SOUTH VALLY UNIVERSITY

FACULTY OF SCIENCE

INTRODUCTION TO THE CHEMISTRY OF ALICYCLIC COMPOUNDS

By

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For 3rd Education Students
(English Program)

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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.

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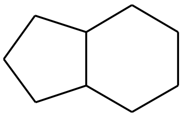


INTRODUCTION

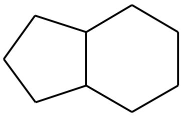
This course presents a brief introduction to the chemistry of alicyclic compounds, it is necessary to understand some of the language used to describe the stereochemistry of alicyclic compounds.

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.

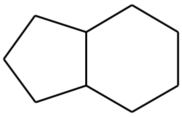
OBJECTIVES OF EACH LESSON

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.

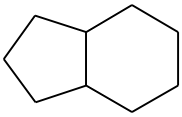
Lesson 11:

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).

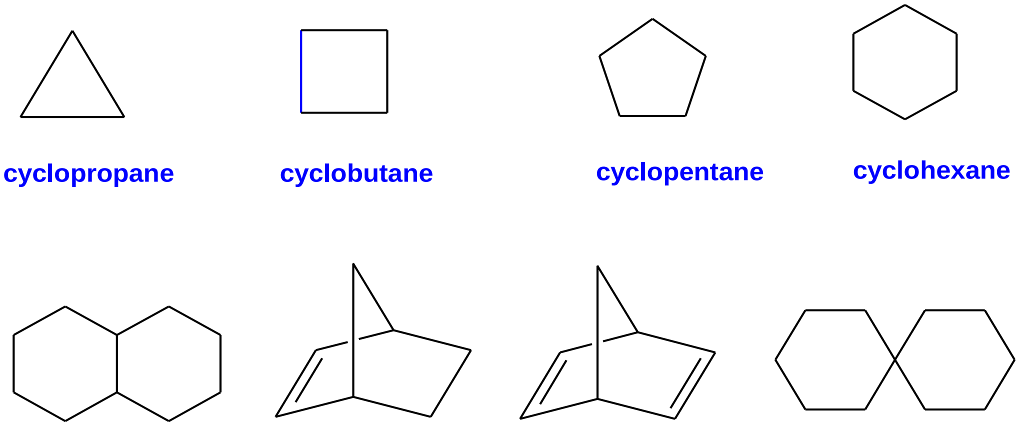

cyclopropane
cyclobutane
cyclopentane
cyclohexane
decalin
norbornene
norbornadiene
spiro[5.5]undecane

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).

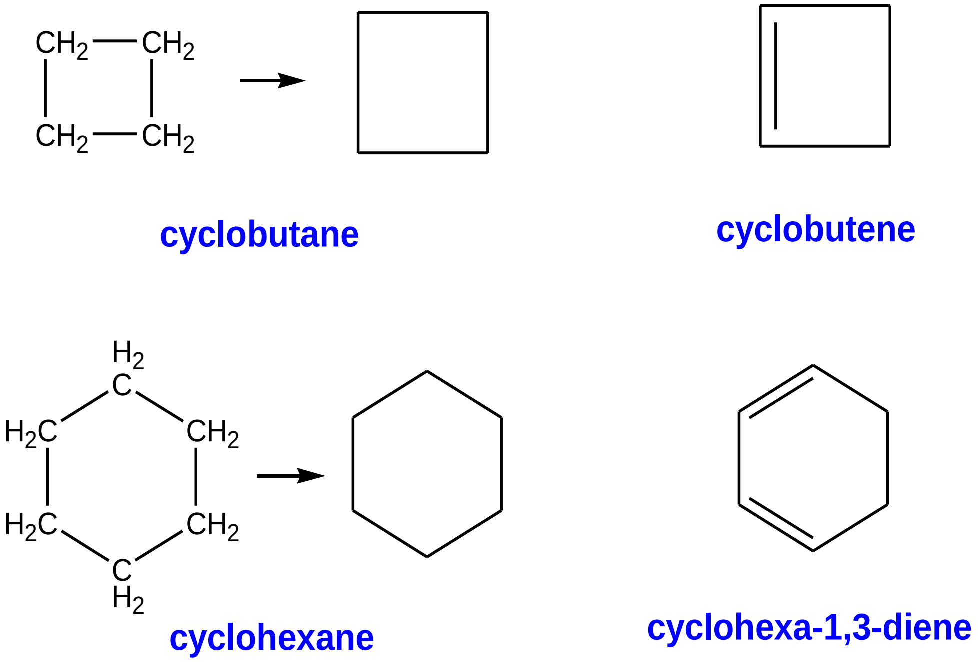
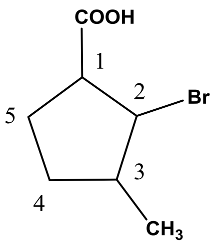
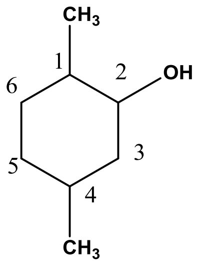


Fig. 1.2

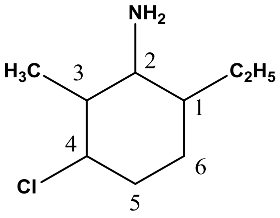
When a monocyclic hydrocarbon has a long and complex side chain, the open chain is named according to the I.U.P.A.C system, and the ring is regarded as a substituent, see examples in (Fig. 1.3).



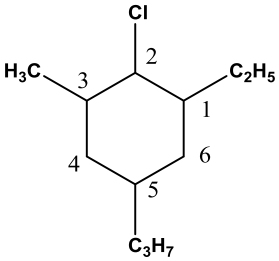
2-bromo-3-methyl-cyclopentane carboxylic acid



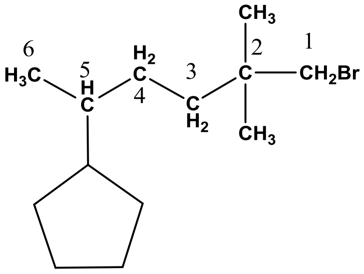
1,4-dimethyl-2-cyclohexanol



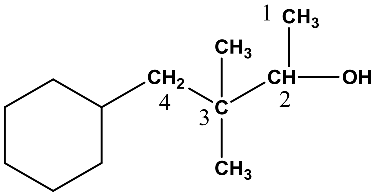
4-chloro-1-ethyl-3-methyl-2-cyclohexylamine



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



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



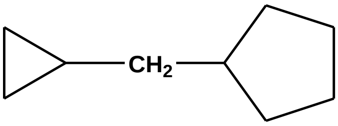
4-cyclohexyl-3,3-dimethyl-2-butanol

Fig. 1.3

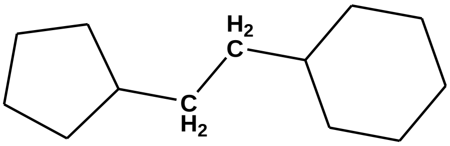
B- Bicyclic system:

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;

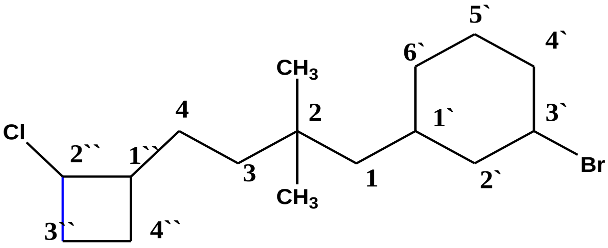


cyclopropylcyclopentylmethane

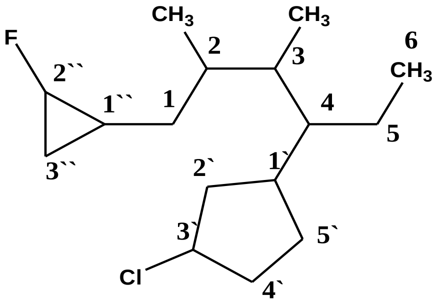


cyclopentylcyclohexylethane

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

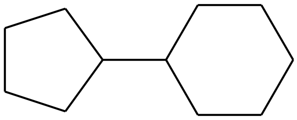


2,3-dimethyl-4-(3`-chlorocyclopentyl)-1-(2``-flourocyclopropyl)-hexane

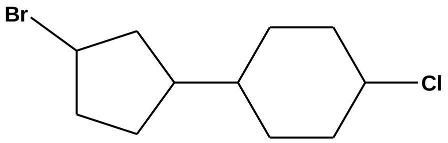
Fig. 1.4

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.,



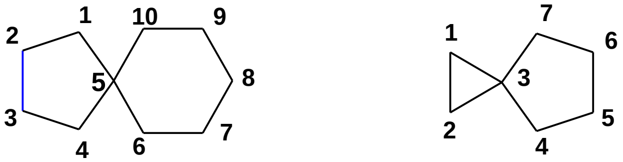
cyclopentyl-cyclohexane



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

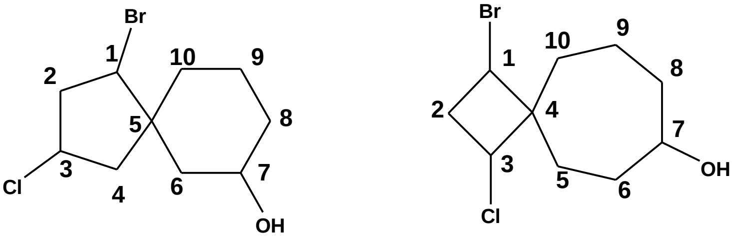
3- Bicyclic compounds with rings having one common atom (Spirans):

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



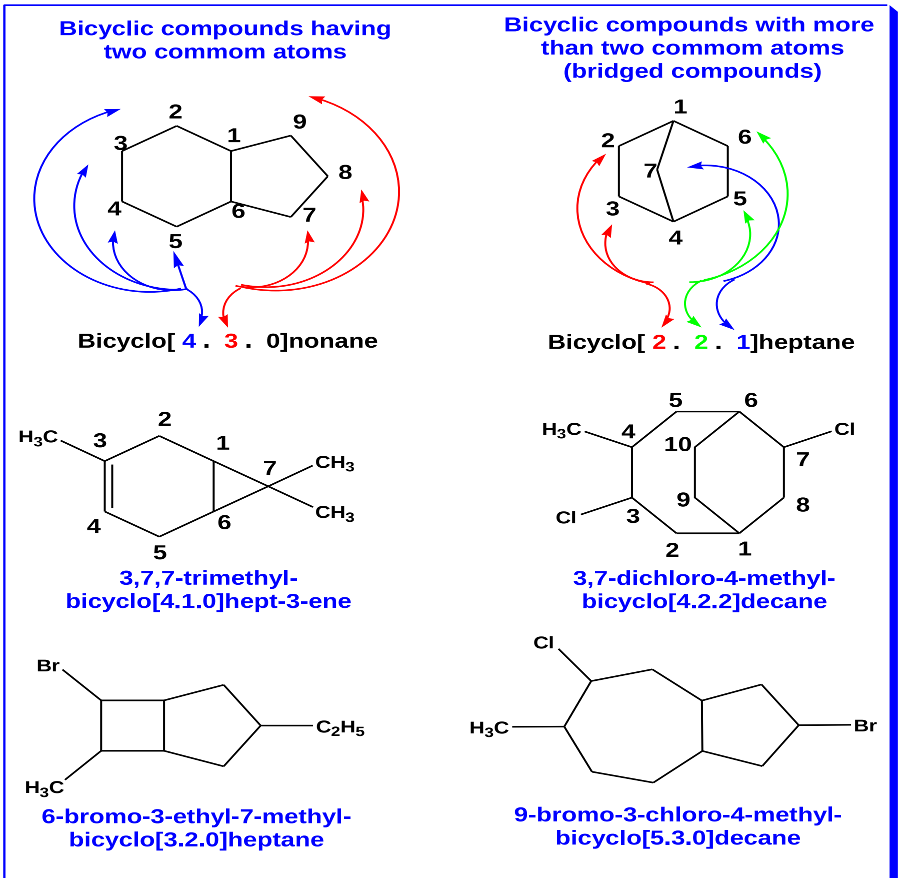
1-Bromo-3-chloro-spiro[4.5]decan-7-ol

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

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

Bicyclo[4.3.0]nonane

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

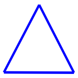
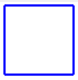
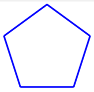
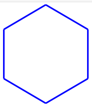
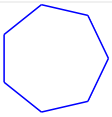
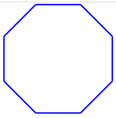
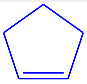
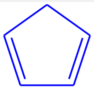
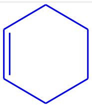
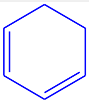
Five and six membered paraffins occur in petroleum (The naphthenes); three, four and five membered rings occur in terpenes which are the most important class of alicyclic compounds.

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):

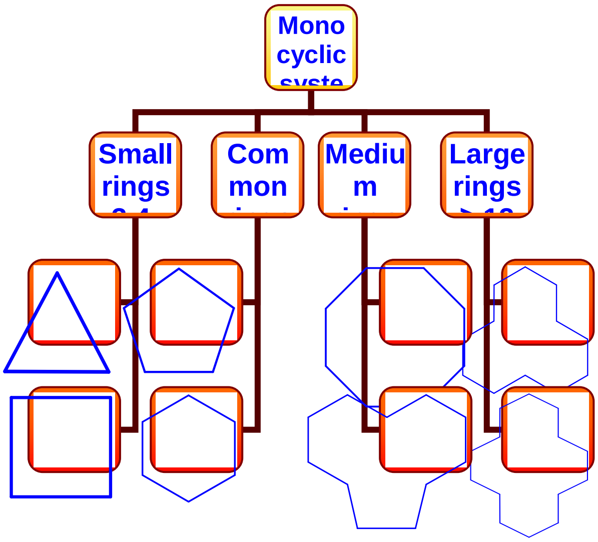


Diagram 2.2

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:

(α) = 1/2 (109º 28` - 60) = + 24º 44`

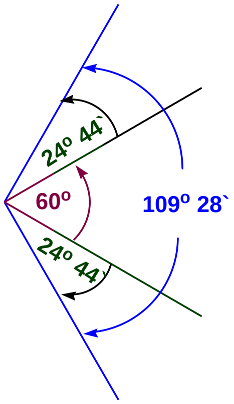


Fig. 2.3

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) = 0º 44`. Hence, cyclopentane must posses the lowest energy and the highest stability.

- The bond angle in the planar cyclohexane is (120º), which is larger than the tetrahedral angle, so, the strain (α) = - 5º 16`. Also the stain in cycloheptane will be (α) = - 9º 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 (60º). This value is impossible, since, the carbon valency angle never be less than (90º). Furthermore, according to Coulson *et al.* calculation has shown that the smallest carbon valency angle is (104º), 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):

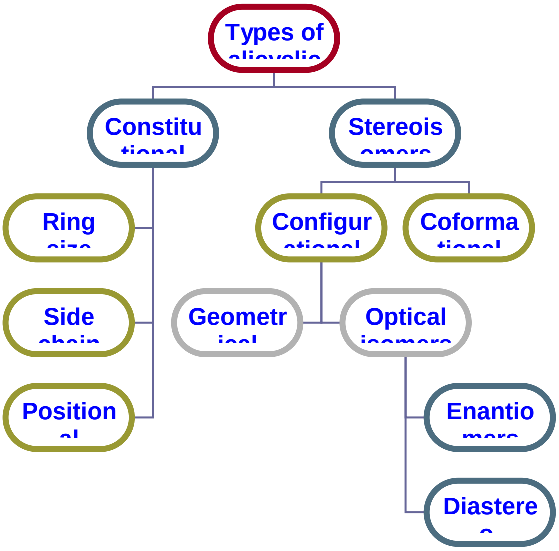


Diagram 3.1

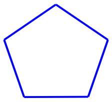
3.2 Constitutional isomers:

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

Types of constitutional isomers in alicyclic compounds:

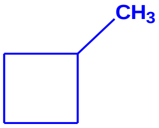
I- Ring size isomers:

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



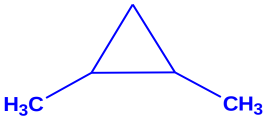
Cyclopentane

MF: C_5H_{10}



Methyl-cyclobutane

C_5H_{10}

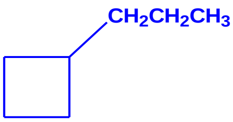


1,2-Dimethyl-cyclopropane

C_5H_{10}

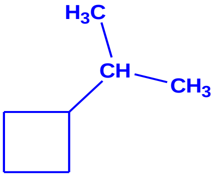
II- Side chain isomers:

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



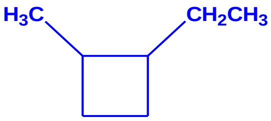
Propyl-cyclobutane

MF: C_7H_{14}



Isopropyl-cyclobutane

C_7H_{14}

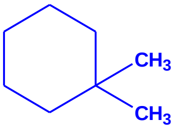


1-Ethyl-2-methyl-cyclobutane

C_7H_{14}

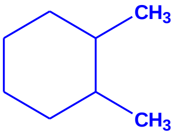
III- Positional isomers:

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



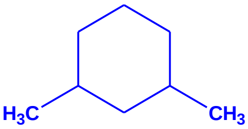
1,1-Dimethyl-cyclohexane

MF: C_8H_{16}



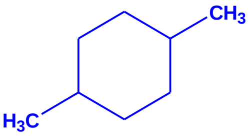
1,2-Dimethyl-cyclohexane

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.

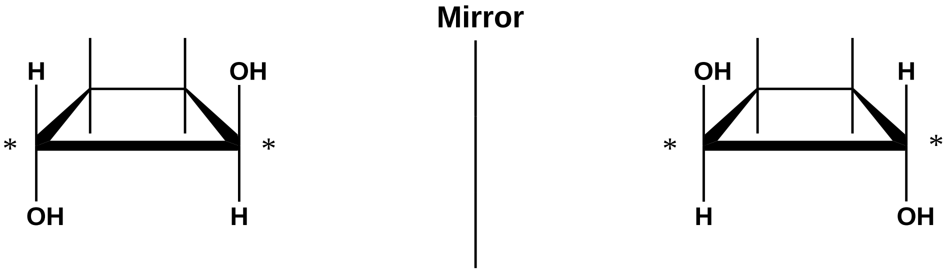
IV- Meso-form:

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.

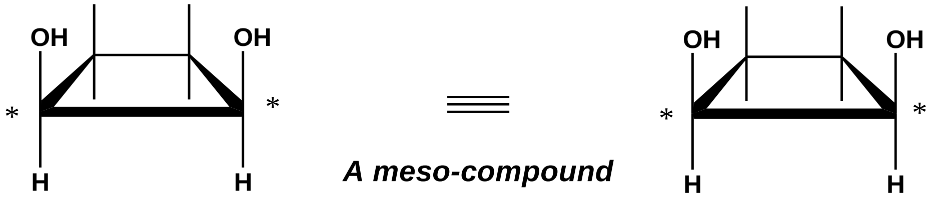
The ***trans***-isomer exists in two optically active enantiomers, whereas, the ***cis***-isomer has a plane of symmetry and is therefore optically inactive Meso-form.



2 enantiomers

non-superimposable

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



A meso-compound

superimposable

cis-cyclobutane-1,2-diol

*** - chiral carbon atom**

Fig. 3.3

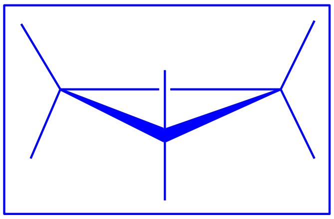
Unit 1

Lesson 4: Conformations of cycloalkanes

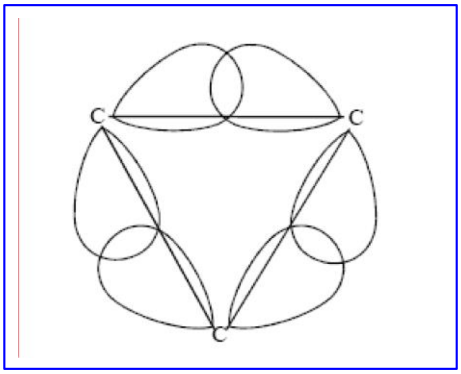
4.1 Geometrical shape of the rings

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}.



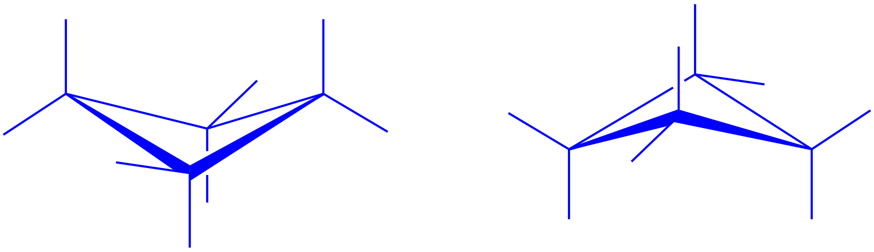
Propane molecule



Banana-bond of cyclopropane

Fig. 4.1

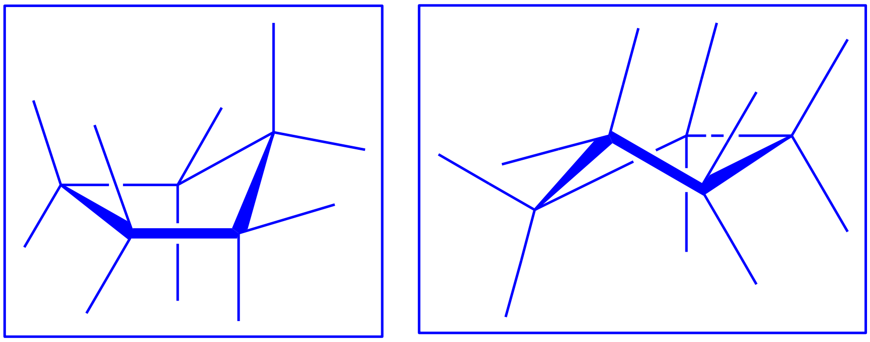
B- Cyclobutane: (Flat bond angles will be = 90^{O}) is puckered, even through the puckered causes more-strained bond angles (Fig. 4.2).



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).



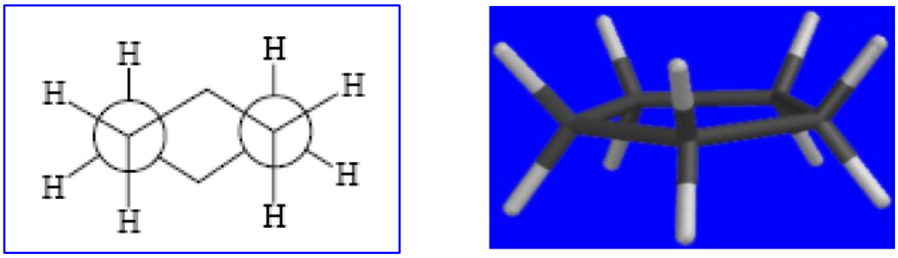
Envelop-form

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

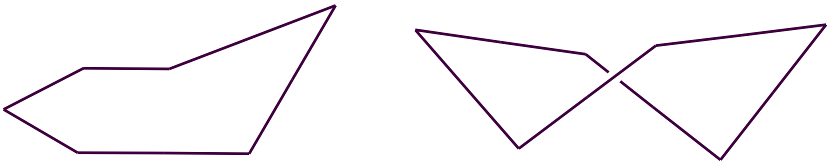
Fig. 4.4

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

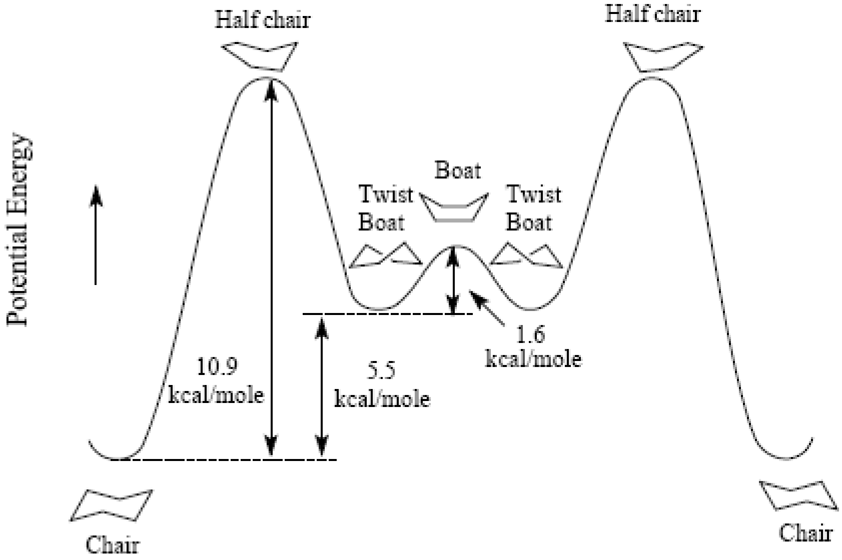


The half-chair form of cyclohexane

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).

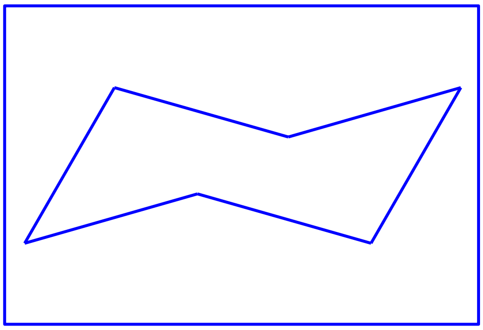


The energy diagram for the ring inversion of cyclohexane.

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

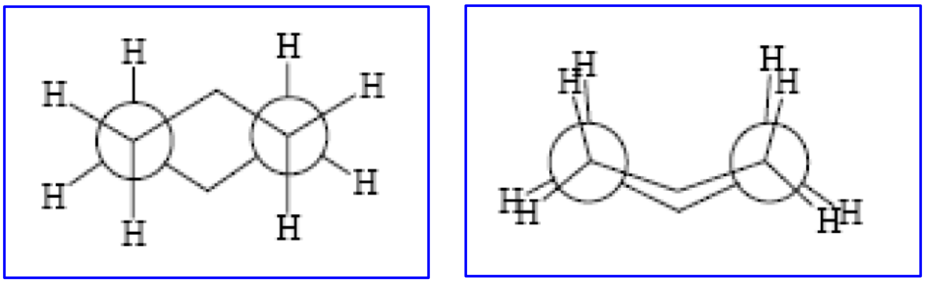
The stability of the chair-form is due to the following reasons:

(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).

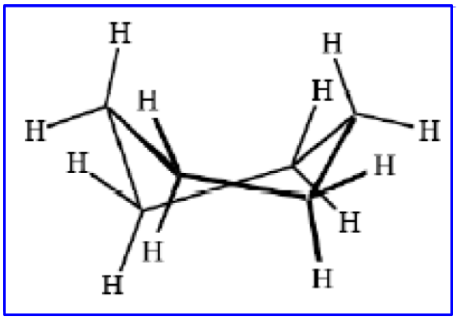


Newman projection of the chair-form

Newman projection of the boat-form

Fig. 4.8

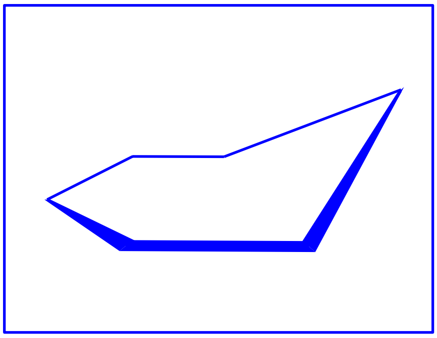
3- A third conformation of cyclohexane is the twist-boat (Fig. 4.9), there is a relieving in this form minimizes the torsional strain and make the twist-boat is lower in energy than the boat-conformation.



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).

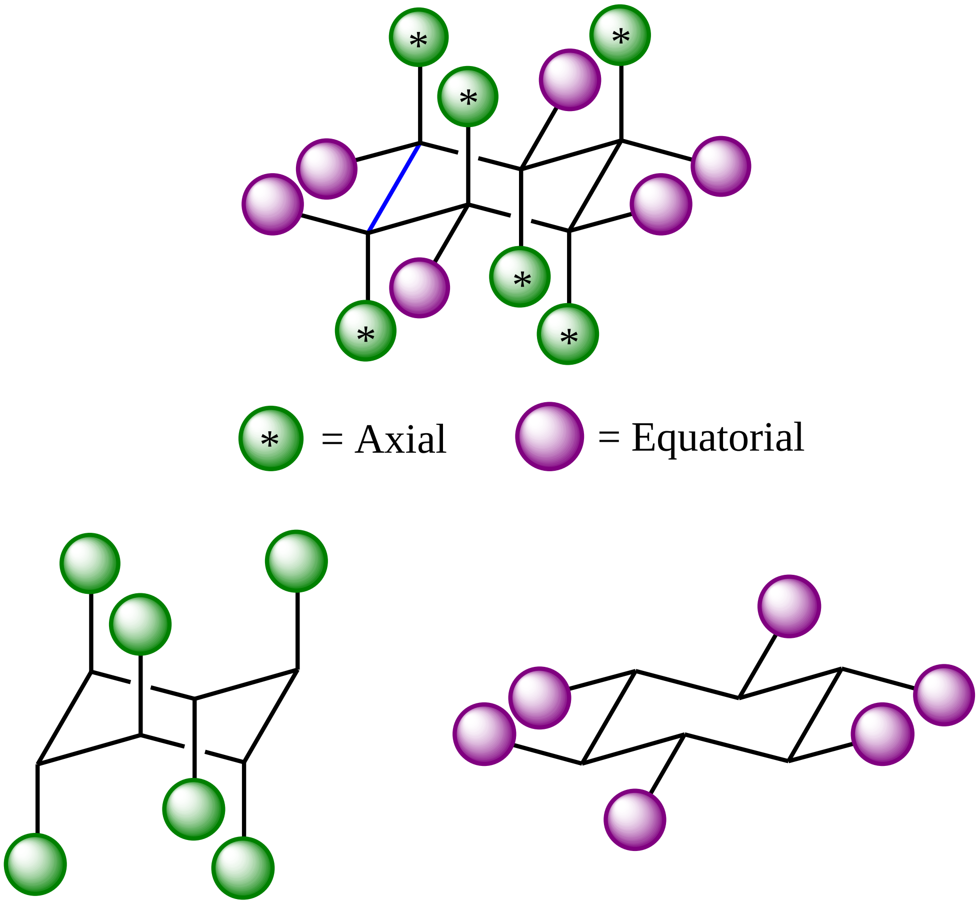


The half-chair form of cyclohexane

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).



