Chm 102 Chemisstry II BTC

المادة كيمياء عضوية Organic Chemistry

الفرقة الاولي كلية العلوم

شعبة بيوتكنولوجي

Dr Awatef Mohamed Elmaghraby

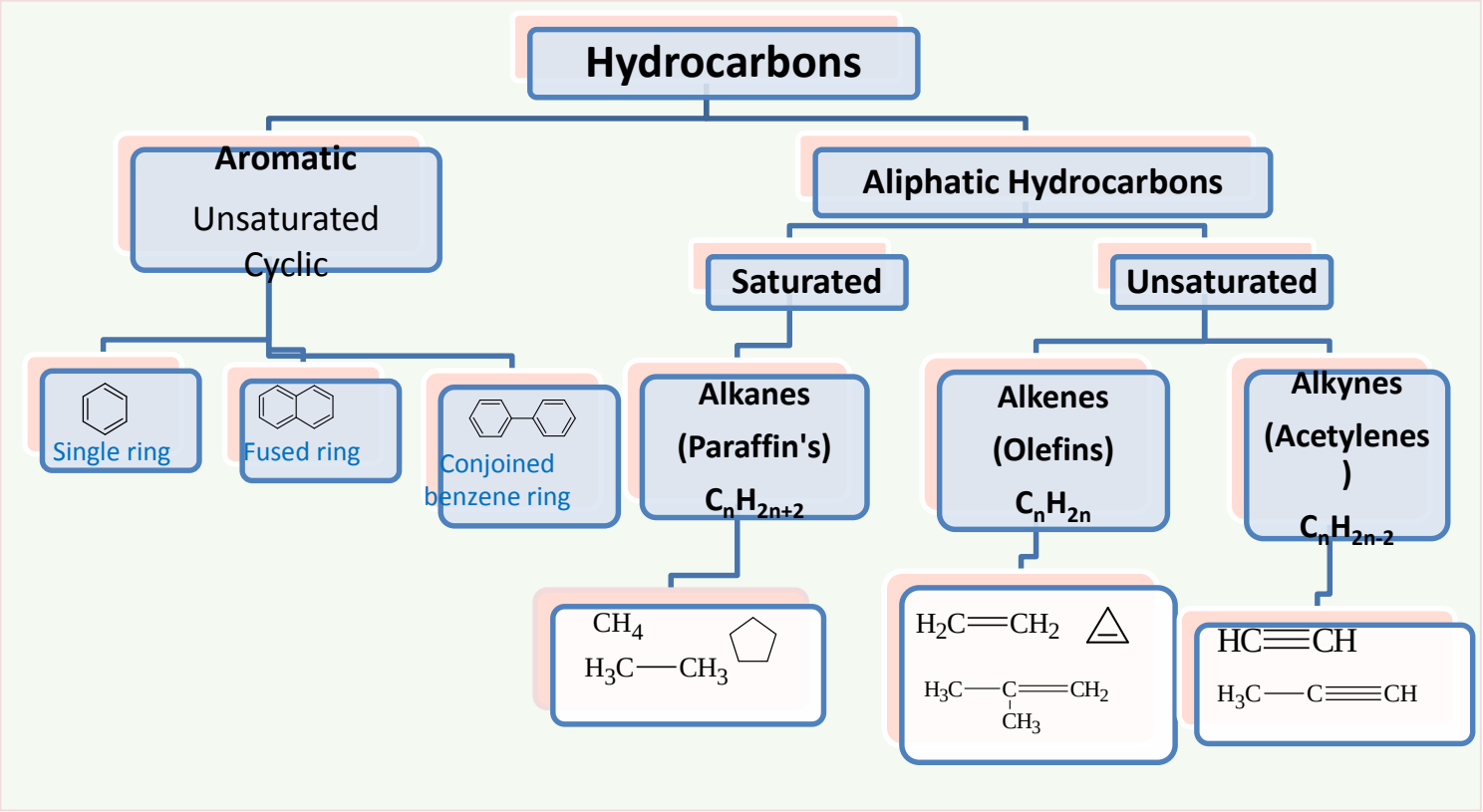
Chemistry Department

Faculty of science

Content

Hydrocarbons

Hydrocarbons are Organic Compounds, which contain only the two elements carbon and hydrogen.



Names and Molecular Formulas of the First Ten Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Alkyl Group Nomenclature

An alkyl group is formed by loss of a hydrogen atom from the corresponding alkane.

General formula C_nH_{2n+1}.

The letter **R** is used as a general symbol for an **alkyl group**.

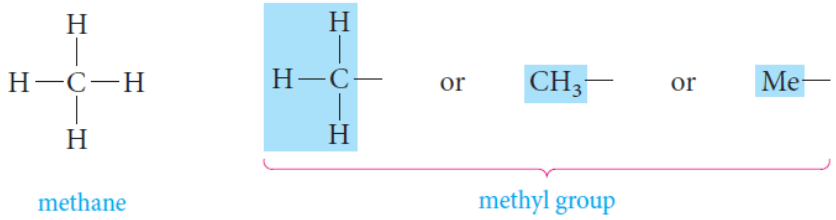
An alkyl group is named by replacing the suffix ***–ane*** of the parent alkane by *–yl.*

i.e. Alkane – ane + yl = Alkyl

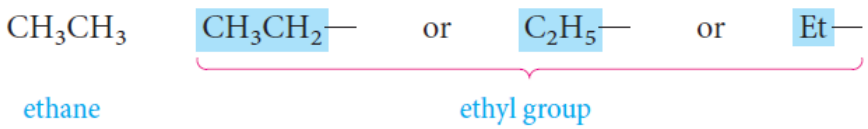
Alkyl Group Nomenclature

Examples: ○

- **Derived from methane** by removing one of the hydrogens, a one-carbon substituent is called a **methyl group**.



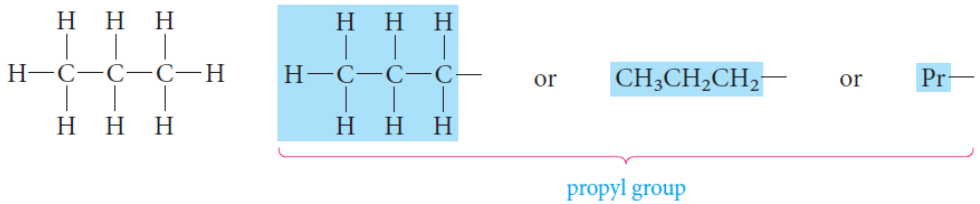
- Thus the two-carbon alkyl group is called the **ethyl group**, **from ethane**.



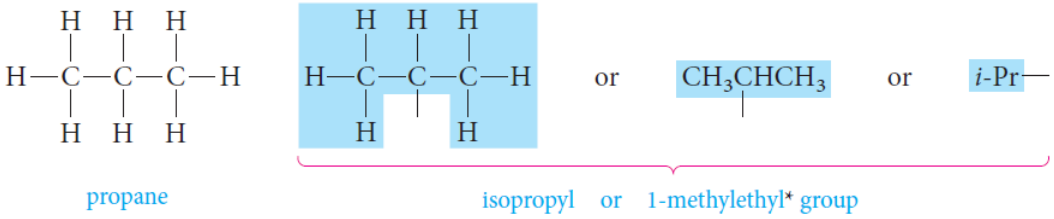
Alkyl Group Nomenclature

- When we come to **propane**, there are two possible alkyl groups, depending on which type of hydrogen is removed.

- If a *terminal* hydrogen is removed, the group is called a **propyl group**.

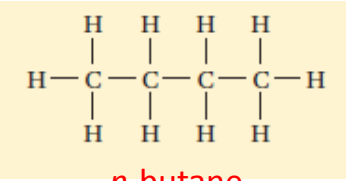


- If a hydrogen is removed from the *central* carbon atom, we get a different isomeric propyl group, called the **isopropyl group**.

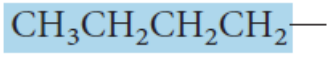


Alkyl Group Nomenclature

- For four-carbon alkyl group, there are four different butyl groups.
  - The butyl and *sec*-butyl groups are based on ***n*-butane**.
  - The isobutyl and *tert*-butyl groups come from **isobutane**.



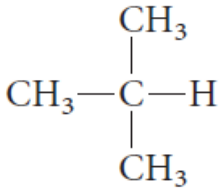
n-butane



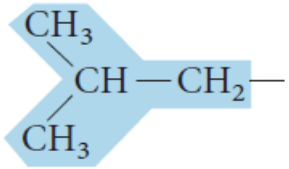
butyl

and

sec-butyl
(or 1-methylpropyl)

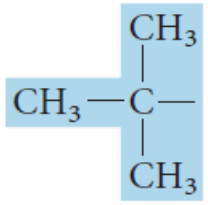


isobutane



isobutyl
(or 2-methylpropyl)

and



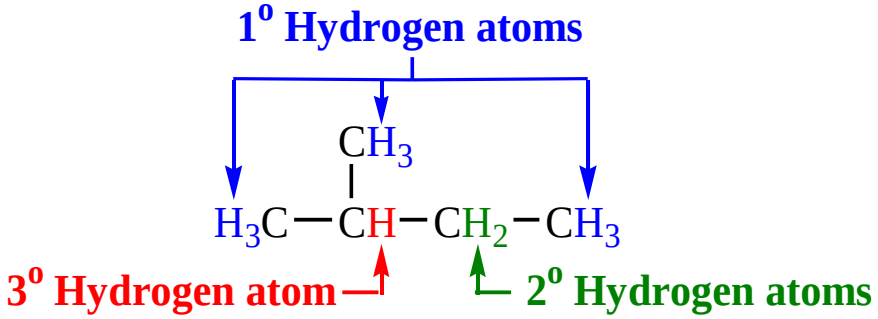
tert-butyl
(or 1,1-dimethylethyl)

Classes of Carbons and Hydrogen

A primary (1°) carbon is one that is bonded to only one other carbon.

A secondary (2°) carbon is one that is bonded to two other carbons.

A tertiary (3°) carbon is one that is bonded to three other carbons.



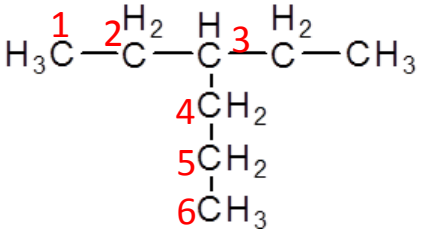
Hydrogens are also referred to as 1°, 2°, or 3° according to the type of carbon they are bonded to.

Nomenclature of Saturated Hydrocarbons

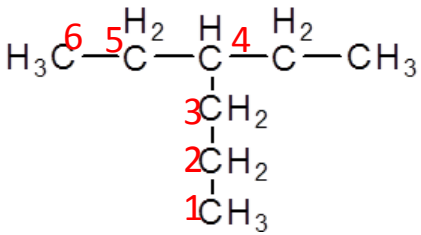
Nomenclature of Alkanes

2) **Number** the carbons in the parent chain

starting from the end which gives the lowest number for the substituent



not



3- Ethyl hexane

4- Ethyl hexane ✗

To name the compound;

1) The position of the substituent on the parent carbon chain by a number.

2) The number is followed by a hyphen (-).

3) The combined name of the substituent (ethyl).

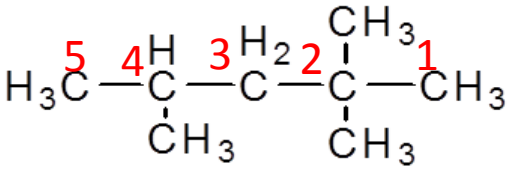
4) The parent carbon chain (hexane).

3 - Ethyl hexane

Nomenclature of Saturated Hydrocarbons

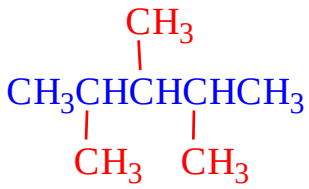
Nomenclature of Alkanes

3) If the **same alkyl substituent** occurs more than once on the parent carbon chain, the prefixes **di-**, **tri-**, **tetra-**, **penta-**, and so on are used to indicate **two**, **three**, **four**, **five**, and so on.

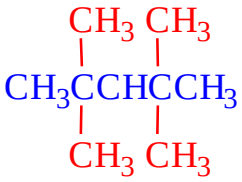


2,2,4- Trimethylpentane

2,3-Dimethylbutane



2,3,4-Trimethylpentane



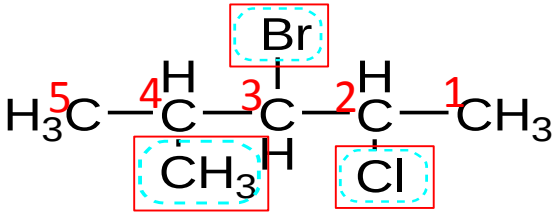
2,2,4,4-Tetramethylpentane

Nomenclature of Saturated Hydrocarbons

Nomenclature of Alkanes

7) If substituents other than alky groups are also presents on the parent carbon chain;

all substituents are named alphabetically
-F fluoro -Cl chloro -Br bromo -I iodo
-NO2 nitro -NH2 amino -CN cyano .



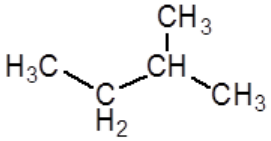
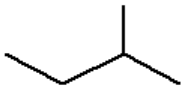
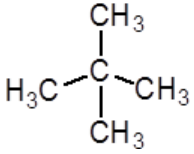
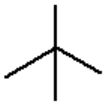
3-bromo -2- chloro-4-methyl pentane

2- choro
3-bromo
4- methyl

Nomenclature of Saturated Hydrocarbons

Nomenclature of Alkanes

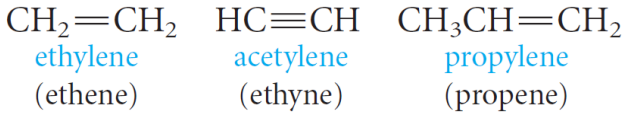
Examples

		Common name:	IUPAC name:
$CH_3CH_2CH_2CH_2CH_3$		n-Pentane	Pentane
		Isopentane	2-Methylbutane
		Neopentane	2,2-Dimethylpropane

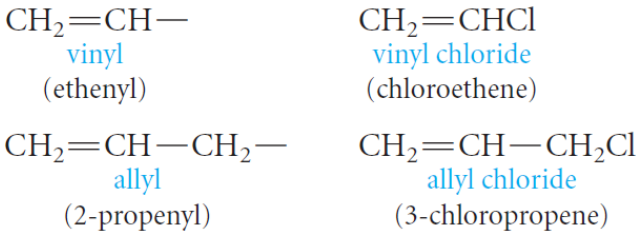
Nomenclature of Unsaturated Hydrocarbons

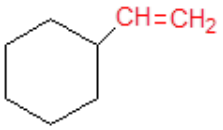
Common Names

- The simplest members of the **alkene and alkyne** series are frequently referred to by their older common names, ethylene, acetylene, and propylene.



- Two important groups also have common names; They are the **vinyl** and **allyl** groups and are used in common names.





Common name: Vinyl cyclohexane
IUPAC name: Cyclohexylethene

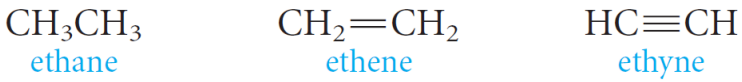
Nomenclature of Unsaturated Hydrocarbons

The IUPAC Rules

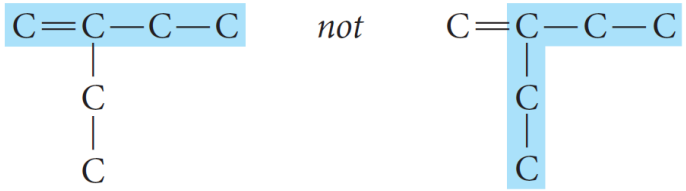
The IUPAC rules for naming alkenes and alkynes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

The ending ***-ene*** is used to designate a carbon–carbon double bond.

The ending ***-yne*** is used to designate a carbon–carbon triple bond.



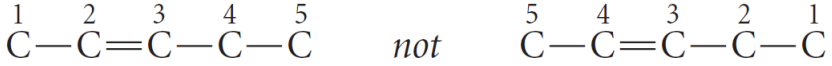
2. Select the longest chain that includes *both* *carbons of the double (triple) bond*.



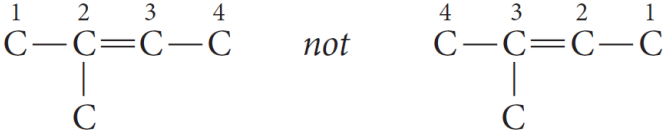
The IUPAC Rules

Nomenclature of Unsaturated Hydrocarbons

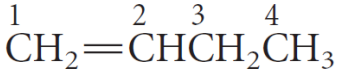
3. **Number the chain from the end nearest the double (triple) bond** so that the carbon atoms in that bond have the lowest possible numbers.



If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



4. Indicate the **position of the multiple bond using the *lower numbered carbon atom*** of that bond.



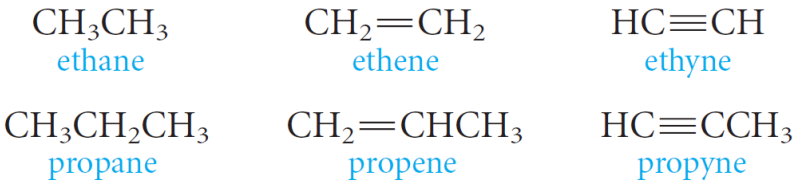
1-butene, *not* 2-butene

Nomenclature of Unsaturated Hydrocarbons

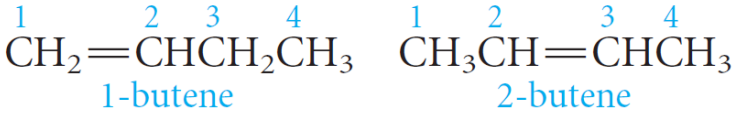
The IUPAC Rules

NOTES

- The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane, -ene,* or *-yne*) tells us whether the bonds are single, double, or triple.
- *No number is necessary in these cases, because in each instance, only one structure is possible.*



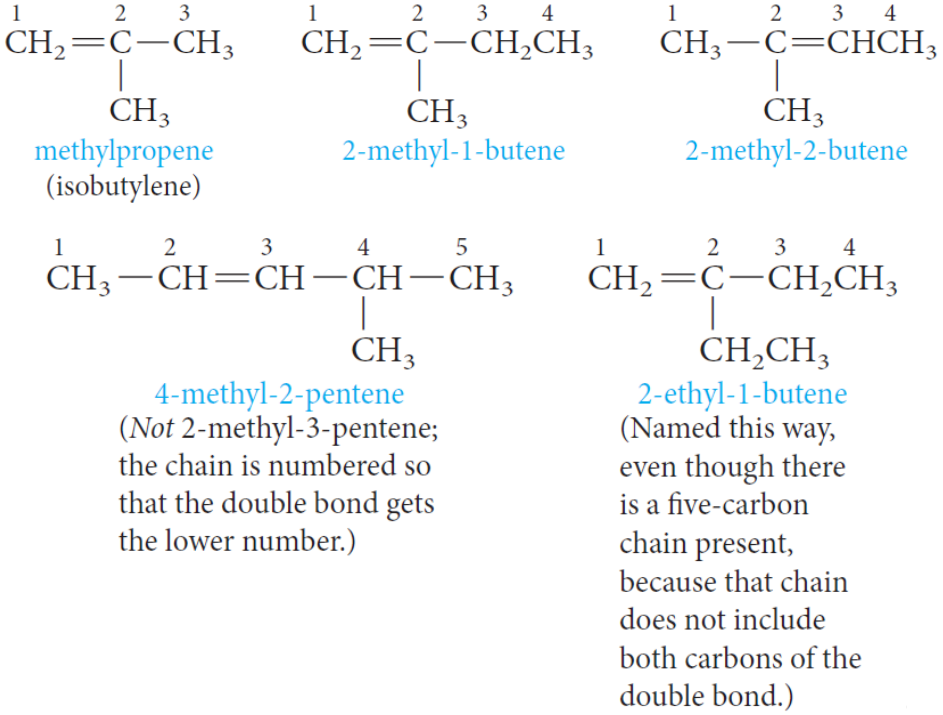
- *With four carbons, a number is necessary to locate the double bond.*



The IUPAC Rules

Nomenclature of Unsaturated Hydrocarbons

Branches are named in the usual way. ○



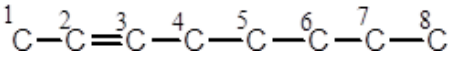
The IUPAC Rules

Nomenclature of Unsaturated Hydrocarbons

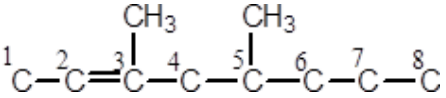
Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

1) The parent carbon chain is an **Octene**.

