood?
a) solvent spirit
b) petroleum coke
c) tar
d) gasoline
View Answer
15. What is the boiling range of diesel oil?
a) $120-180^{o}C$
b) $180-250^{o}C$
c) $320-400^{o}C$
d) $250-320^{o}C$
View Answer
Answer: d

Explanation: Diesel oil’s boiling point is $250-320^{o}C$. So, in cracking the high temperatures are applied.

Questions & answers

Answer all questions.

1. List and explain the classification of petroleum crude

2. Write briefly about the catalysts used in cracking

3. Write a note on white spirit

4. Distinguish between fire point and smoke point

5. Differentiate between thermal cracking and visbreaking

6. Explain how the API scale is useful in evaluating crude

7. Compare isomerization and reforming

8. Give the purpose of clay treatment in petroleum processing

9. Draw a neat flow diagram of isoprene production

10. How is Phthalic anhydride made? Give its uses

11. a) Discuss the various theories related to the origin of petroleum.

11 b) Write a note on petroleum drilling operations

12. a) What is sweetening? With reference to petroleum processing describe any sweetening process with a neat flow sheet.

12 b) Write a note on solvent extraction of kerosene.

13. With a neat flow diagram, explain the furfural process for the manufacture of lubricating oil

13a) With a neat flow diagram, explain the fluid catalytic cracking process

13 b) Discuss the following refining processes -i. Alkylation ii. Thermal Cracking

14. a) Write short notes on : i. Dealkylation ii. Hydrocracking iii. Isomerization

iv. Dehydrogenation

15 b) What is reforming? Explain in detail catalytic reforming

16 a) Describe the manufacture of acetylene from hydrocarbons

16 b) Write short notes on petroleum waxes

17)Describe the synthesis of methanol

1-What chemical property was used to separate the hydrocarbons in the distillation process?

(It was the boiling point.)

2-Based on size, where are the smallest hydrocarbons after distillation?

(They are at the top of the distillation column.)

3-Where are the largest hydrocarbons?

(They are at the bottom of the distillation column.)

4-What are the two processes that are used to remove sulfur?

(They are amine sweetening and hydrotreating.)

5-Why might it be important to remove sulfur from the hydrocarbons?

(Encourage students to think of different ideas. Emphasize that impurities such as sulfur can damage equipment in the refinery and the quality of the products. There are also legal limits set by the Environmental Protection Agency on the amount of sulfur that can stay in the products.)

6-What is a catalyst?

(It is something that changes the rate of reaction and is not permanently changed in the reaction.)

7-Would the reaction still happen without the catalyst?

In hydrotreating, a metal surface is usually used as a catalyst. These metals include palladium, nickel, platinum, cobalt, and iron. Draw a general reaction formula for students to understand hydrotreating.

$S + H_2 (g) \rightarrow H_2S (g)$ *(Catalyst, heat, and pressure)*

If possible, project the treatment page of the interactive for the class. Click on one of the fuels and then on the hydrotreating box to show students an example of one of the types of reactions that happen in the hydrotreating unit. Solid sulfur is converted to hydrogen sulfide gas, which is then removed.

$S_8 (s) + 8H_2 (g) \rightarrow 8H_2S (g)$ *(Catalyst, heat, and pressure)*

Tell students that the hydrotreating process also removes nitrogen compounds, which if not removed, would react with the oxygen in the air and produce nitric acid (HNO_3).

Do large hydrocarbons have high or low boiling points? Why?

(They have high boiling points due to factors such as a

		heavier molecular weight, hydrogen bonding, and the amount of branching.) 8-What is the first treatment process for the gas oil fraction? (It is hydrotreating.) 9-What is the goal of hydrotreating? (The goal is to remove impurities.) 10-What are the other two treatment processes that gas oil undergoes after hydrotreating? (It undergoes hydrocracking and catalytic cracking.) 11-What is the first treatment process for the gas oil fraction? (It is hydrotreating.) 12-What is the goal of hydrotreating? (The goal is to remove impurities.) 13-What are the other two treatment processes that gas oil undergoes after hydrotreating? (It undergoes hydrocracking and catalytic cracking.) Cracking processes break down heavy hydrocarbons (you may want to use the term large hydrocarbon molecules) into lighter products (smaller hydrocarbon molecules). Different types of cracking processes are used. Focus on catalytic cracking, telling students that this process uses high heat and a catalyst to break larger molecules into smaller, more useful ones. Draw the following reaction to show students how catalytic cracking works: $C_{22}H_{46}$ + heat + catalyst → $C_{12}H_{26} + C_6H_{12} + C_4H_8$ The catalyst used is often silica or alumina. In the above reaction, docosane is converted to dodecane, cyclohexane, and butene. The smaller hexane and butene can be combined with other smaller compounds to make gasoline stock. The larger dodecane is a component of diesel stock, which can be used to fuel ships and factories. 14-Describe an example of the third process (Reshaping or building hydrocarbons from smaller ones) by clicking the red circle next to "light naphtha" on the treatment page of the interactive. Doing so will show two treatment processes: hydrotreating and isomerization. Ask students: 15-Are the hydrocarbons in light naphtha large or small relatively? (They are small.)