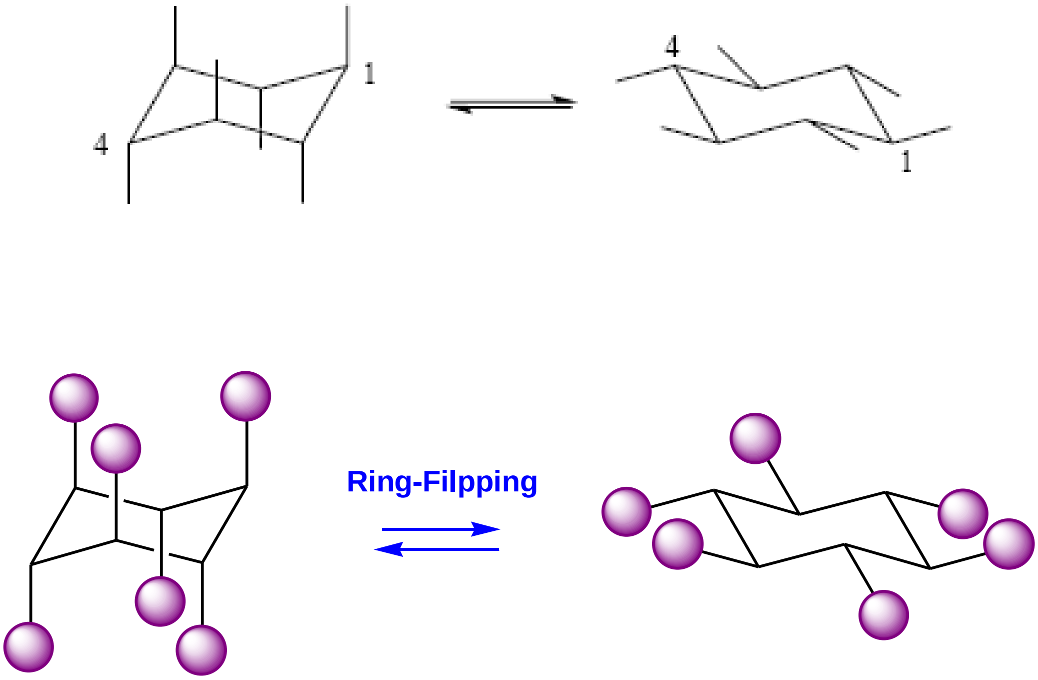
Axial hydrogens of cyclohexane

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.

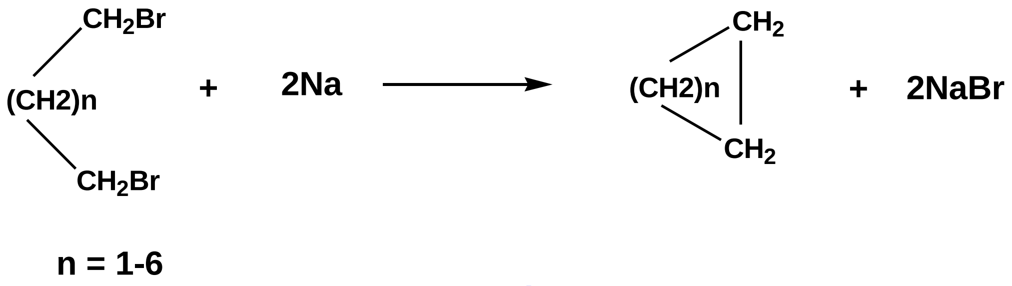
Unit 2

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):

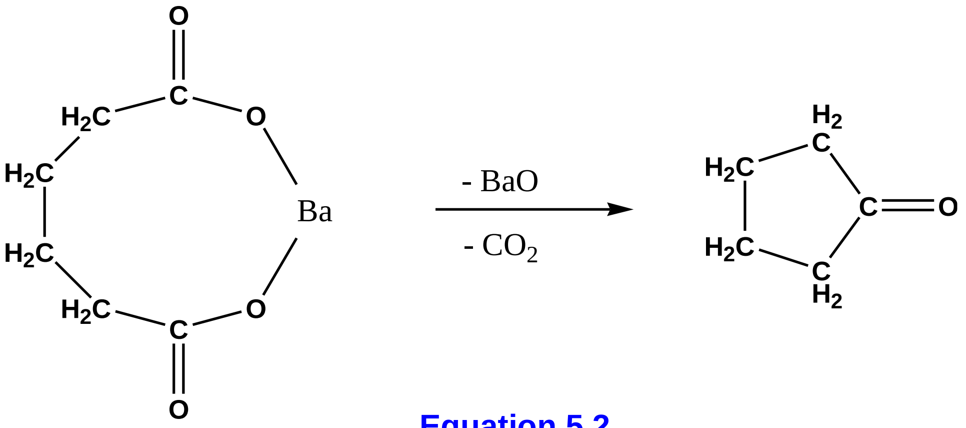
Treatment of an alkyl dihalide with sodium or zinc gives the corresponding cycloalkane (Equation 5.1).



Equation 5.1

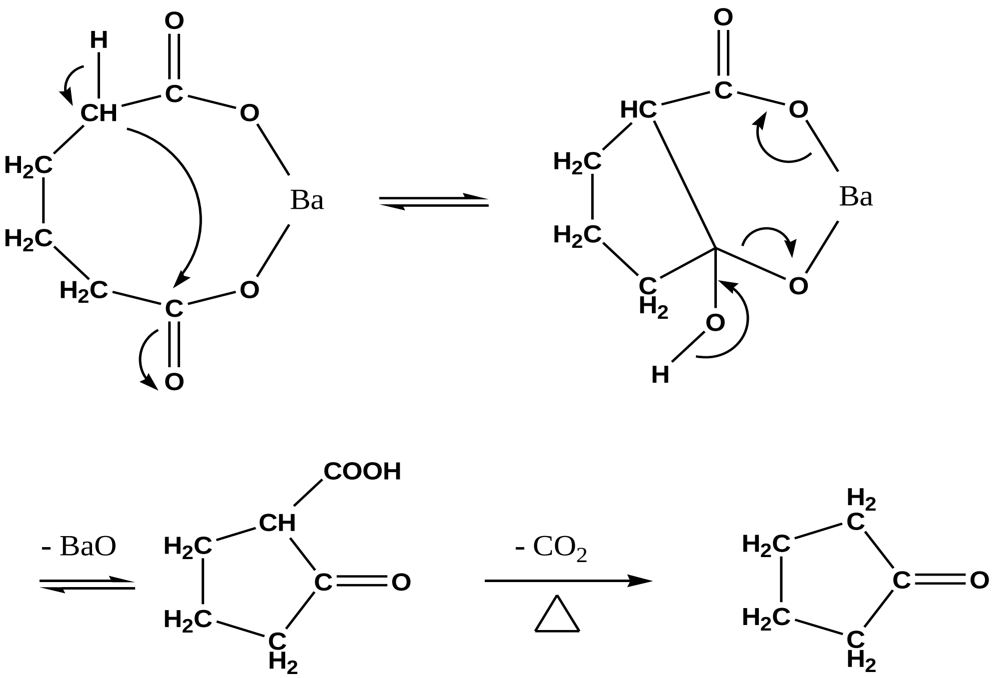
2. Pyrolysis of the salts of dibasic acid:

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).



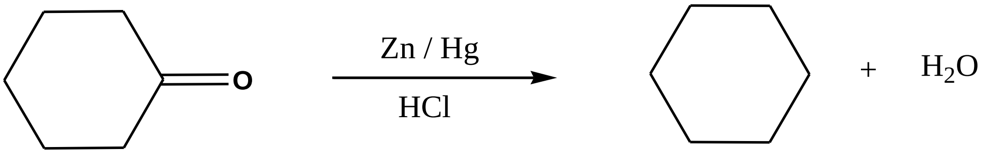
Equation 5.2

The reaction mechanism;



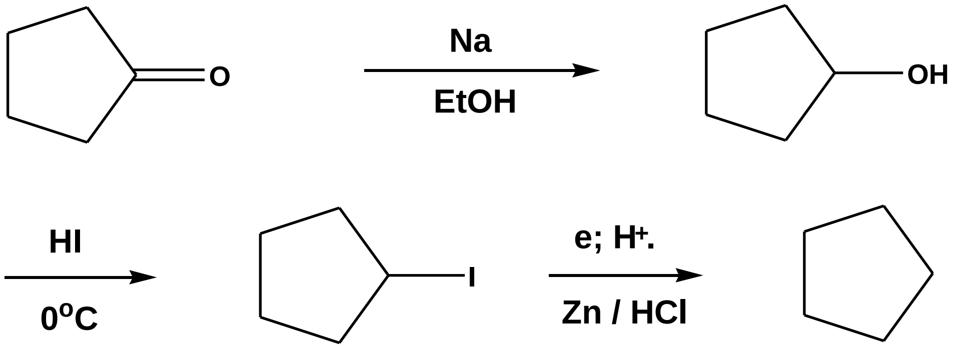
3. Reduction of cyclic ketones:

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

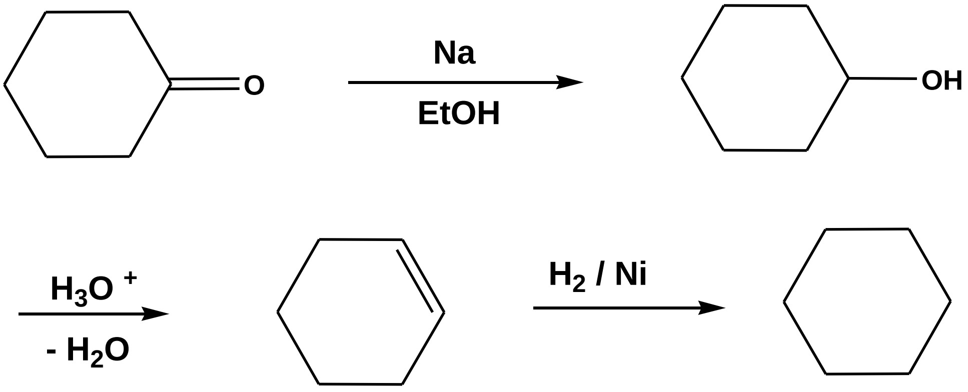


Equation 5.3

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



Equation 5.4



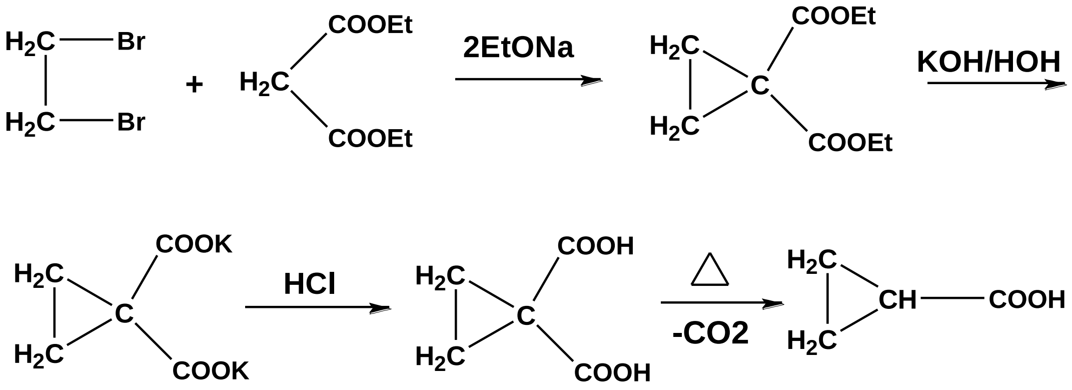
Equation 5.5

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.

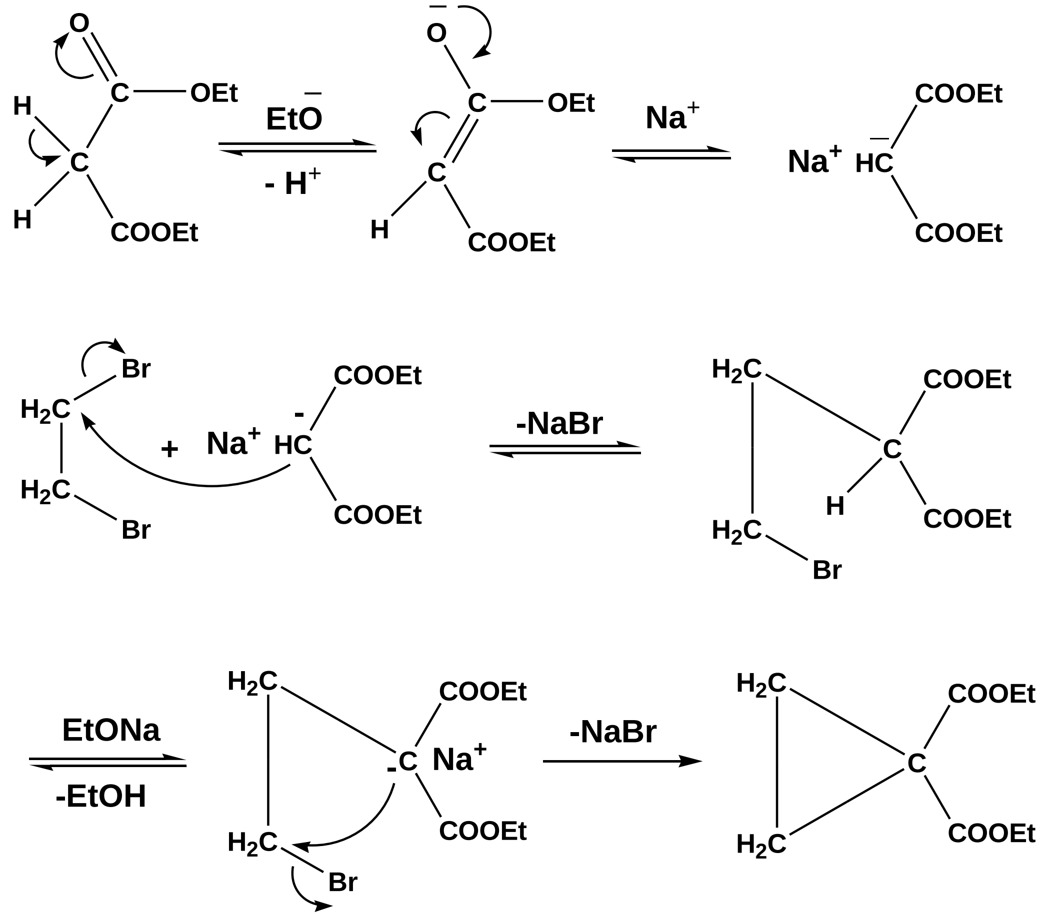
I- Condensation with malonic ester:

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).



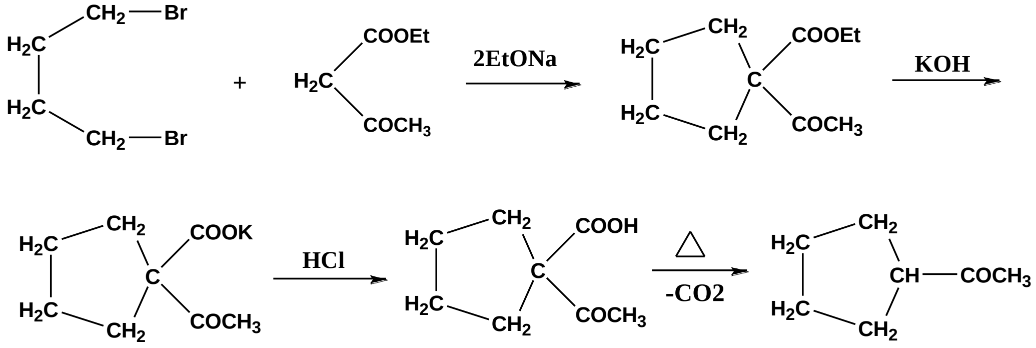
Equation 5.6

The reaction mechanism;



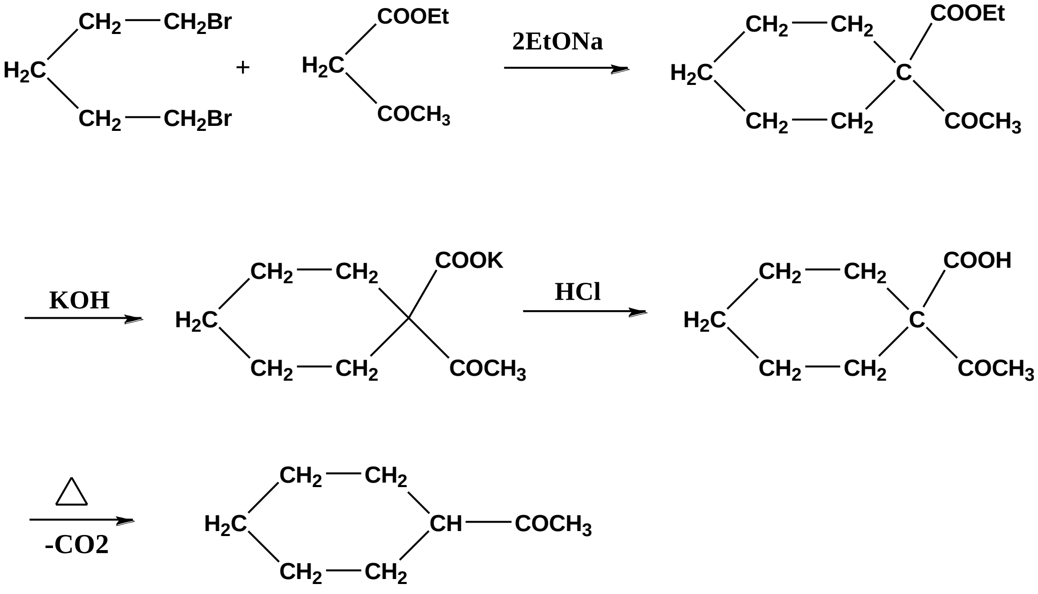
I- Condensation with ethylacetoacetate:

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



cyclopentylmethylketone

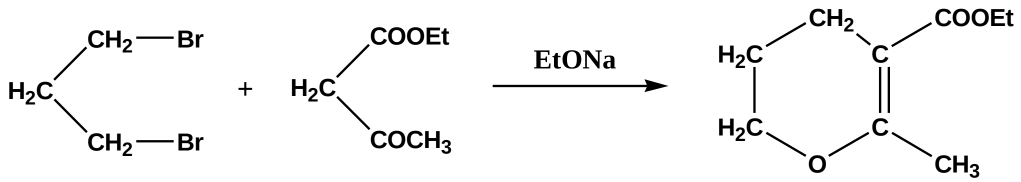
Equation 5.7



cyclohexylmethylketone

Equation 5.8

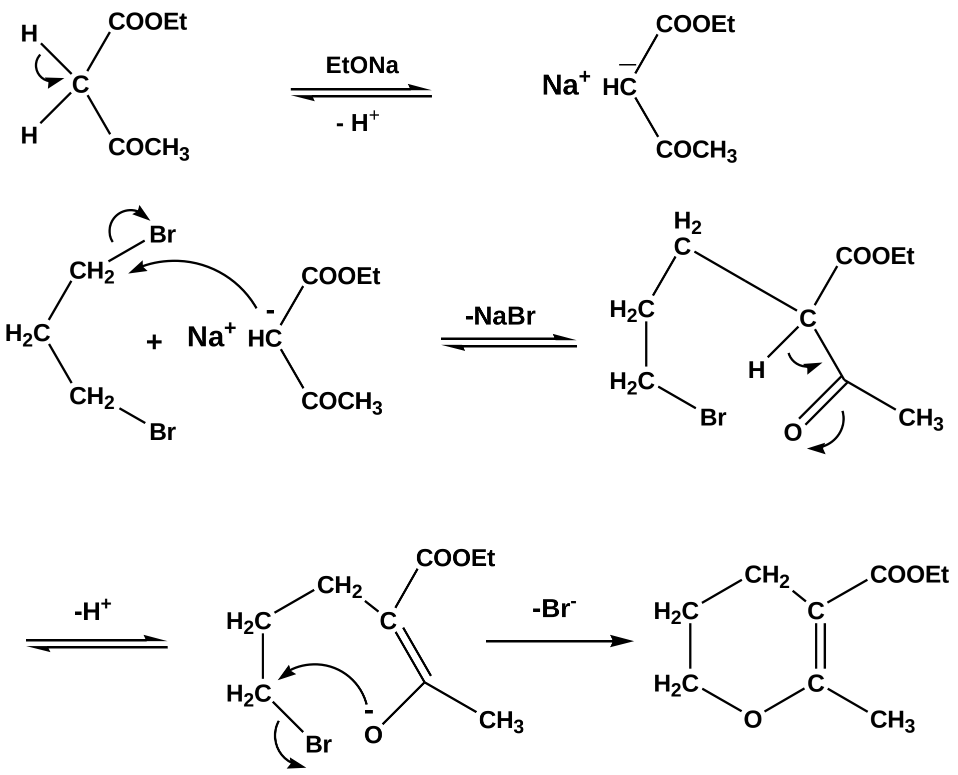
All attempts to prepare a four-membered ring result in the formation of a dihydropyran derivative (Equations 5.9).



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

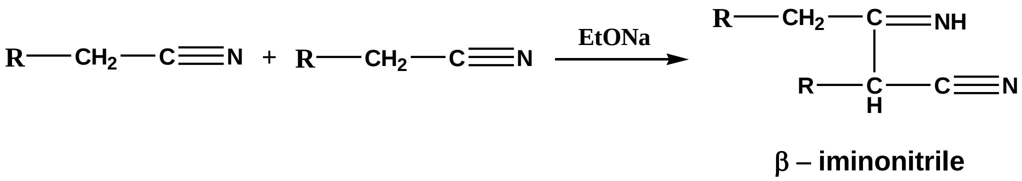
Equation 5.9

The reaction mechanism;



5. Ziegler-Thorpe reaction:

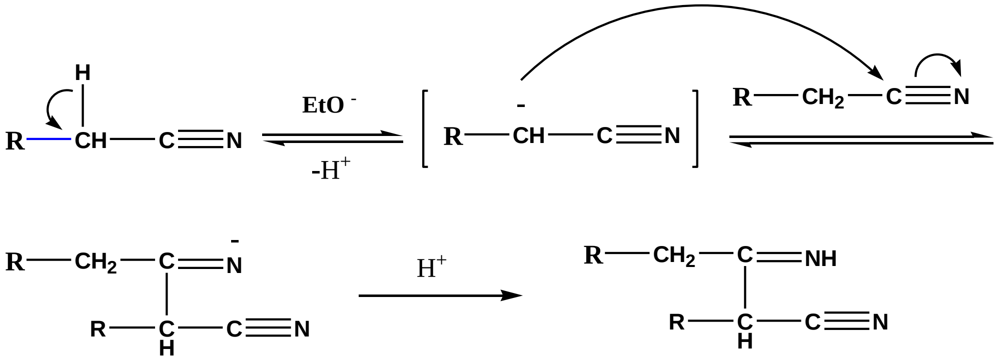
Thorpe nitrile reaction is a base catalyzed condensation of two nitrile molecules to yield a **β-iminonitrile** (Equation 5.10).



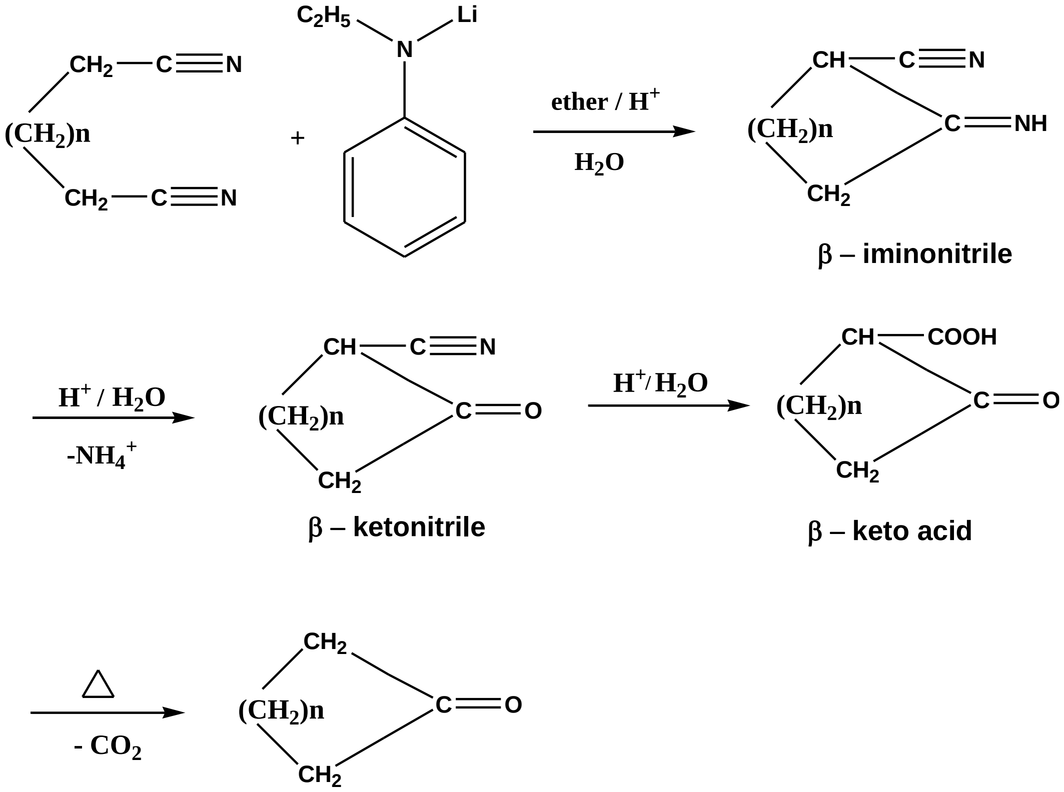
Equation 5.10

The Mechanism of this reaction shown as follows:

The reaction Mechanism;



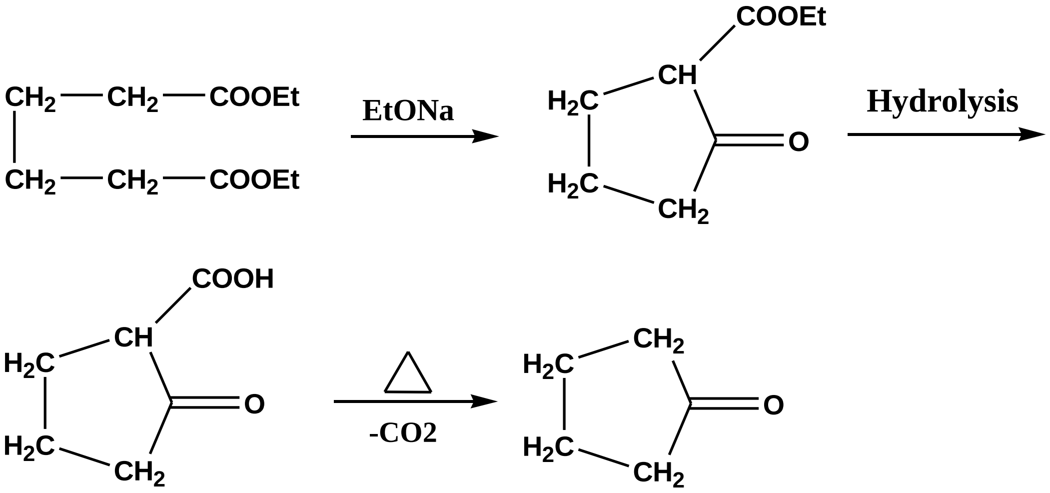
Ziegler used **Thorpe** reaction to yield a **cyclic iminonitrile** using Lithium n-ethylaniline as a basic catalyst, then the product hydrolyzed with aqueous acid to yield the **cyclic ketonitrile**. Boiling the later with aqueous acid converts the nitrile group to a carboxylic acid to yield **β-ketoacid**,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



Equation 5.11

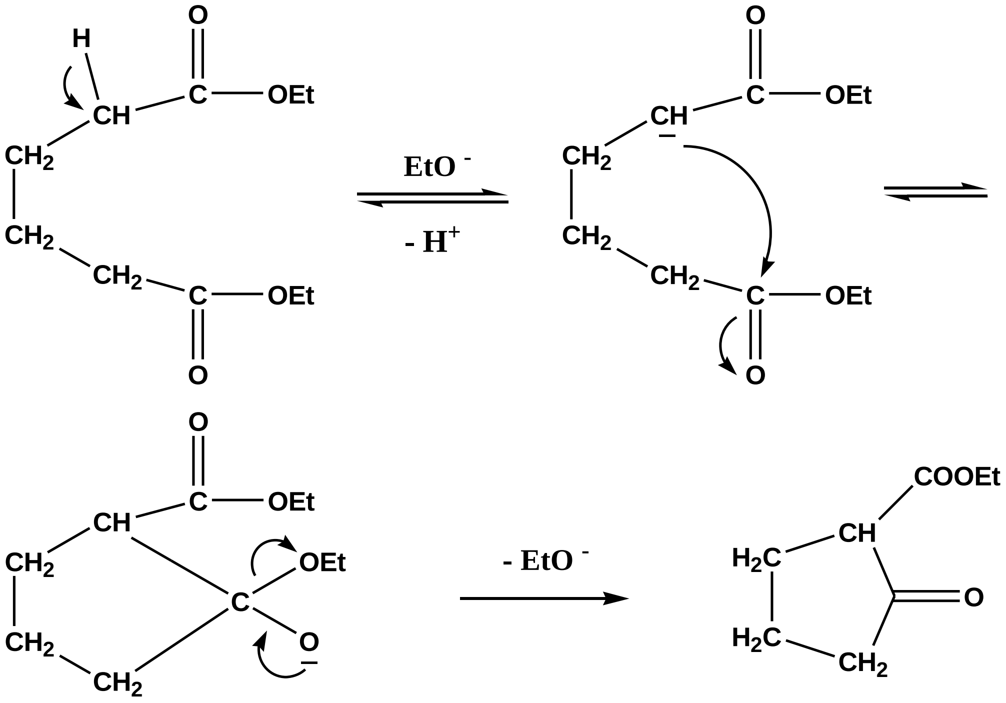
6. Dieckmann condensation:

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).

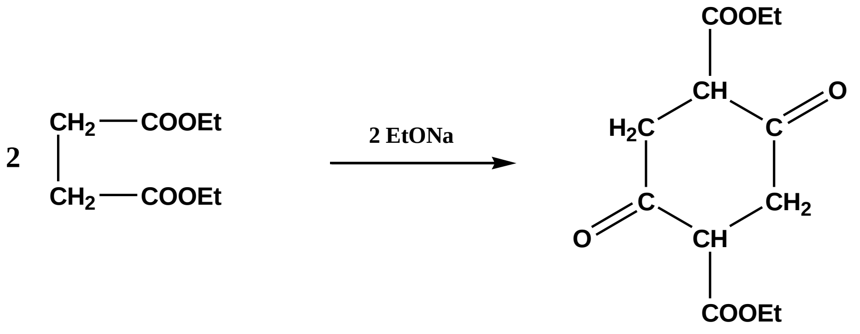


Equation 6.1

The reaction mechanism;



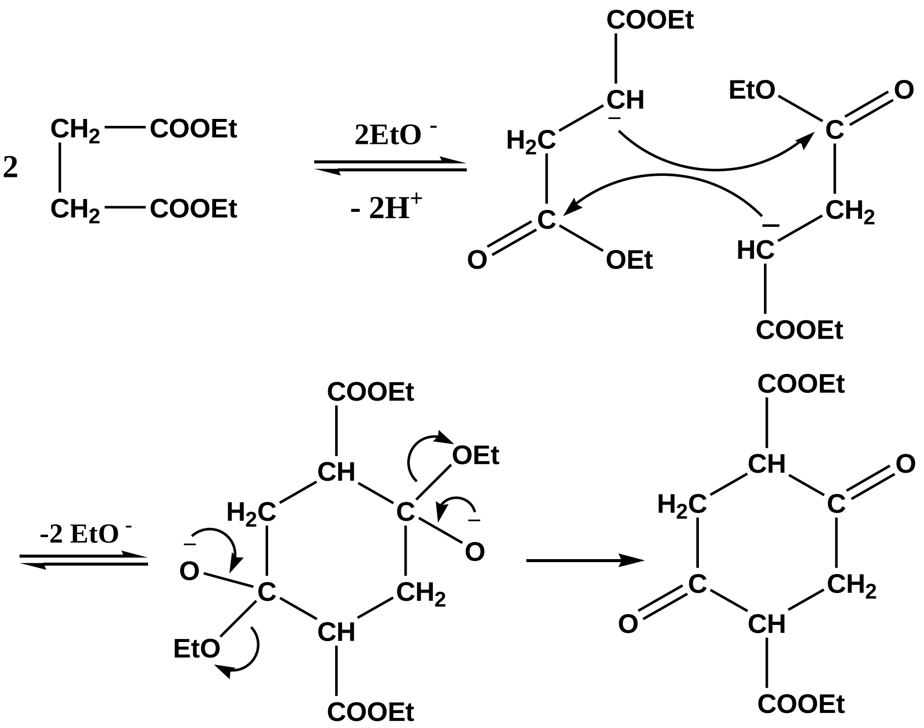
Esters lower than adipic ester may form cyclic products through the intermolecular condensation and cyclization, e. g., treatment of ethyl succinate in presence of sodium ethoxide forms succino-succinic ester (cycohexane-2,5-dione-1,4-carboxylic ester) (Equation 6.2).