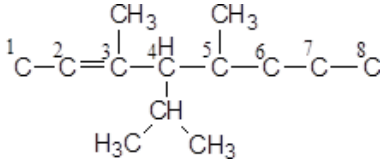
The double bond is located between the 2nd and 3rd carbons.



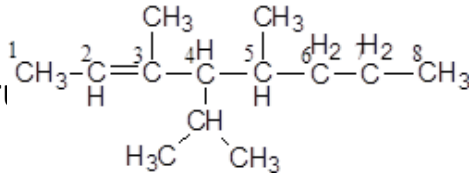
2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



3) An isopropyl group is attached on carbon 4.



4) Put the missing hydrogens to get the correct str

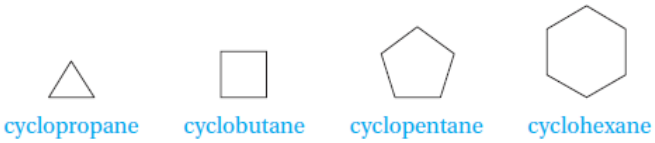


Nomenclature of Cycloalkanes

Nomenclature of Cycloalkanes and Cycloalkenes

Cycloalkanes are saturated hydrocarbons that have at least one ring of carbon atoms.

Cycloalkanes are named by placing the prefix *cyclo-* before the alkane name that corresponds to the number of carbon atoms in the ring.

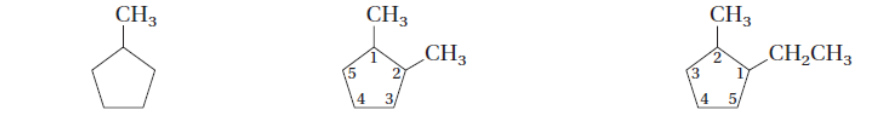


cyclopropane cyclobutane cyclopentane cyclohexane

If only one substituent is present, no number is needed to locate it.

If there are several substituents, numbers are required.

With different substituents, the one with highest alphabetic priority is located at carbon 1.



methylcyclopentane (*not* 1-methylcyclopentane)

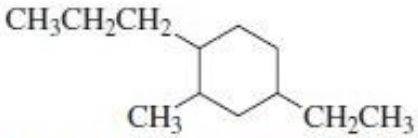
1,2-dimethylcyclopentane (*not* 1,5-dimethylcyclopentane)

1-ethyl-2-methylcyclopentane (*not* 2-ethyl-1-methylcyclopentane)

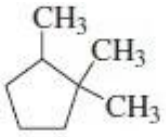
Nomenclature of Cycloalkanes

Nomenclature of Cycloalkanes and Cycloalkenes

- If there are more than two substituents on the ring, they are cited in alphabetical order.
- The substituent given the number 1 position is the one that results in a second substituent getting as low a number as possible.
- If two substituents have the same low number, the ring is numbered in the direction that gives the third substituent the lowest possible number.
- **Examples,**



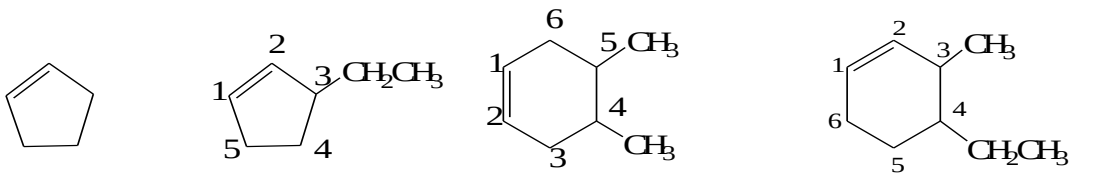
4-ethyl-2-methyl-1-propylcyclohexane
not
1-ethyl-3-methyl-4-propylcyclohexane
because 2 < 3
not
5-ethyl-1-methyl-2-propylcyclohexane
because 4 < 5



1,1,2-trimethylcyclopentane
not
1,2,2-trimethylcyclopentane
because 1 < 2
not
1,1,5-trimethylcyclopentane
because 2 < 5

Nomenclature of Cycloalkenes

- We start numbering the ring with the carbons of the double bond.
- A number is not needed to denote the position of the functional group, because the ring is always numbered so that the double bond is between carbons 1 and 2.
- Put the lowest substituent number into the name not in the direction that gives the lowest sum of the substituent numbers.



Cyclopentene

3-Ethylcyclopentene

4,5-Dimethylcyclohexene

4-Ethyl-3-methylcyclohexene

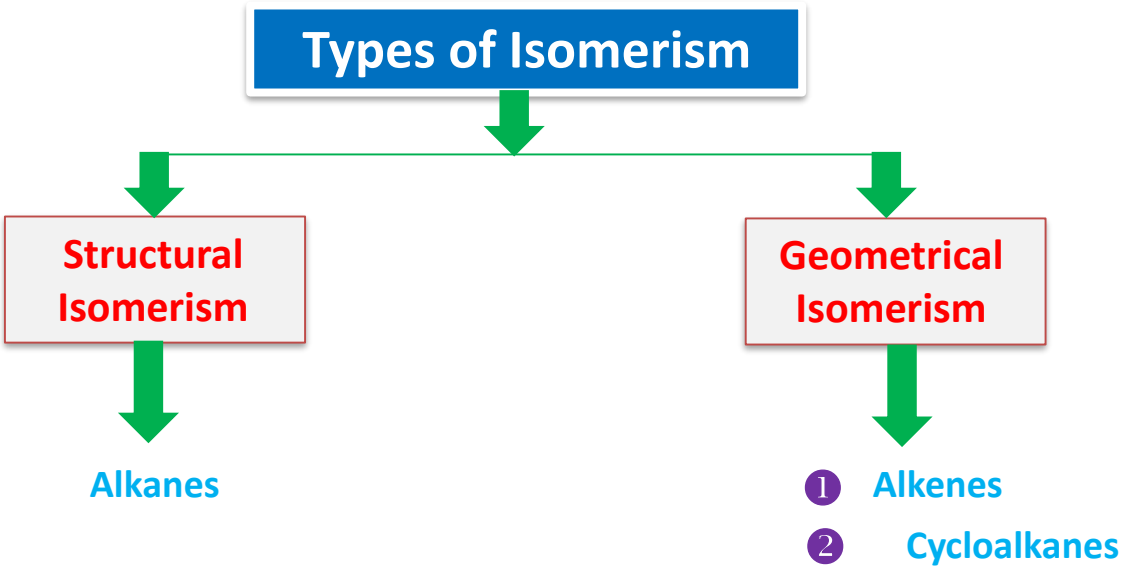
2-Cyclopentene

5-Ethylcyclopentene

Isomerism

Isomers are different compounds with identical molecular formulas.

The phenomenon is called ***isomerism***.

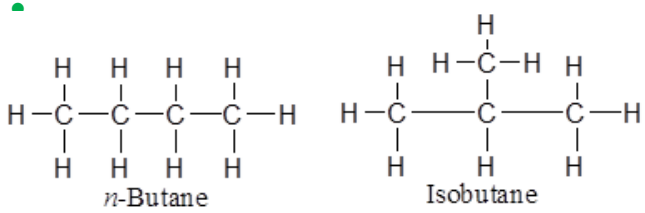


Structural Isomerism in Alkanes Isomerism

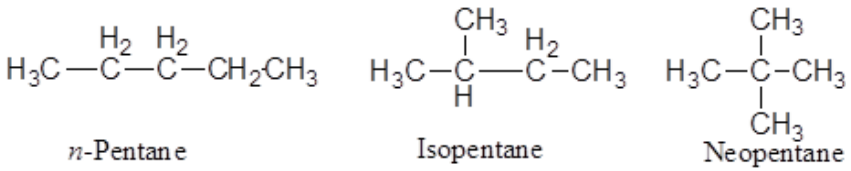
Structural or **constitutional isomers** are isomers which differ in the sequence of atoms bonded to each other.

Examples:

- **Butanes, C_4H_{10}**



- **Pentanes, C_5H_{12}**

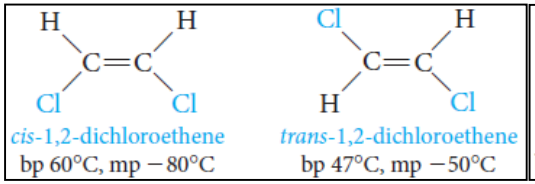


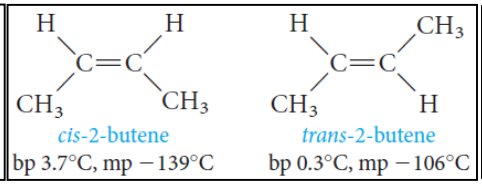
Geometric Isomerism in Alkenes Isomerism

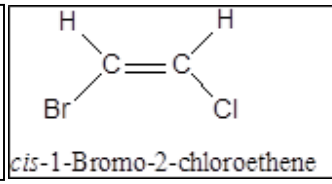
In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.

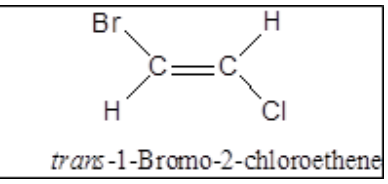
Geometric isomers

A) when W differs from X and Y from Z, Alkenes exist as geometric isomers









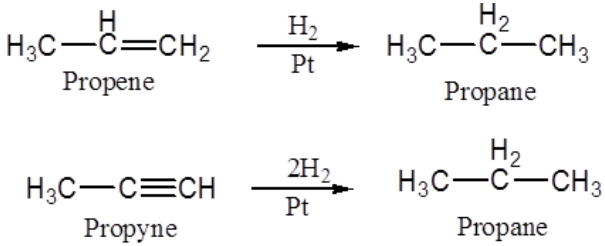
***cis* isomer;** when two similar groups are on the same side of the double bond.

***trans* isomer;** when two similar groups are on the opposite sides of the double bond.

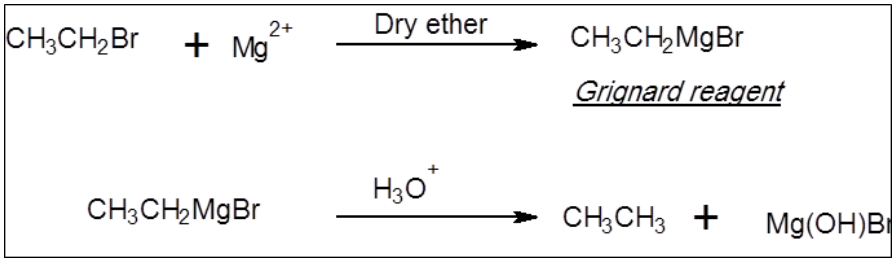
They have different physical properties and can be separated by fractional crystallization or distillation.

Preparation of Alkanes

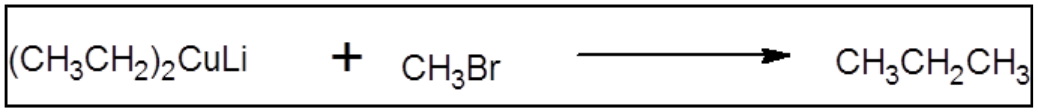
1. Hydrogenation of unsaturated hydrocarbon:



2. Hydrolysis of Grignard reagent

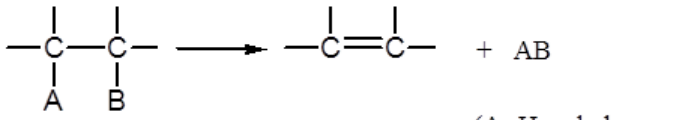


3. Reduction of Alkyl halides By lithium dialkyl cuprate



Preparation of Unsaturated hydrocarbons

Unsaturated hydrocarbons are prepared by ***Elimination*** of an atom or group of atoms from adjacent carbons to form *carbon-carbon double or triple bond*.



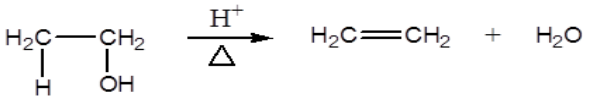
(A=H or halogen;
B=OH or halogen)

Preparation of Unsaturated Hydrocarbons

Preparation of Alkenes

1) Dehydration of Alcohols

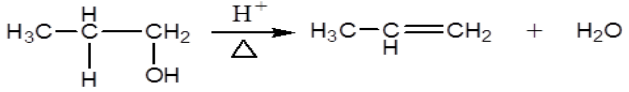
- *When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.*



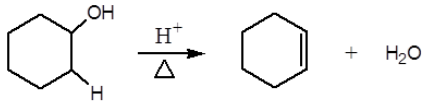
IUPAC name: Ethanol — Ethene
Common name: Ethyl alcohol — Ethylene

- *The acid catalysts most commonly used are mineral acids as **sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.***

- Removal of OH group and a proton from two adjacent carbon atoms using mineral acids.



IUPAC name: 1-Propanol — Propene
Common name: *n*-Propyl alcohol — Propylene



IUPAC name: Cyclohexanol — Cyclohexene
Common name: Cyclohexyl alcohol

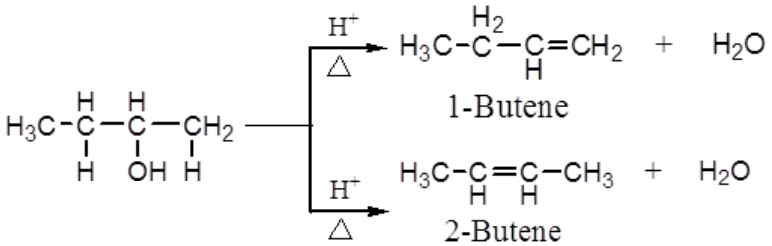
Preparation of Unsaturated Hydrocarbons

Preparation of Alkenes

Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: *the dehydration of 2-butanol.*



2-butene is the major (with two alkyl substituents attached to C=C)

Saytzeff's Rule applies

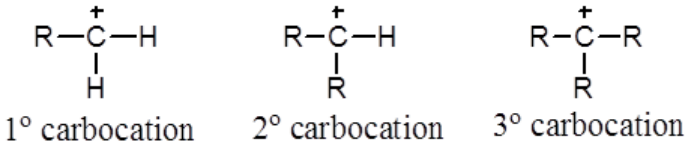
In every instance in which more than one Alkene can be formed

The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

Preparation of Unsaturated Hydrocarbons

Preparation of Alkenes

Classes of Carbocations ○



according to the number of carbon atoms attached to the positively charged carbon.

The ease of formation and the stabilities of carbocations follow the order

$3^{\circ} > 2^{\circ} > 1^{\circ}$

Ease of formation and stabilities of carbocations

Generally ○

1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeffs rule.
3. The reaction proceeds *via* a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order $3^{\circ} > 2^{\circ} > 1^{\circ}$.

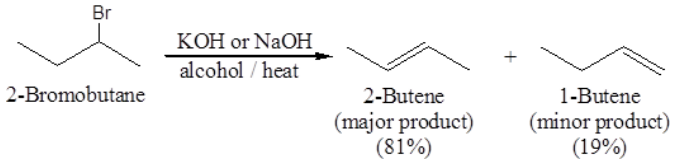
Preparation of Unsaturated Hydrocarbons

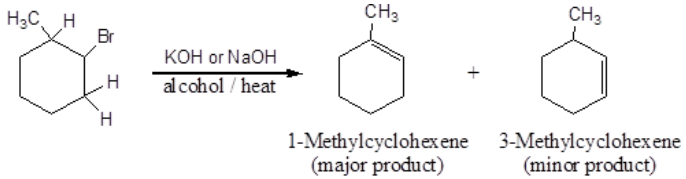
Preparation of Alkenes

2) Dehydrohalogenation of Alkyl Halides

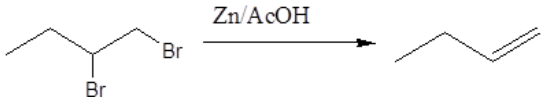
Alkenes can also be prepared under alkaline conditions. ○

heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.





3) Dehalogenation of Vicinal Dibromides

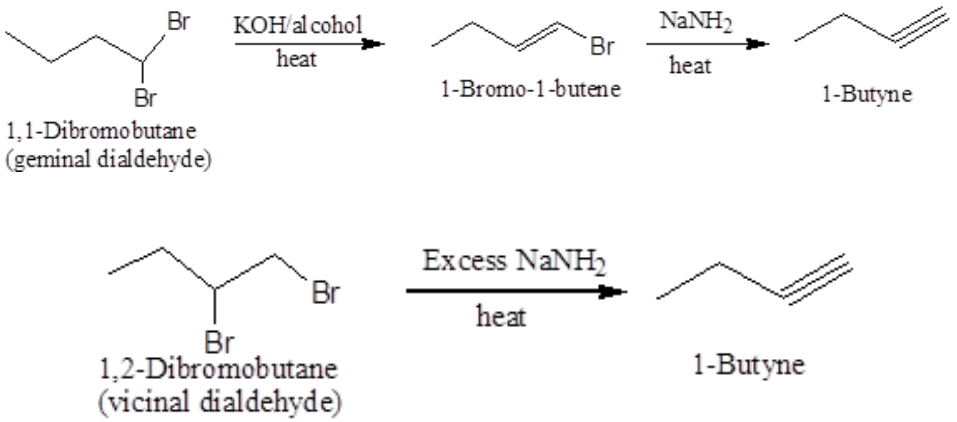


Preparation of Unsaturated Hydrocarbons

Preparation of Alkynes

1) Dehydrohalogenation of Alkyl dihalides

Alkynes can be prepared under alkaline conditions via deydrohalogenation of alkyl dihalides.