15-Tell students that light naphtha is a mixture of mostly pentane and hexane. Have students draw the chemical structures of pentane and hexane. If possible, provide models of each structure. Ask students:

16-What is an isomer?

(It is a compound with the same molecular formula as another, but with a different structure.)

17-What do you think happens in the isomerization process in the refinery?

(The hydrocarbons are made into isomers.)

18-If we start with hexane and pentane, after isomerization, will the chemical formulas of the products change?

(No.)

19-Write the following reaction on the board:

$C_5H_{12} \quad \rightarrow \quad C_5H_{12}$

This is the reaction for pentane to isopentane. Ask students to draw the chemical structure of isopentane. Using the model for pentane, remove the fifth carbon from the chain and move it to the second carbon. This new structure is isopentane (also called methylbutane or 2-methylbutane), which has the same chemical formula as straight-chained pentane. Tell students that this isomerization is important in the petroleum treatment process because isomers improve the quality of gasoline as opposed to the straight-chained molecules. In fact, isomers improve the octane rating for gasoline.

20-Describe the processes for gases treatment?

Removal of solids, Sulfur,and water using amines and glycols

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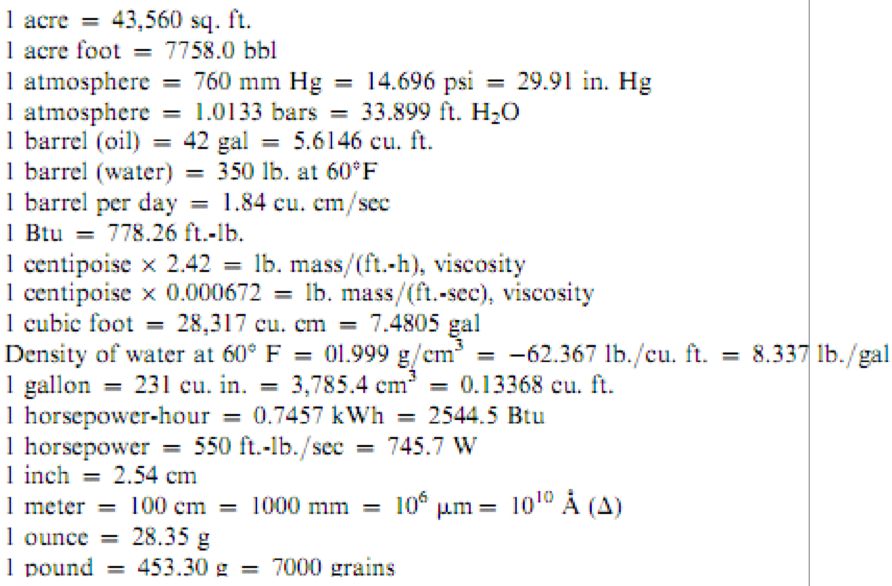
Conversion Factors



1 acre = 43,560 sq. ft.
1 acre foot = 7758.0 bbl
1 atmosphere = 760 mm Hg = 14.696 psi = 29.91 in. Hg
1 atmosphere = 1.0133 bars = 33.899 ft. H_2O
1 barrel (oil) = 42 gal = 5.6146 cu. ft.
1 barrel (water) = 350 lb. at 60°F
1 barrel per day = 1.84 cu. cm/sec
1 Btu = 778.26 ft.-lb.
1 centipoise × 2.42 = lb. mass/(ft.-h), viscosity
1 centipoise × 0.000672 = lb. mass/(ft.-sec), viscosity
1 cubic foot = 28,317 cu. cm = 7.4805 gal
Density of water at 60° F = 01.999 g/cm^3 = −62.367 lb./cu. ft. = 8.337 lb./gal
1 gallon = 231 cu. in. = 3,785.4 cm^3 = 0.13368 cu. ft.
1 horsepower-hour = 0.7457 kWh = 2544.5 Btu
1 horsepower = 550 ft.-lb./sec = 745.7 W
1 inch = 2.54 cm
1 meter = 100 cm = 1000 mm = 10^6 μm = 10^{10} Å (Δ)
1 ounce = 28.35 g
1 pound = 453.30 g = 7000 grains

SI METRIC CONVERSION FACTORS
(E = EXPONENT; I.E. E + 03 = 10^3)

Acre-foot × 1.233482 E + 03 = meter cube
Barrels × 1.589873 E − 01 = meter cube
Centipoises × 1.00000 E − 03 = pascal seconds
Darcy × 9.869233 E − 01 = micrometer square
Feet × 3.048000 E − 01 = meters
Pounds/acre-foot × 3.677332 E − 04 = kilograms/meter cube
Pounds/square inch × 6.894757 E − 00 = kilopascals
Dyne/cm × 1.000000 E + 00 = mN/m
Parts per million × 1.000000 E + 00 = milligrams/kilograms