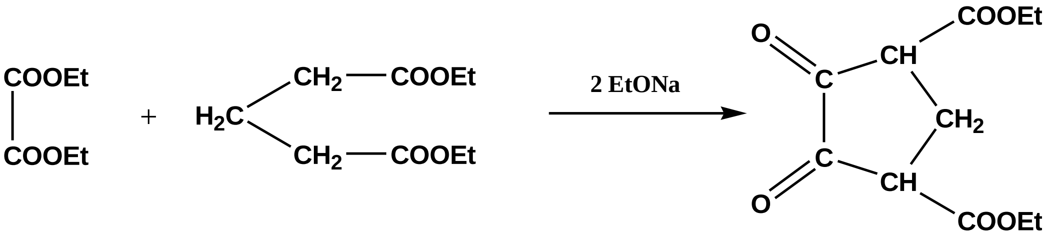
succino-succinic ester

Equation 6.2

The reaction mechanism;



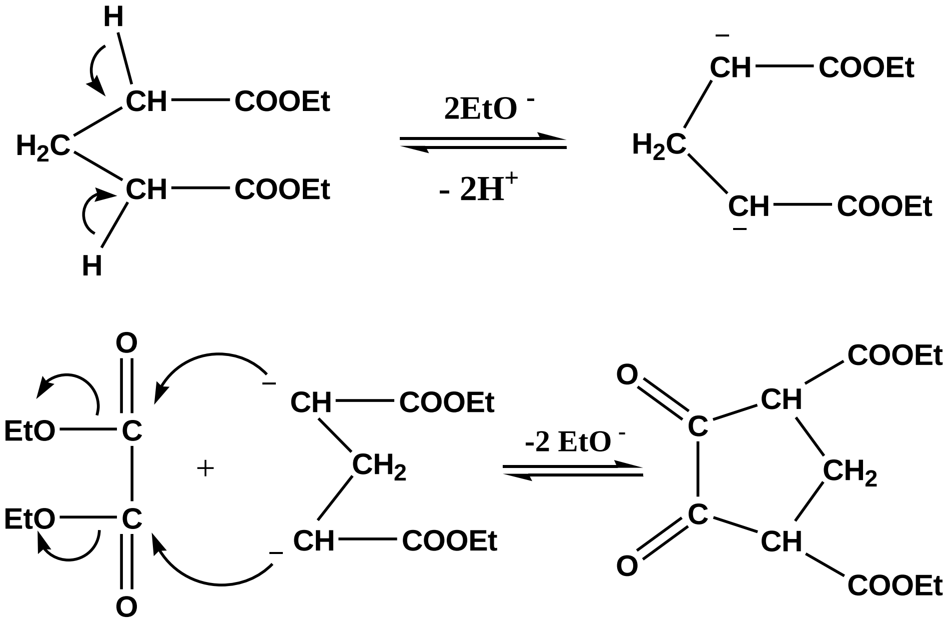
Also, five-membered ring cycloalkanes may be obtained through the intermolecular condensation between two different esters, such as, ethyl oxalate and ethyl glutarate (Equation 6.3).



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

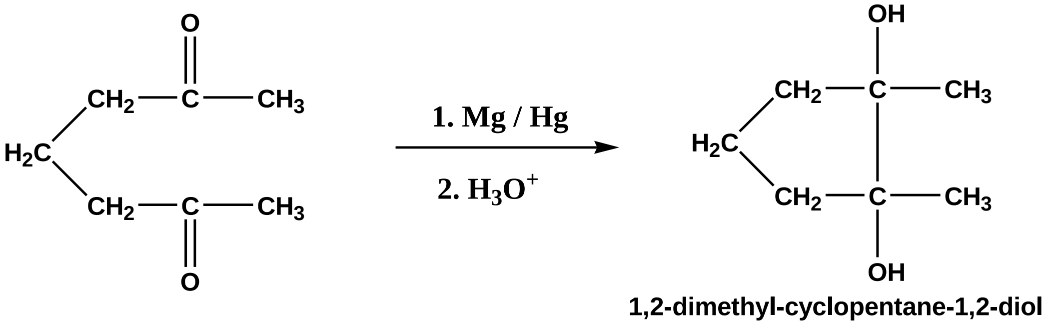
Equation 6.3

The reaction mechanism;



7. Reduction of diketones:

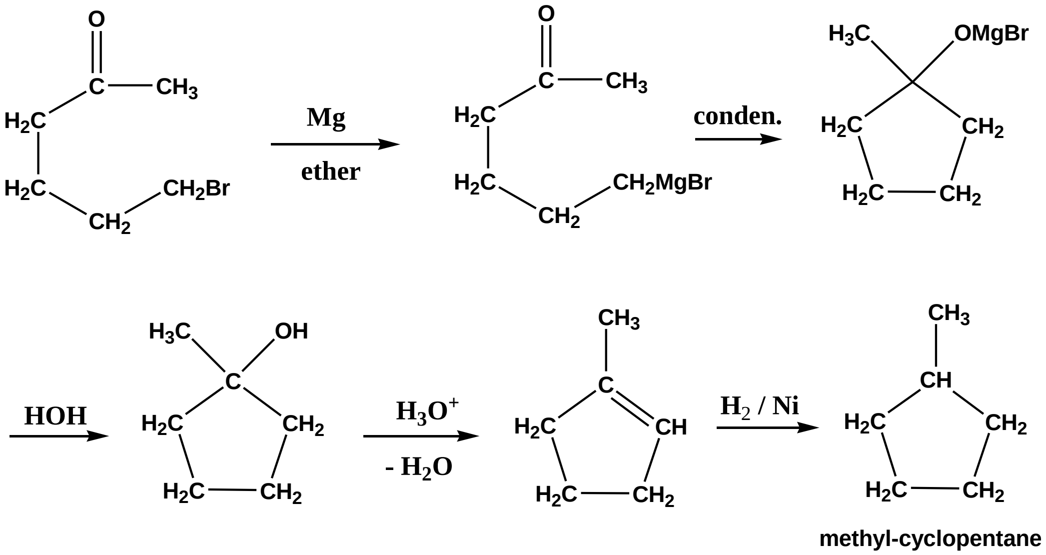
Five- or six-membered ring can be obtained through an intramolecular cyclization of certain diketones with magnesium amalgam, e. g., reduction of heptane-2,6-dione to form 1,2-dimethylcyclopentane-1,2-diol (Equation 6.4).



Equation 6.4

8. The Grignard method:

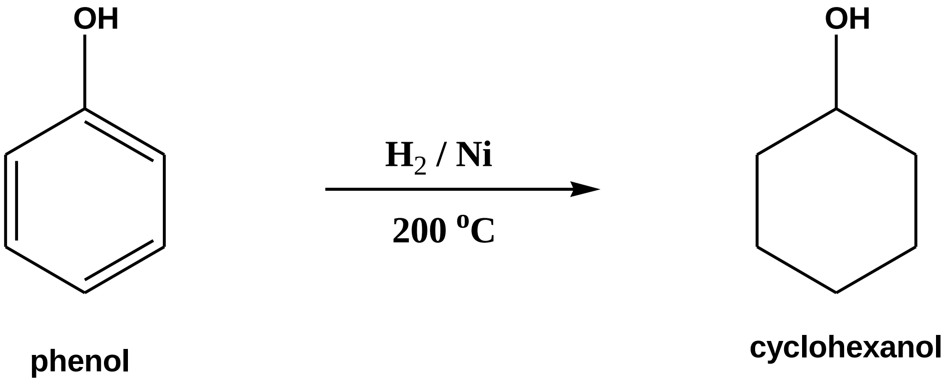
Certain halogen compounds react with magnesium which condenses internally to give cycloalkane derivatives, e. g., 6-bromo-2-hexanone reacts with **Mg** to give 1-methylcyclopentanol, which up on hydrolysis then reduction gives methylcyclopentane (Equation 6.5).



Equation 5.6

9. Reduction of benzene and its derivatives:

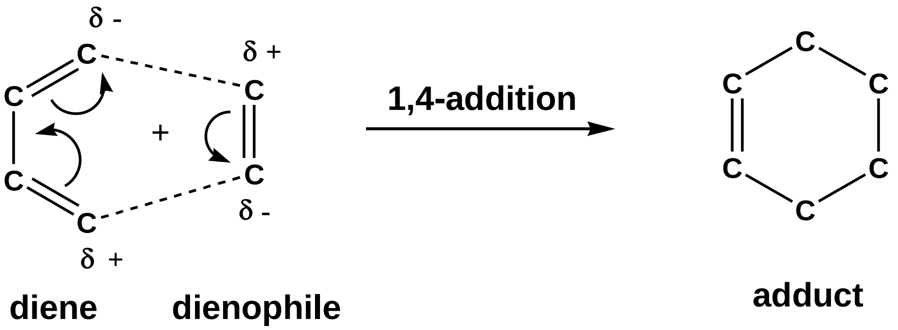
Catalytic reduction under pressure using nickel converted benzene or its derivatives into the corresponding six-membered cycloalkanes (Equation 6.6).



Equation 6.6

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

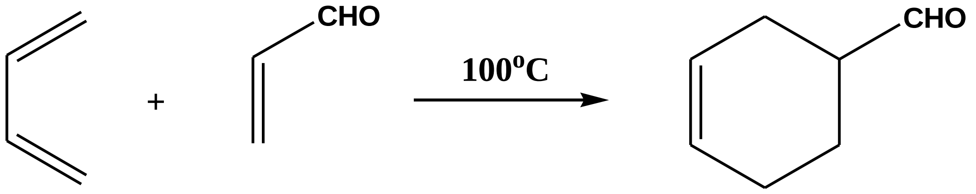
Diels-Alder reaction is an addition reaction between the diene (a compound containing conjugated double bonds) and the dienophile (unsaturated hydrocarbon) to yield a product known as the adduct. The adduct is usually a six-membered ring, the addition taking place in the 1,4-positions. In general terms,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



Equation 6.7

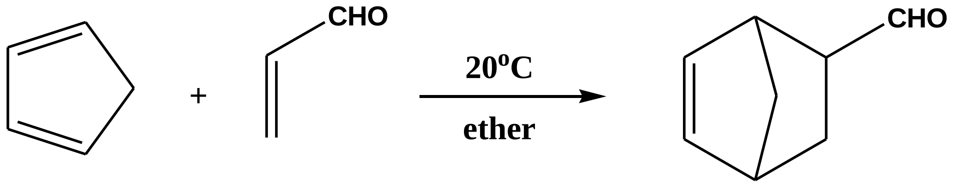
The diene may be of various types: acyclic, cyclic, semicyclic, bicyclic,

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).



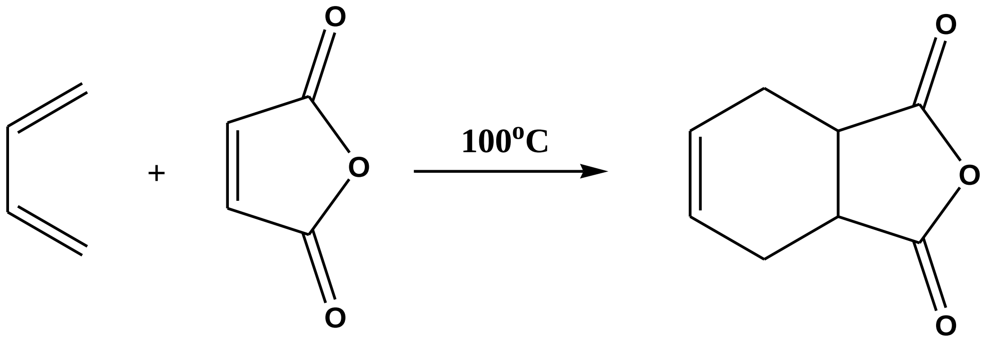
3-cyclohexene-carbaldehyde

Equation 6.8



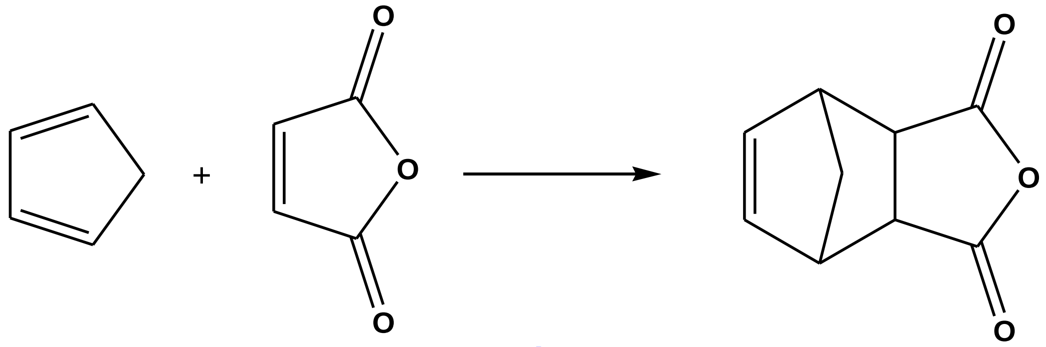
**bicyclo[2.2.1]hept-5-ene-
2-carbaldehyde**

Equation 6.9

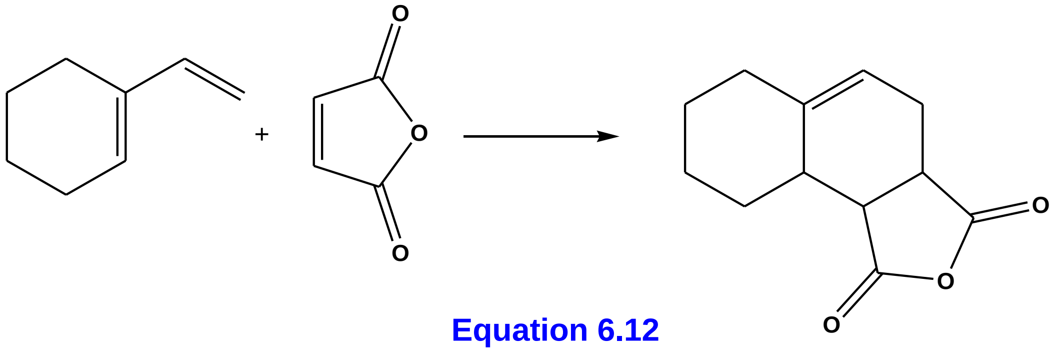


tetrahydrophthalic anhydride

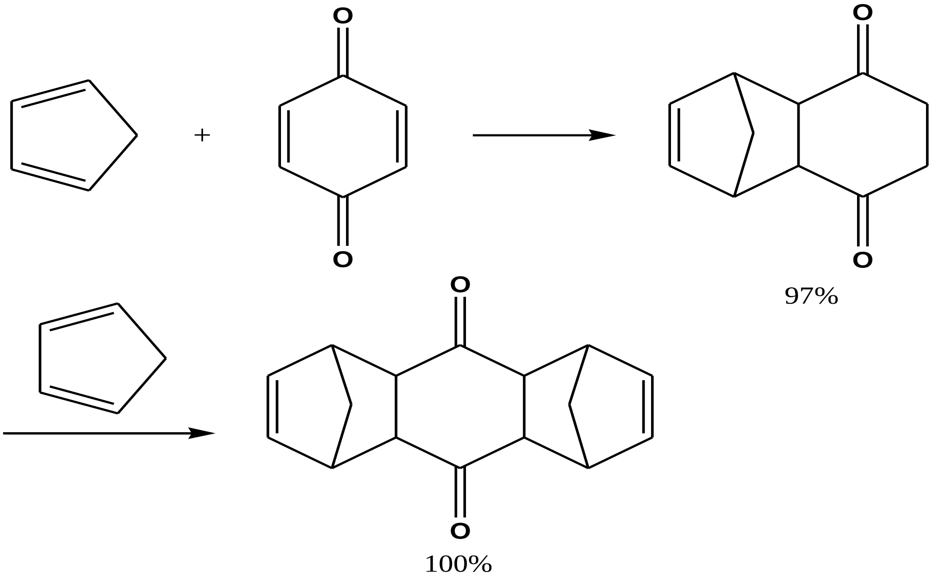
Equation 6.10



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).

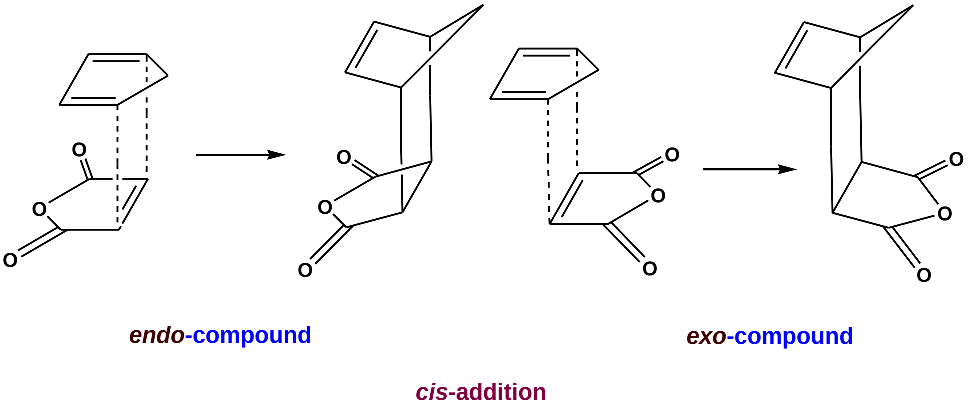


Fig. 6.14

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.

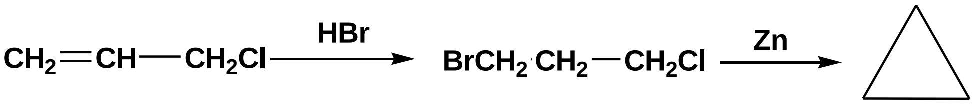
6.2 Chemical properties:

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

I- Methods of preparation:

1. Gustavson method:

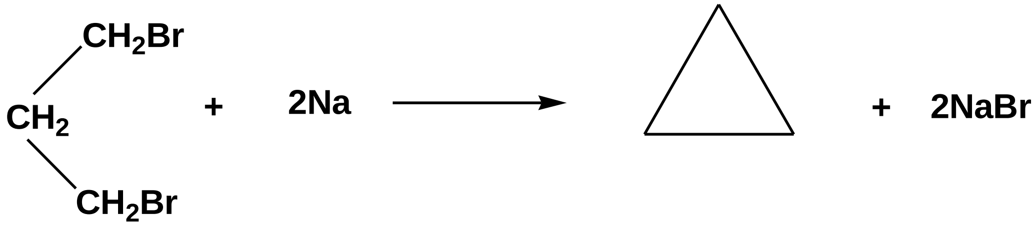
Cyclopropane is produced on an industrial scale by the action of zinc on 1,3-chlorobromo-propane, which prepared by addition of HBr to allylchloride (Equation 6.1).



Equation 6.1

2. Freund method:

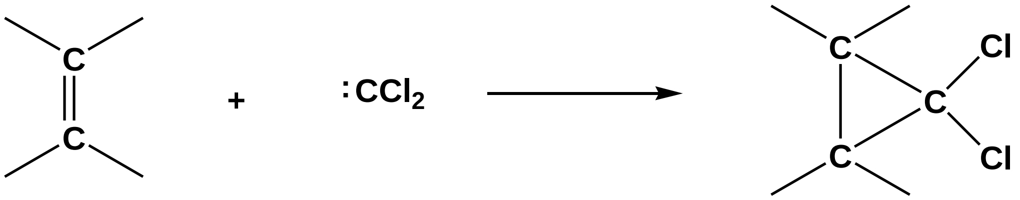
Treatment of 1,3-dibromopropane with metallic sodium gives the cyclopropane (Equation 6.2).



Equation 6.2

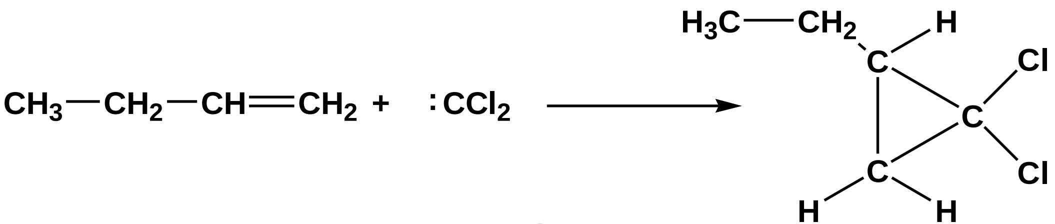
3. Action of carbenes on unsaturated compounds:

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

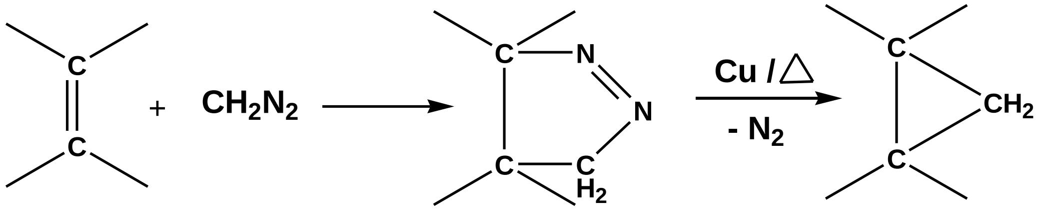
For example, (Equation 6.4).



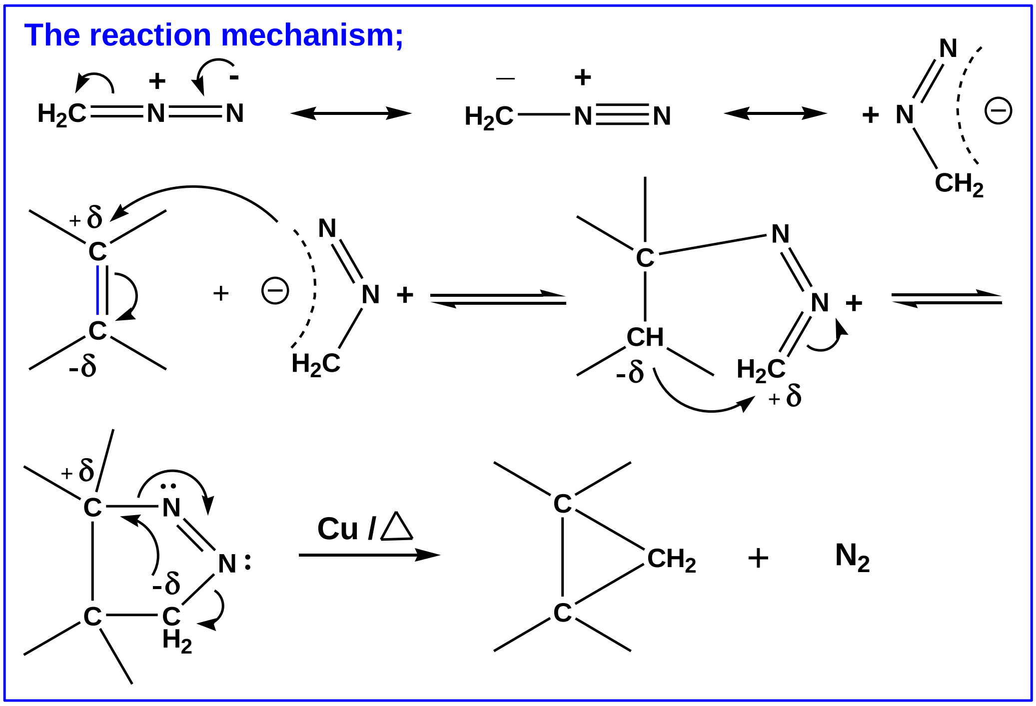
Equation 6.4

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).

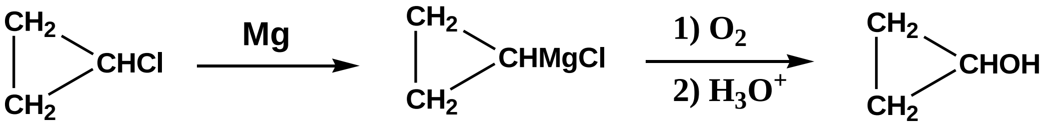


Equation 6.5



5. Synthesis of cyclopropanol:

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

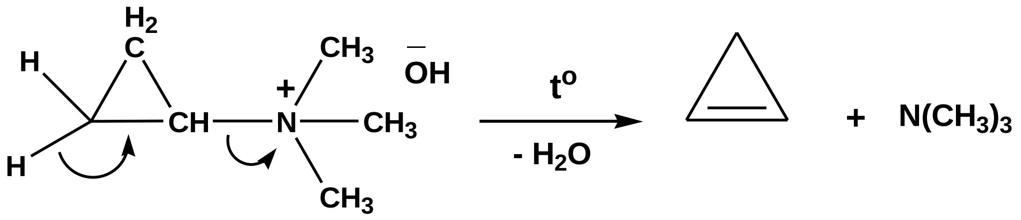


Equation 6.6

6. Synthesis of cyclopropenes:

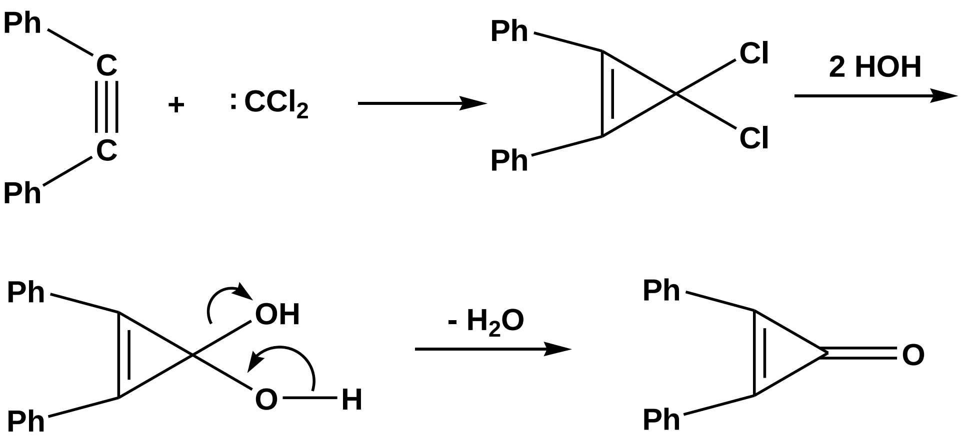
Two methods described the preparation of cyclopropene and cyclopropenenone as follows:

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



Equation 6.7

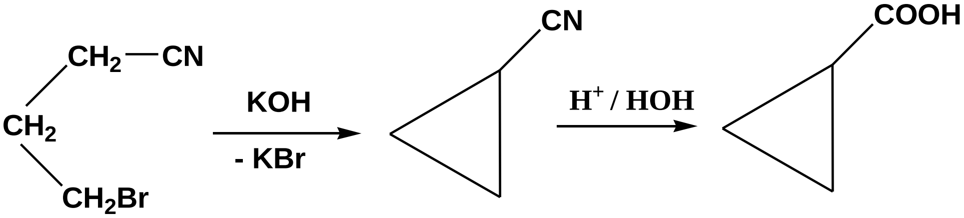
ii- Action of carbenes on acetylenes (Equation 6.8).



Equation 6.8

7. Synthesis of cyclopropanecarboxylic acid:

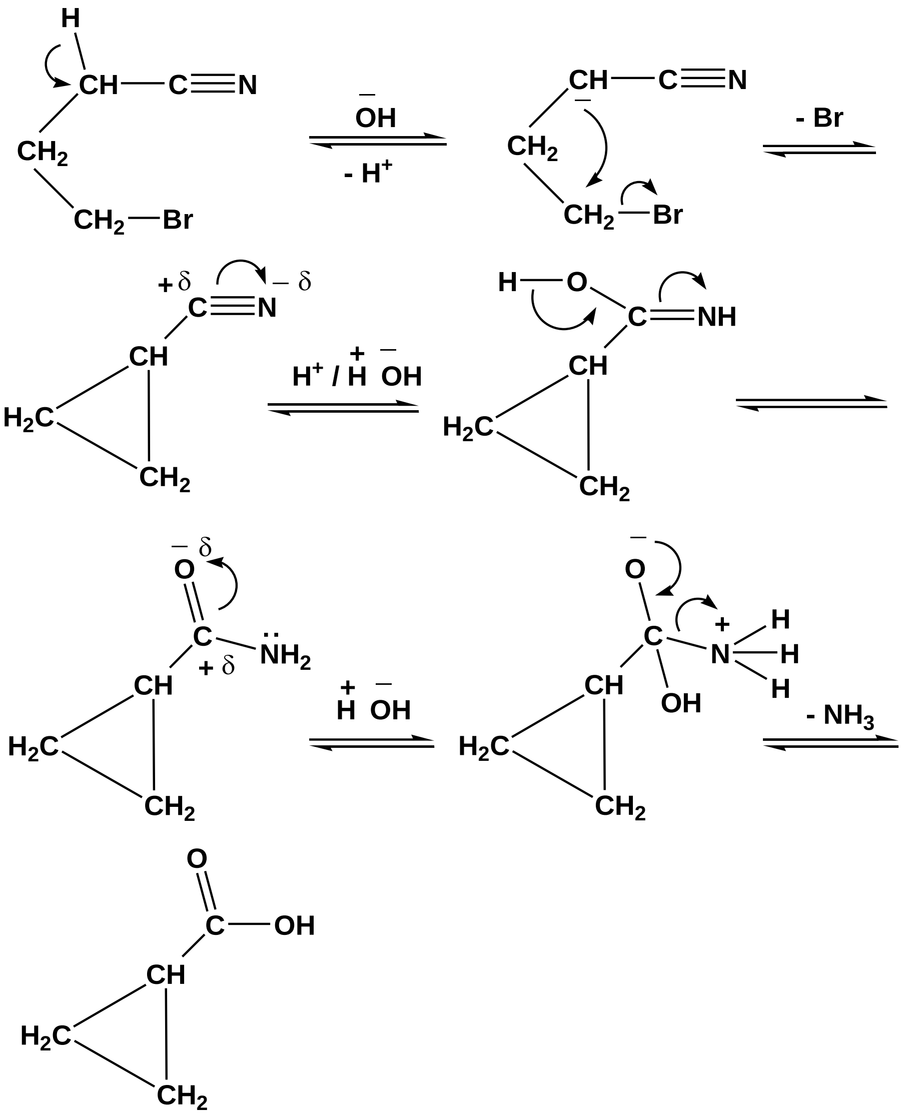
Cyclopropanecarboxylic acid has been prepared by the action of potassium hydroxide on 4-bromo-butyronitrile followed by hydrolysis of cyclopropanecarbonitrile (Equation 6.9).



cyclopropanecarboxylic acid

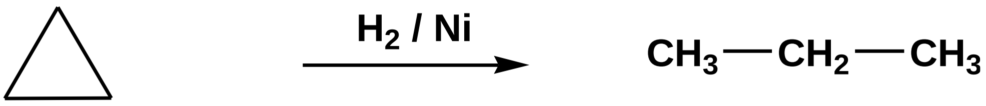
Equation 6.9

Mechanism;



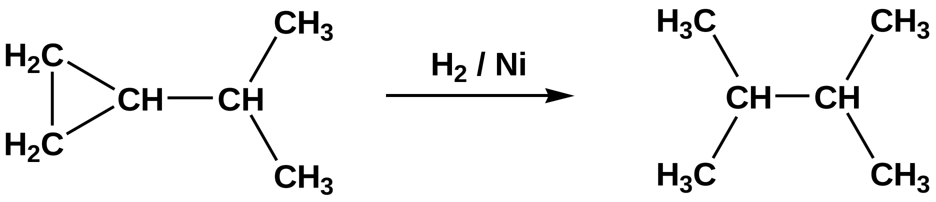
II- Chemical reactions of cyclopropane and its derivatives:

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).