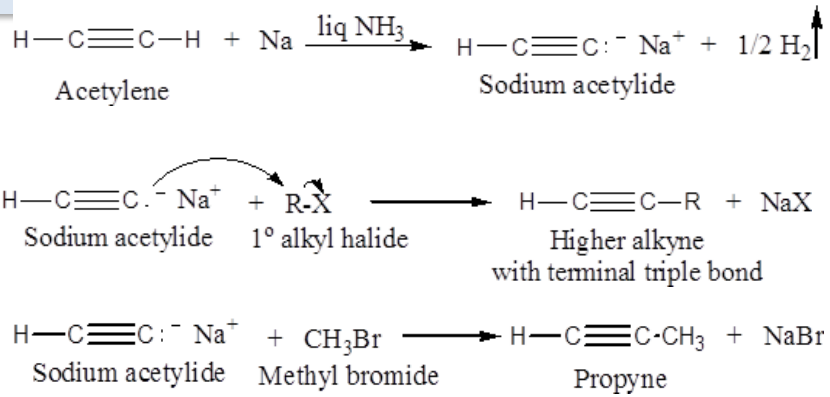


Preparation of Unsaturated Hydrocarbons

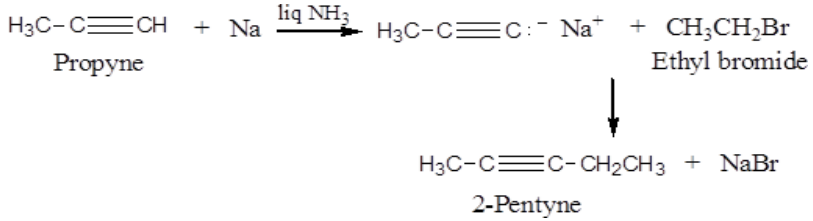
Preparation of Alkynes

2) Reaction of Sodium Acetylide with Primary Alkyl Halides

Acetylene ○



Monosubstituted Acetylenes ○



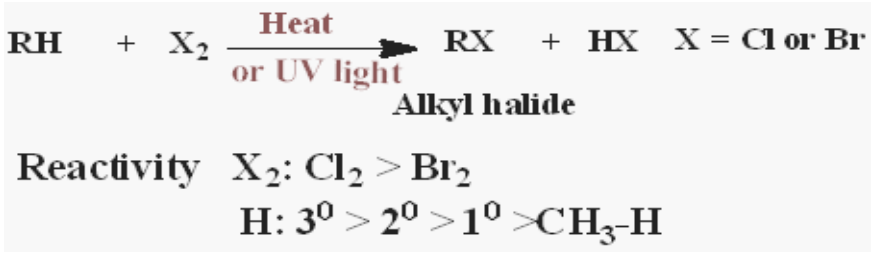
Reactions of Saturated Hydrocarbons

Reactions of Alkanes

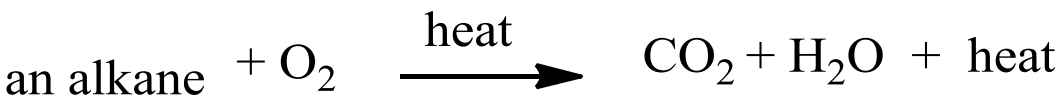
Saturated hydrocarbons undergo very few reactions, so they are called Paraffinic hydrocarbons.
(Latin *parum*, little; *affinis*, affinity)

Halogenation

The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed



Combustion



Reactions of Saturated Hydrocarbons

Reactions of Alkanes

A) Halogenation

Substitution reaction of alkanes, ○

i.e. replacement of hydrogen by halogen,
usually chlorine or bromine, giving alkyl chloride or alkyl bromide.

Flourine reacts explosively with alkanes ○

It is unsuitable reagent for the preparation of the alkyl flourides.

Iodine is too unreactive ○

It is not used in the halogentaion of alkanes.

Halogenation of alkanes take place at ○

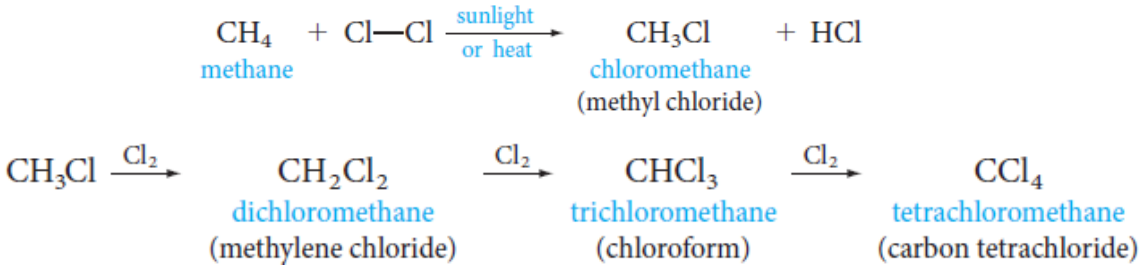
high temperatures or under the influence of ultraviolet light

Reactions of Saturated Hydrocarbons

Reactions of Alkanes

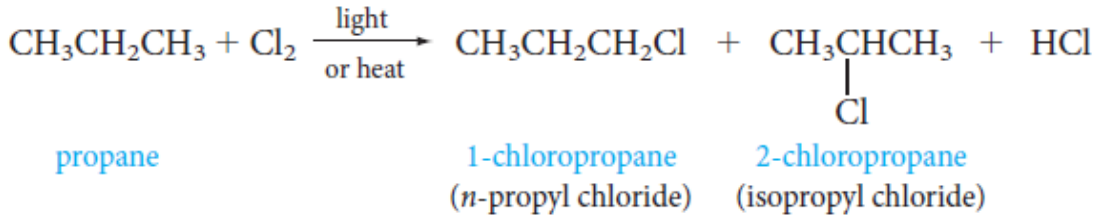
A) Halogenation

Chlorination of an alkane usually gives a mixture of products ○



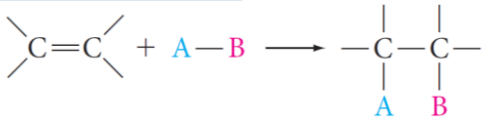
With longer chain alkanes, mixtures of products may be obtained even at the first step. ○

For example, with propane,



Reactions of Unsaturated Hydrocarbons

(1) Electrophilic Addition Reactions



Addition of Symmetric and Unsymmetric Reagents to symmetric Alkenes.

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule.

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

(2) Oxidation Reactions

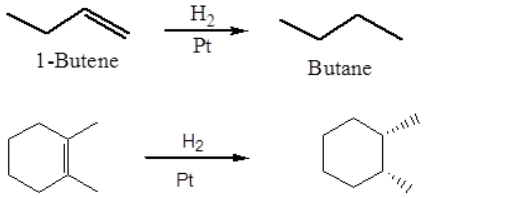
1. Ozonolysis
2. Oxidation Using $KMnO_4$

Reactions of Unsaturated Hydrocarbons

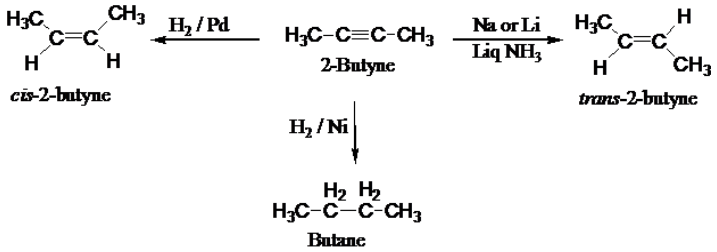
Electrophilic Addition Reactions

1. Addition of Hydrogen: Hydrogenation

- *Addition of a mole of hydrogen to carbon-carbon double bond of **Alkenes** in the presence of suitable catalysts to give an Alkane.*



- With an ordinary nickel or platinum catalyst, ***Alkynes*** are hydrogenated all the way to alkanes.

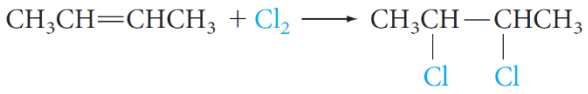


Reactions of Unsaturated Hydrocarbons

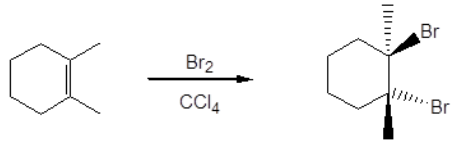
Electrophilic Addition Reactions

2. Addition of Halogen: Halogenation

*When an **alkene** is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons)*

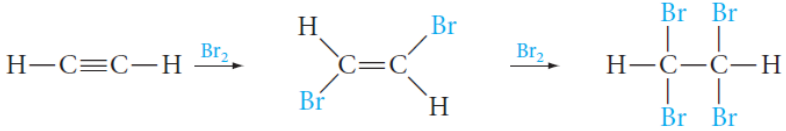


2-butene — 2,3-dichlorobutane



1,2-Dimethylcyclohexene — *trans*-1,2-Dibromocyclohexane

Bromine adds to **alkynes** as follows; In the first step, the addition occurs mainly *trans.*



ethyne — *trans*-1,2-dibromoethene — 1,1,2,2-tetrabromoethane

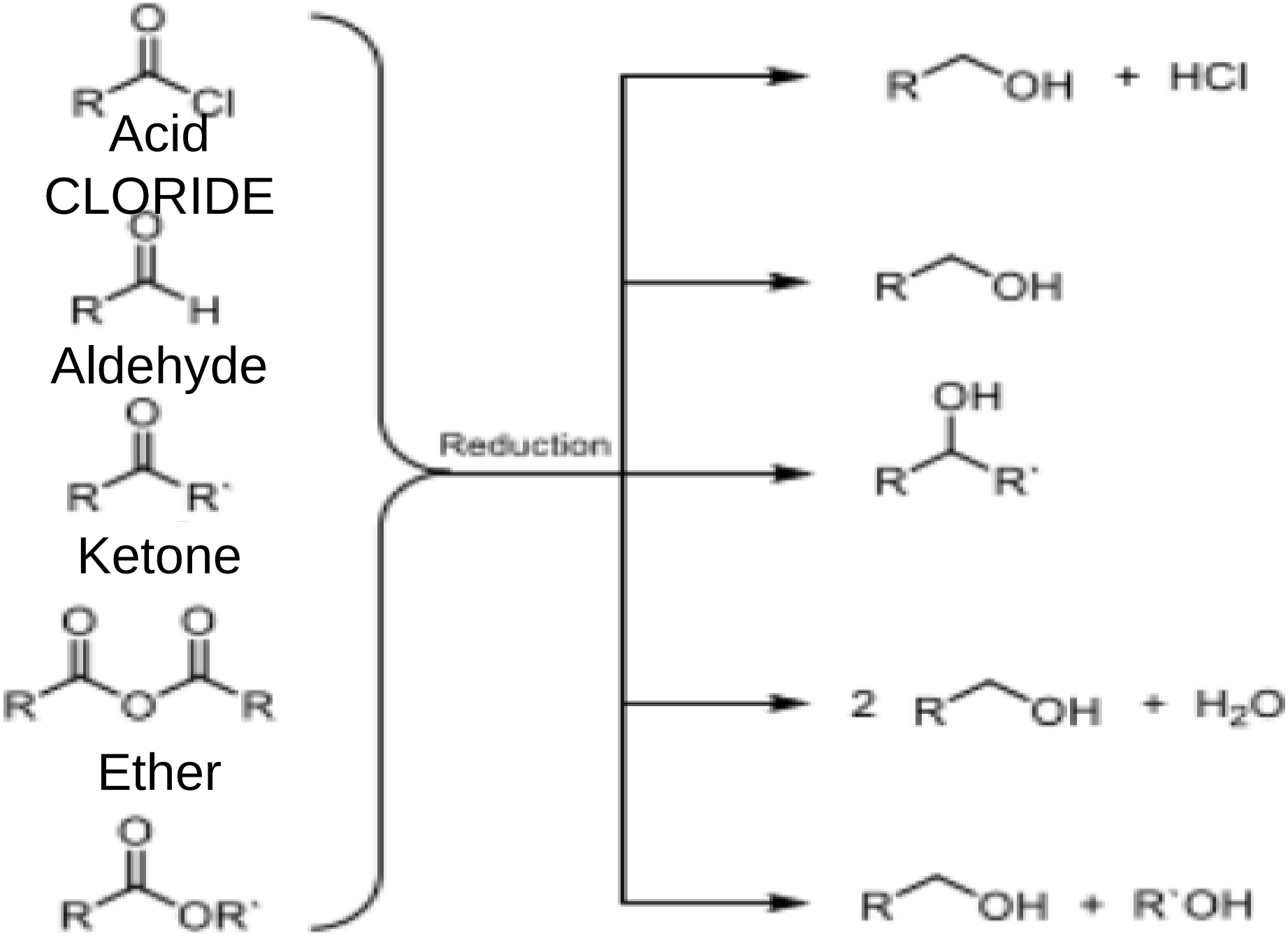
Alcohols

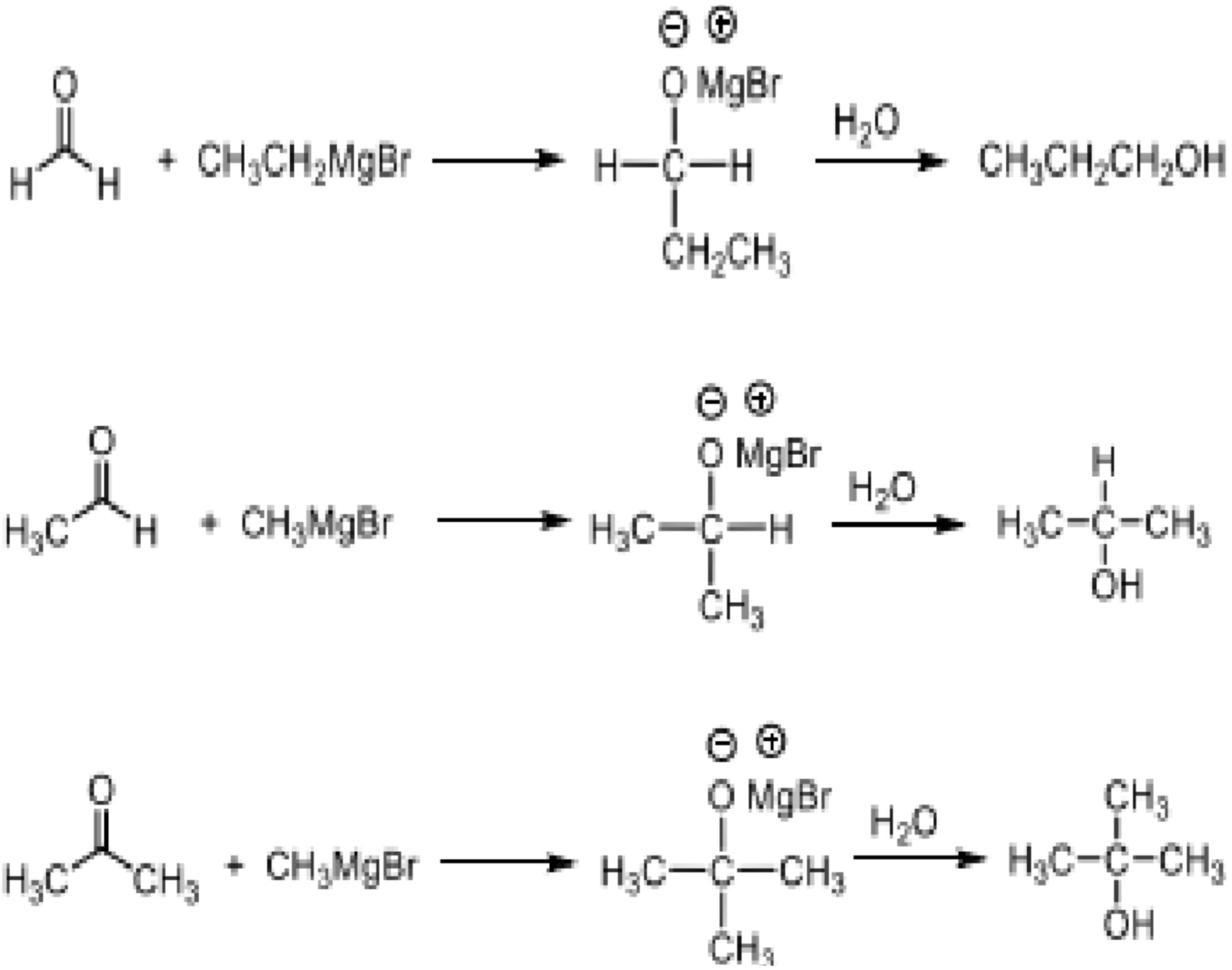
Methods of preparation:

$CH_2 = CH_2 + H_2SO_4 \longrightarrow CH_3 - CH_2 - O - SO_3H$

$\downarrow$ HOH

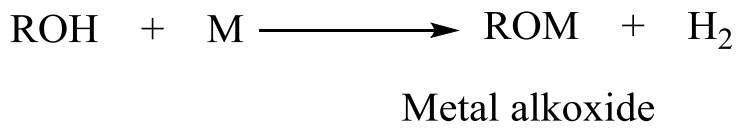
$H_2SO_4 + CH_3 - CH_2 - OH$

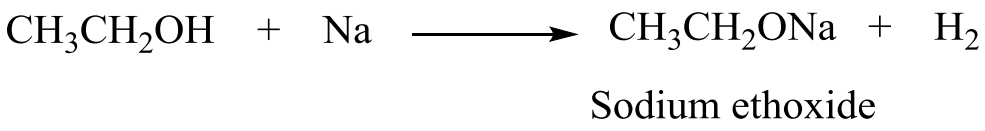

Acid
CLORIDE
Aldehyde
Ketone
Ether
Ester
Reduction
+ HCl
2
+ H_2O
+


+ CH3CH2MgBr
O MgBr
H2O
CH3CH2CH2OH
+ CH3MgBr
O MgBr
H2O
+ CH3MgBr
O MgBr
H2O

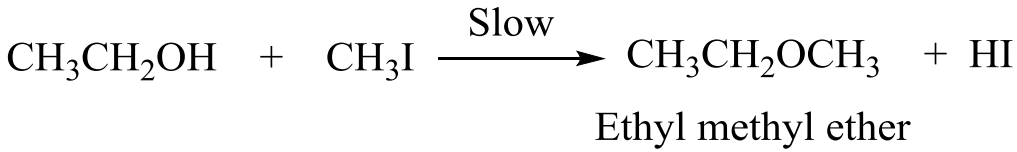
Reactions

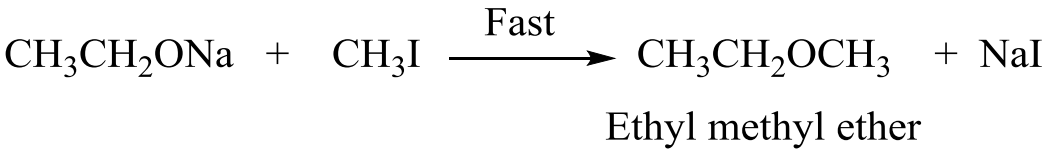
1- Reaction with metals (salt formation)



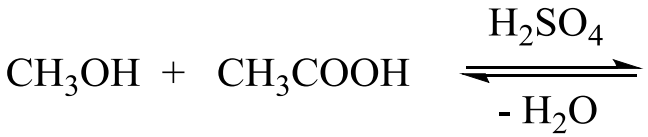


2- Ether formation

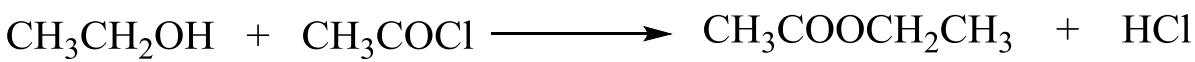




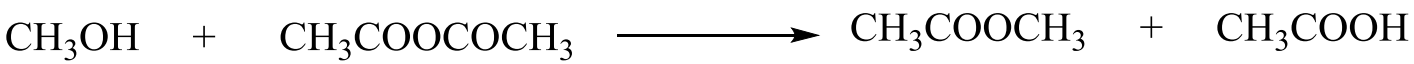
3- Ester formation



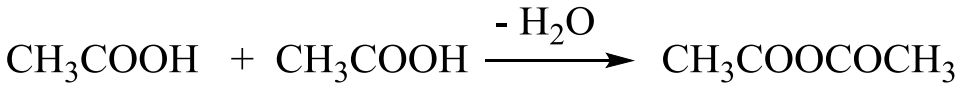
Methyl acetate



Ethyl acetate



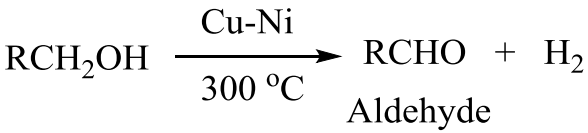
Acetic anhydride

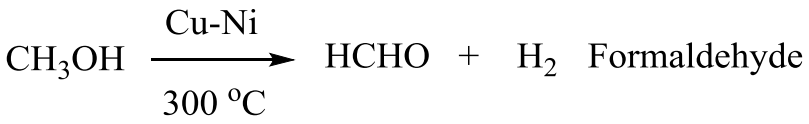


Acetic anhydride

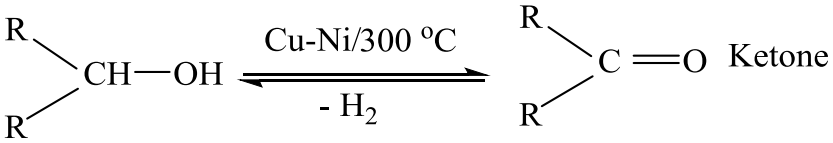
4- Dehydrogenation

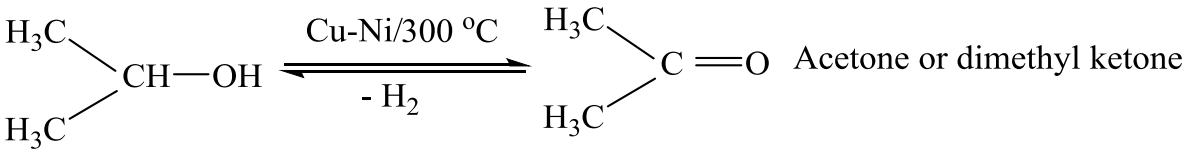
a- Primary alcohols





b- Secondary alcohols

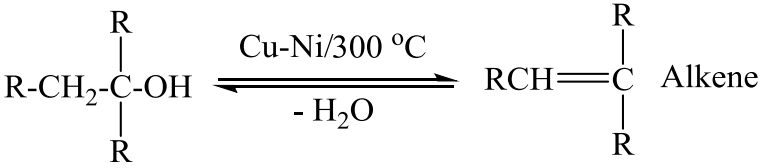


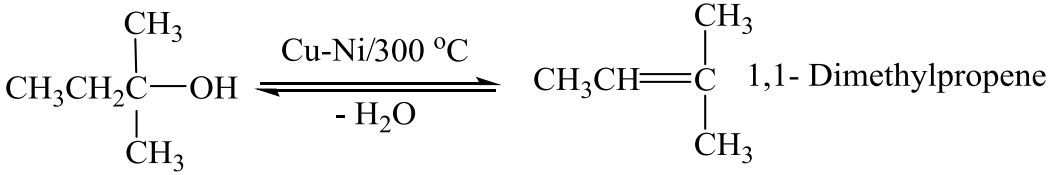


2- Propanol or isoprpanol

c- Tertiary alcohols

(Dehydration)