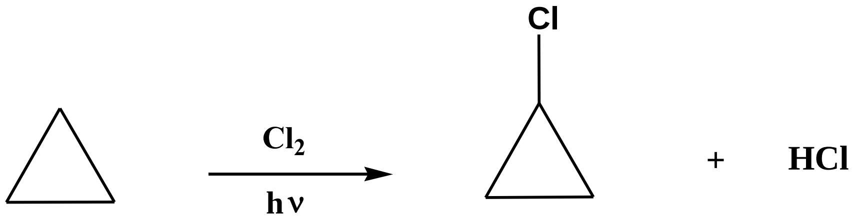
2,3-dimethyl-butane

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).

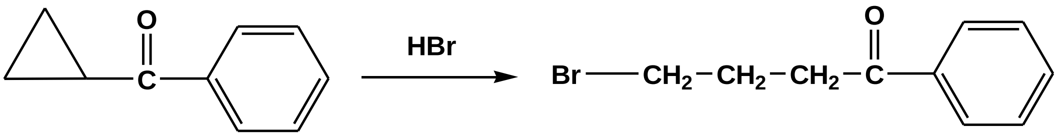


Equation 6.13

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

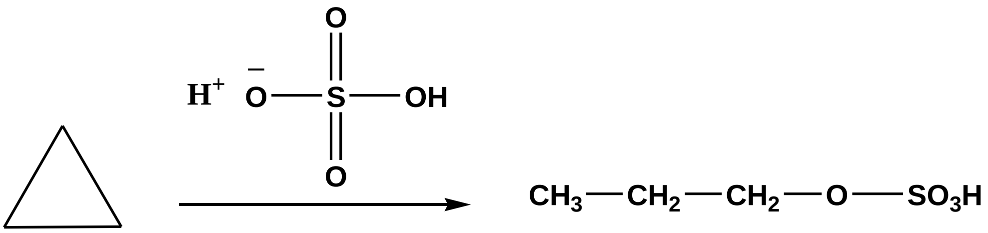
Equation 6.14

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.

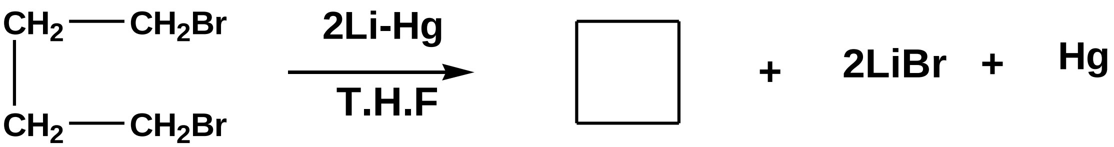
7.2 Chemical properties:

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

I- Methods of preparation:

1. Connor and Wilson reaction (1967):

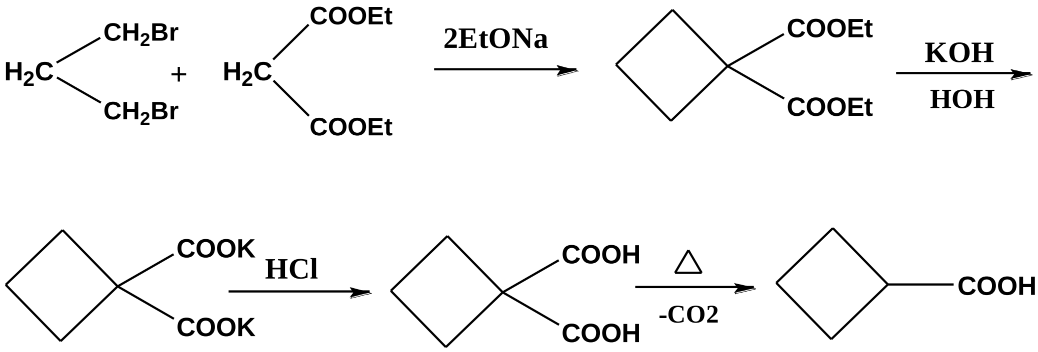
When 1,4-dibromobutane reacted with lithium amalgam in tetrahydrofuran, cyclobutane in a good yield was obtained (Equation 7.1).



Equation 7.1

2- Perkin's reaction:

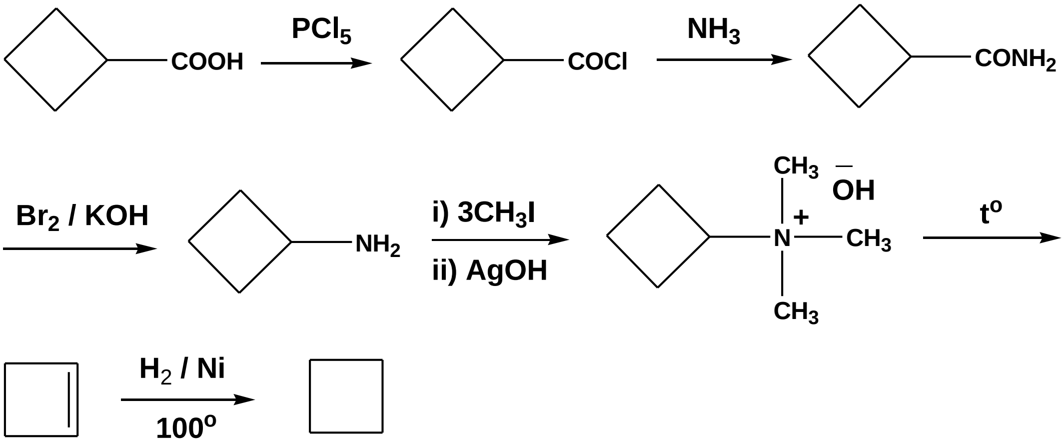
1,3-dibromobutane reacts with diethyl malonate in presence of sodium ethoxide to give cyclobutane dicarboxylic esters, which converts to cyclobutanecarboxylic acid (Equation 7.2).



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).



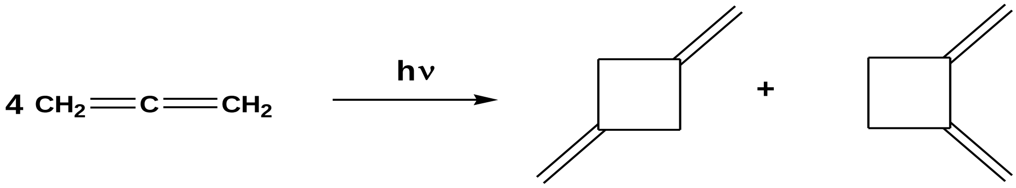
Equation 7.3

4- By photochemical reactions:

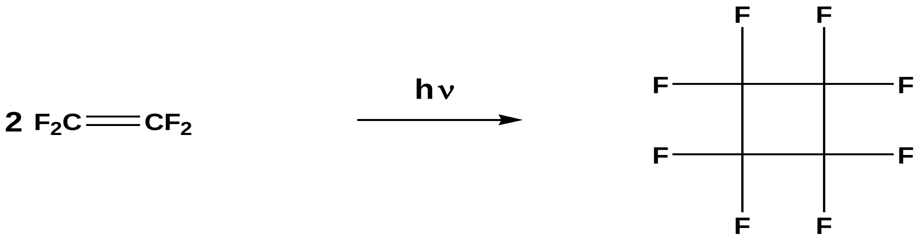
Cyclobutane or its derivatives can be prepared photochemically according to the following methods:

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).

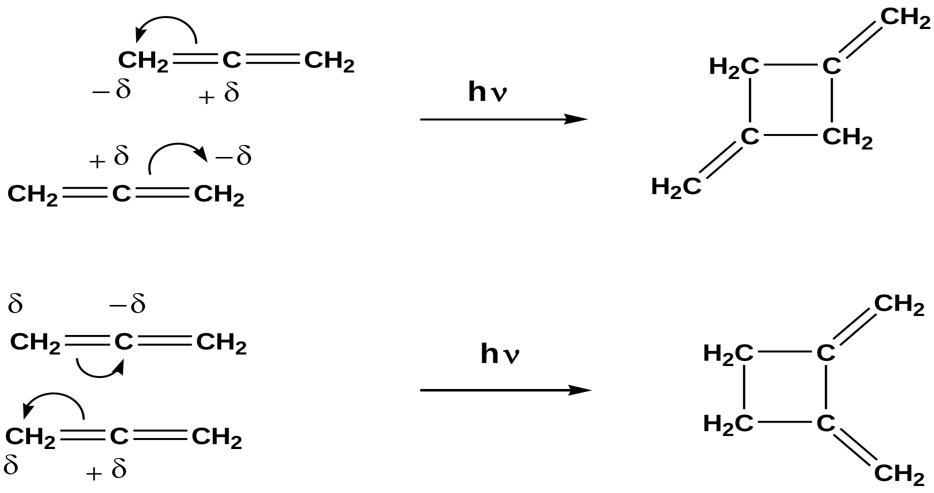


Equation 7.4



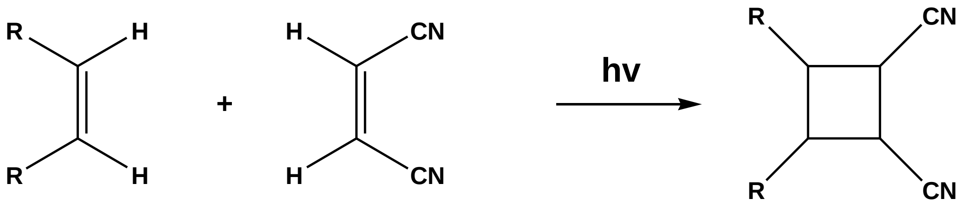
Equation 7.5

The reaction Mechanism;

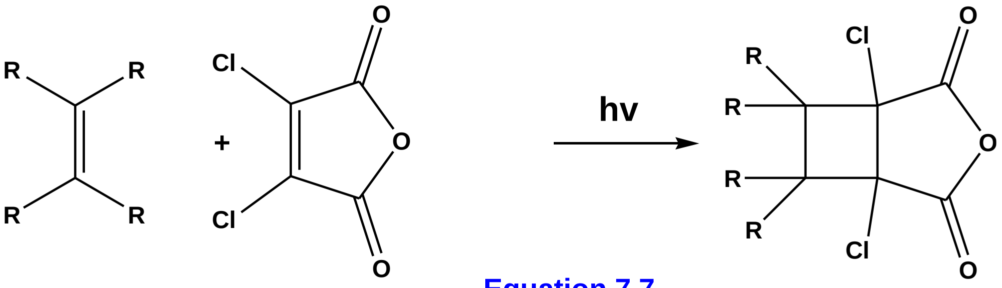


b- Olefin- Olefin addition:

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).



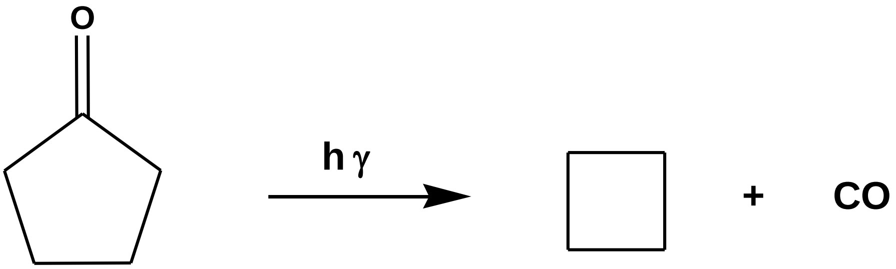
Equation 7.6



Equation 7.7

c- Proteolysis of cyclopentanone:

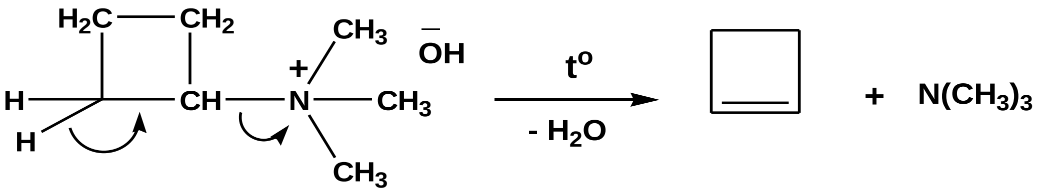
cyclobutane and carbon monoxide are the products of the proteolysis of cyclopentanone (Equation 7.8).



Equation 7.8

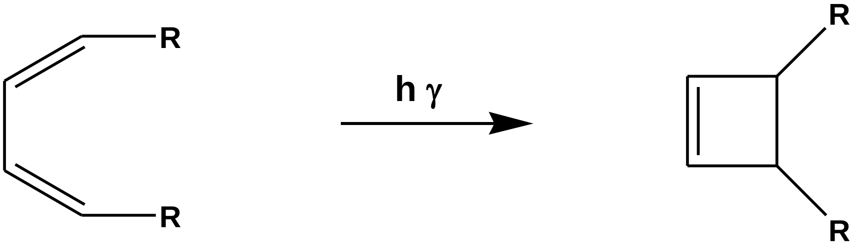
5- Preparation of cyclobutenes:

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).

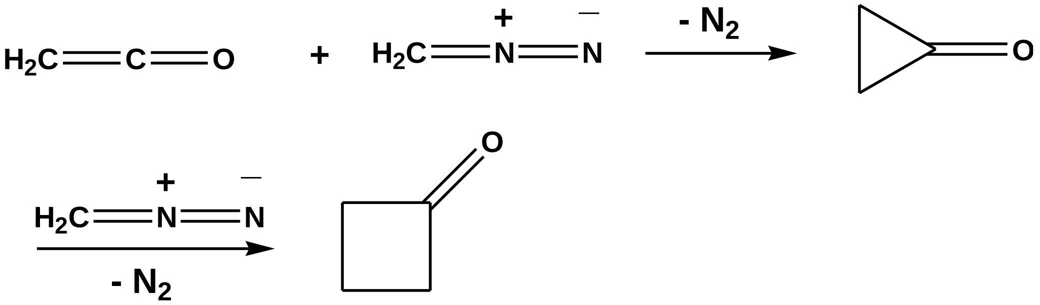


Equation 7.10

6- Carbonyl compounds of cyclobutane:

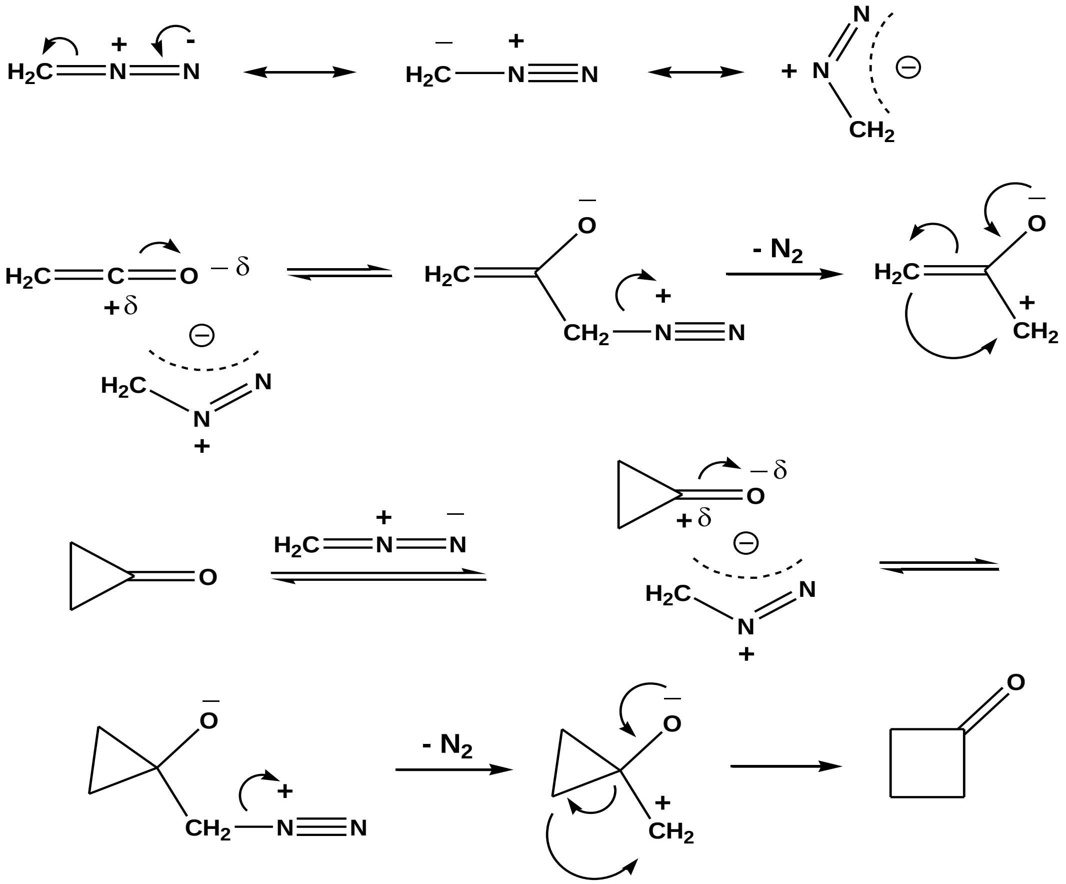
a- Cyclobutanone:

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



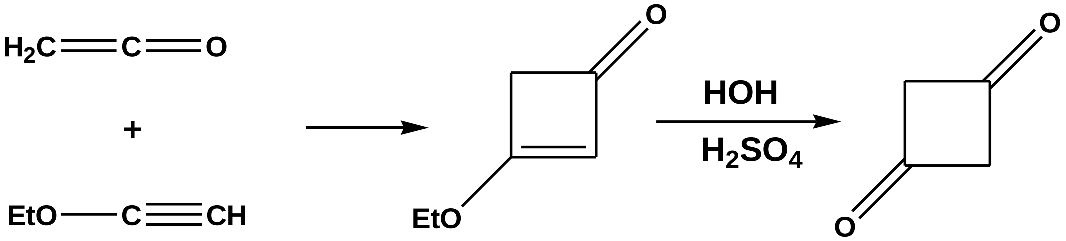
Equation 7.11

The reaction mechanism;



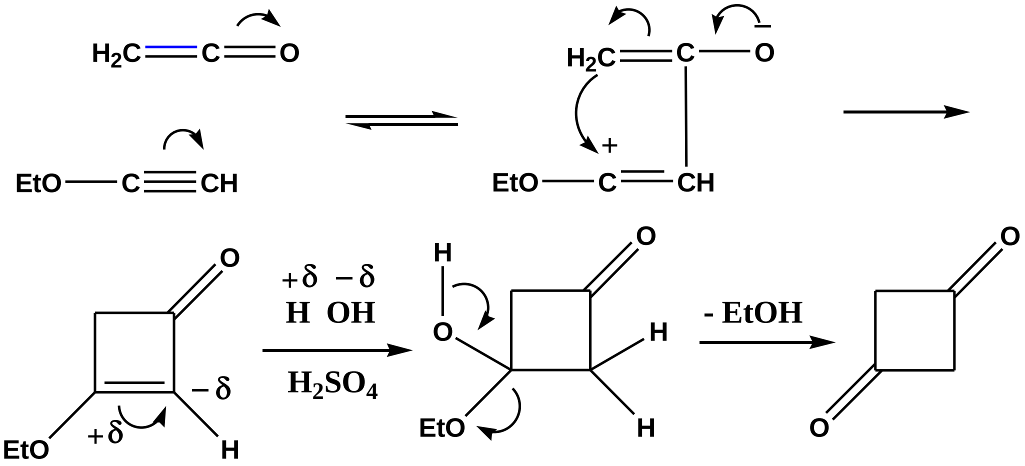
b- Cyclobutanedione:

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



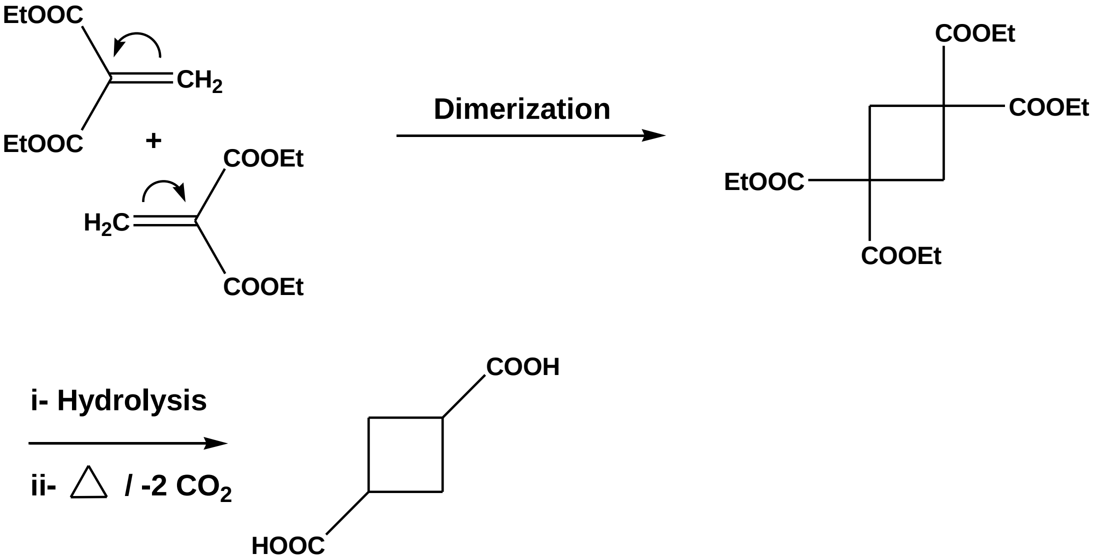
Equation 7.12

The reaction mechanism;



7- Cyclobutanecarboxylic acids:

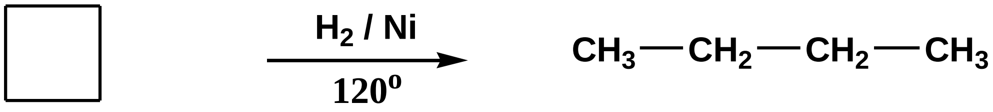
Cyclobutane-1,3-dicarboxylic acid as an example was prepared by the dimerization of 2-methylene-malonic acid diethyl ester (Equation 7.13).



Equation 7.13

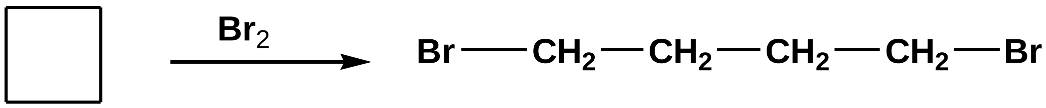
II- Chemical reactions of cyclobutane and its derivatives:

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).

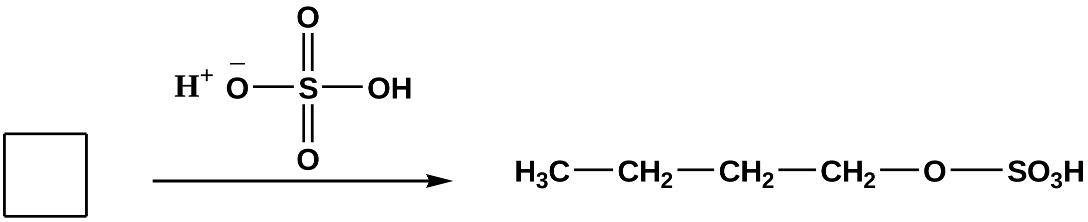


Equation 7.15

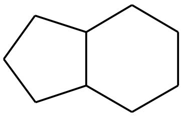
3- Hydrohalogenation: Cyclobutane reacts with hydrogen bromide to give the bromobutane (Equation 7.16).

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.

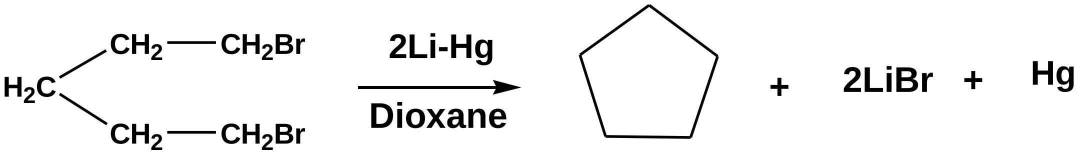
8.2 Chemical properties:

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

I- Methods of preparation:

1. Connor and Wilson reaction:

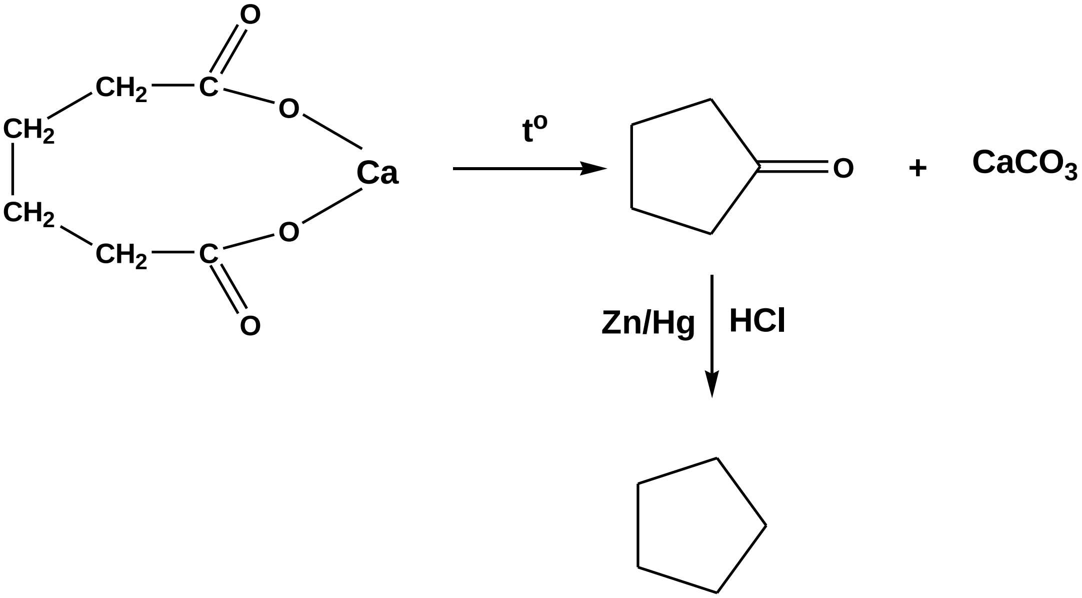
Action of lithium amalgam on a dioxane solution of 1,5-dibromopentane can give cyclopentane in 75% yield (Equation 8.1).



Equation 8.1

2. Pyrolysis of calcium salt of adipic acid:

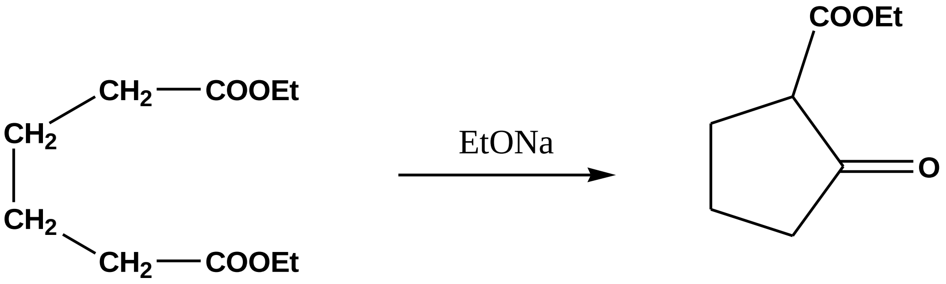
This method can be used to synthesize cyclopentanone with good yield under pyrolysis of the calcium adipate. Cyclopentanone may be converted into cyclopentane by means of the Clemmenson reduction (Equation 8.2).



Equation 8.2

3. Dieckmann condensation:

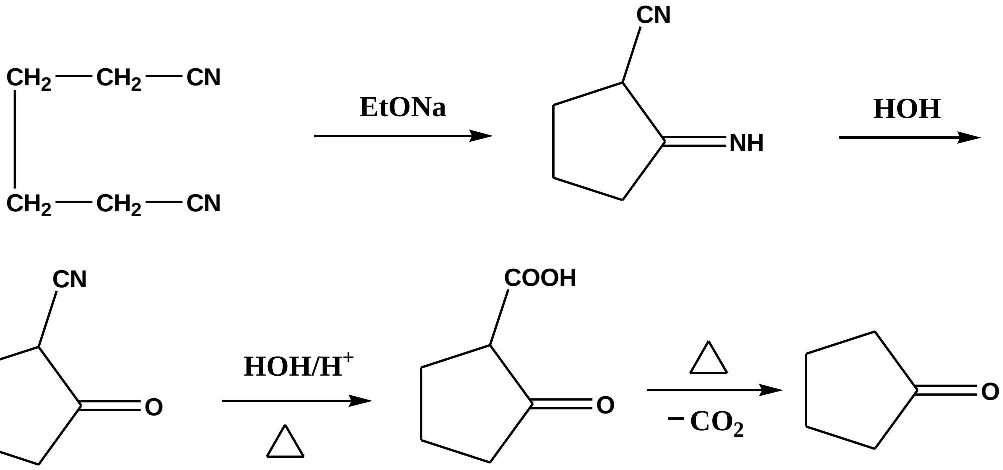
Treatment of diethyl adipate with excess of sodium ethoxide can give 2-cyclopentanonecarboxylic acid ethyl ester (Equation 8.3).



Equation 8.3

4. Ziegler-Thorpe reaction:

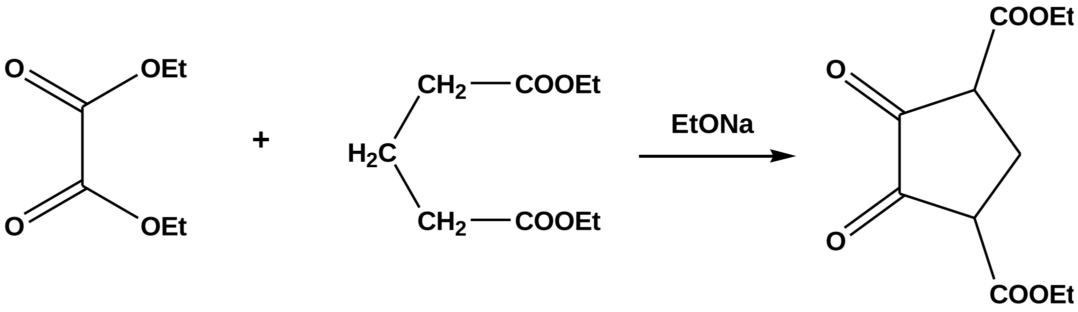
Condensation of hexanedinitrile in presence of sodium ethoxide gives 2-cyclopentanonecarbonitrile, which up-on hydrolysis affords 2-cyclopentanonecarboxylic acid. Decarboxylation of the later gives cyclopentanone (Equation 8.4).



Equation 8.4

5. Condensation of oxalic ester with glutatric ester:

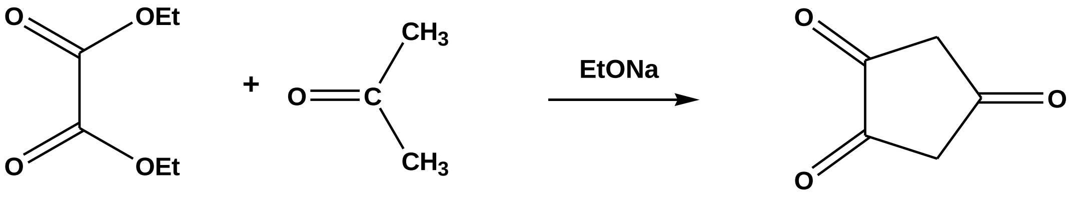
Treatment of ethyl oxalate with ethyl glutrate in presence of sodium ethoxide gives cyclopentan-4,5-dione-1,3-dicarboxylic acid diethyl ester (Equation 8.5).



Equation 8.5

6. Condensation of oxalic ester with acetone:

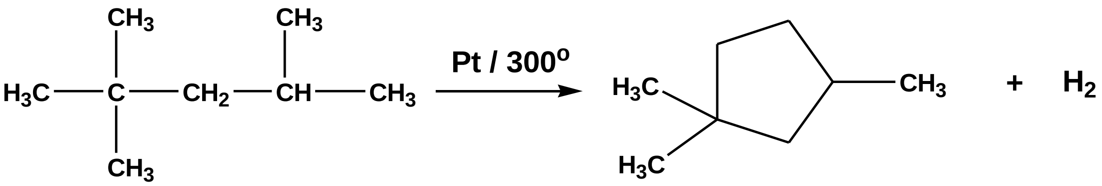
Treatment of acetone with ethyl oxalate in presence of sodium ethoxide gives cyclopentane-1,2,4-trione (Equation 8.6).



Equation 8.6

7. Dehydrocyclization of hydrocarbon chains:

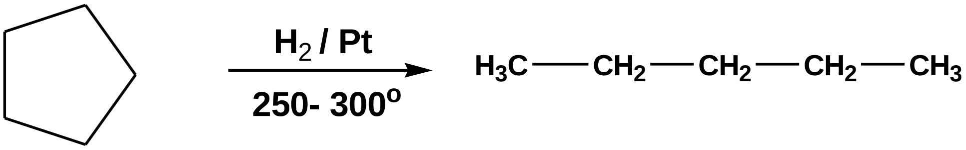
When a five carbon atoms chain contains a quaternary carbon atom is passed over a platinium catalyst at 300 ^oC, cyclopentane derivative was obtained (Equation 8.7).



Equation 8.7

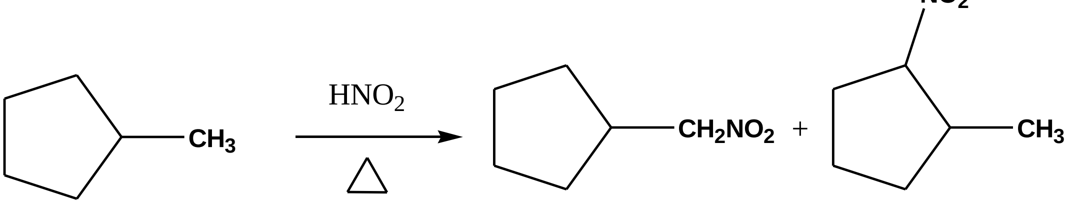
II- Chemical reactions of cyclopentane and its derivatives:

1. Hydrogenation: cyclopentane undergoes hydrogenation over platinium at 250-300 ^{o}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).

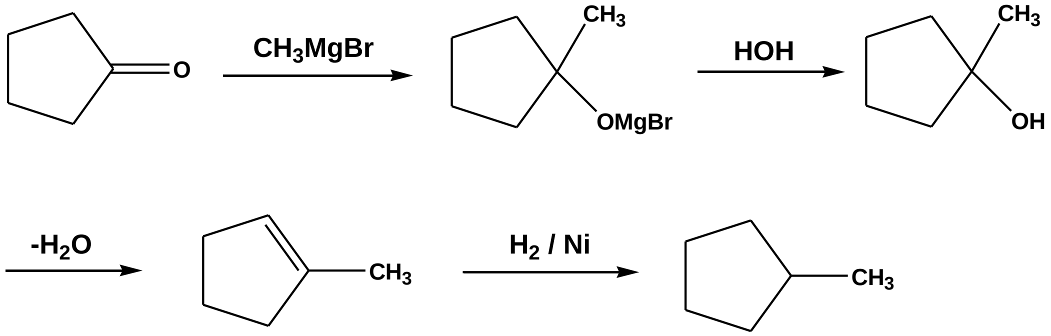


Equation 8.9

3. Cyclopentanone:

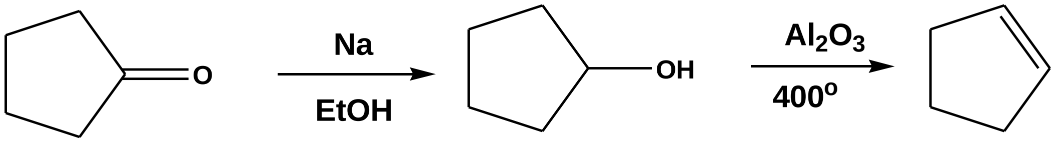
a- Grignard reaction: treatment of cyclopentanone with Grignard reagent (CH_3MgBr) followed by hydrolysis gives 1-

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



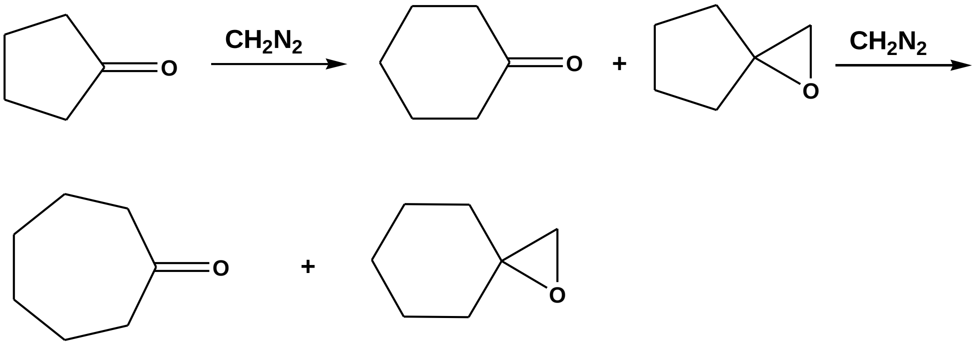
Equation 8.10

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



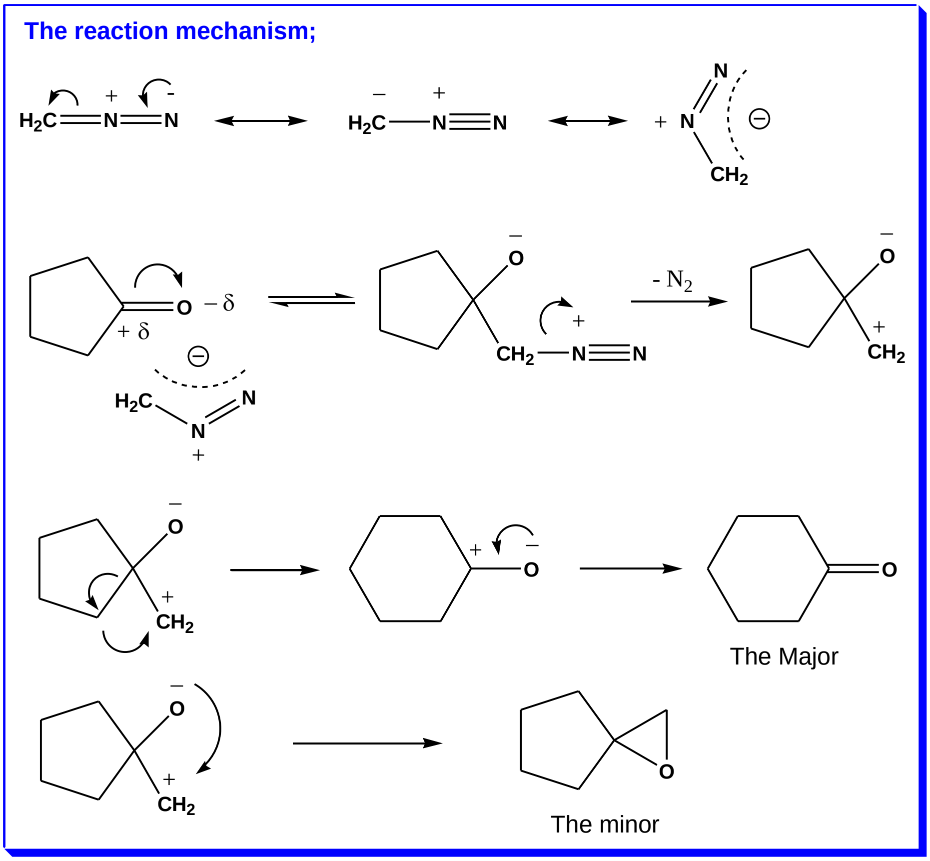
Equation 8.11

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);

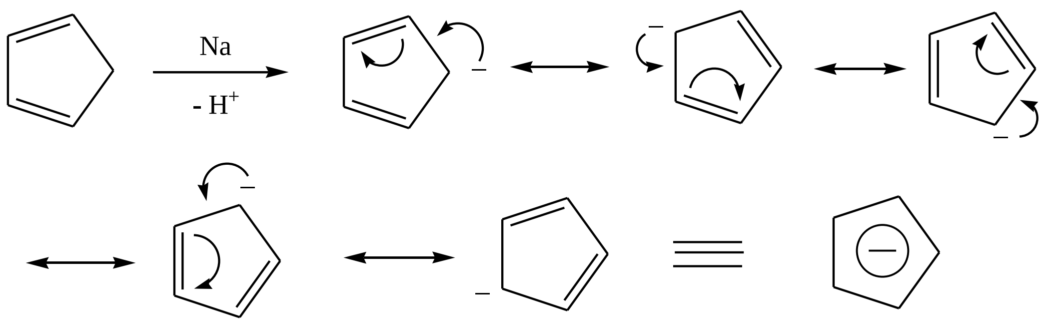
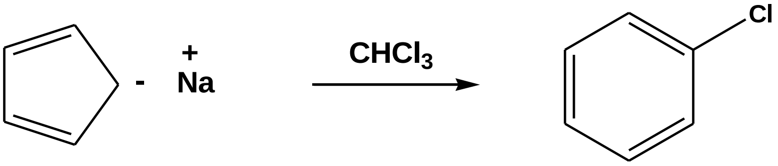


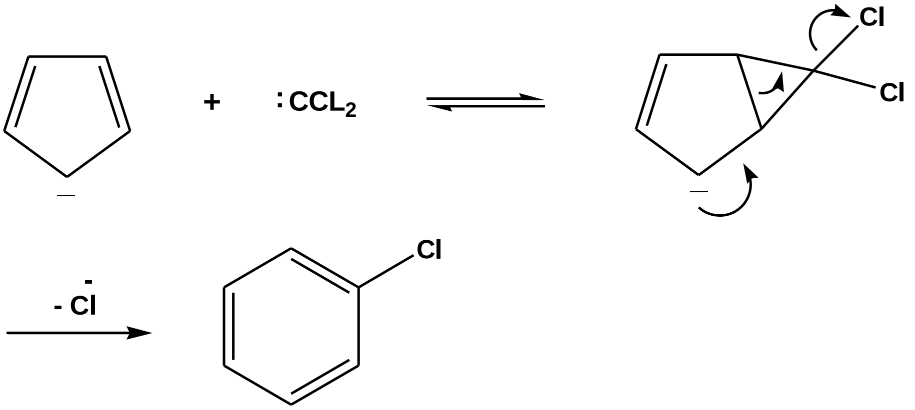
Figure 8.13

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

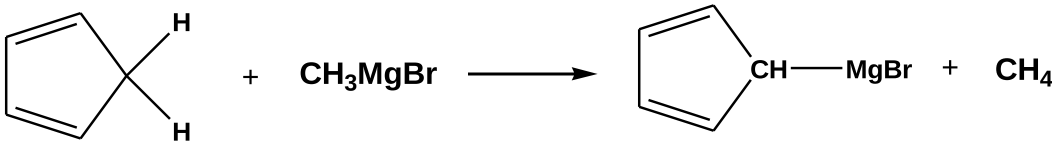


Equation 8.14

The reaction mechanism;

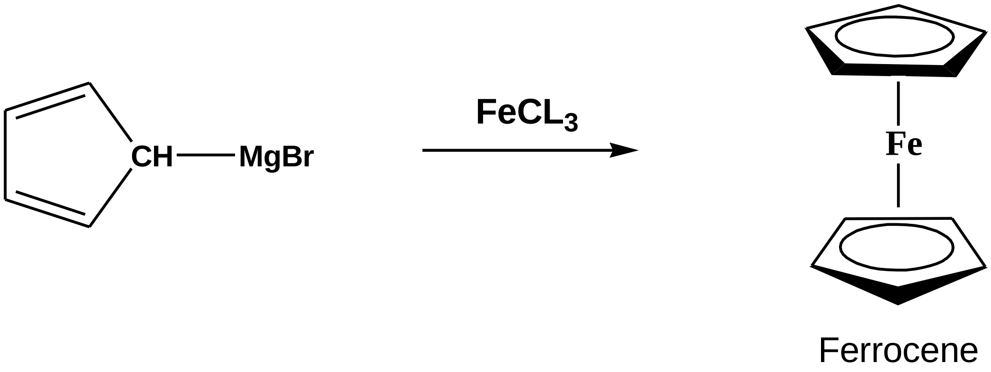


b- Grignard reaction: cyclopentadiene reacts with Grignard reagents to form cyclopentadienyl magnesium halide and the corresponding hydrocarbon (Equation 8.15).



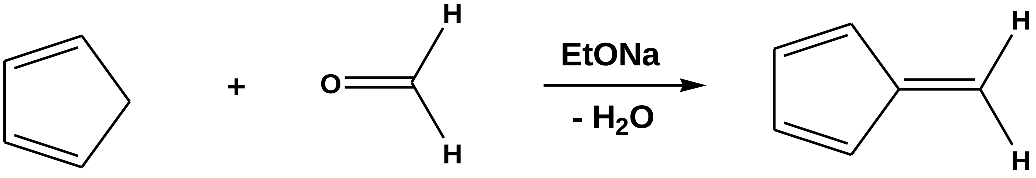
Equation 8.15

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).



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.

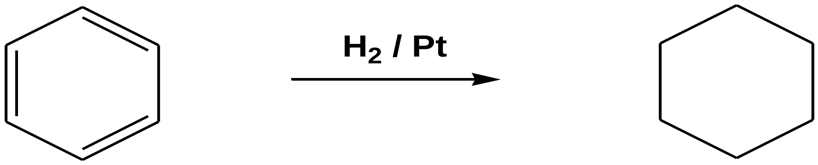
9.2 Chemical properties:

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

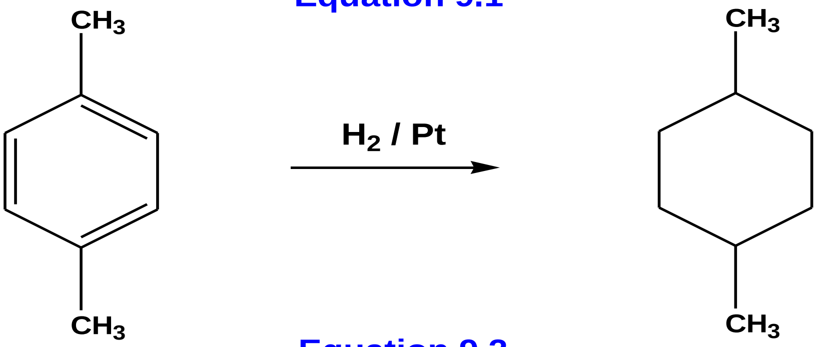
I- Methods of preparation:

1. Hydrogenation of benzene and its derivatives:

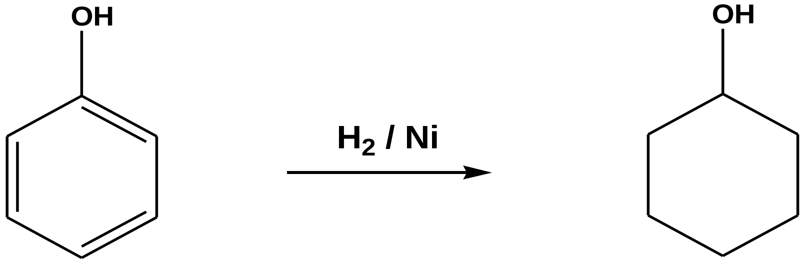
Cyclohexane is prepared commercially by catalytic hydrogenation of benzene. Certain derivatives of cyclohexane are mainly prepared by catalytic hydrogenation of certain aromatic compounds over platinum or nickel (Equations 9.1-9.4).



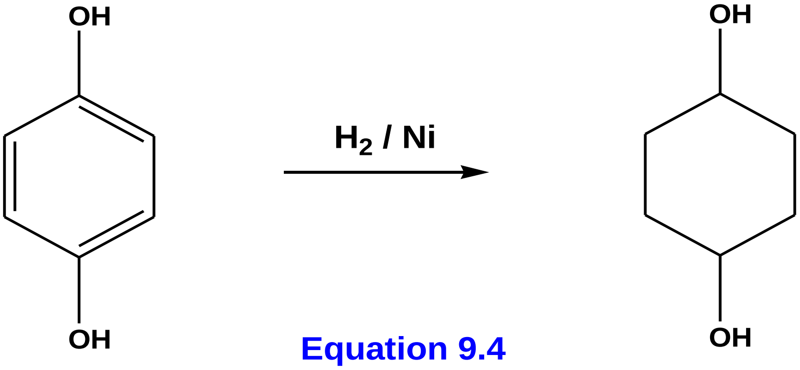
Equation 9.1



Equation 9.2



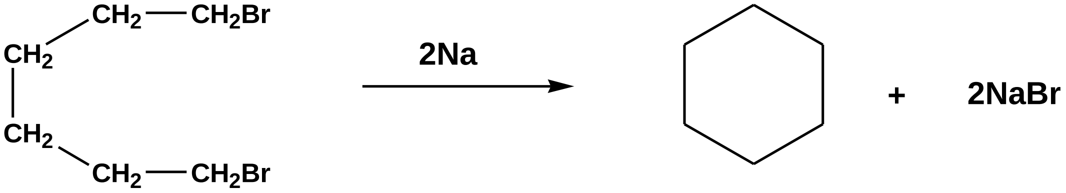
Equation 9.3



Equation 9.4

2- Freund reaction:

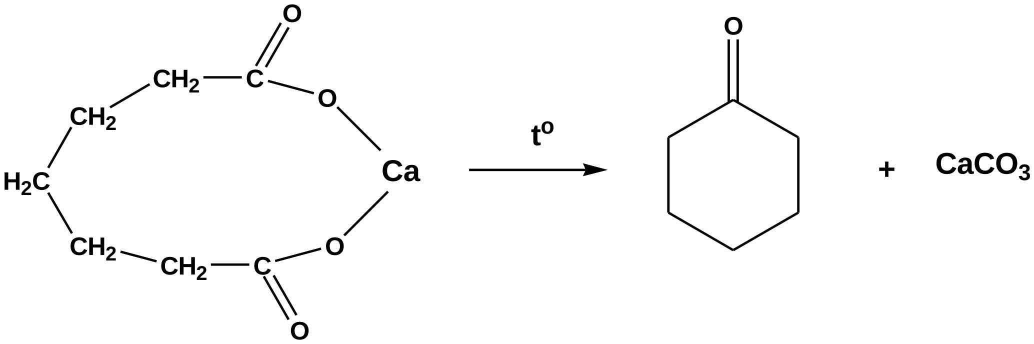
Treatment of 1,6-dibromohexane with a metal like sodium or zinc gives cyclohexane (Equation 9.5).



Equation 9.5

3. Pyrolysis of calcium salt of pimelic acid:

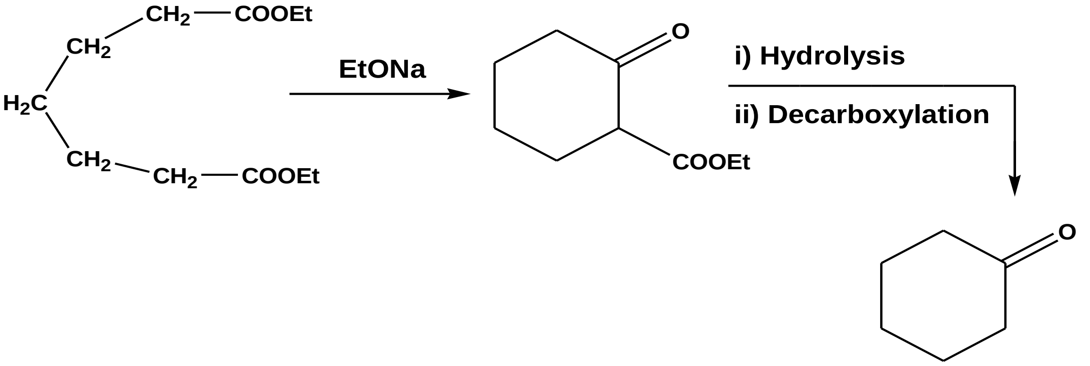
Cyclohexanone can be obtained under the pyrolysis of calcium pimelate (Equation 9.6).



Equation 9.6

4. Dieckmann condensation:

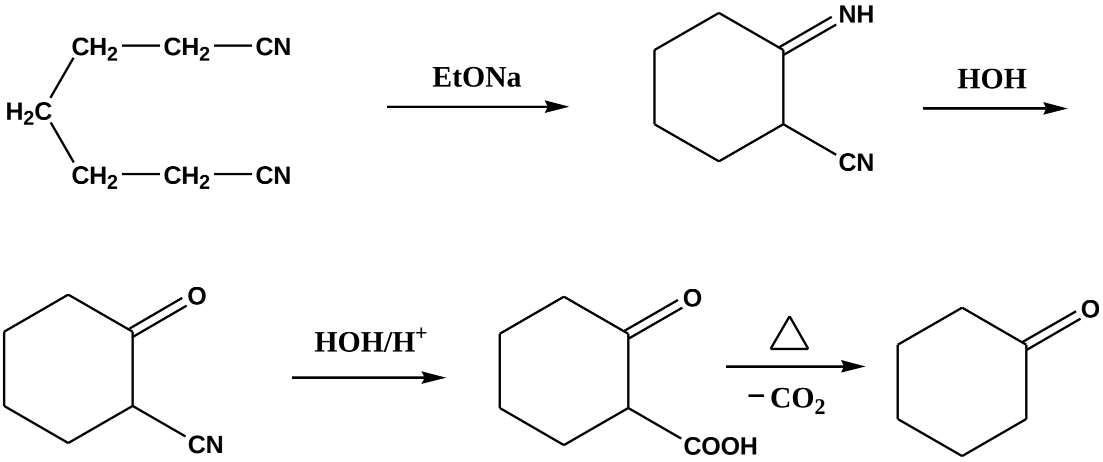
Treatment of diethyl pimelate with sodium ethoxide can give 2-cyclohexanonecarboxylic acid ethyl ester, which upon hydrolysis and decarboxylation turns to cyclohexanone (Equation 9.7).



Equation 9.7

5. Ziegler-Thorpe reaction:

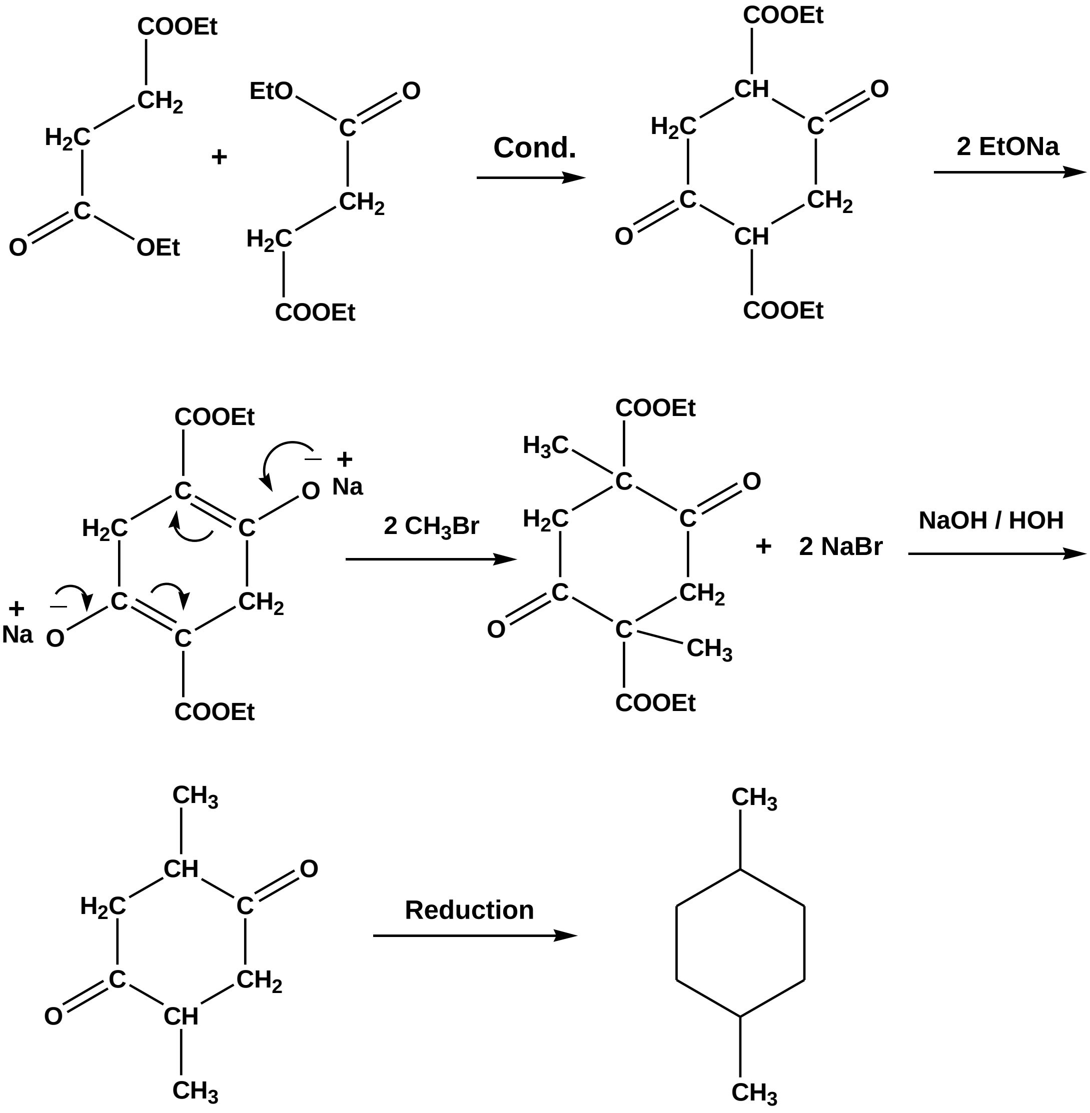
When heptanedinitrile treated with sodium ethoxide followed by hydrolysis affords 2-cyclohexanonecarbonitrile. After hydrolysis and decarboxylation of the later, cyclohexanone was obtained (Equation 9.8).



Equation 9.8

6. Ester condensation of succinic ester:

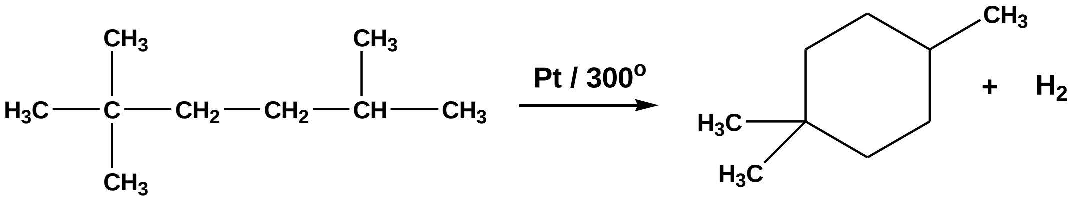
Condensation of two molecules of diethylsuccinate in presence of sodium ethoxide gives succinosuccinic ester. The sodium salt of the later was treated with alkyl halide followed by saponification and then finally Clemmenson reduction to afford 1,4-disubstituted-cyclohexane (Equation 9.9).



Equation 9.9

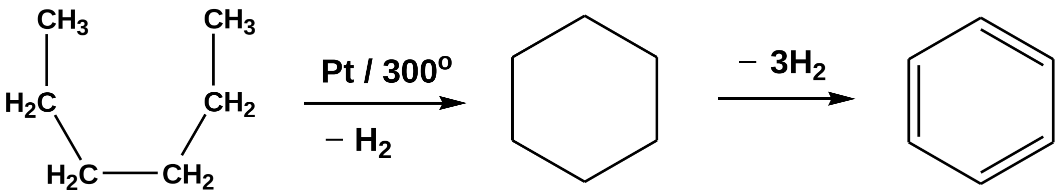
7. Dehydrocyclization of hydrocarbon chains:

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

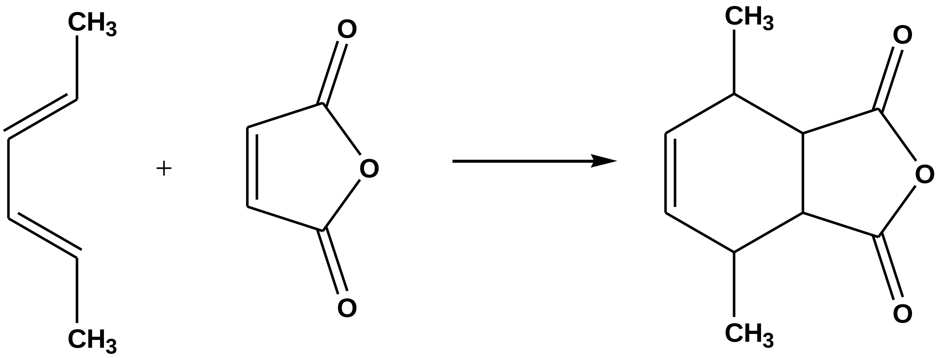
Absence of a quaternary carbon atom in the carbon chain makes the produced cyclohexane dehydrogenated to benzene (Equation 9.11).