Tertiary pentanol

Reactions

$$CH_3\text{-}CH_2\text{-}OH + HCl \longrightarrow CH_3\text{-}CH_2\text{-}Cl + H_2O$$

Iodoform Reaction

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow[Ox]{I_2} CH_3\text{-}CHO \xrightarrow{3I_2} Cl_3\text{-}CHO + 3HI$$

$$Cl_3\text{-}CHO \xrightarrow{NaOH} CHI3 + HCOONa$$

Ethers

1- Synthesis

From alkyl halides

$$RX + RONa \longrightarrow ROR \text{ (ethers)} + NaX$$

$$CH_3Br + CH_3ONa \longrightarrow CH_3OCH_3 + NaBr$$

Dimethyl ether

$$CH_3Br + C_2H_5ONa \longrightarrow CH_3OC_2H_5 + NaBr$$

Ethyl methyl ether

2- Reactions

1- Cleavage by halogen acids

$$ROR + HX\ (conc.) \xrightarrow{\text{high temp.}} RX + ROH$$

$$(CH_3CH_2)_2O + HI\ (conc.) \xrightarrow{\text{high temp.}} CH_3CH_2I + CH_3CH_2OH$$

$$(CH_3CH_2)_2O + 2HI\ (conc.) \xrightarrow{\text{high temp.}} 2CH_3CH_2I + H_2O$$

2- Reaction with phosphorus pentasulphide

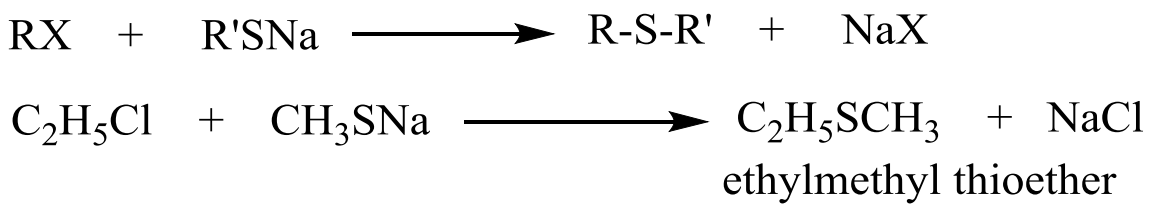
$$5C_2H_5OC_2H_5 + P_2S_5 \xrightarrow{\Delta} 5C_2H_5SC_2H_5 + P_2O_5$$

(diethylthioether)

Thioethers

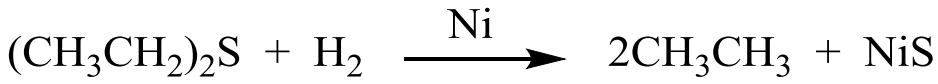
Synthesis

From alkyl halide and sodium mercaptide

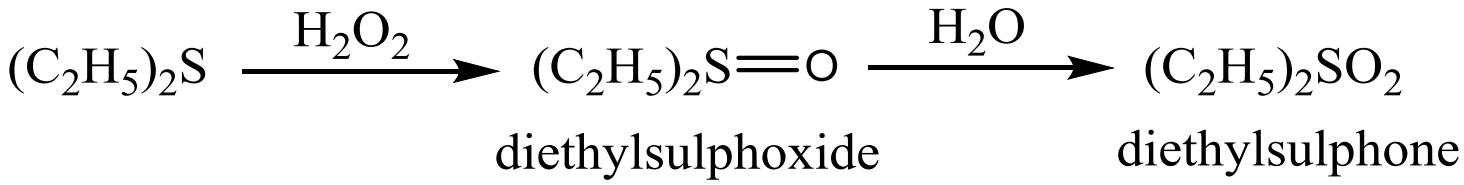


Reactions

1- Desulphurization



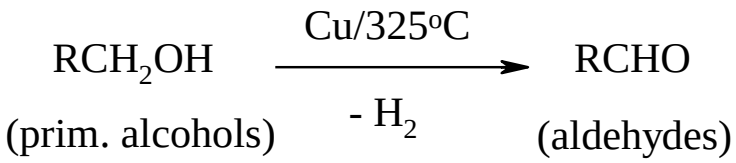
2- Oxidation



Aldehydes

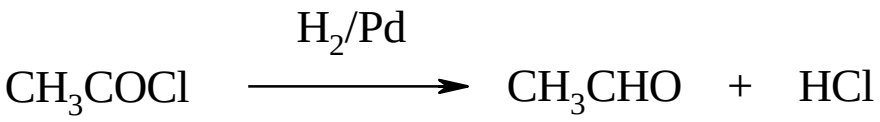
Synthesis

1- Via dehydrogenation of alcohols



2- From acid derivatives

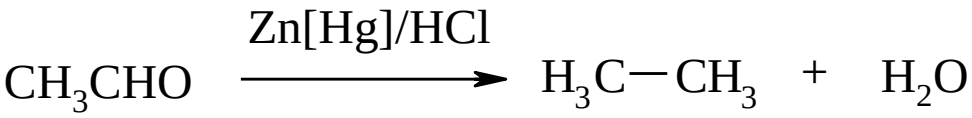
From acetyl chlorides



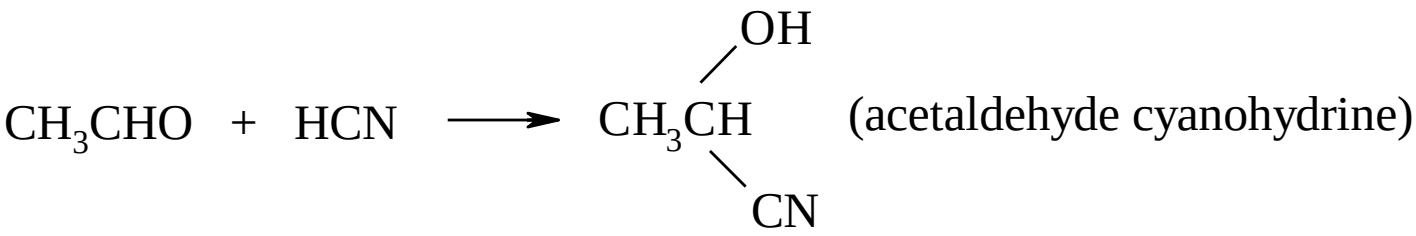
Reactions

1- Addition of hydrogen

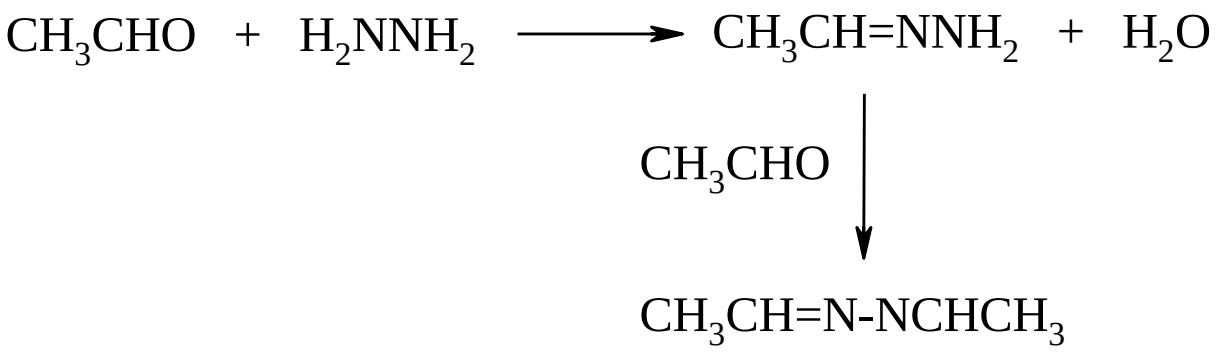
Reduction to alkanes:- *via* Clemensen reduction



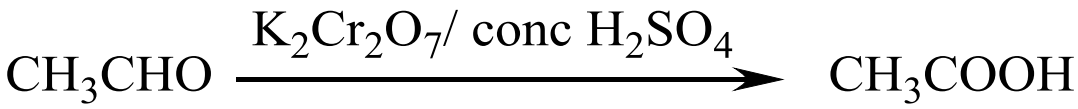
2- Addition of hydrogen cyanide



3- Addition of hydrazine (H_2N-NH_2)



4- Oxidation

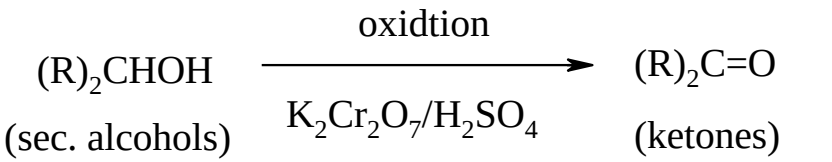


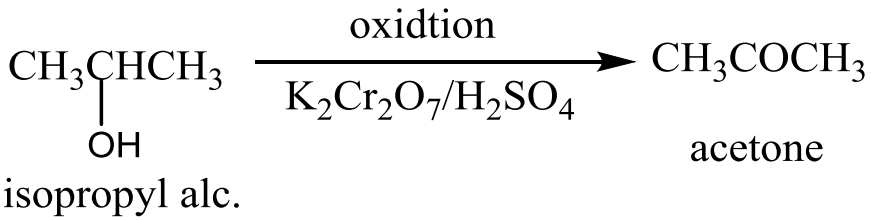
Ketones

Synthesis

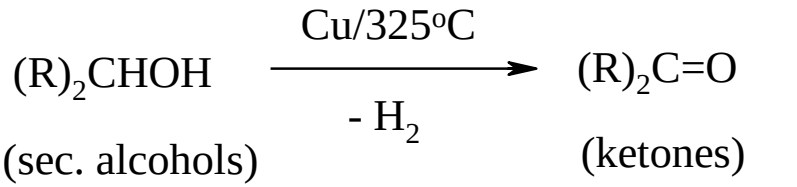
1- From alcohols

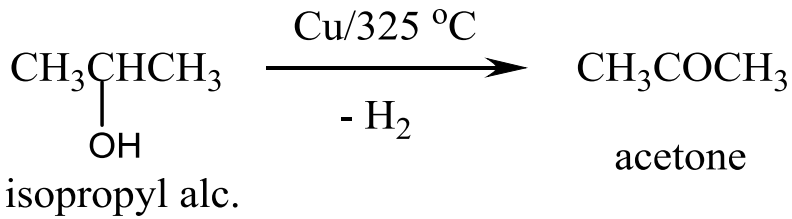
a- Via oxidation





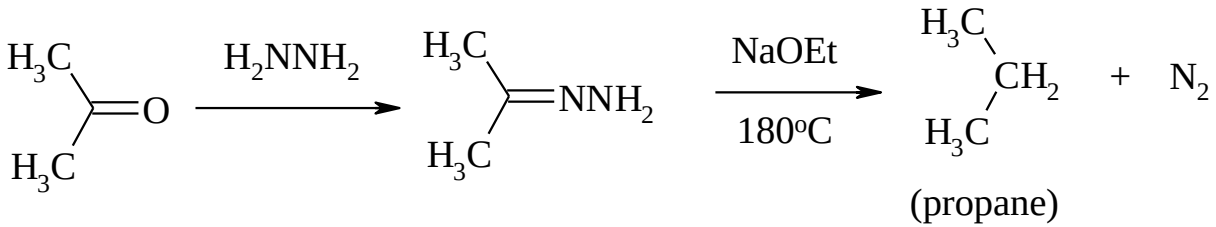
b- Via dehydrogenation





Reactions

1- Reduction to alkanes



(propane)

2- Addition of ammonia derivatives

a- With hydroxyl amine

$$(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C{=}NOH \quad \text{(acetoxime)}$$

b- With hydrazine

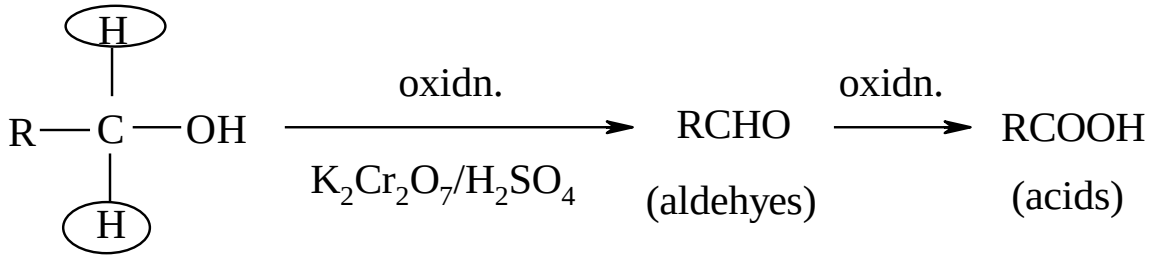
$$(CH_3)_2CO + H_2NNH_2 \longrightarrow (CH_3)_2C{=}NNH_2 \xrightarrow{(CH_3)_2CO} (CH_3)_2C{=}NNC{=}(CH_3)_2$$

(hydrazone) (azine)

Carboxylic acids

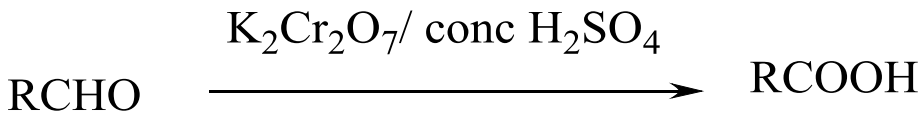
1- Synthesis

1- From primary alcohols:- (via oxidation)



(prim. alcohols)

2- From aldehydes :- (via oxidation)



3- Hydrolysis of acid derivatives:-

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

(acetyl chloride)

2- Reactions

1- Salt formation:-

Acids react with metals, metal oxides, hydroxides, carbonates to form salts of carboxylic acids.

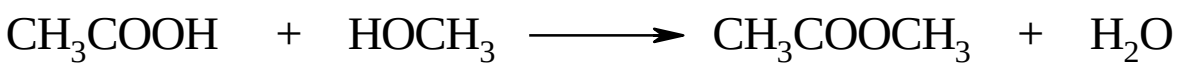
$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2\uparrow$$

$$2CH_3COOH + CuO \longrightarrow (CH_3COO)_2Cu + H_2O$$

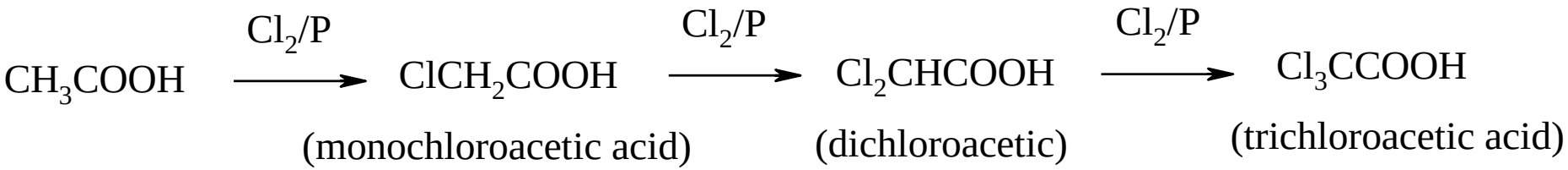
$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

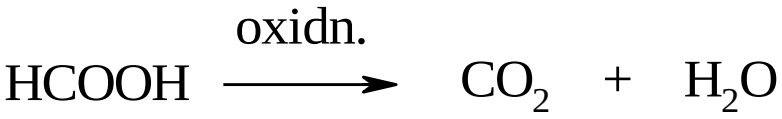
2- Esterification:-



3- Halogenation:-



4- Oxidation:- (only formic acid)



Reactions on carboxylic acid salts

1- Silver salts:-

$$RX + R'COOAg \longrightarrow R'COOR \text{ (esters)} + AgX$$

2- Heating of ammonium salts:-

$$RCOONH_4 \xrightarrow{\triangle} RCONH_2 + H_2O$$

(amide)

Esters

1- Synthesis

1- From acids:-

$$CH_3CH_2OH + CH_3COOH \underset{}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

(ethyl acetate)

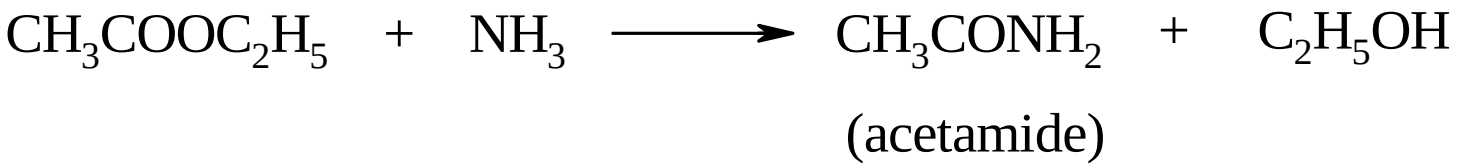
2- From acylhalides:-

$$ROH + R'COCl \longrightarrow R'COOR + HCl$$

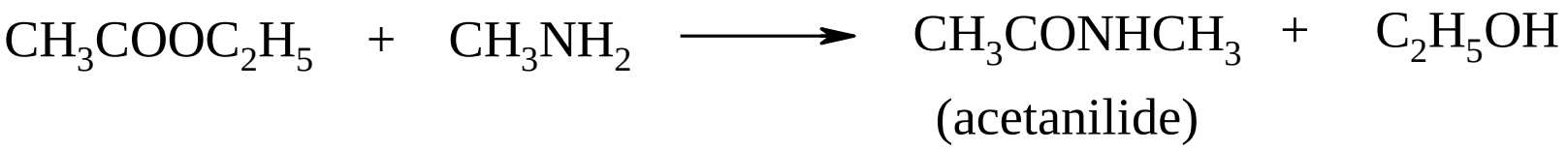
(acid chloride) (estrers)

2- Reactions

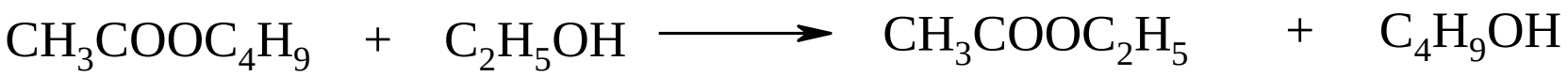
1- Ammonolysis:-



2- Aminolysis:-



3- Transesterfication:- (with lower alcohols)



Acid halides

1- Synthesis

From acids:-

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

2- Reactions

1- Hydrolysis to acids:-

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

(acetyl chloride)

2- Alcoholysis to esters:-

$$ROH + \underset{\text{(acid chloride)}}{R'COCl} \longrightarrow \underset{\text{(estrers)}}{R'COOR} + HCl$$

Anhydrides

1- Synthesis

From acyl halides:-

$$RCOCl + RCOONa \longrightarrow (RCO)_2O + NaCl$$

(anhydrides)

2- Reactions

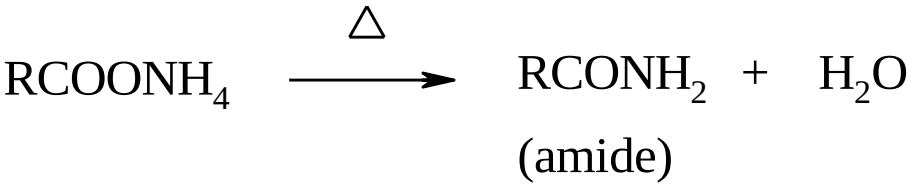
Hydrolysis to acids:-

$$RCOOCOR + H_2O \xrightarrow{\triangle} 2RCOOH$$

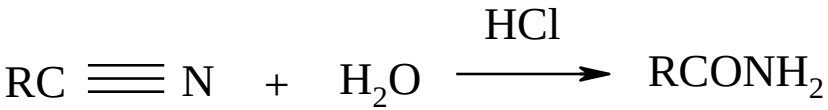
Amides

Synthesis

1- From ammonium salts. (via pyrolysis)



2- Partial hydrolysis of nitriles.