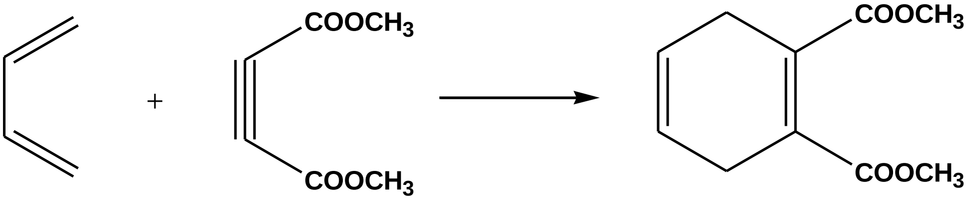
Equation 9.11

8. Diels-Alder reaction:

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



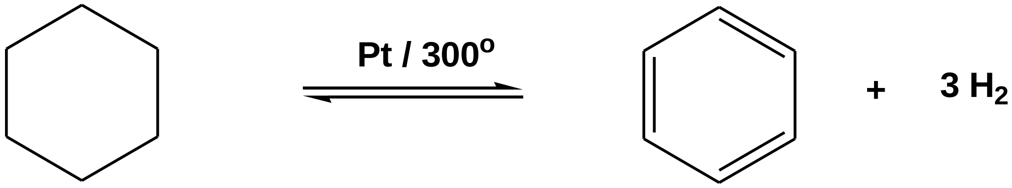
Equation 9.12



Equation 9.13

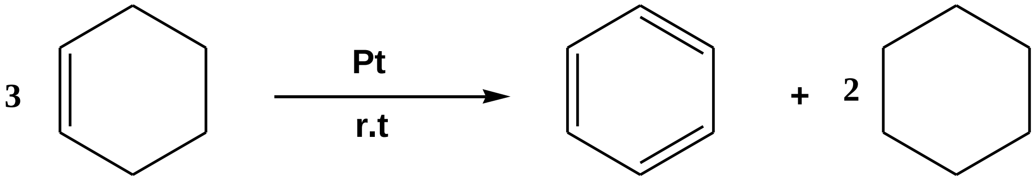
II- Chemical reactions of cyclohexane and its derivatives:

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



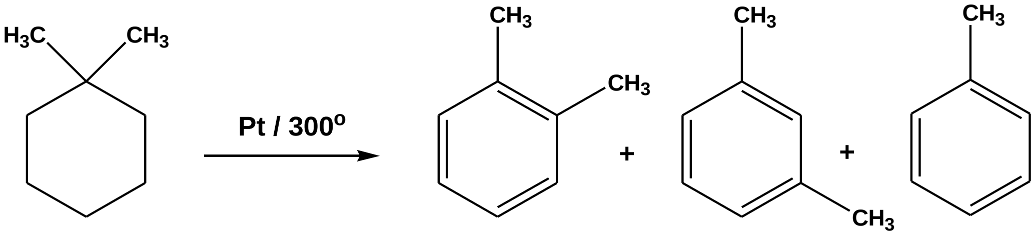
Equation 9.14

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).



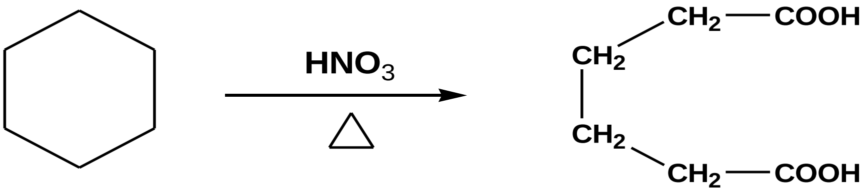
Equation 9.15

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

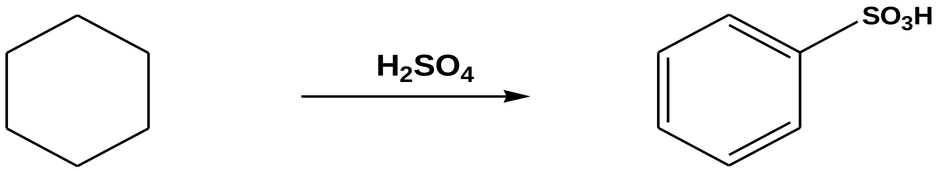
2. Nitration: in hot concentrated nitric acid, cyclohexane can be oxidized to adipic acid (Equation 9.17).



Adipic acid

Equation 9.17

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

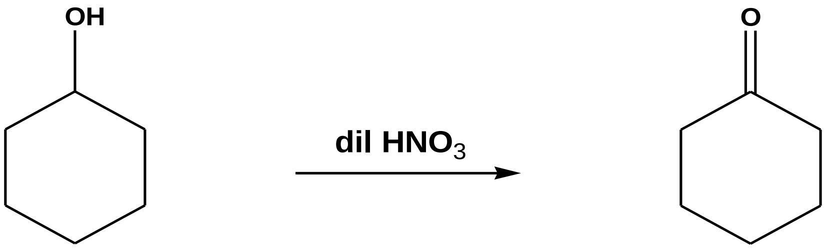


Benzenesulphonic acid

Equation 9.18

4. Cyclohexanol:

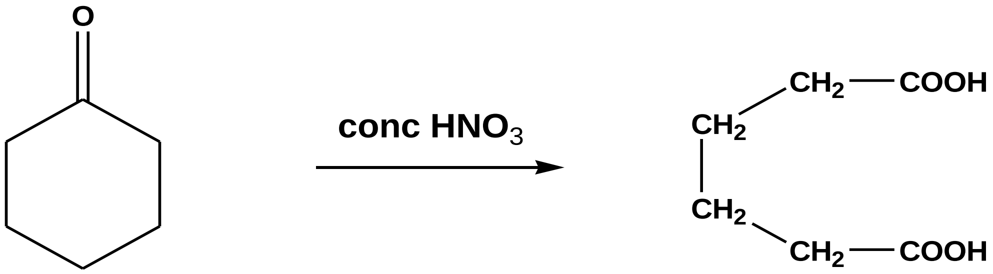
Cyclohexanol is converted by oxidation with dilute nitric acid into cyclohexanone (Equation 9.19).



Equation 9.19

5. Cyclohexanone:

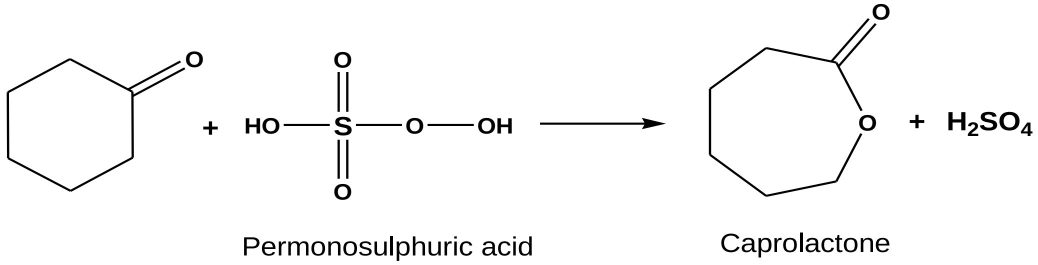
a- Oxidation with nitric acid: The vigorous oxidation of cyclohexanone with *conc* nitric acid produces adipic acid (Equation 9.20).



Adipic acid

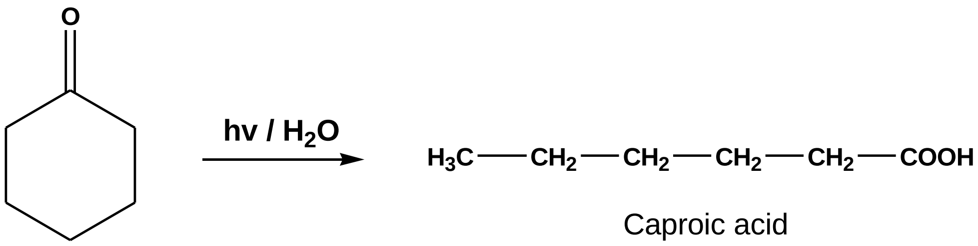
Equation 9.20

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.

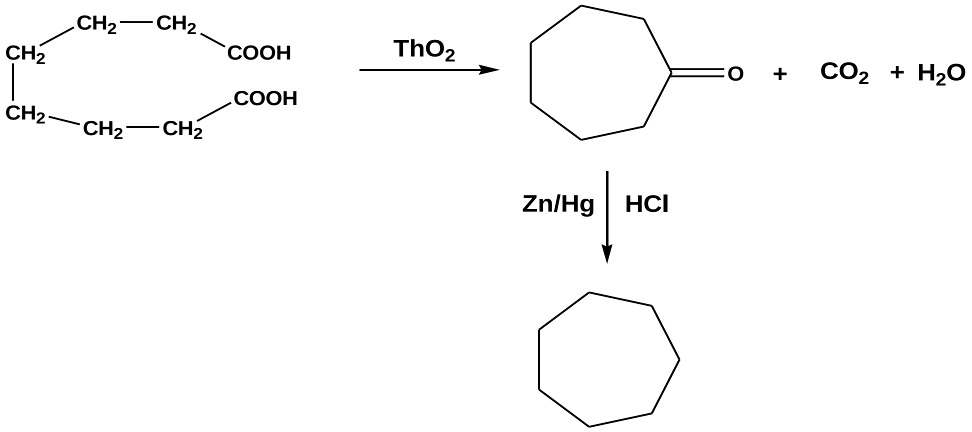
10.2 Chemical properties:

I- Methods of preparation:

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

1. Pyrolysis of dibasic acids:

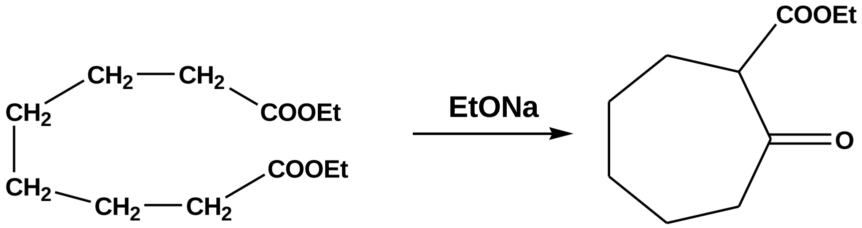
Pyrolysis of suberic acid over **ThO_2** gives cycloheptanone, which turns to cycloheptane by Clemmenson reduction (Equation 10.1).



Equation 10.1

2. Dieckmann condensation:

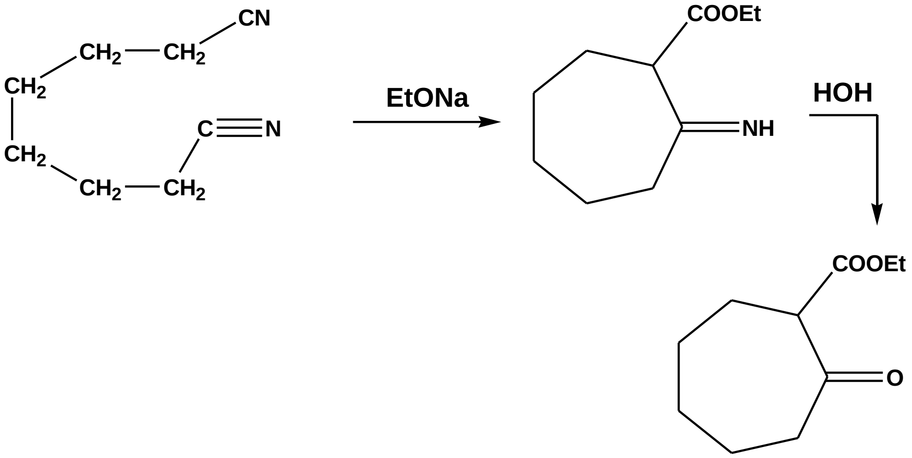
Ester condensation of octanedioic acid diethyl ester in a basic medium (sodium ethoxide) affords 2-cycloheptanonecarboxylic acid ethyl ester (Equation 10.2).



Equation 10.2

3. Thorpe reaction:

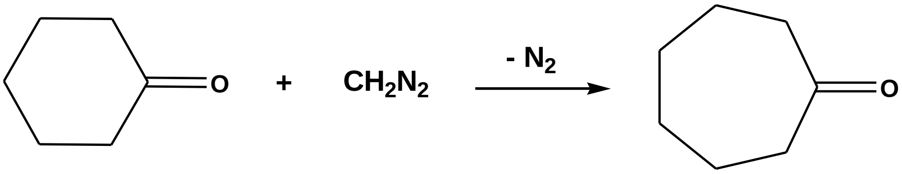
Condensation of octanedinitrile in presence of sodium ethoxide followed by hydrolysis affords 2-cycloheptanonecarbonitrile (Equation 10.3).



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).



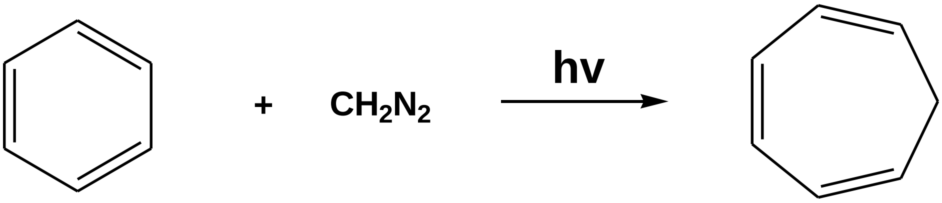
Equation 10.4

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).

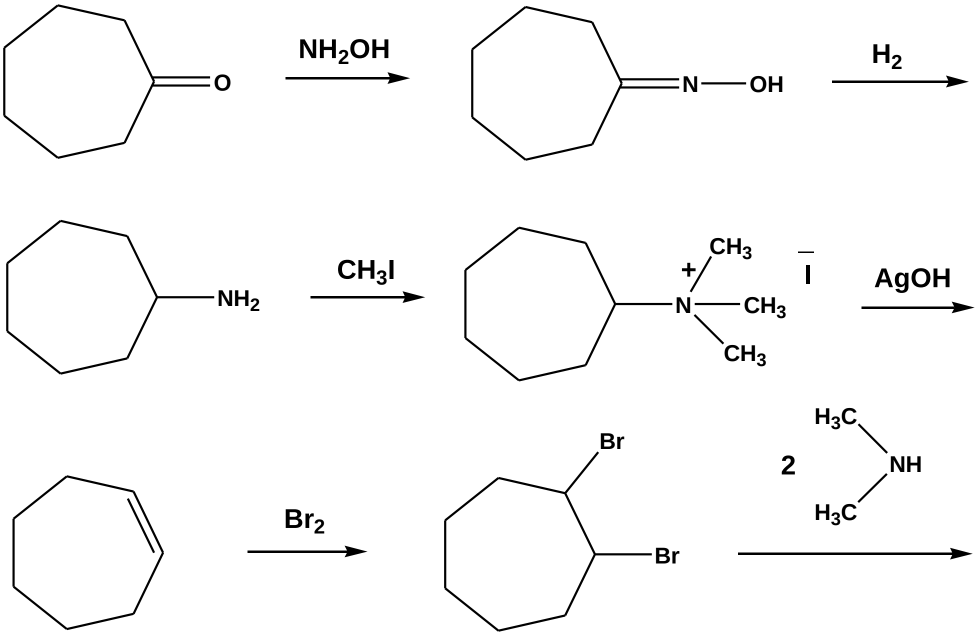


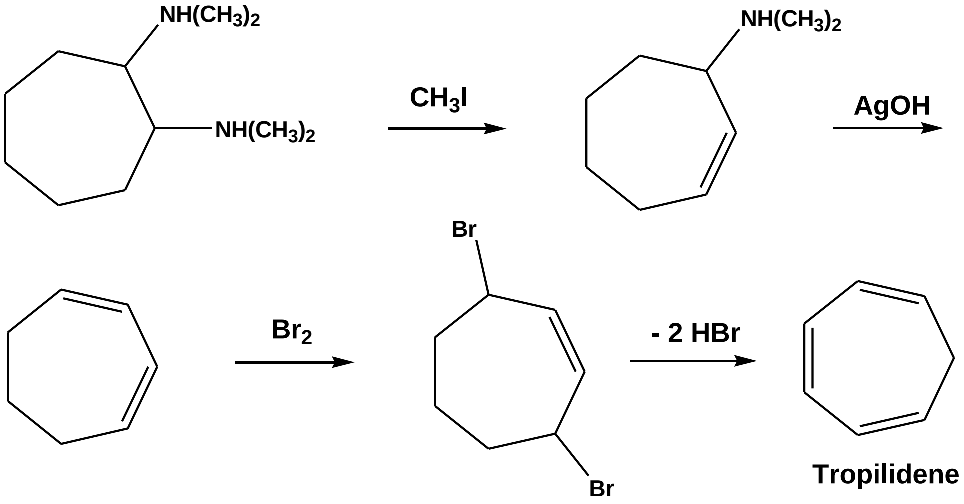
Tropilidene

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

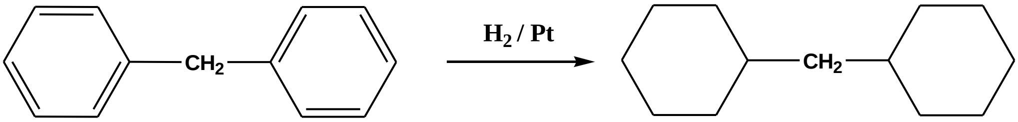
11.1 Bicyclic compounds with isolated rings.

- **Methods of preparation:**

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

1- Hydrogenation:

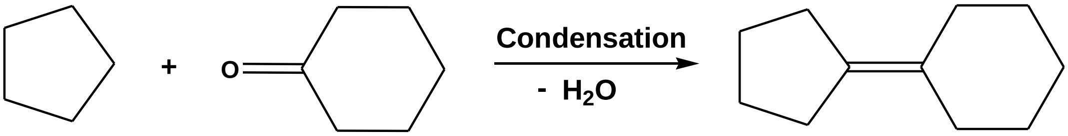
In presence of platinum as a catalyst, hydrogenation of certain aromatic compounds gave the corresponding bicyclic rings (Equation 11.1).



Equation 11.1

2- Condensation of cyclic aldehydes or ketones:

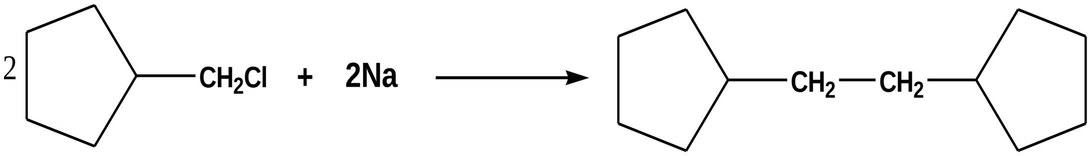
Cyclohexanone and cyclopentane may be condenses to give the cyclopentylidene-cyclohexane (Equation 11.2).



Equation 11.2

3- Wurtz reaction:

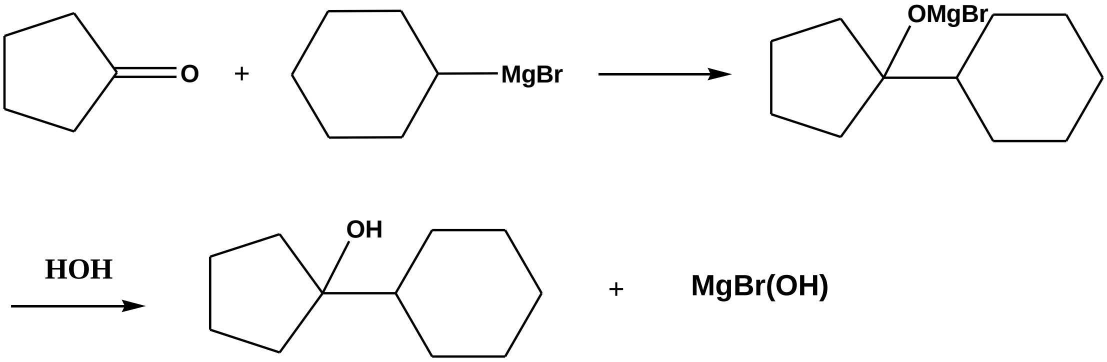
According to Wurtz reaction, the treatment of the chloromethyl-cyclopentane with sodium metal can give 1,2-dicyclopentyl-ethane (Equation 11.3).



Equation 11.3

4- By using organomagnesium compounds:

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

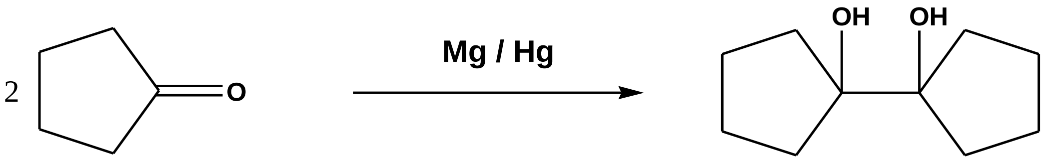


1-cyclohexyl-cyclopentanol

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

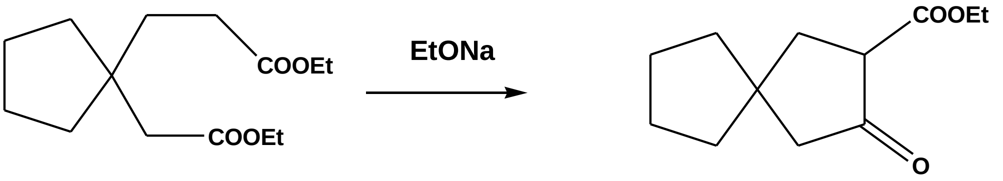
Equation 11.5

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:

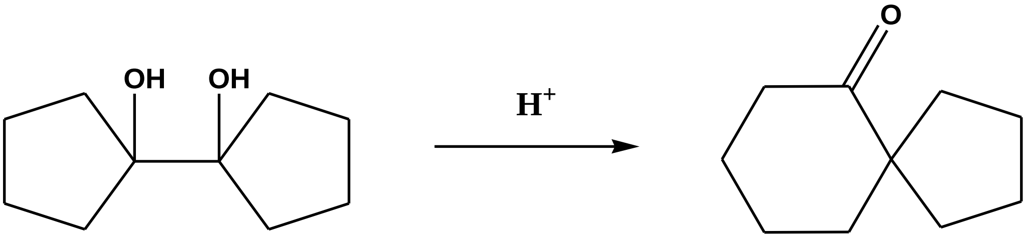
Example 1: (Equation 11.6).



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

Equation 11.6

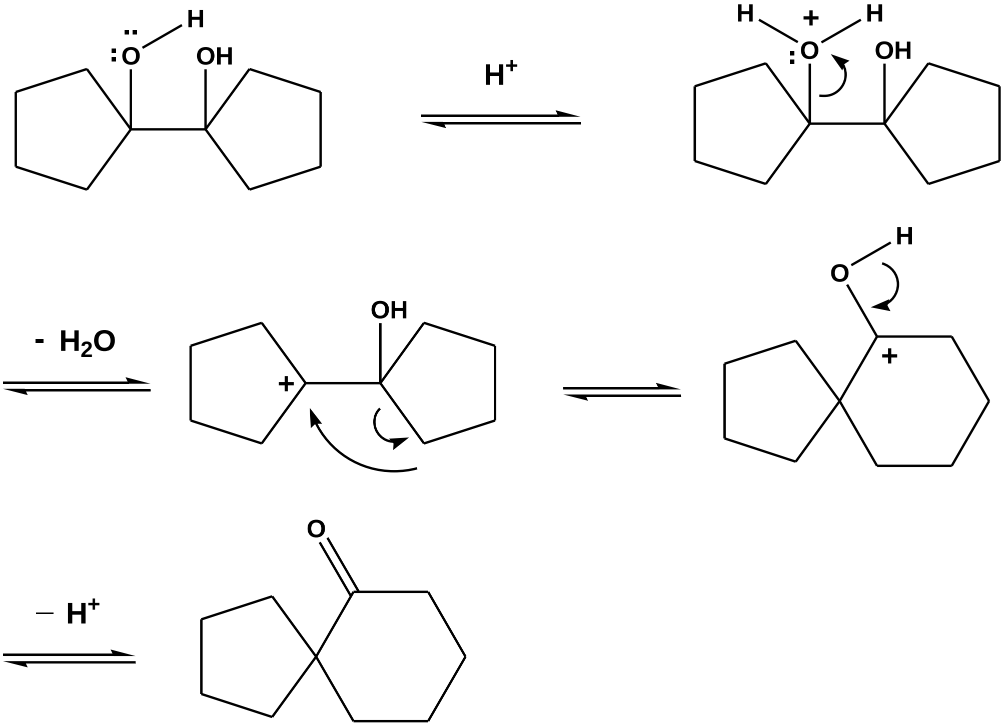
Example 2: Extension of the rings of certain bicyclic compounds (Equation 11.7).



Spiro[4.5]decan-6-one

Equation 11.7

The reaction mechanism;



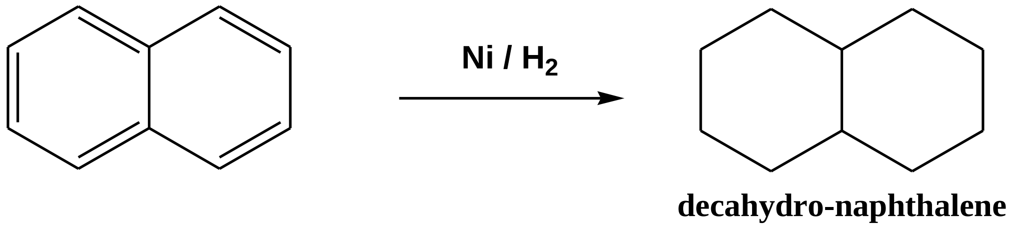
11.3 Alicyclic compounds with fused rings

- **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:

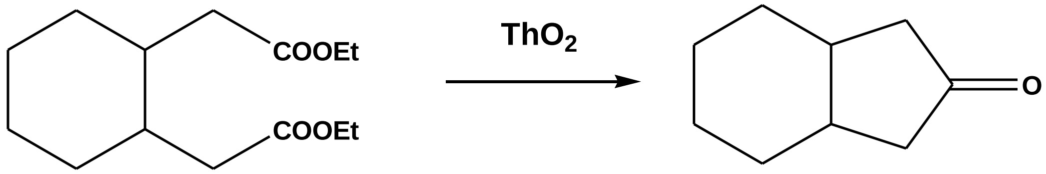
Catalytic hydrogenation of naphthalene, anthracene or phananthrene can give fused rings (Equation 11.8).



Equation 11.8

2- Cyclization of a compound containing one ring:

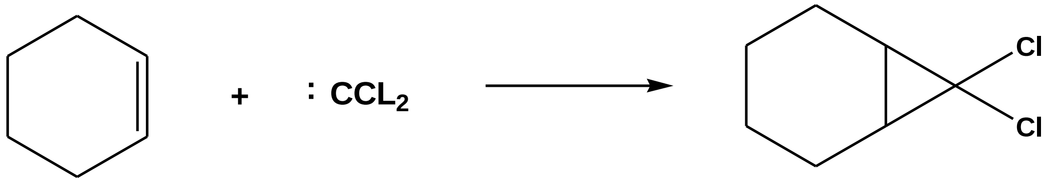
Treatment of 1,2-diethoxycarbonylmethyl-cyclohexane with thorium oxide (**ThO_2**) gives octahydro-inden-2-one (Equation 11.9).



Equation 11.9

3- Addition of carbenes to unsaturated monocyclic compounds:

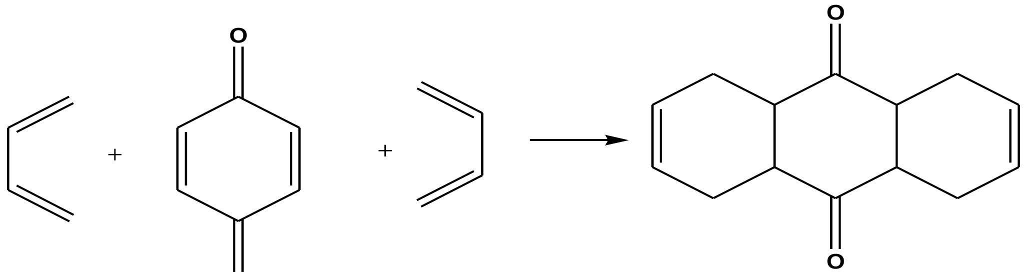
Cyclohexene reacts with carbenes to give bicyclo[4.1.0]heptane (Equation 11.10).



Equation 11.10

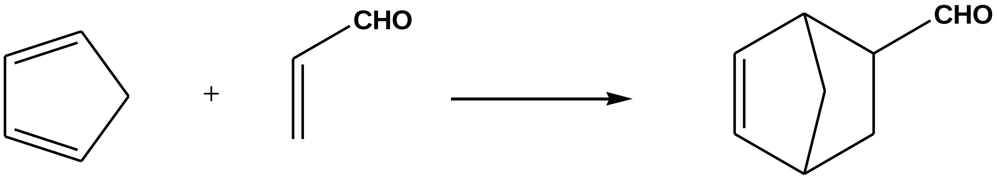
4- Diels-Alder reaction:

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



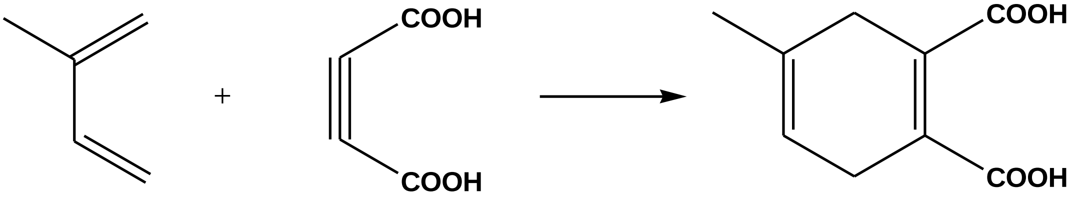
1,4,4a,5,8,8a,9a,10a-octahydro-anthraquinone

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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- http://www.chem.qmul.ac.uk/iupac/hetero/De.html
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SOUTH VALLY UNIVERSITY

FACULTY OF SCIENCE
AT QENA

Chemistry of polymer

اعداد

د. امنية سيد زكي

كلية العلوم – قسم الكيمياء

العام الجامعي

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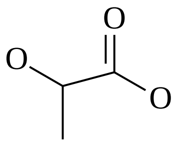
Polymeric material

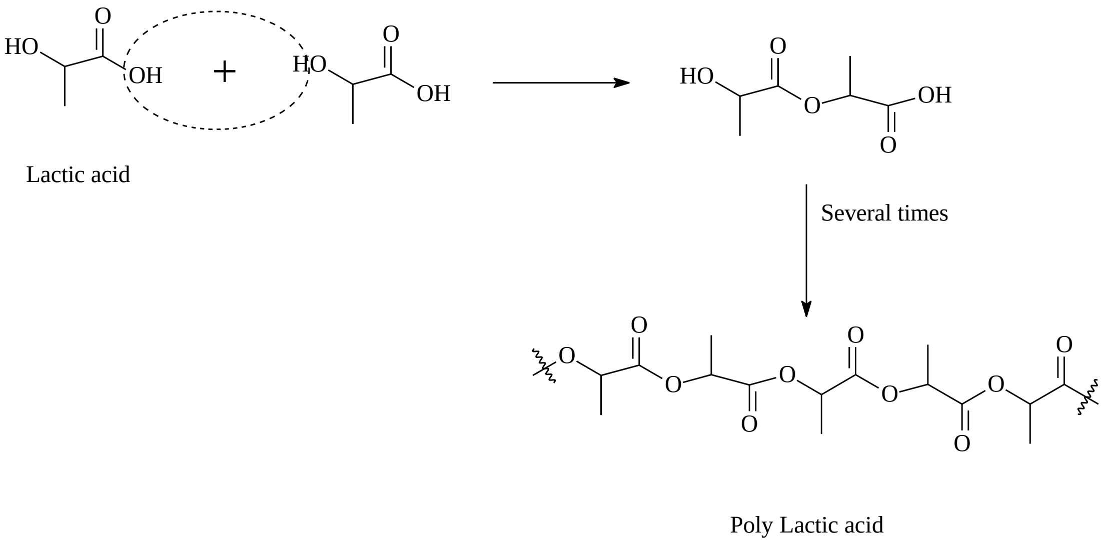
Up to this point we have studied the properties of small molecules. However, life is fall with extremely large molecules. The basic molecules of life starch, cellulose, proteins and nucleic acids are formed of large number of repeated similar or unsimilar small molecules weight unites. Such molecules are called polymers a term introduced by Berzelius in 1830. We will now look at how such polymers can be making and examine some of their characteristics then will look into molecules of nature.

Monomers and polymers:

If we look at polymer poly lactic acid we can readily note that it is composed of units and



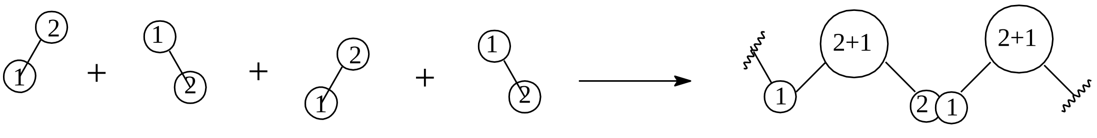
Should have resulted from consecutive esterification of carboxylic group of that acid with its hydroxyl group.



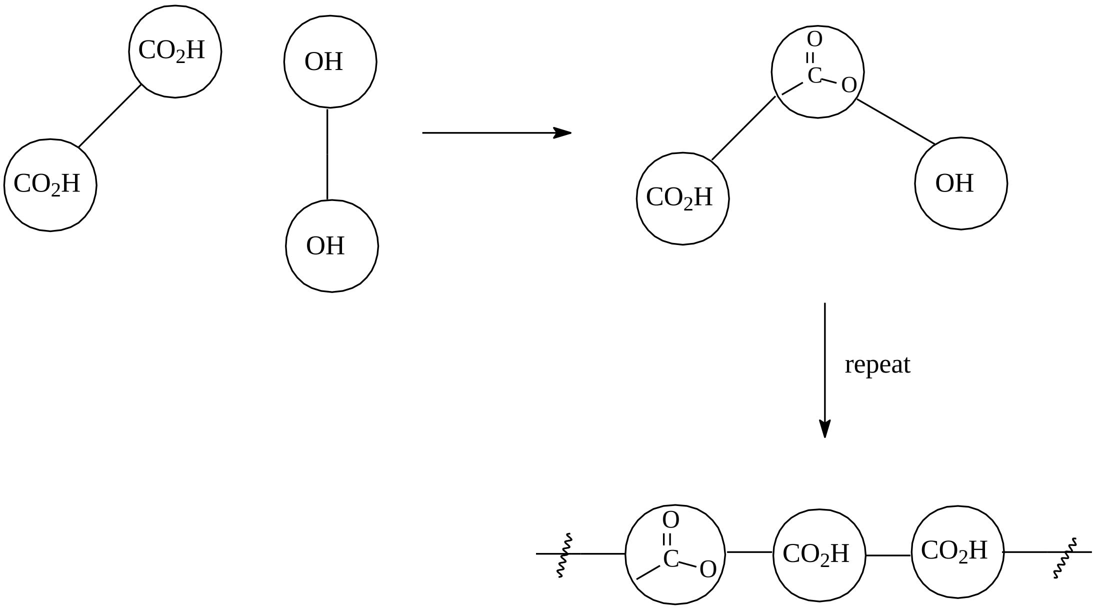
The process by with polylactic acid is formed from lactic acid is called polymerization. Lactic acid is thus a monomer and when self condensed it produces a dimmer and the letter when condensed with further one molecule it produces a trimmer.

The concept of polymerization can be illustrated graphically in general sense

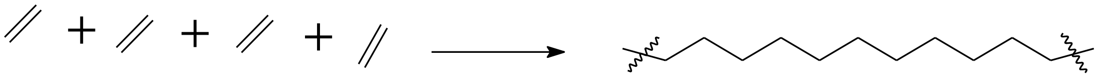
By representing the "monomer" as astic and represent the functional group as ball (1) and (2)



In lactic acid 2 and 1 are different but this is not a condition: polyesters can be formed via condensation of a dicarboxylic acid and a diol.



It is easy to visualize the monomer units required to from a poly ester. The functional group in the polymer, an ester, is directed to functional groups from which it is made. However, as we will see, many polymers are formed by linking monomer units to getter by a carbon-carbon bond. It is all way difficult, if not impossible, to distinguish C-C bonds between monomer units from those in the monomer it self. For example ethylene undergoes polymerization to form long hydrocarbon chains in which C-C bonds are indistinguishable.

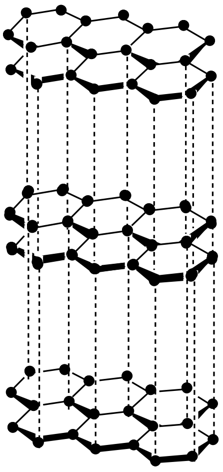


Linear and branched polymers:

In polyethylene and polylactic acid. Similar polymers monomer molecule are linked to each other linearly and such monomer are called "linear polymers" polymer molecules are attracted thus to each other only by vander wall's forces and by dipole interaction although these are very weak the fact that they are repeated hundreds of times makes these enough to give such polymers rigidity and they are thus either solids or viscous liquids. The rigidity decreases by raising temperature as result of rupture of the attraction forces.

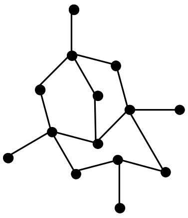
In contrast, other extremely large, multi dimensional molecules have distinctly different properties from those of linear polymers. These polymers are said to be branched or cross-linked. In such a polymer, chemical bonds interconnect chains, resulting in a complex network. One example is diamond, is which the smallest repeat unit is a single carbon that is connected to four other carbon bonds. In fact diamond is made under such extreme conditions of high temperature and pressure that scientists have been unable to define in detail how it is formed. Non etheles the bonding of each carbon to four partners in diamond lictice results in a material that is connected in three dimensions by very strong, carbon-carbon bonds. As a consequence, diamond does not melt or soften as it is heated and is totally insoluble in all known solvents.

The structure graphite is some what analogies, except that the carbon bonds are SP^2 hyperdised and thus each carbon is linked to only three neighboring carbons. Because of the planner arrangement of bonding to such a carbon, graphite is composed of sheets resembling fused polyaromatic arrays.



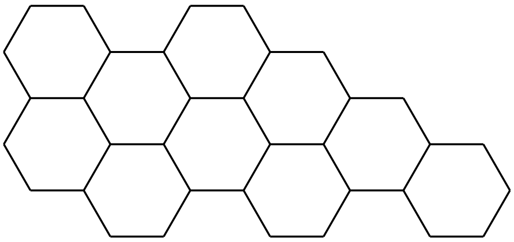
Graphite

SP^2



Diamond

SP^3



Graphite

SP^2

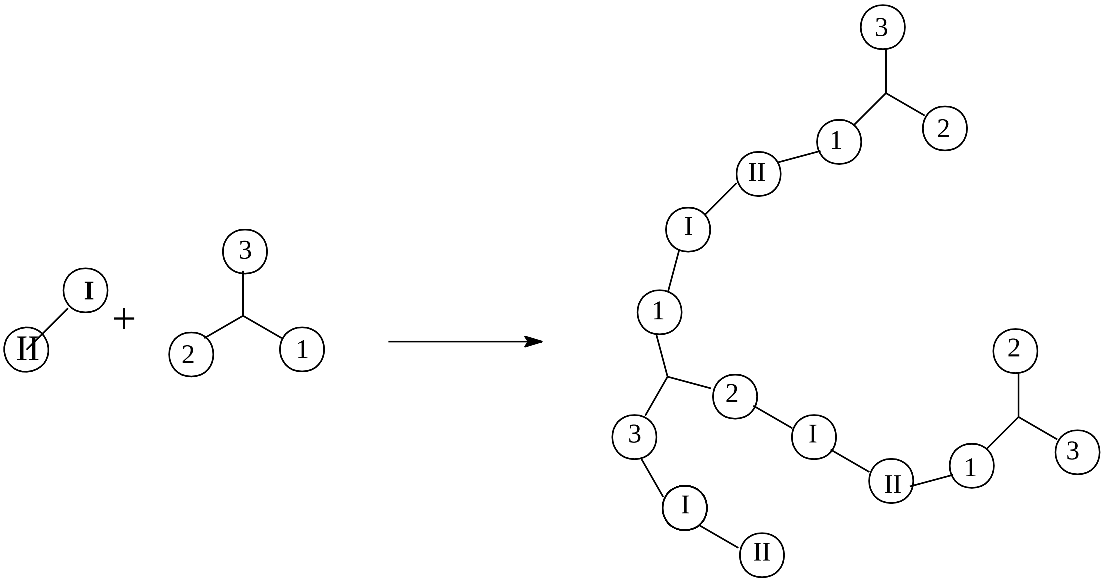
Because each sheet is planner, these is a fairly strong attraction between the carbon nuclei of one sheet and the π electrons cloud of the adjust sheets, and graphite exhibit the same isolubility as dose diamond. Although these vander waals interaction are relatively strong, the attraction between the sheets changes very little as one sheet slides on the other. Thus sheets can be moved with virtually no resistance making graphite excellent lubercant. Diamond and graphite are examples of the three dimensional and two dimensional polymers respectively, in which the monomer units are identical.

Now we have looked at

1- **Linear polymers**: Derived from monomer that have only two possible attachment points.

2- **Branched polymers**: These are polymers that has three ar four attachment points

A three dimension network of chemical bonds in a polymer generally leads to a material that is less harder and less flexible than the corresponding linear polymer with similar functional groups. Polymers can also be made from mixtures of different monomer, which one unite having three bonds and other only two:

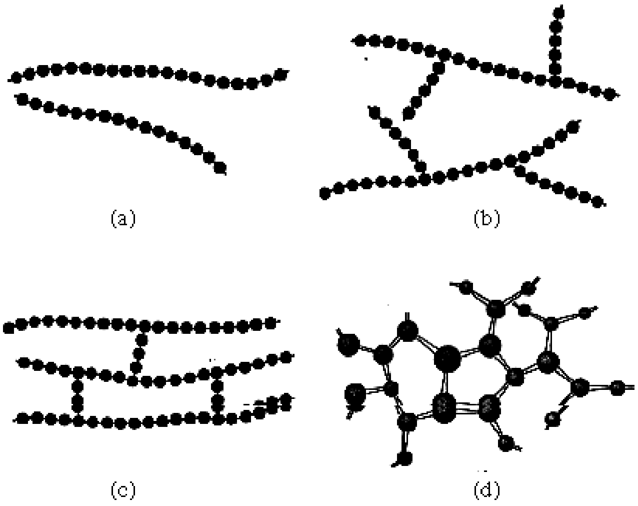


I & II represent alcohol which 1 & 2 &3 represent carboxylic acid derivatives.

Molecular Structure of Polymers

- **a- Linear**
  - High Density Polyethylene (HDPE), PVC, Nylon, Cotton

- **b- Branched**



1. Low Density Polyethylene (LDPE)

- **c- Cross-linked**
    - Rubber
- **d- Network**
    - Kevlar, Epoxy

<u>Types of polymerization</u>:

The chemical transformations that result in polymers can be divided into two major classes:

(A)- <u>Condensation polymerization</u>: As an example OH fraction in hydroxy acid can condense with its carboxulic group producing polyester via elimination of water.

(B)- <u>Addition polymerization</u>: This results ferom addition of one molecule to another link can of polyethaylene.

Type of polymer according to their physical properties

- **thermoplastics**

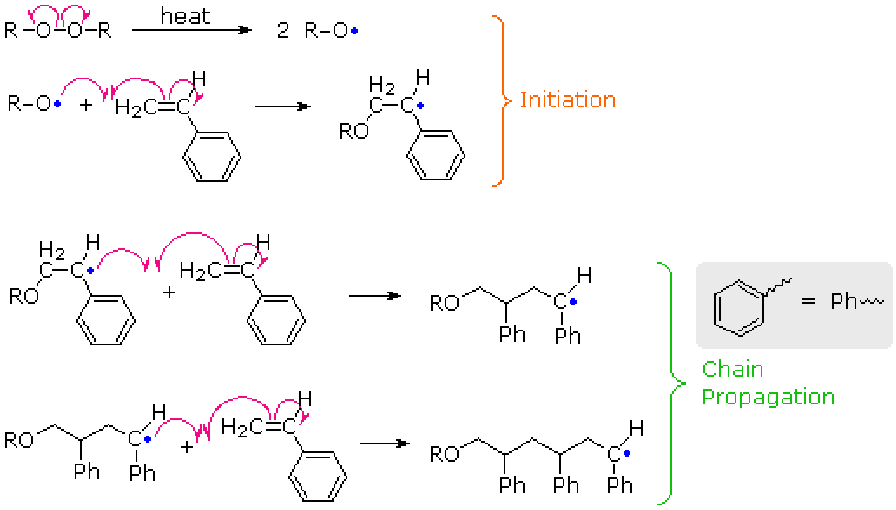
It is a solid material at normal temperatures, but it softens with heat and turns into something like a paste, and if the heat is increased, it melts, and it is used in the manufacture of plastics and synthetic fibers, such as Polyethylene - polystyrene - polyvinyl chloride – polypropylene

- **thermosetting polymers**

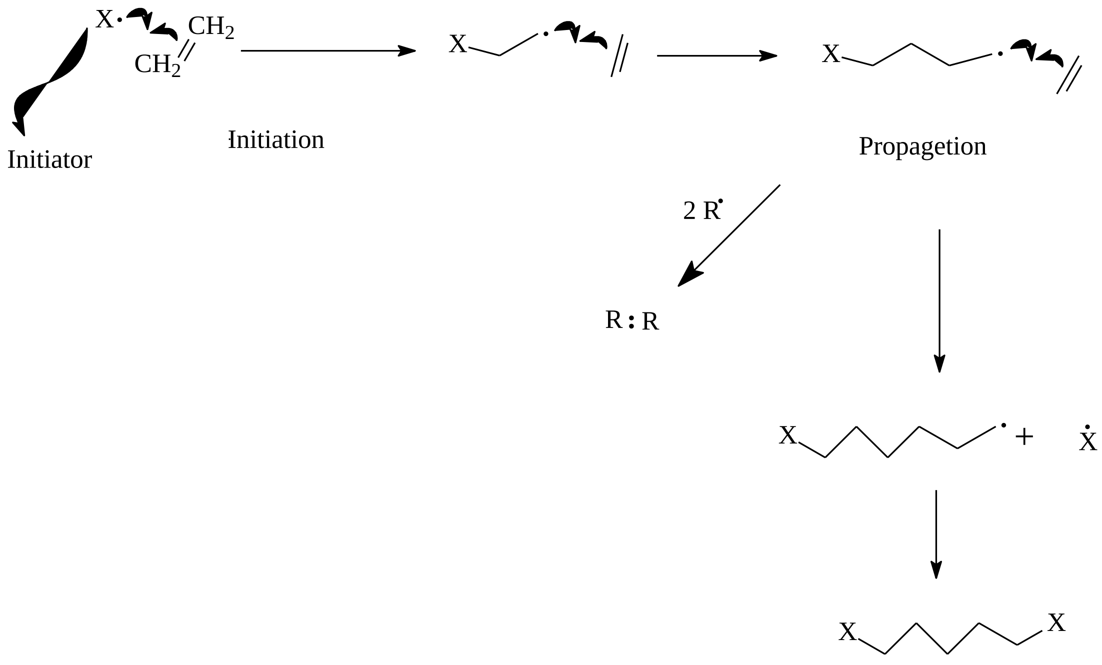
  These polymers undergo chemical changes when heated, so the polymer chains become entangled in them, and after their thermal treatment, these polymers become insoluble,, poor conductivity of heat and electricity. These polymers are used as insulating materials in household electrical industries, such as phenol-formaldehyde resins, urea-formaldehyde resins.

Addition polymerization

Radical polymerization: example (Polystyrene)



a growing polystyrene chain



Polymers up to 1,400,4000 mw (50,000 unit) can be made link other linear polymers it is flexible and some are even stretshiabl and can these be shaped if heated. Materials this is called plastics from greek plastikos that mean.

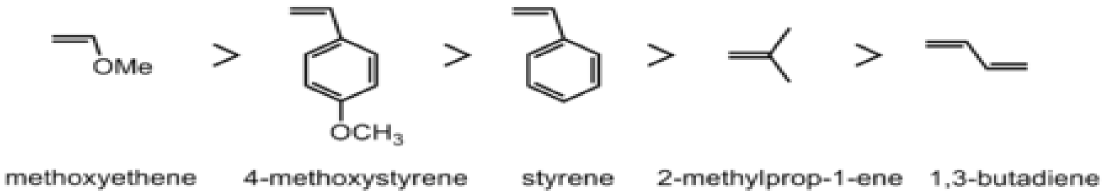
Ionic polymerization:

i) Cationic polymerization:

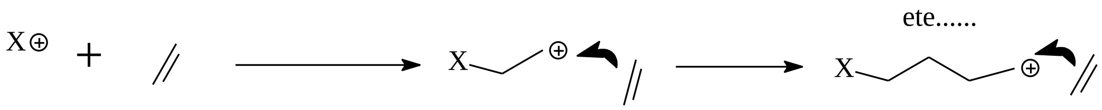
The types of monomers necessary for cationic polymerization are limited to olefins (alkene)with electron-donating substituent's (oxygen and nitrogen-based functionalities)and heterocycles

- **Olefins**

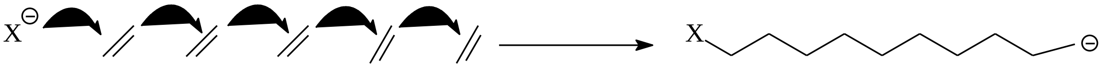
  Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electron-donating groups make the olefin nucleophilic enough to attack electrophilic initiators or growing polymer chains. Some reactive olefin monomers are shown below in order of decreasing reactivity, with heteroatom groups being more reactive than alkyl or aryl groups.



Example of cationic polymer



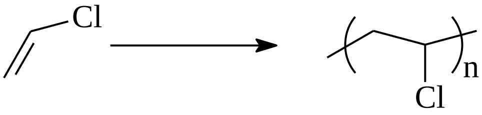
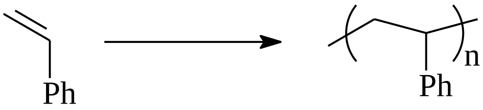
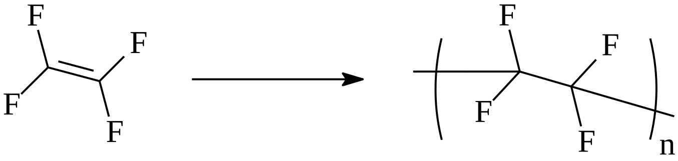
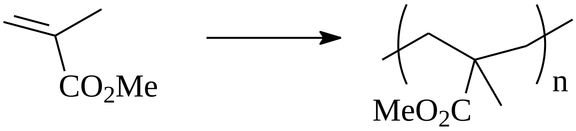
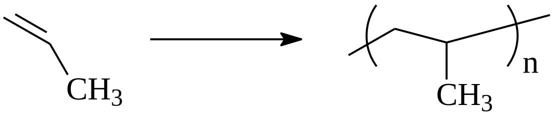
ii) Anionic polymerization:



Cationic polymerization link anionic polymerization have not to terminate and the length of polymer chain can be increased by addition more monomers. Such polymers are called living polymers. Cationic polymerization can be initiated by adding alkyl lithium to ethylene. All types of polymerization are exothermic with 20 kal / mol for each addition. Cationic and anionic polymers can have higher mol.wt rigid and insoluble

Poly ethylene:

Substituted ethylene are also polymerisable grieves new polymers with different properties.

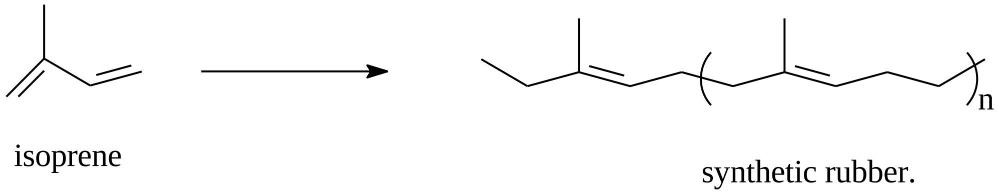
 	 Poly vinyl chloride (PVC)  Poly styrene used in making styrofann and plastic bags or water pipes
	 Teflon
	 Plexiglas, Lucite
	 polypropylene

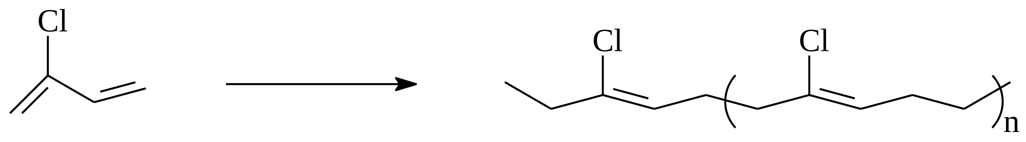
Natural rubber :-

Rubber, also called India rubber, latex, Amazonian rubber, *caucho*, or *caoutchouc*, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds. Thailand and Indonesia are two of the leading rubber producers. Types of polyisoprene that are used as natural rubbers are classified as elastomers.

Butadiene polymerization:

(Rubber: Butadiene and other conjugated diene also form polymers. For example, the polymer derived from isoprene (2-methyl butadiene) is synthetic rubber. The rubber tree and several other plants produce a similar natural polymer known as latex rubber, which differ from synthetic rubber in that essentially all of its double bonds have a cis configuration. Chloroprene (2-chlorobutadiene) a monomer structurally similar to isoprene, lead to a synthetic rubber called neoprene.



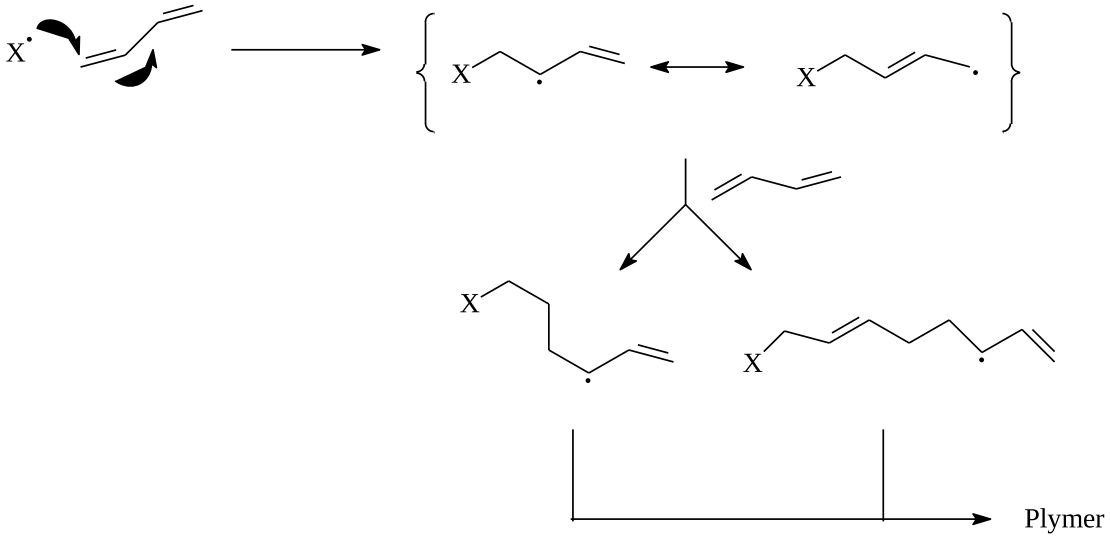


Chloroprene

Neoprene

Replacement of the methyl group of isoprene with a chlorine atom reduces the ability of neoprene is not resistant to gasoline and oils than synthetic rubber.

Although synthetic and naturally occurring rubbers are similar in many ways, some of their properties differ. The synthetic polymer consists of very diverse mixture of structures, whereas the structure of natural polymer is very constant. Radical polymerization begins by formation of bond between a radical initiator and one of the terminal atoms, resulting in a stabilized allyl radical.

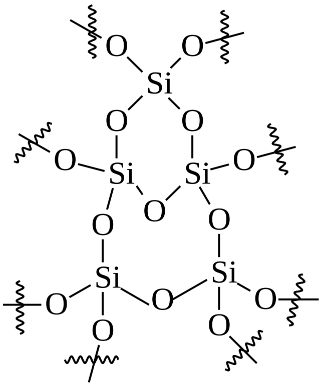


Two sites in an allyl radical bear radical character. Therefore; addition of these type of species to another butadiene molecule occurs with two different region chemical outcomes; bond formation occurs either at C-2 or at C-3. Two dimmers are formed, one linear and one branched. As each additional butadiene molecule adds to a growing chain, there are two possible outcomes: Linear or branched addition. Furthermore, both cis and trans geometrical isomers will be formed, further expanding the number of different species formed. Thus, synthetic rubber is quite a complex mixture.

In contrast to synthetic rubber, latex rubber is produced in living plant through catalysis by enzymes. These natural catalysts produce a polymer in which essentially all double bonds have the cis geometry. For this reason, there is structure diversity a many the polymer molecules found in natural rubber.

Cross-Linking in polymers:

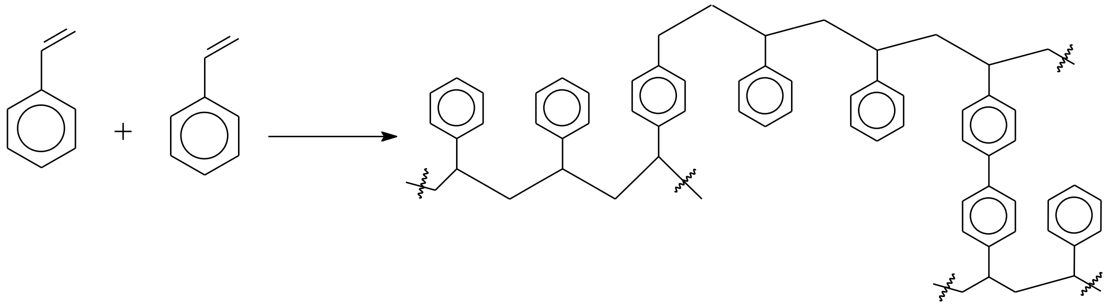
Most of the polymers described so far are derived from monomers with two bonding sites. As a result, the polymer chains are held together only by relatively weak vander wals attractive interactions. In contrast, glass is a rigid polymeric material in which tetravalent dimensional covalent net work



Glass

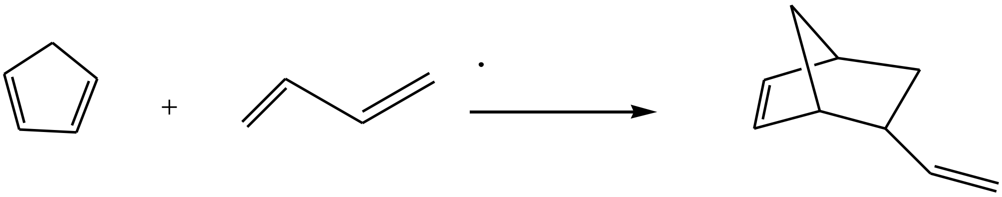
Cross-linking is a process in which a bifunctional molecule (such as a diene) participates in polymerization and is incorporated into two separate polymer chains.

Polymerisation of a mixture of simple alkene (such as styrene) with a diene (such as P-divinyl benzene) allows each of two alkene units of the diene to be incorporated into a separate chain, thus linking the chains together. A molecule such as divinyl benzene an believed a monomer capable of forming four bonds and these of establishing cross links between growing monomer chains.



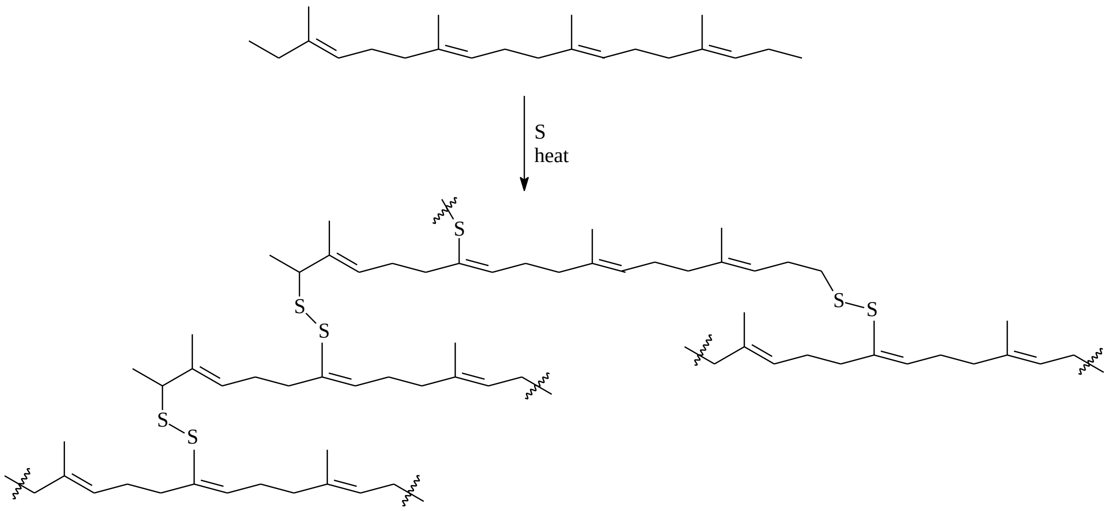
The extent of cross-linking attained depends on the relative concentration of styrene and divinyl benzene. But, if divinyl benzene constitutes only very small % of the mixture, the resulting Plastic is much more rigid than polystyrene itself because of additional covalent bonds between the chains.

Diene polymers such as latex or neoprene rubber can also be made more rigid by cross-linking with nonconjugated dienes. One such linking agent is 5-vinylnor bornene, large quantities of with which is produced each year by the Diels –Alder reaction of butadiene with cyclopentadiene



The stretched double bond in 5-vinylnorbornen is more reactive them the monosubstituted alkene substituent and these the former is in corporated in individual chains while the majority of the latter remain unreacted. When polymerization has consumed most of the available alkene, the less reactive double bond participate in cross-linking of polymer chains. In this way cross-linking is delayed until late in polymerization, resulting in quite long chains. The incorporation of 5-vinylmorbornene in a monomer nature resulting a more rigid polymer by enhancing degree of cross linking between chains.

Attentively, polymer chains can be linked by sulfur bridges. Transformation of the rather of common and soft latex rubber into the much more rigid material used as example in automobile tires is a accomplished by heating with sulfarin a process known as **vulcanization**, which was discovered by accedant by chairles goody ear (the term vefes tovealcan, the roman god of fire, who was thought to be very strong). The reaction almost certainly invrus radicals, but the mechanism is not well understood. The bridges are depicted here as resulting from simple allylic substitution of sulpher for hydrogen



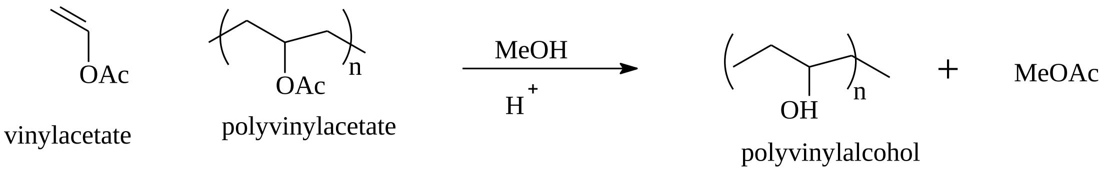
Neither the original polymer nor the cross linked rubber derived from isoprene only functionality that produces color. **The characteristic black color of the rubber is caused by the presence of carbon black**, a material similar to graphite, which ads as lubricant and impedes a greater life time to the rubber under conditions of repeats flexing. Large quantities carbon black is produced in easter Europe. Unfortunately, the outdated technologies in this region have resulted in emission of substantial amounts of carbon black into the atmosphere causing, significant industrial pollution.