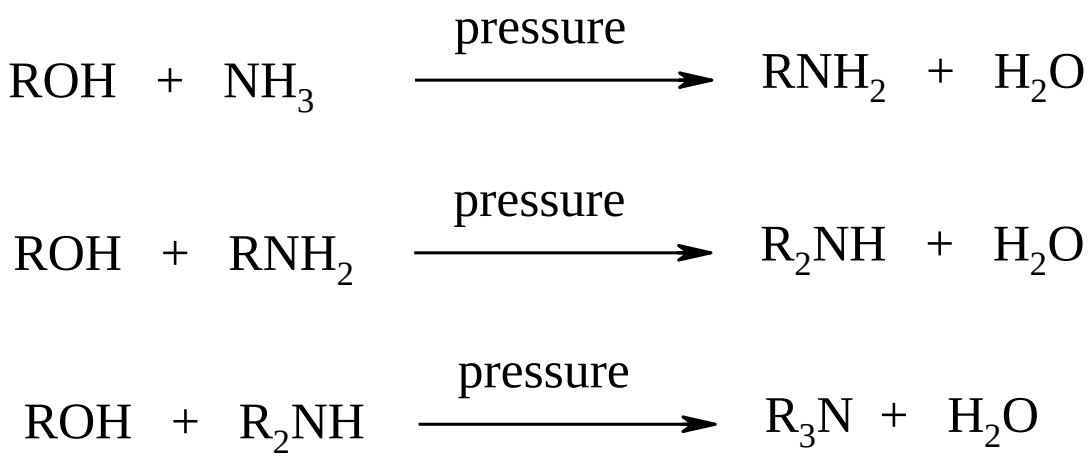
Reactions

1- Dehydration to nitrils

Amines

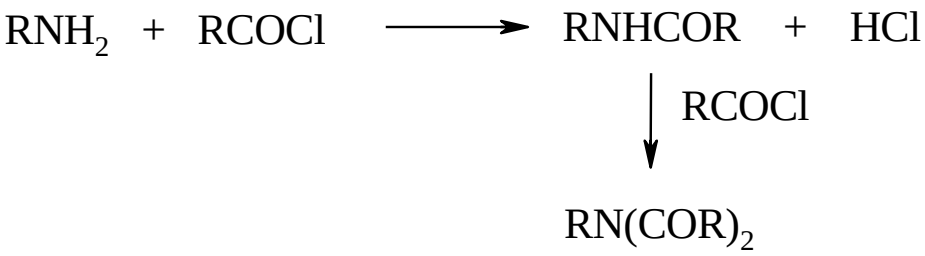
Synthesis

1- Synthesis of primary, secondary and tertiary amines from alcohols (mixture)



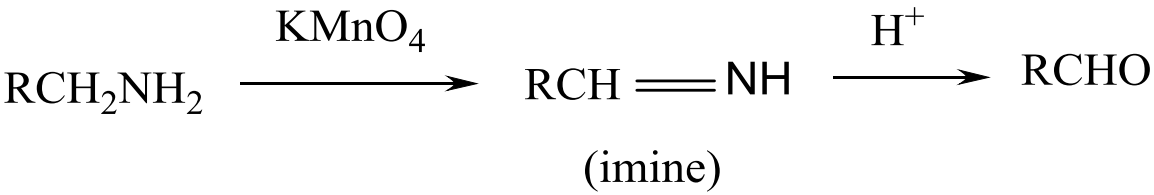
2- Reactions

1- Acylation

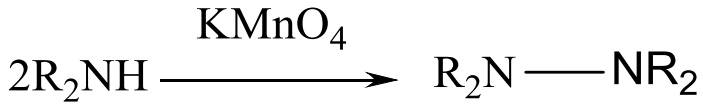


2- Oxidation

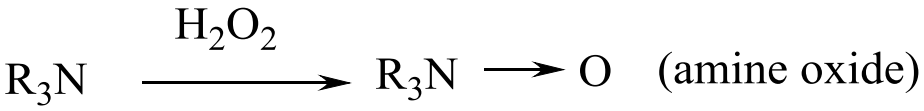
1- Primary amines:-



2- Secondary amines:-



3- Tertiary amines:-

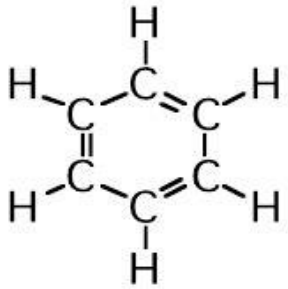


Aromatic Compounds

Aromatic compound: A hydrocarbon that contains one or more benzene-like rings.

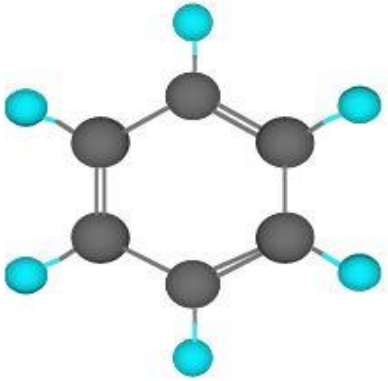
Arene: A term used to describe aromatic compounds.

- Ar-: A symbol for an aromatic group derived by removing an -H from an arene.
- Kekulé structure for benzene (1872).



A Kekulé structure showing all atoms

A Kekulé structure as a line-angle formula



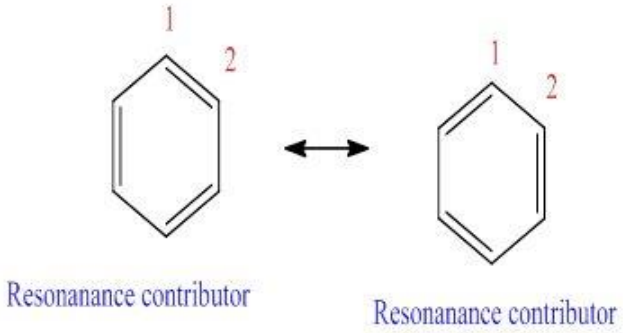
Benzene

- General properties:
- Display aromaticity.
- The carbon-hydrogen ratio is high.
- They burn with a sooty yellow flame because of the high carbon-hydrogen ratio.
- They undergo electrophilic subsitution and nucleophilic substitution
- Give both pleasant and unpleasant odors

Benzene

Resonance structure for benzene (1930s)

- The theory of resonance developed by Linus Pauling provided the first adequate description of the structure of benzene.
- According to the theory of resonance, certain molecules and ions are best described by writing two or more Lewis structures. The real molecule or ion is a resonance hybrid of these structures.
- Each individual Lewis structure is called a contributing structure.
- We show that the real molecule is a resonance hybrid of the two or more Lewis structures by using a double-headed arrow between them.

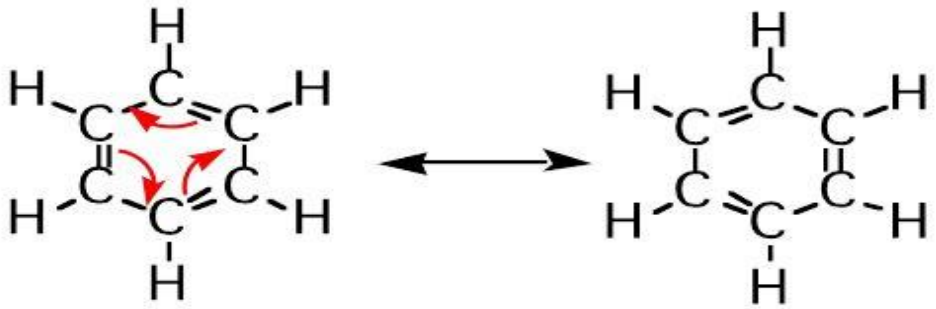


Resonance hybrid
The real structure

electron delocation

Benzene

- Here are two contributing structures for benzene;

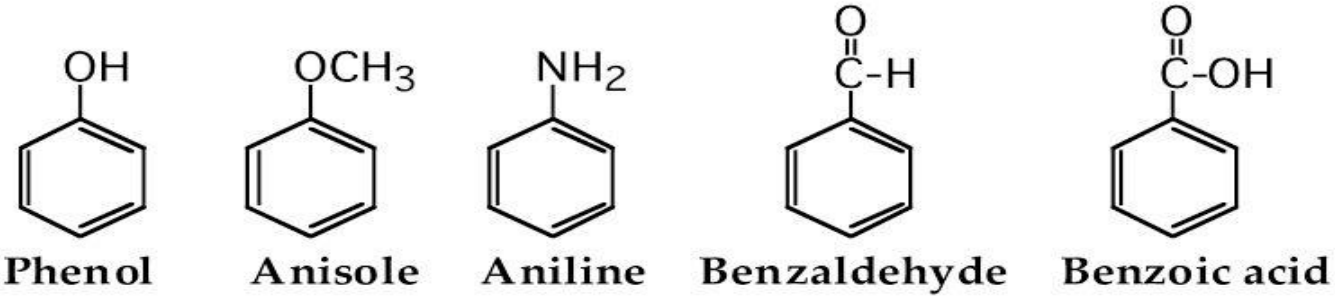


- The resonance hybrid has some of the characteristics of each Lewis contributing structure.
- The length of a carbon-carbon bond in benzene, for example, is midway between that of a carbon-carbon single bond and a double bond.

Benzene and its derivatives

Nomenclature

- The common names for these monosubstituted benzenes are also retained

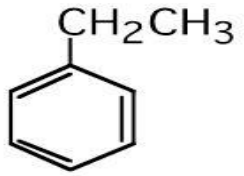


Phenol **Anisole** **Aniline** **Benzaldehyde** **Benzoic acid**

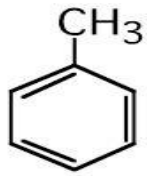
Benzene and its derivatives

Nomenclature

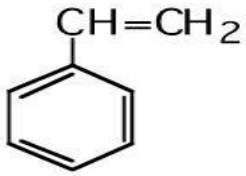
- Monosubstituted alkylbenzenes are named as derivatives of benzene; for example, ethylbenzene.
- The IUPAC system retains certain common names for several of the simpler monosubstituted alkylbenzenes.



Ethylbenzene



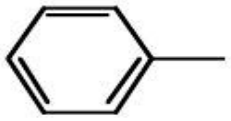
Toluene



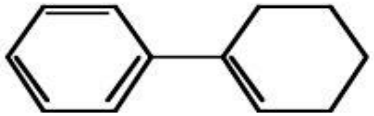
Styrene

Nomenclature

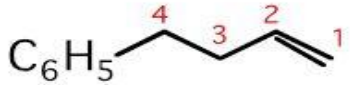
- Phenyl group (C_6H_5- or Ph-): The substituent group derived by removal of an H from benzene.



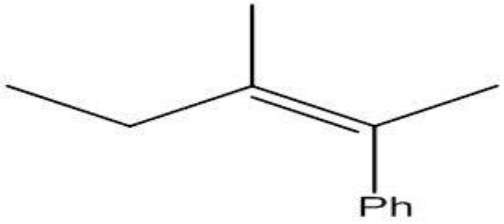
Phenyl group



1-Phenylcyclohexene



4-Phenyl-1-butene



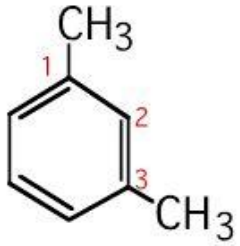
3-methyl-2-phenyl-2-pentene

Nomenclature

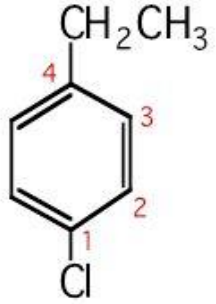
When two substituents occur on a benzene ring, three isomers are possible; they may be located by:

- numbering the atoms of the ring or
- using the locators **ortho (*o*)**, **meta (*m*)**, and **para (*p*).**

2-Bromobenzoic acid
(*o*-Bromobenzoic acid)



1,3-Dimethylbenzene
(*m*-Xylene)



1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)

Nomenclature

For three or more substituents:

- If one of the substituents imparts a special name, name the molecule as a derivative of that parent.
- If none of the substituents imparts a special name, number the substituents to give the smallest set of numbers, and list them in alphabetical order before the ending "benzene".

4-Chloro-2-nitrotoluene

2,4,6-Tribromophenol

2-Bromo-1-ethyl-4-nitrobenzene

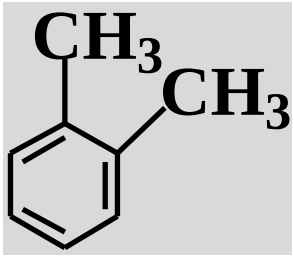
Examples

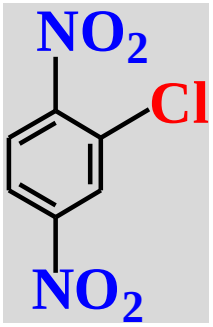
- Draw the structure of the following compounds

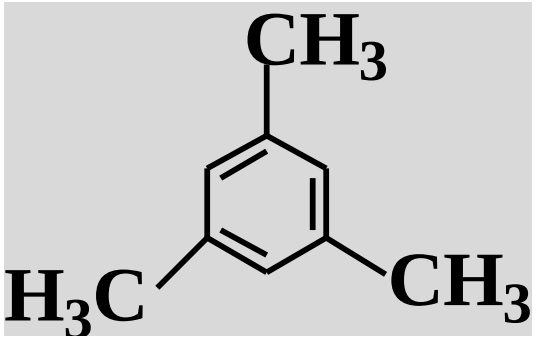
a. 2-phenyl-4-hexyne

b. m-ethylphenol

Name the following compounds



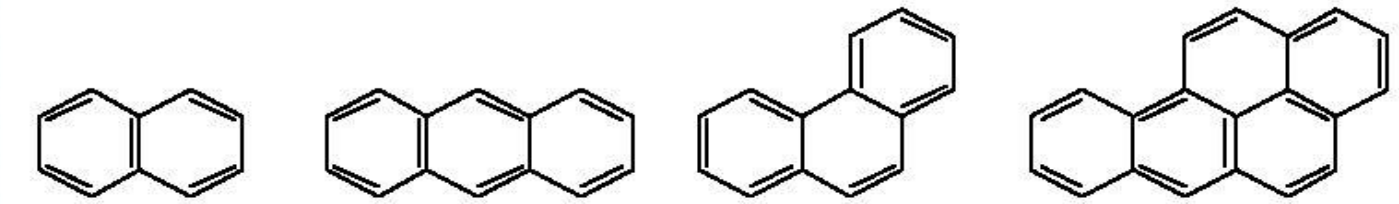




PAHs

Polynuclear aromatic hydrocarbon (PAH)

- A hydrocarbon that contains two or more benzene rings, with each pair of rings sharing two adjacent carbon atoms.



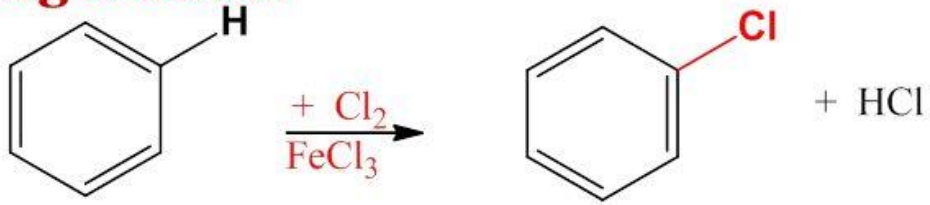
Naphthalene Anthracene Phenanthrene Benzo[a]pyrene

Reactions of Benzene

By far the most characteristic reaction of aromatic compounds is substitution at a ring carbon.

- This reaction is called **aromatic substitution**.
- Some groups that can be introduced directly on the ring are the halogens, the nitro ($-NO_2$) group, and the sulfonic acid ($-SO_3H$) group.

Halogenation:



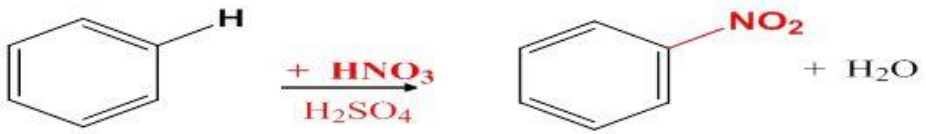
Benzene

Chlorobenzene

Hydrogen from the bezene is replaced by Cl

Reactions of Benzene

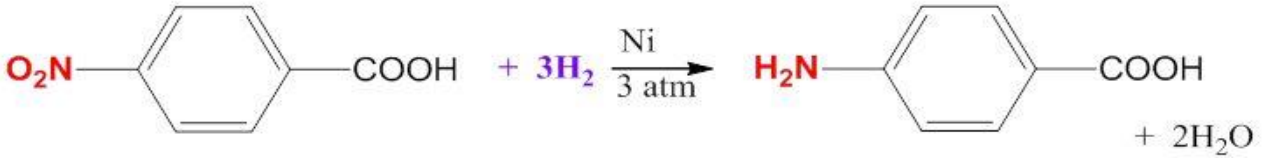
Nitration:



Benzene — Nitrobenzene

——NO_2 replaces one of the Hydrogens from the ring

- A value of nitroarenes is that the nitro group can be reduced to a primary amino group.



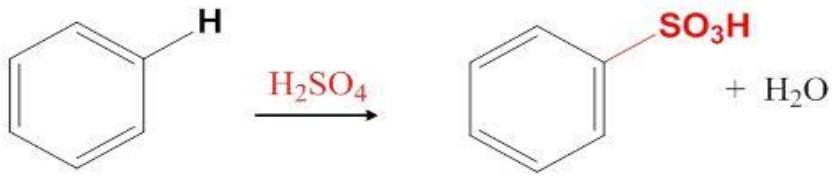
4-Nitrobenzoic acid (p-nitrobenzoic acid)

4-aminobenzoic acid (p-aminobenzoic acid)

——NO_2 is reduced to ——NH_2

Reactions of Benzene

Sulfonation:

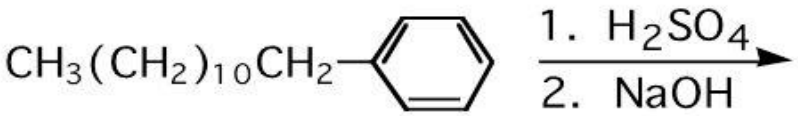


Benzene

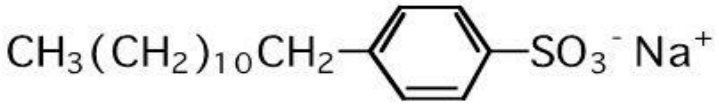
Benzenesulfonic acid

——SO_3H replaces one of the Hydrogens from the ring

- An application of sulfonation is in the preparation of synthetic detergents.



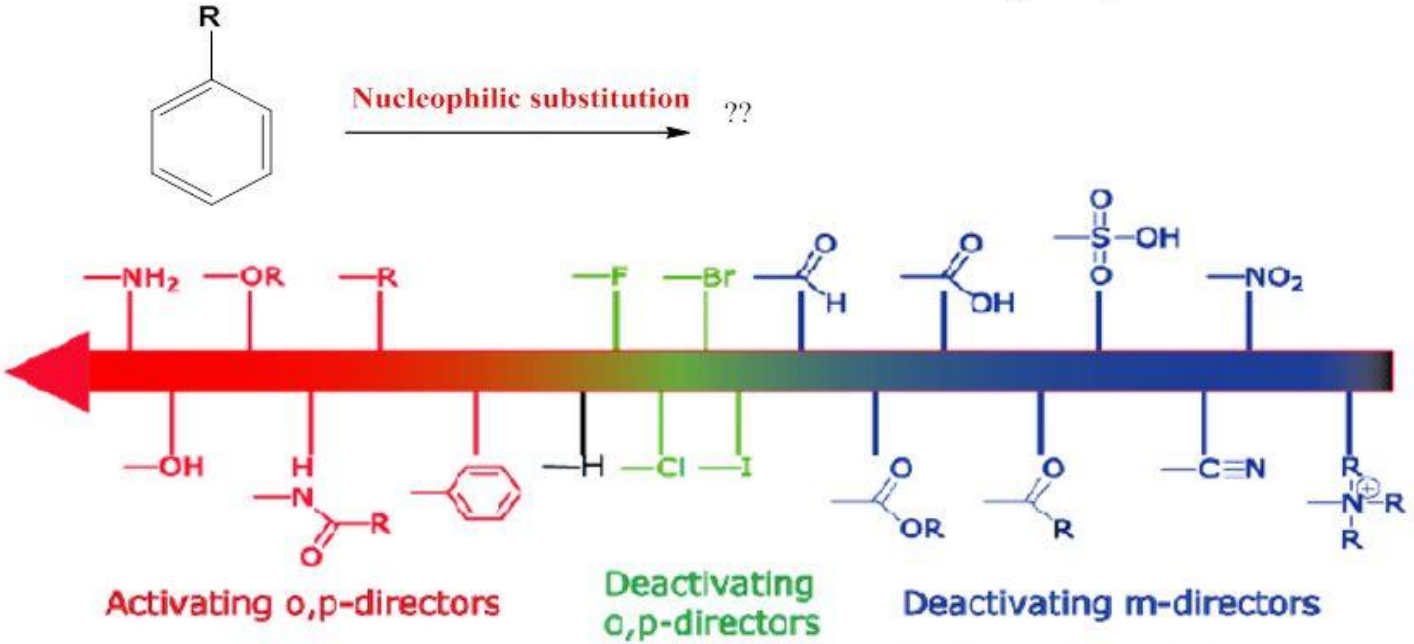
Dodecylbenzene



Sodium 4-dodecylbenzenesulfonate, SDS (an anionic detergent)

The effects of subsituents on Reactivity of a Benzene ring

What if benzene is a monosubsituted with one –R group?

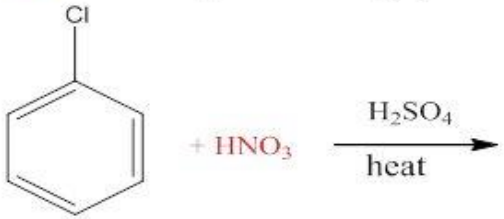


Make benzene more reactive toward substitution

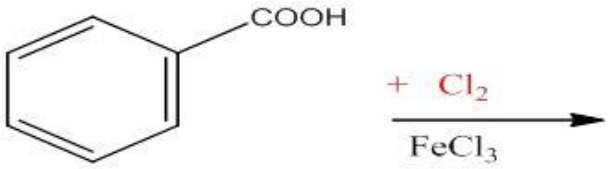
Make benzene less reactive toward substitution

Example

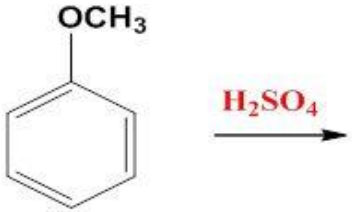
- What product(s) would result from the following compounds



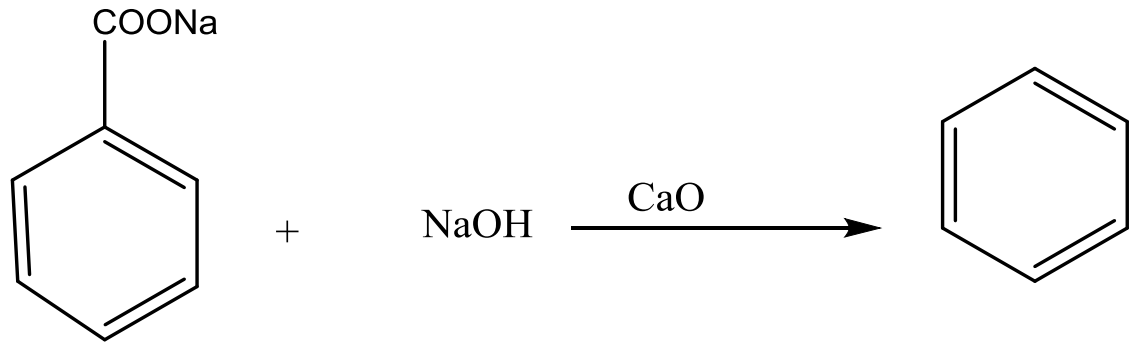
chlobenzene

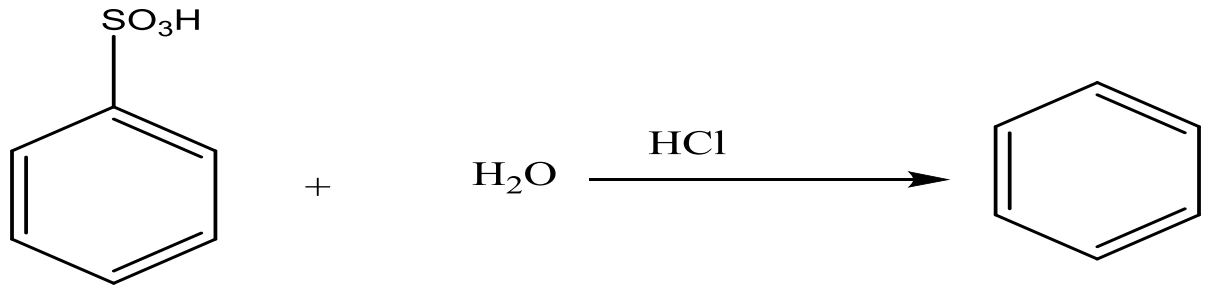


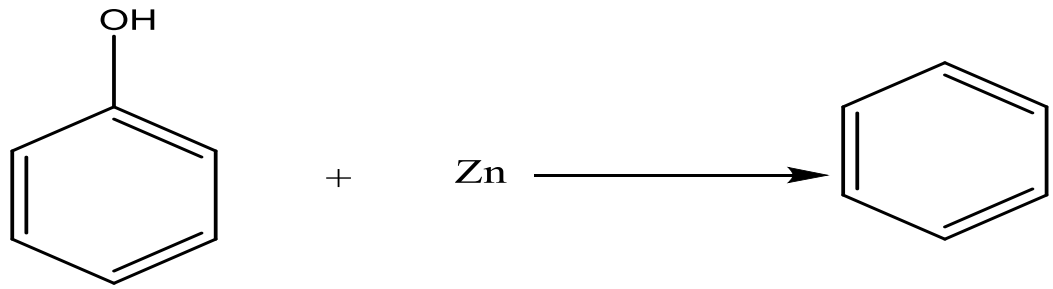
Benzoic acid

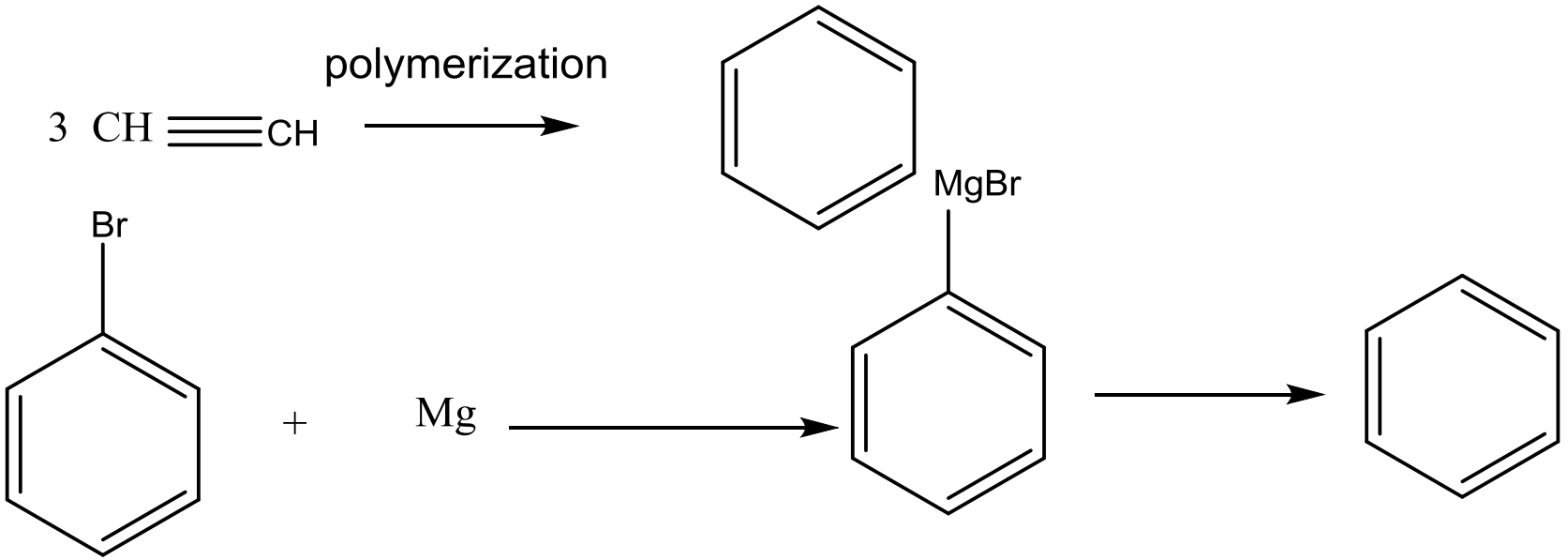


Preparation of benzene



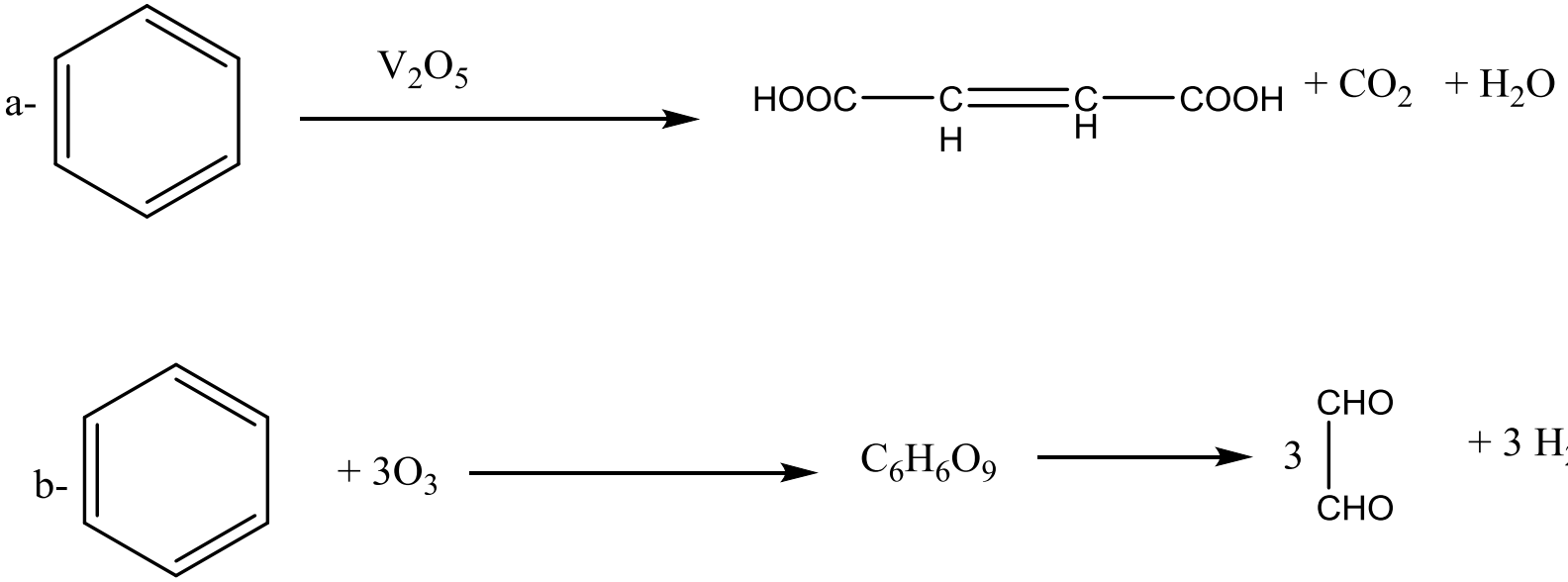




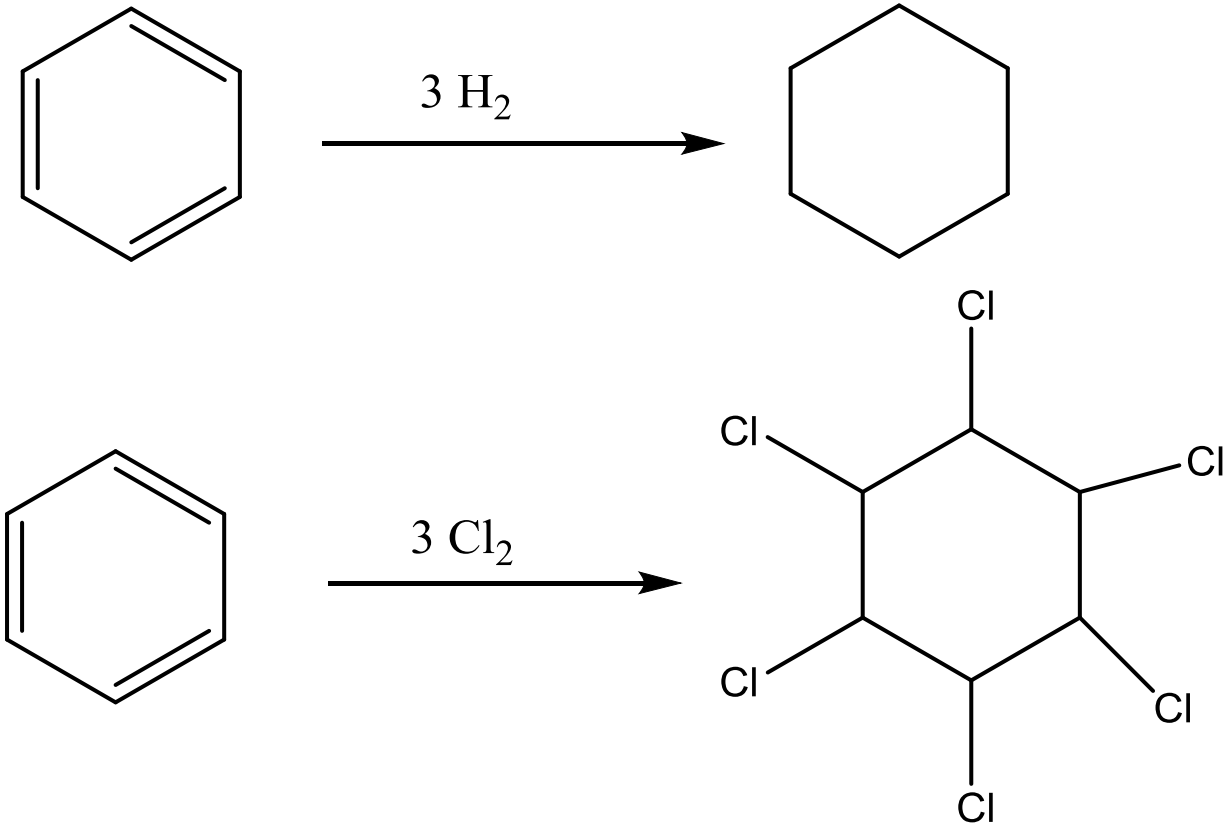

polymerization
3 CH CH
Br
+
Mg
MgBr

Chemical properties
Reactions lead to break the ring

- OXidation
- A- By Vandium Oxide
- B - Oxidation by Ozone



- Addition reactions



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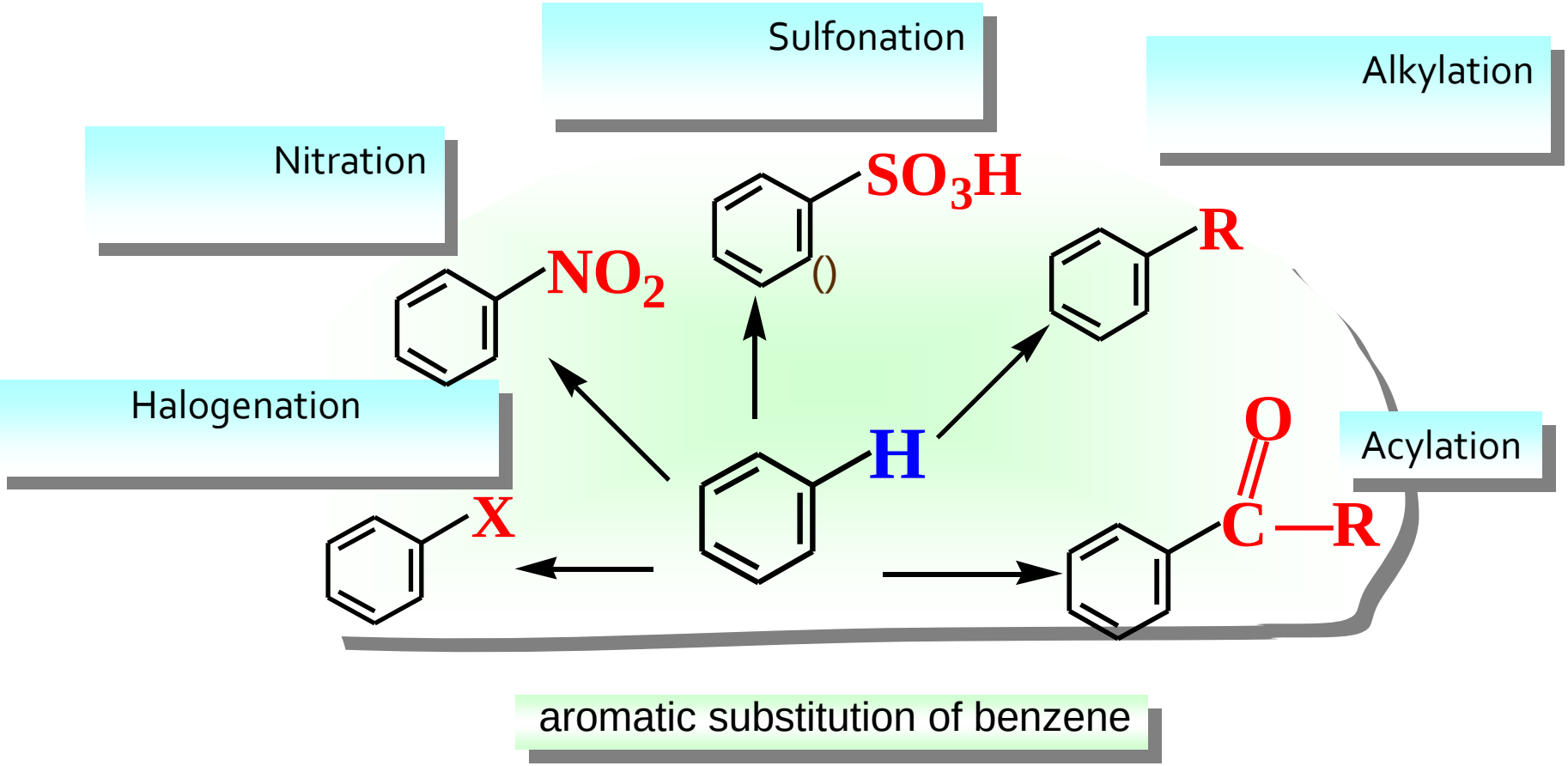
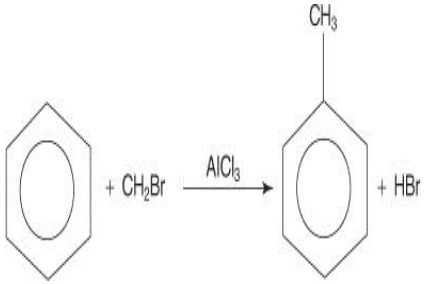
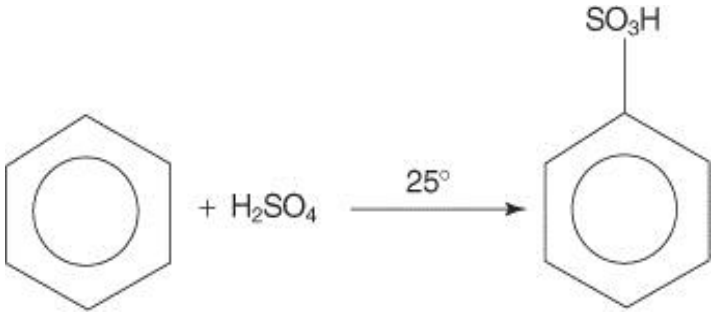
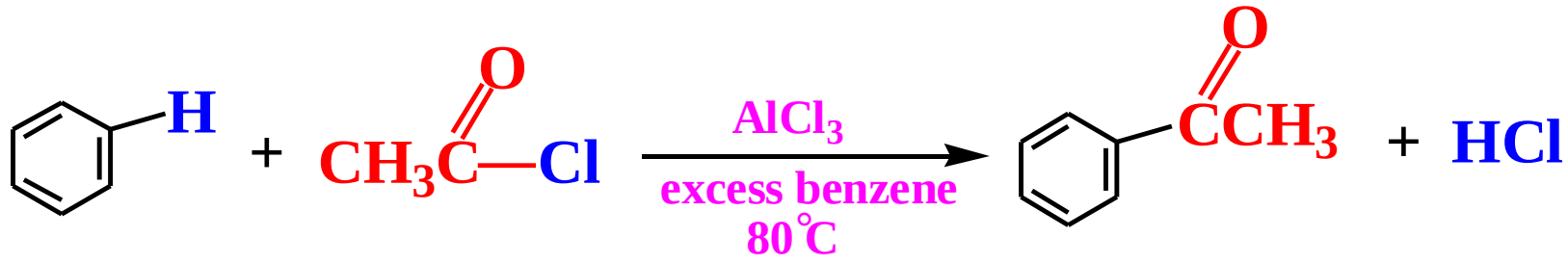
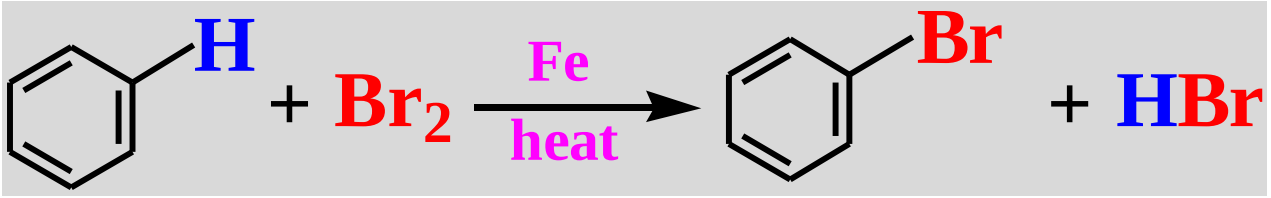


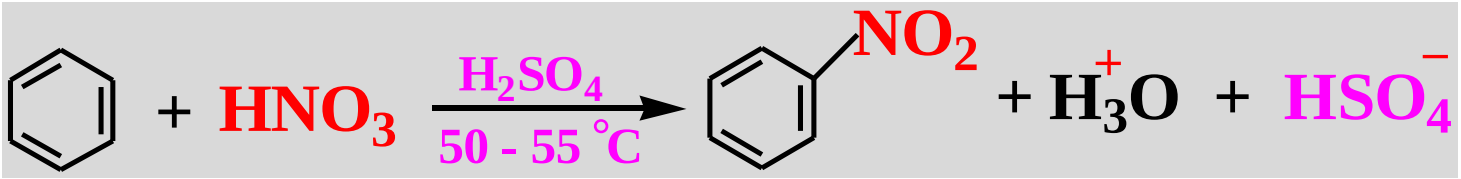
aromatic substitution of benzene


CH3
+ CH2Br
AlCl3
+ HBr

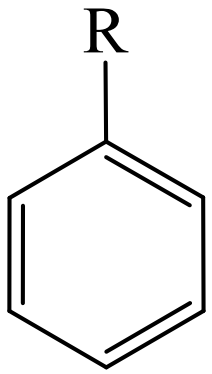

SO3H
+ H2SO4
25°


H
+ CH3C—Cl
O
AlCl3
excess benzene
80℃
CCH3
O
+ HCl


H
+ Br2
Fe
heat
Br
+ HBr

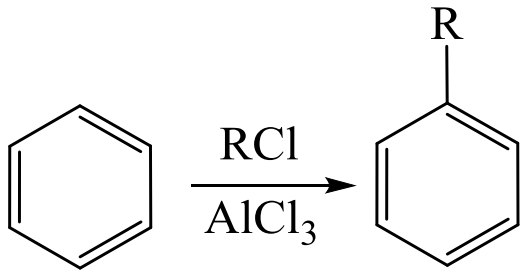

+ HNO3
H2SO4
50 - 55 ℃
NO2
+ H3O+
+ HSO4−

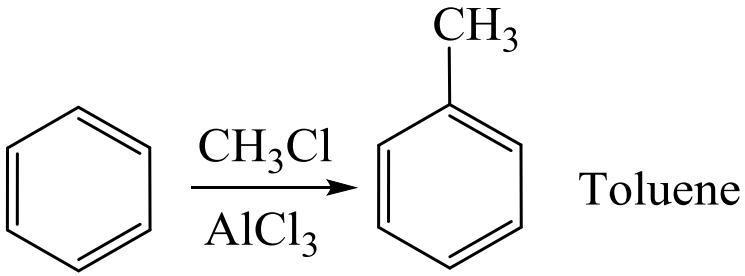
Alkylbenzene



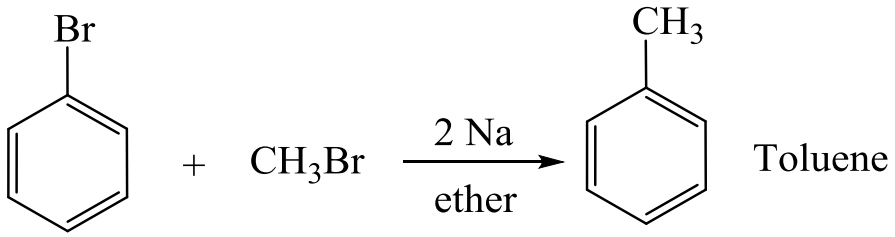
Synthesis of alkylbenzene

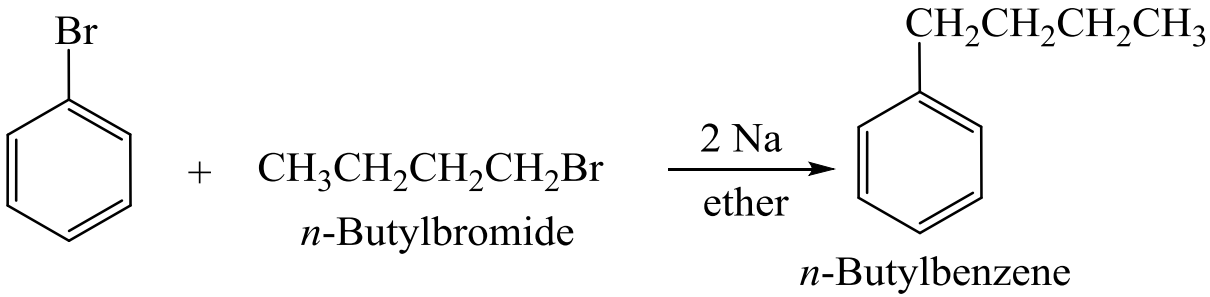
1- Via Friedel-Crafts reaction



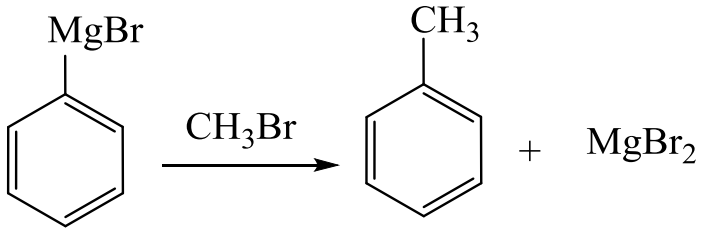


2- Wurtz-Fittig reaction



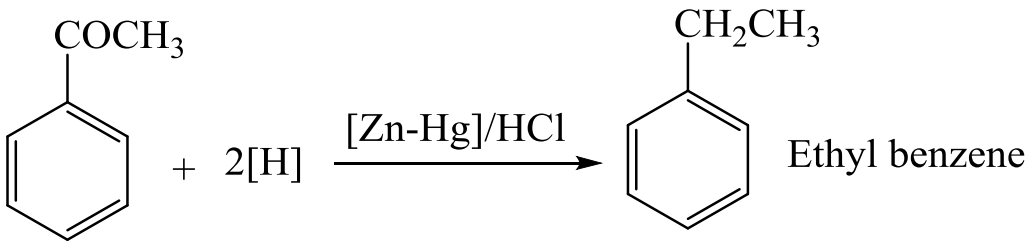


3- From Grignard reagents



Phenyl magnesium bromide
Grignard reagent

4- Via Clemensen reduction

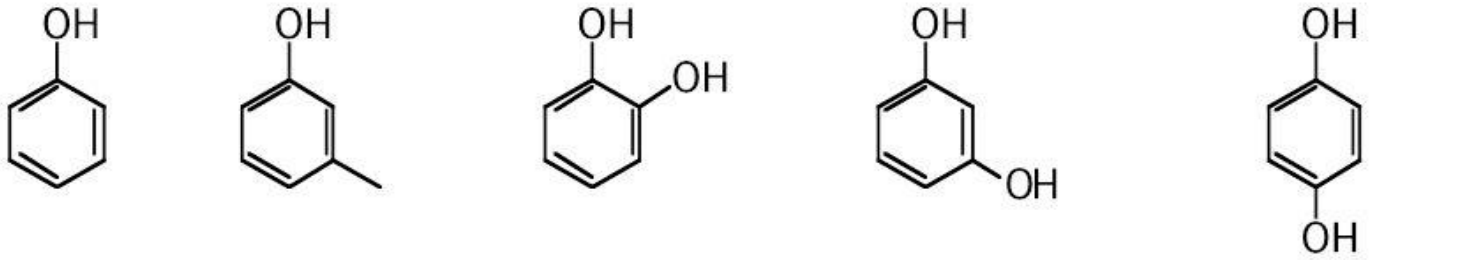


Acetophenone

Phenols

The functional group of a phenol is a hydroxyl (-OH) group bonded to a benzene ring.

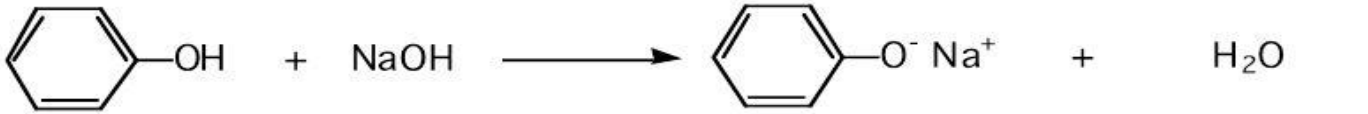
- Name substituted phenols either as derivatives of phenol or by common names.



Phenol | **3-Methylphenol (*m*-Cresol)** | **1,2-Benzenediol (Catechol)** | **1,3-Benzenediol (Resorcinol)** | **1,4-Benzenediol (Hydroquinone)**

Phenols

- Most phenols are weak acids, with pK_a values approximately 10.
- They are insoluble in water but react with strong bases, such as NaOH and KOH to form water-soluble salts.



Phenol
pK_a 9.95
(stronger acid)
(only slightly soluble in water)

Sodium hydroxide (stronger base)

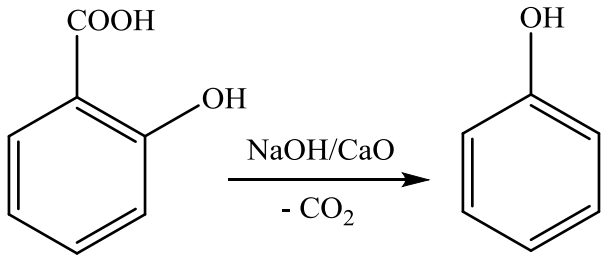
Sodium phenoxide
(weaker base)
(very soluble in water)

Water
pK_a 15.7
(weaker acid)

Phenols

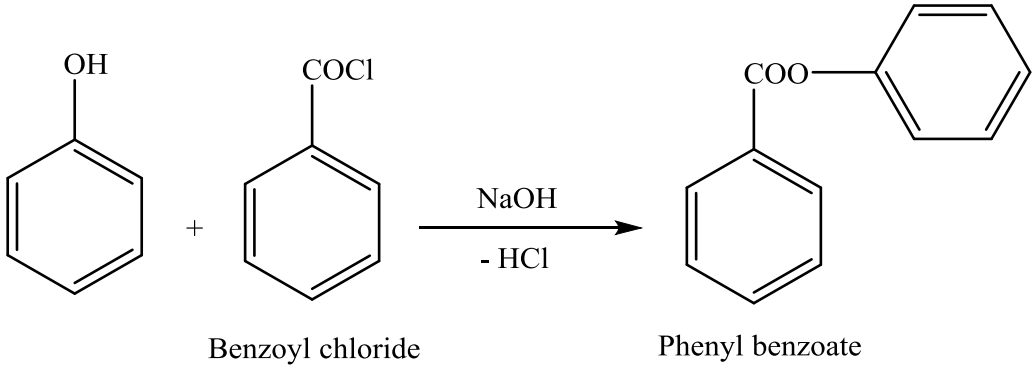
Synthesis

From salicylic acid

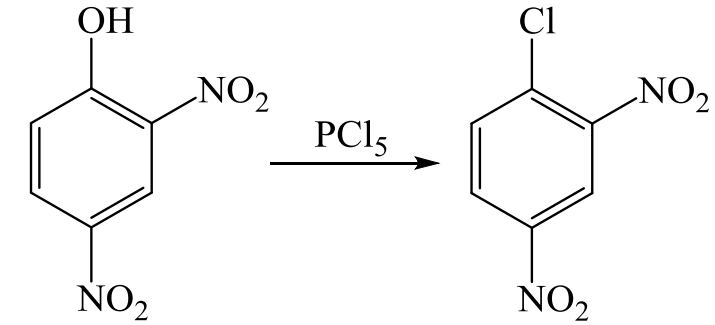


Reactions

1- Ester formation

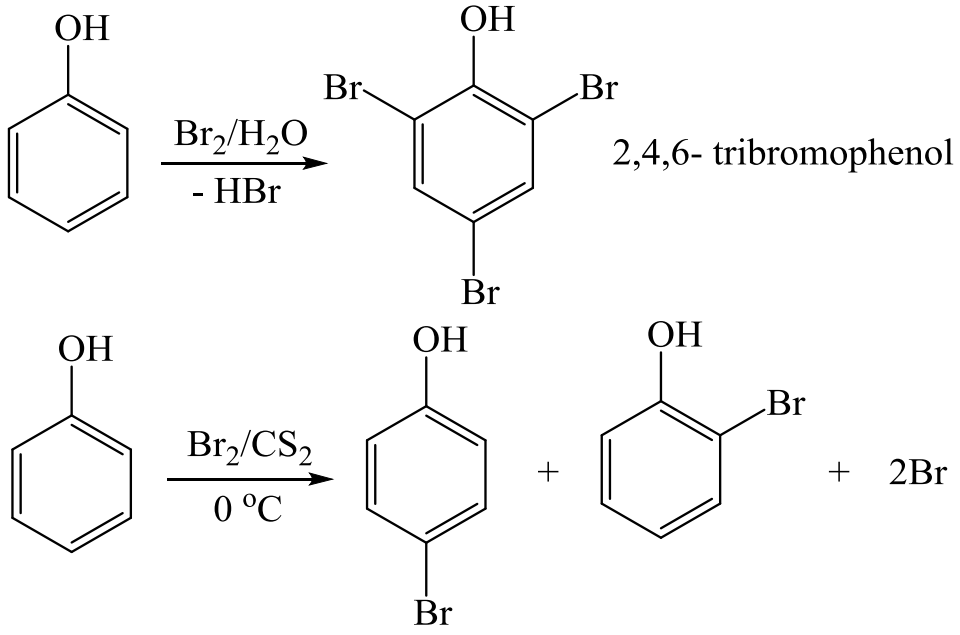


2- With phosphorous pentachloride

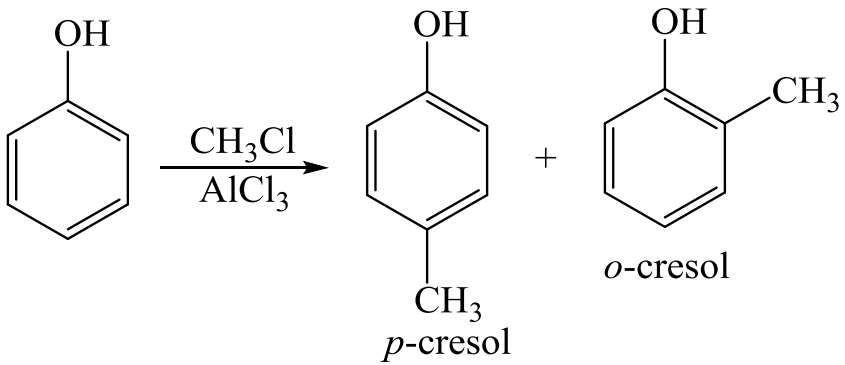


2,4-dinitrophenol

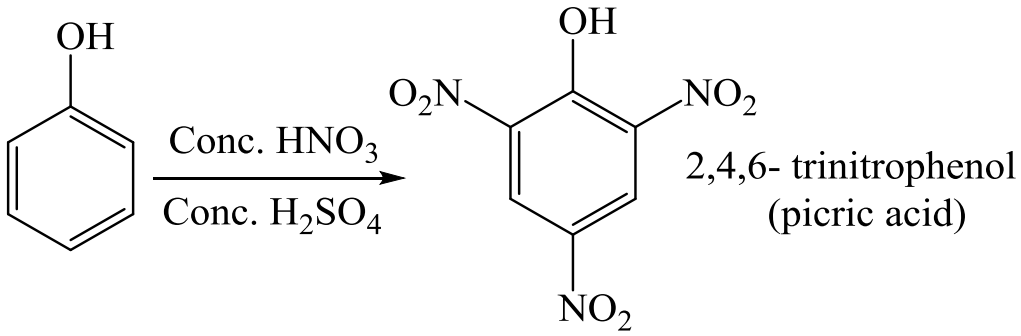
3- With bromine



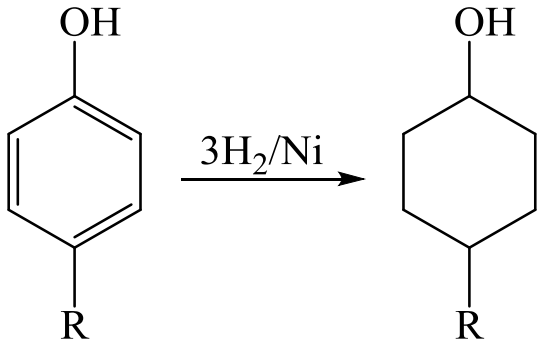
4- Alkylation



5- Nitration



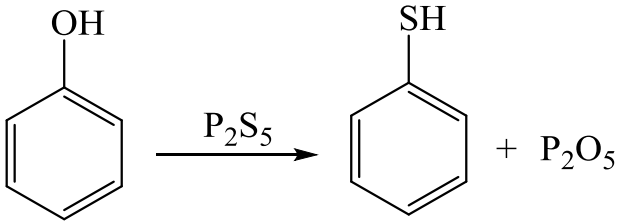
6- Reduction



Aryl thiols

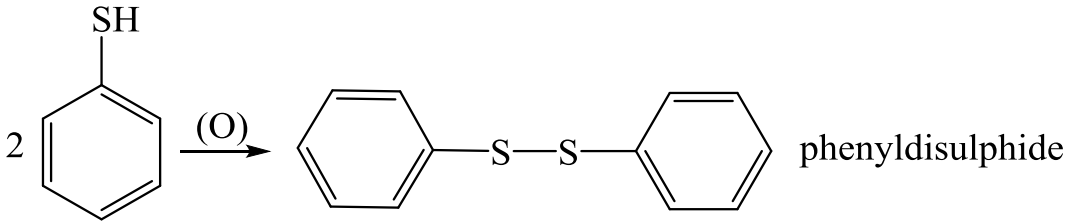
Synthesis

From phenols

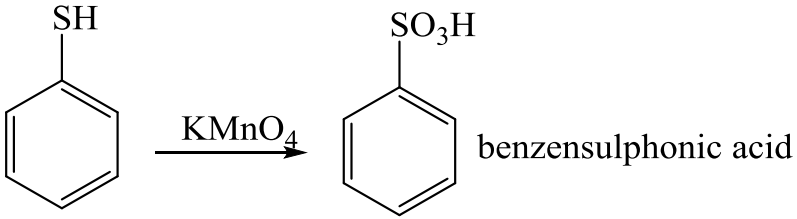


Reactions

1- With mild oxidizing agent



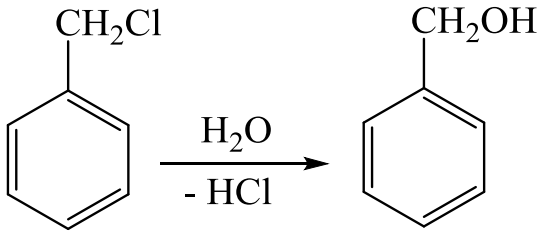
2- With strong $KMnO_4$



Aromatic alcohols

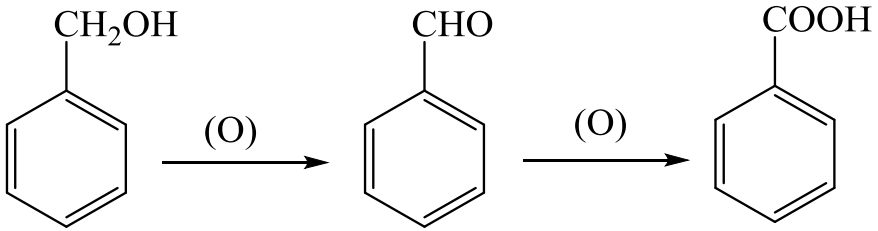
Synthesis

From benzyl chloride

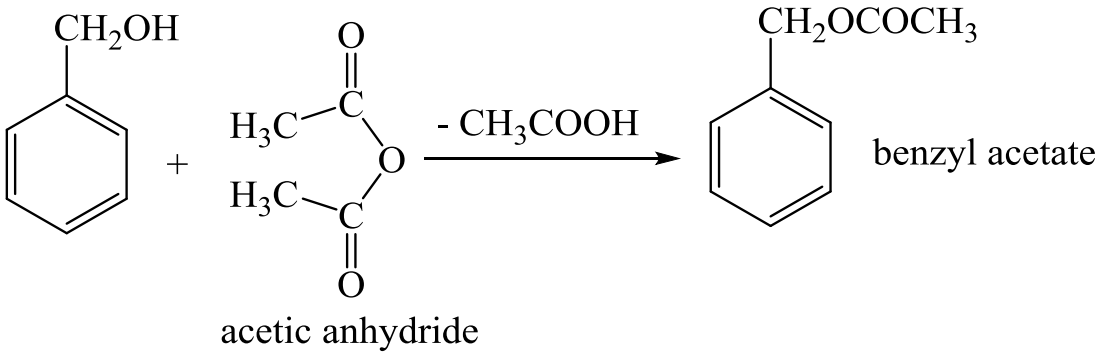


Reactions

1- Oxidation



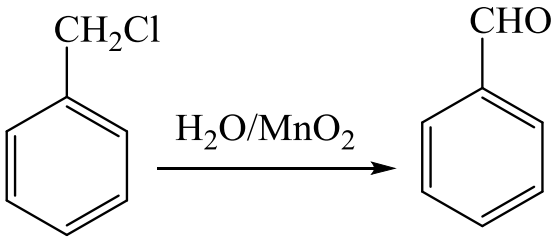
2- Esterformation



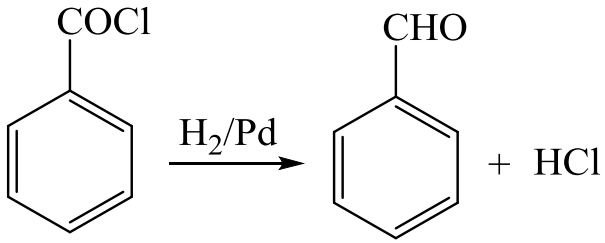
Aromatic aldehydes

Synthesis

1- From benzyl chloride

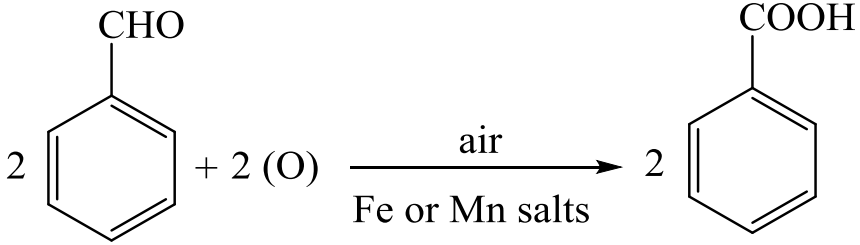


2- From benzoyl chloride

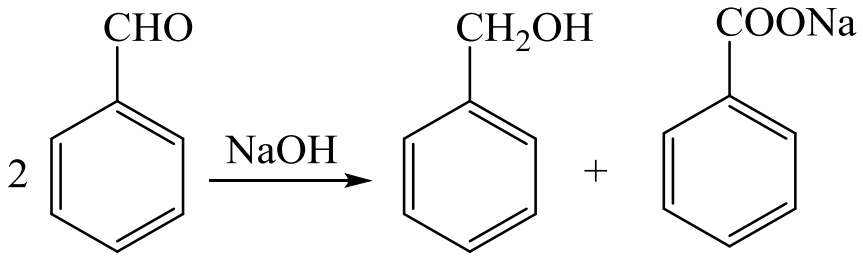


Reactions

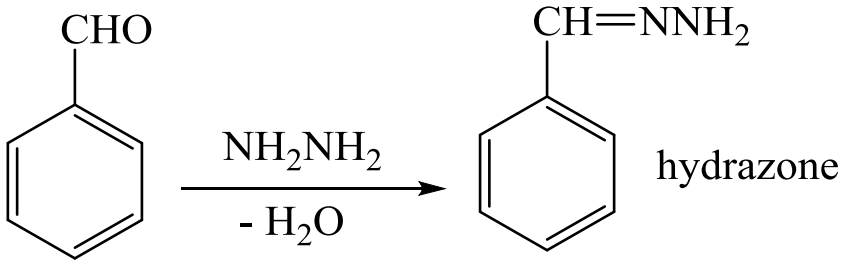
1- Oxidation



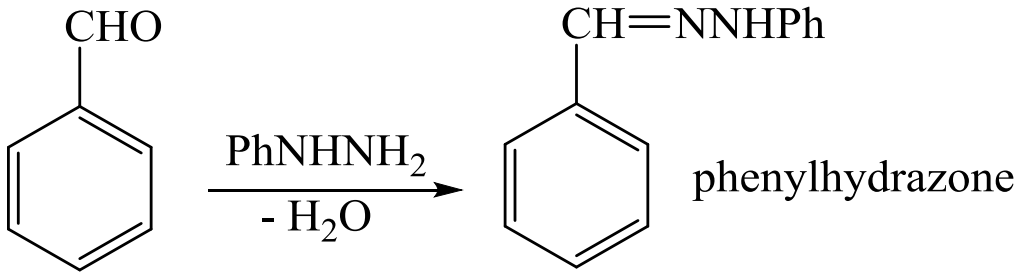
2- Cannizaro reaction



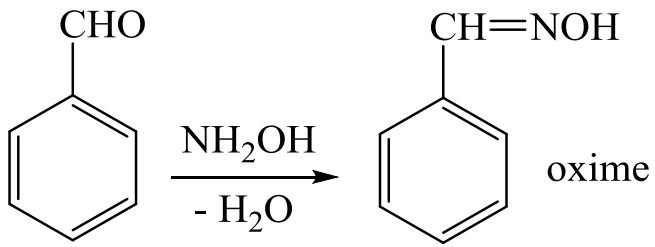
3- With hydrazine



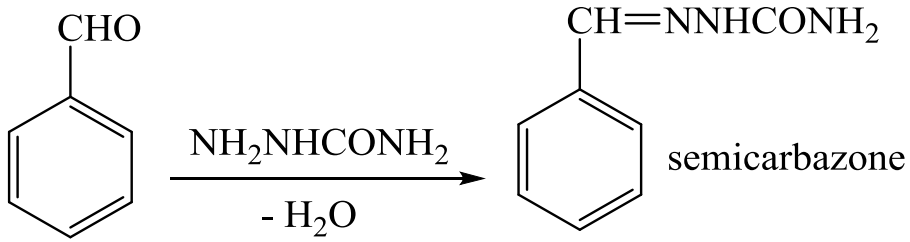
4- With phenylhydrazine



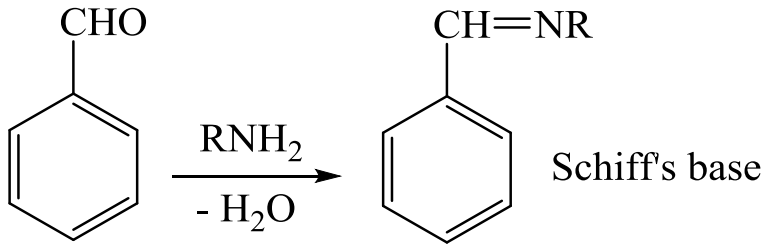
5- With hydroxyl amine



6- With semicarbazide



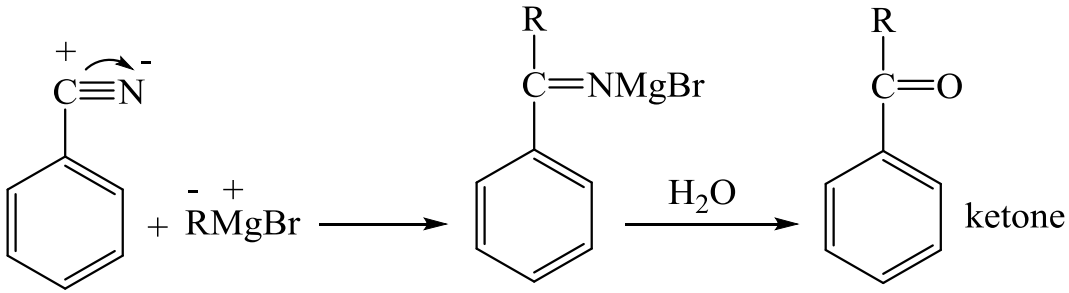
7- With amines



Aromatic ketones

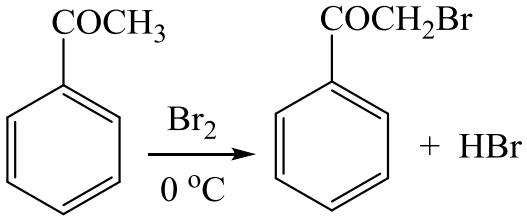
Synthesis

By the reaction of Grignar reagents benzonitrile

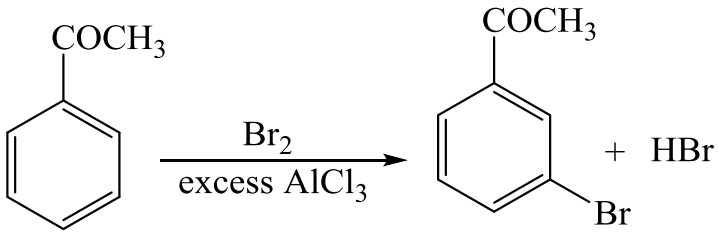


Reactions

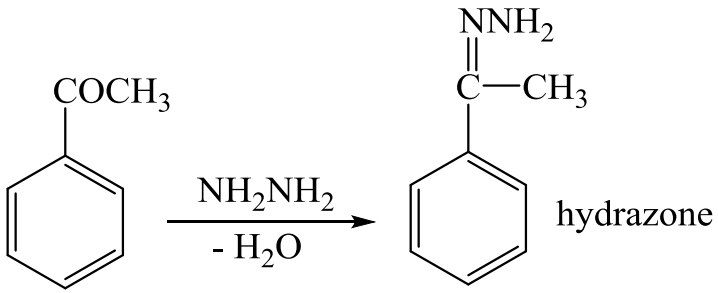
1- With bromine



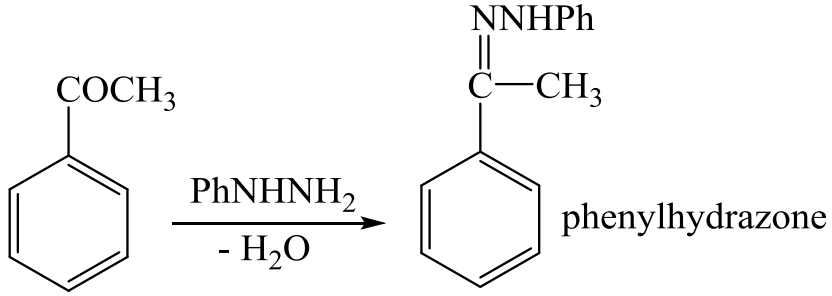
phenacyl bromide



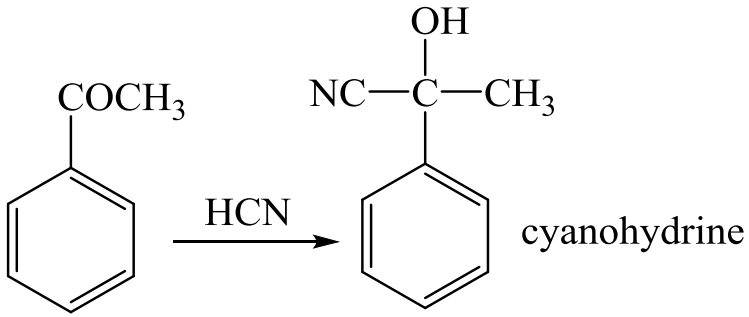
2- With hydrazine



3- With phenyl hydrazine



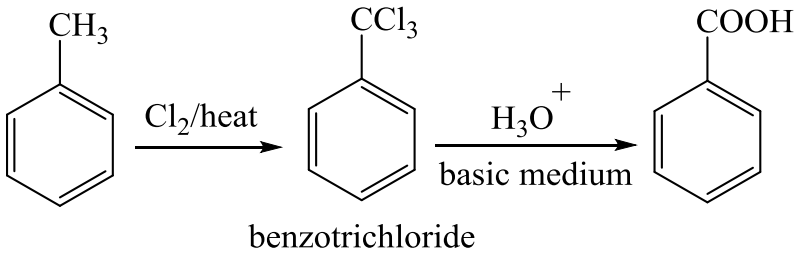
4- With hydrogen cyanide



Aromatic carboxylic acids

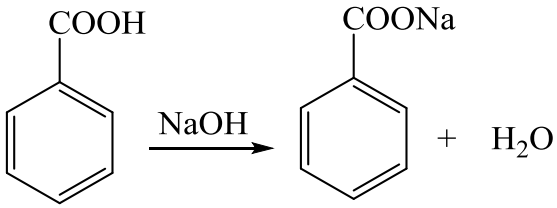
Synthesis

From toluene

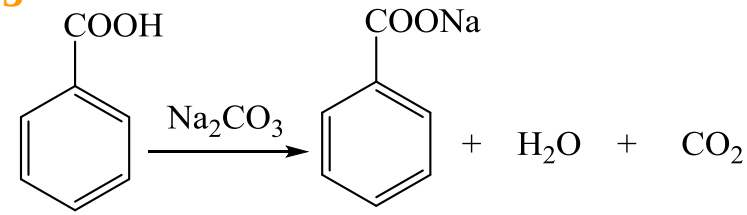


Reactions

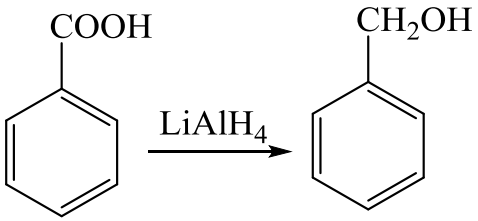
1- With NaOH



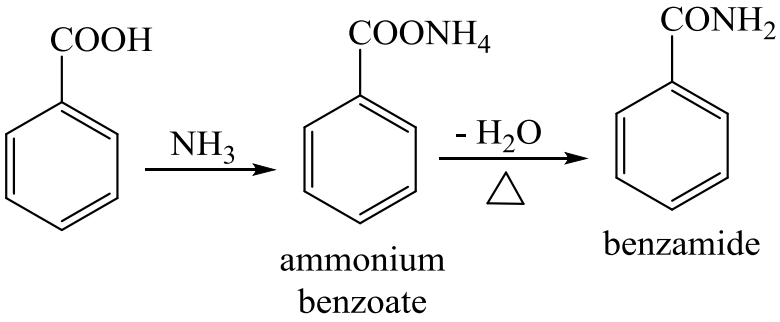
2- With Na_2CO_3



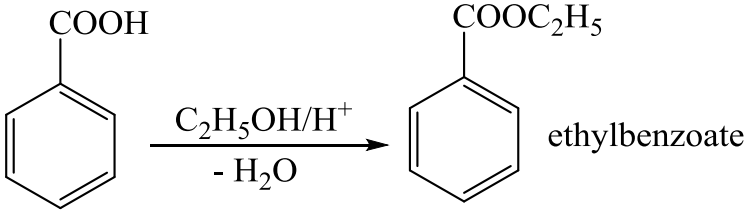
3- With lithium aluminium hydride



4- With ammonia



5- Ester formation



6- Nitration