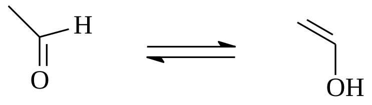
<u>Heteroatom containing additional polymers</u>:

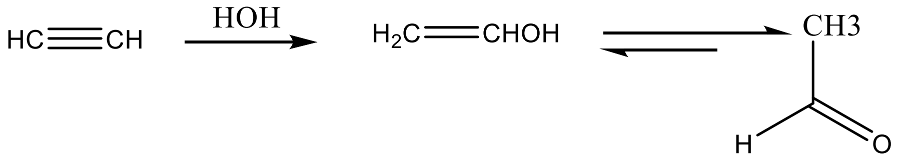
Substituted vinyl polymers have very low solubility in water because they lack any functional group that can form hydrogen bonds. Now we then to polymers that incorporates oxygen in the form of alcohol or ether functional groups. The attachment of heteroatom to a carbon framework increases solvent-solute interactions, enhancing solubility of heteroatom-containing carbons.

Carbon-linked monomer units: polyols:

The polyol known **as poly (vinyl alcohol)**, or **PVA** is highly water-soluble. Its name might seem to imply that, this polymer is made from vinyl alcohol, but this enol is not present in significant amounts in equilibrium with keto form, acetaldehyde.







Radical polymerization of vinyl acetate is used to form poly (vinyl acetate), a polymer with a hydrocarbon chain substituted with acetate ester. The ester are cleaved by awd or base–catalyzed reaction with methanol, forming methyl acetate and PVA. The resulting polymer is mach more soluble in water than are hydrocarbon polymers such as polyethylene and polystyrene but a lower surface tension than pare water. (Viscosity is increased because the long polymer molecules are quite viscous, and the surface tension is partially disrupted by the polymer).

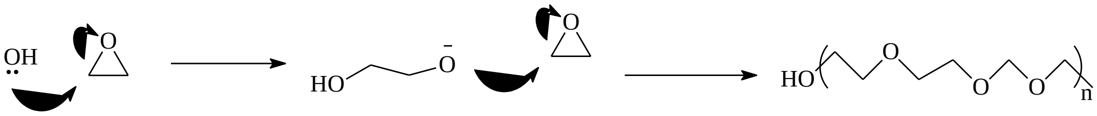
Poly (vinyl alcohol) is therefore included in products ranging from hair spray and styling gels to lubricants for molding rubber.

Heteroatom-linked monomer units:

The addition polymers discussed so far have carbon-carbon bonds linking the polymer units. However, there are also important classes of addition polymers in which the monomer units linked by heteroatoms.

Polyethenes.

A very important class of addition polymers is formed by addition polymerization of simple epoxides. The addition of nucleophile such as OH^- to ethylene oxide results in ring opining and yields the monoanion of ethylene glycol. This ion can also serve as a nucleophile, reacting with another molecule of ethylene oxide.



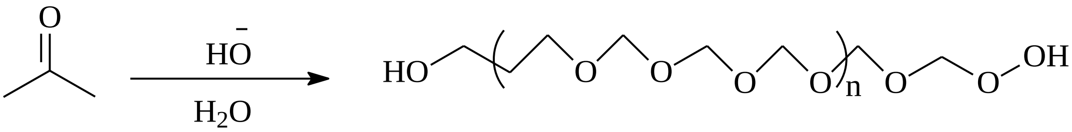
Polyethaylene glycol

This polymerization is quit similar to anionic polymerization of ethylene. Each step in these ring opening polarization releases ring strain of a three membered epoxide ring and is thus exothermic by approximately 15 k cal/mol.

The resulting polymer is called poly (ethylene glycol), or PEG, synthetic PEGS are used in cosmetic creams, lotions, and deodorants and in antistatic agents. These plastics are marketed commercially as carbon waxes and under other trade names. They have high water solubility because of hydrogen bonding to ether oxygen atoms and have many of the same applications as poly (vinyl alcohol). Naturally occurring cyclic polyethenes were important in the biological transport of cations across membranes.

Polyacetals:

Another oxygen-containing polymer is paraformaldehyde, poly acetate formed by addition polymerization of formaldehyde, a reaction that takes place as an agues solution of formaldehyde.



Note that the backbone of the polymer is formed of acetal linkages and that both ends are hemiacetals, which are active sites for further chain growth. Note, also, that all atoms of the monomer are retained within the polyacetal, making it an addition polymer. This addition polymerization is only slightly exothermic. As a result paraformaldehyde undergoes depolymerization in water, reforming formaldehyde. Because formaldehyde is strong antibacterial agent, aqueous solutions of paraformaldehyde are used as disinfectants, and the polymer is the active ingredient in same contraceptive creams.

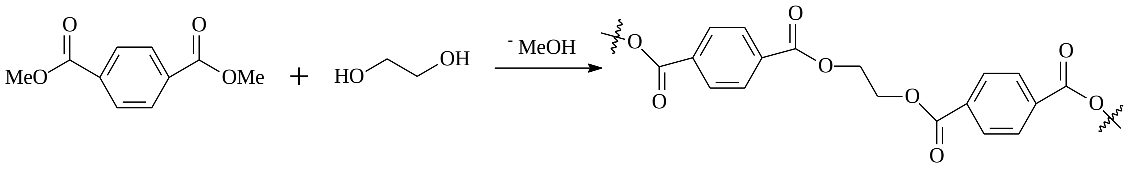
Polyacetals made from formaldehyde, as well as polyacetal and polyketals made from aldehydes and ketanes are strong plastics that are resistant to fatigue (breaking after repeated flexing) and have high electrical resistance, making them quite useful as components for computer hard were and automobile parts. To stabilize these materials toward hydrolysis, the hemiacetals (or hemiketals) at the ends or "capped" by reaction ether with acetic anhydride (to form esters) or ethylene oxide. Polyacetals or (polyketals) require more strongly acidic or basic condition for their hydrolysis than does paraformaldehyde.

Condensation polymers

Unlike an addition reaction in all atoms of the reactants are incorporated with in the product, a condensation reaction forms a more complex organic molecule from two or less complex one, with the expulsion of a small molecule. Some examples of condensation reactions include esterification, aldol, and claisan condensation. In all these water is formed as a byproduct. When such a reaction is repeated many times with an appropriately functionalized monomer, a condensation polymer is produced.

Polyesters:

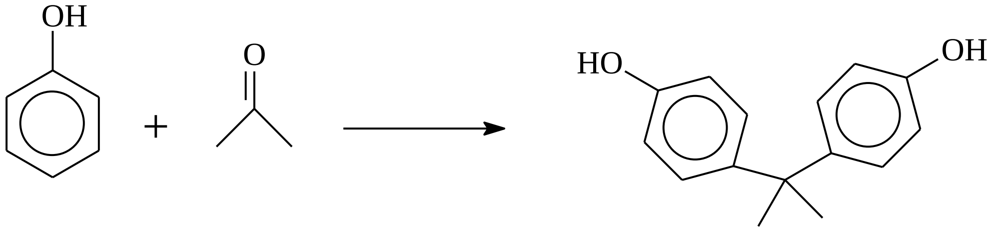
Because interaction of dicarboxylic acids with diols to form polyesters produces one equivalent of water for each link formed in polymer chain, poly ester formation is a condensation polymerization. If esters are used in place of the carboxylic acids, the reaction is a trans esterification. Dacron is communally important condensation polymer used as a fiber and also as a film called Mylar. It is formed by reaction of dimethyl terphthalate with ethylene glycol, a trans esterification in which methane is produced as a by-product:



Dacron, Mylar

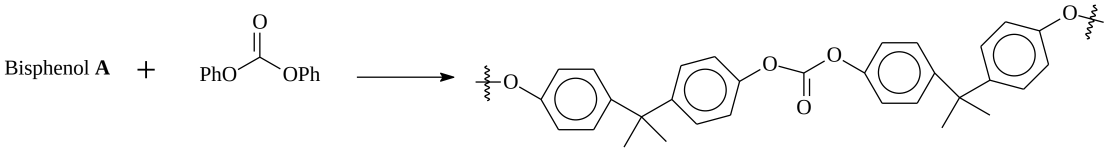
Polycarbonates:

Are condensation polymers that result from trans esterification. A diol often employed reaction is bisphenol **A** (the **A** comes from acetone), produced by reaction of phenol and acetone in presence of lewis acid.



Bisphenol **A**

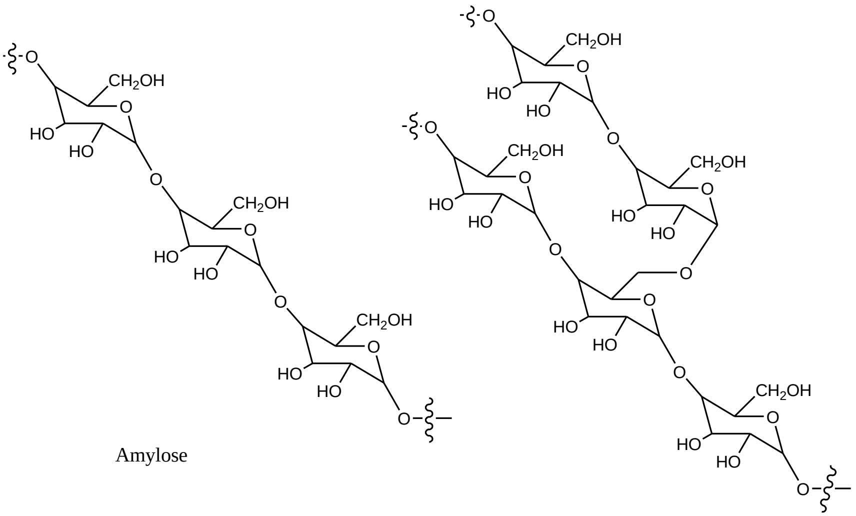
Because phenols are better leaving groups these are aliphatic alcohols, diphenyl carbonate is more reactive in transformation than is, for example dimethyl carbonate. The polycarbonate formed from bisphenol of has many of the same propriates as Plexiglas or polystyrene. All these materials have high optical clarity, but the polycarbonate is more stronger and more rigid, with great impact resistance.



Polycarbonate

Polysaccharides:

Polysaccharides are naturally occurring condensation polymers. In starsh (known as amylose) the acetal function in one molecule condenses with OH group at C-4 of other function though α-linkage. Amylose is water insoluble despite the fact that at is formed from as many as 4000 glucose units. On the other hand amylopectine is also poly glucose but water soluble as a result of the fact that it is braced at C-6 and is of more than million glucose unites.

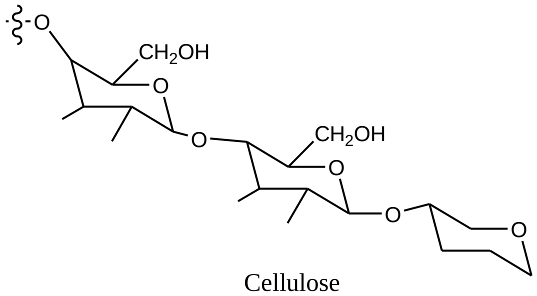


Amylose

Amylopectine

Cellulose

Cellulose is a biological polymer formed via condensation of several anits of β-glucose at C-1 and C-4.



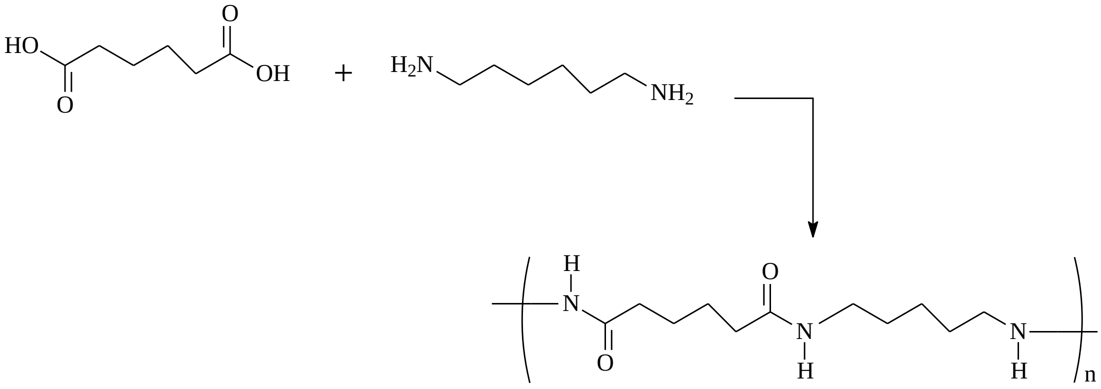
Cellulose

Cellulose is typically formed from 3000 to 3500 glucose units however it is water insoluble as a result of stereochemistry that permit adherence of chins by vander wal forces.

Acylation by acetic anhydride produces acetyl cellulose which is transparent and is used in photographic films.

Polyamides;

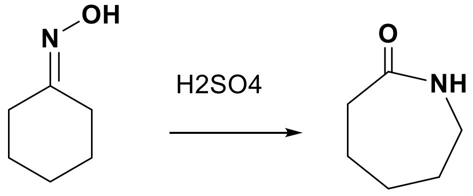
A polymeric condensation product formed from a diacid and a diamine is called polyamide. In a route similar to that for polyester formation adepic acid and 1,6-diaminohexane react at high temperature to form a polyamide known as **nylon 66**. (the numbers refer to the number of carbon atoms of acid and amine).

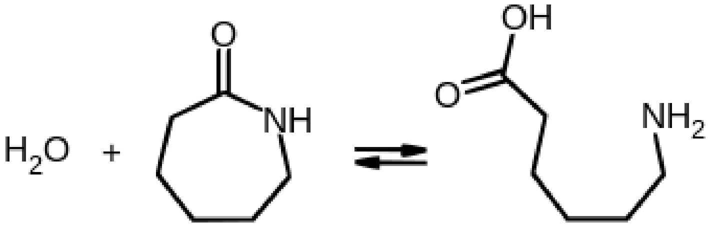


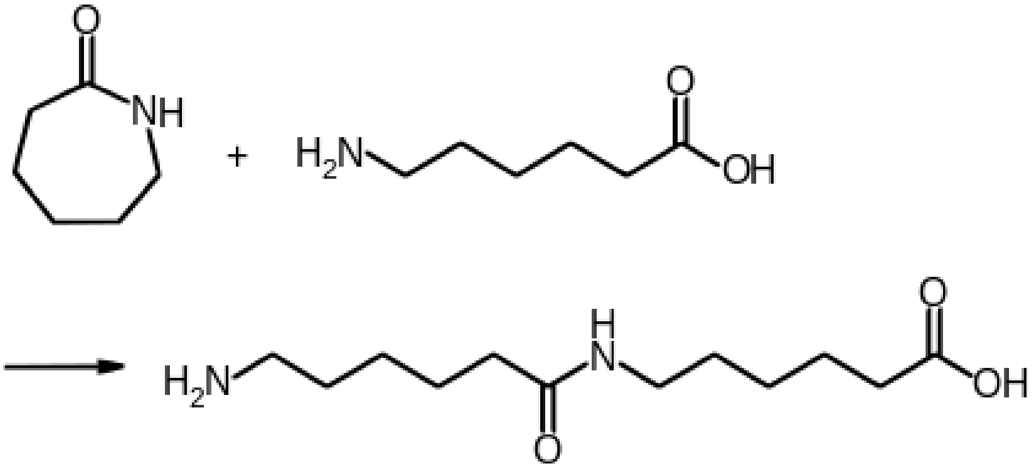
Nylon 66

There is also **nylon 6** produced by the polymeric ring opening induced by the catalytic interaction of Nucleophilic with carpolactan.

Beckmann rearrangement of cyclohexanone oxime







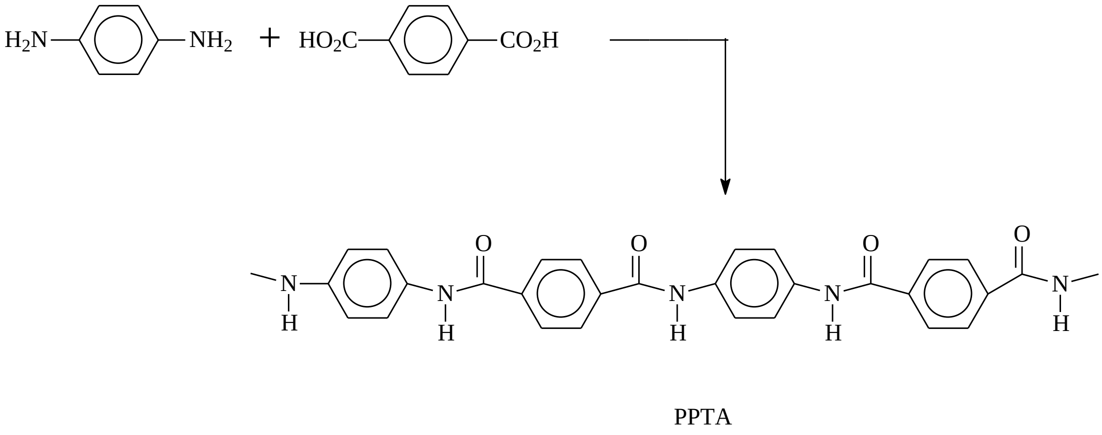
The seven member cyclic amide is produced industrially through Beckmann rearrangement of cyclohexanone oxime. By salphonic acid with is neutralized by ammonia producing ammonia sulphate which solid as fertilizer.

The term condensation and addition refer to the method by which polymers are produced and therefore are not necessarily provide clues to characters of a polymer.

Nylon 66 is produced by the condensation polymerization (with loss of water) of two diffract six-carbon monomers, one of a diacid and other of a diamin. Nylon 6 on the other hand results of addition polymerization of a single six-carbon monomer (the cyclic amide). Both nylon 66 and nylon 6 are useful plastics that form very long lasting, and flexible fibers; the flexibility is due, in part, to conformation at freedom of the chains.

PPTA polymer

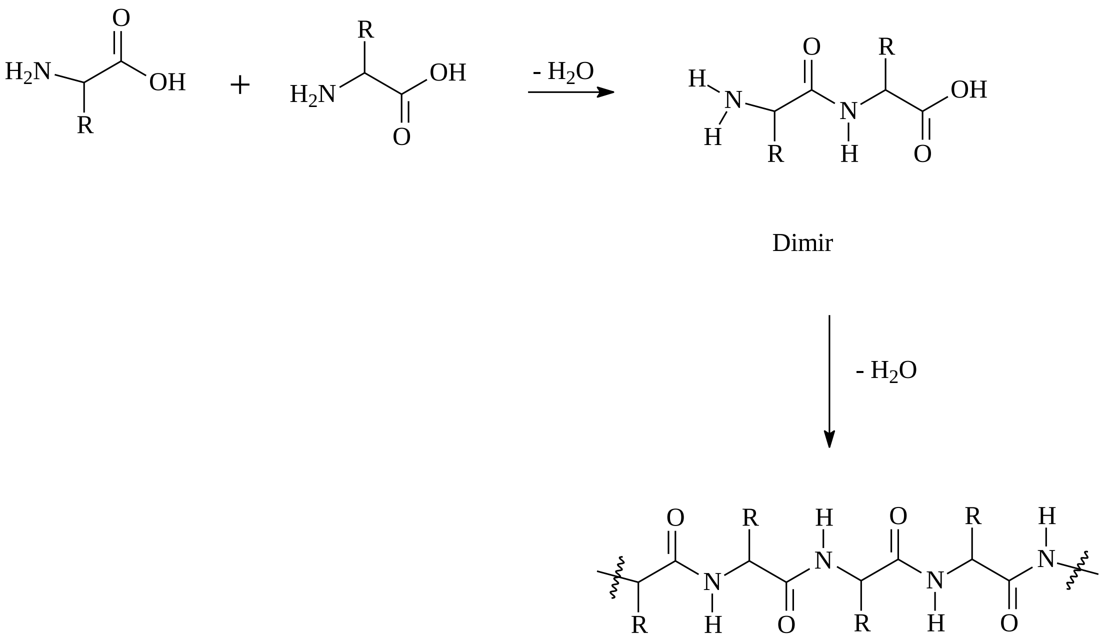
Condensation polymerization of terphthalic acid with p-phenylene diamine results in a polymer known as PPTA (p-phenylenterephdiamine) which have very unusual properties.



In contrast with nylon 6 and 66, which have considerable conformation freedom, PPTA is quite rigid. As a result tris polymer can be formed into fibers that have great tensile strength and resists both compression and elongation. PPTA is five times stronger than steel on a per-weight basis. Fibers spun from this polymer are marketed as Kevlar and are used in applications such as bulletproof vests that require high strength and low weight.

Polypeptides:

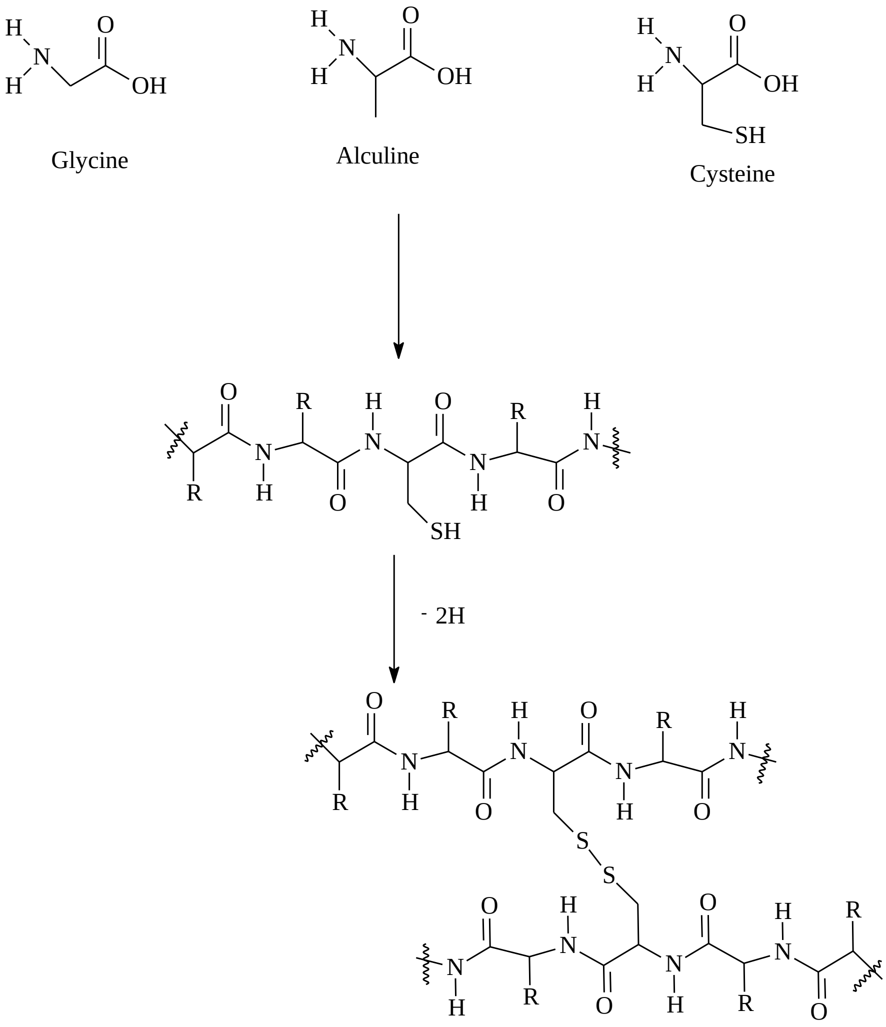
The amide linkage in a polyamide resembles those found in polypeptides and proteins, which are natural polymeric materials derived from a aminoacids. This linkage is referred to us a peptide bond, and thus the term polypeptides explicitly refer to the repeating amide linkage. In polypeptides (and proteins), the monomer units are linked by amide groups formed by a condensation reaction between amino groups of one, α-amino acids and the carboxylic group of another.



Polypeptide

Polypeptides and proteins are naturally occurring polymers that have many different forms and a variety of functions. The difference between the term polypeptide and protein refers to molecular size. Polypeptides are a polymer containing more than 100 amino acids and proteins are larger molecules.

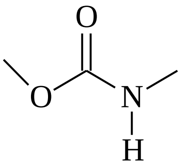
The synthetic (manufacture) polyamides are clavelayzed to minic the properties fond in silic and natural animal hairs such as wool, both composed mainly of polypeptides silk is polymer with amino acid glycine and alanine. **Wool** is structurally more complex, having sulfur sulfur bonds that link individual chains to the another and forms matrix some what like that of vulcanized rubber. These bonds in wool are the result of significant amounts of the sulfur containing amino acid system.



Although a bond between two sulfurs may usual it is non ethelens very easily upon exposed of thiol functional groups to oxidants, and even molecular oxygen will effect this transformation. S-S bonds play a crucial role in many biological processes.

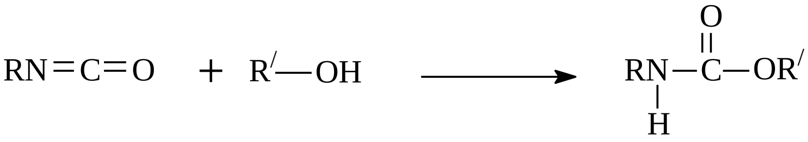
<u>Silk</u>

Poly urethane:



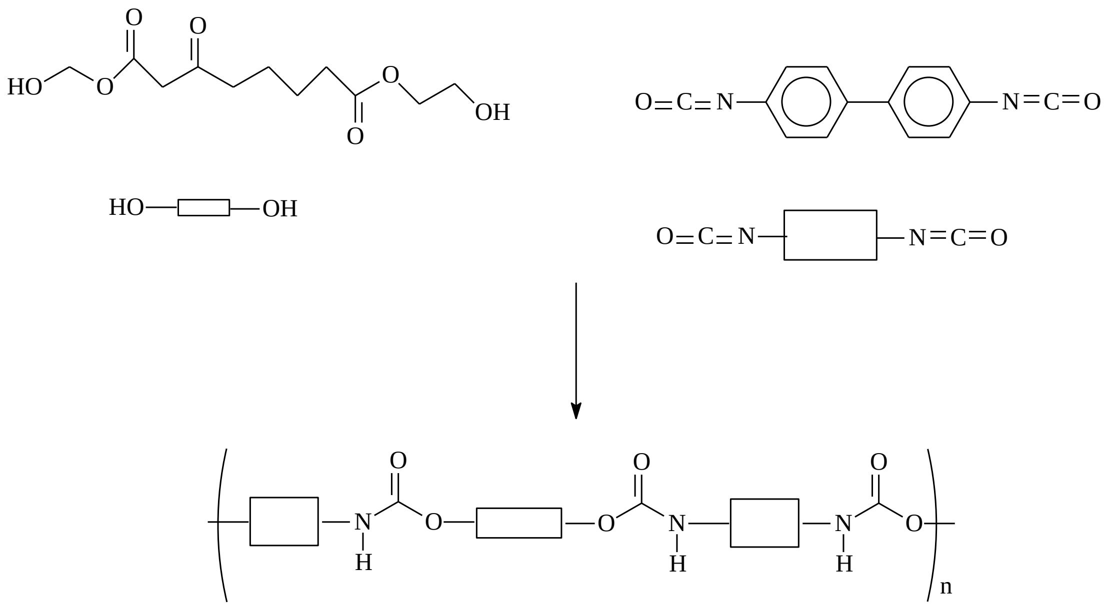
A urithane

Similar in structure to polyamids are poly urethanes, which have one of components of chain a urethane (or carbonate) group. Urethanes are formed by reaction of isocyanets with alcohols.



$$RN{=}C{=}O \quad + \quad R^{/}{-}OH \longrightarrow \underset{\underset{H}{|}}{RN}{-}\overset{\overset{O}{\|}}{C}{-}OR^{/}$$

Typically reacting a low molecular weight polyester with terminal hydroxyl group with pis isocyante.

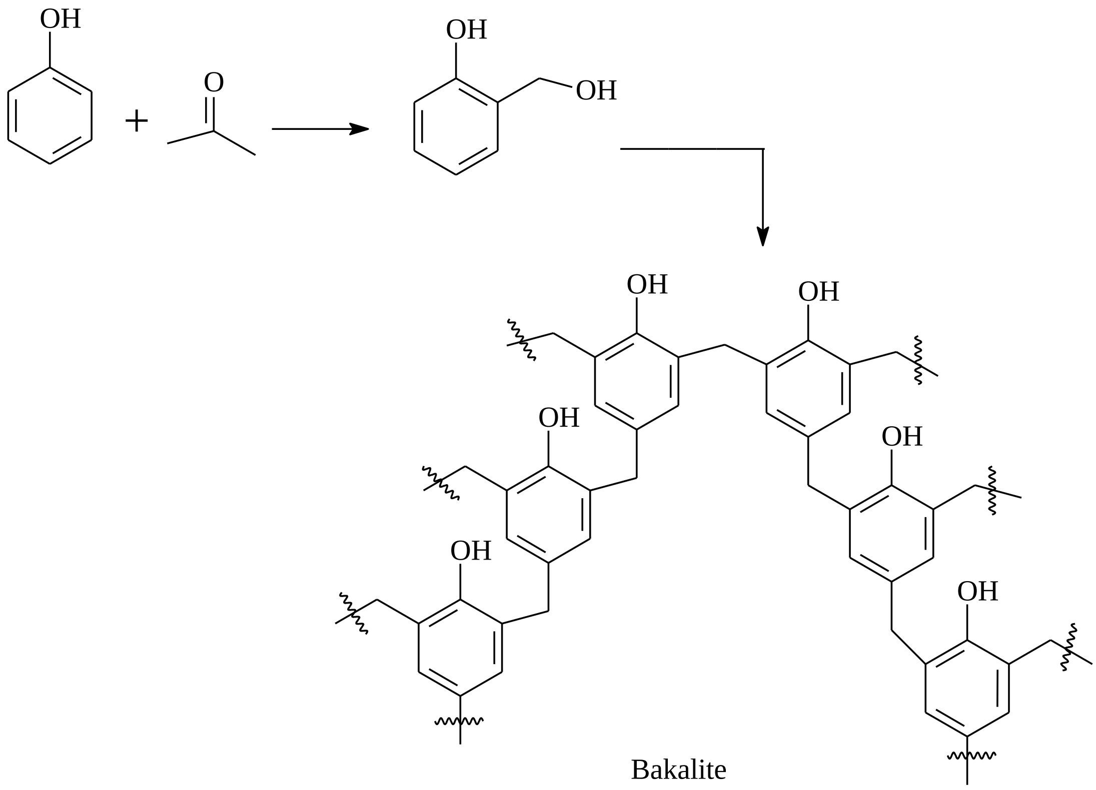


Poly urethane

When a compound with a low boiling point (for example CO_2 or volatile hydrogen such as methane or ethane) is dissolved under pressure in one of starting materials and then allowed to expand and vaporize while polymerization proceeding, the polyurethane obtained has tiny "void" spaces sealed of by surrounding polymer. The resulting poly urethane form is a valuable lightweight material for building insulations and padding.

Extensively Croos-Linked Polymers

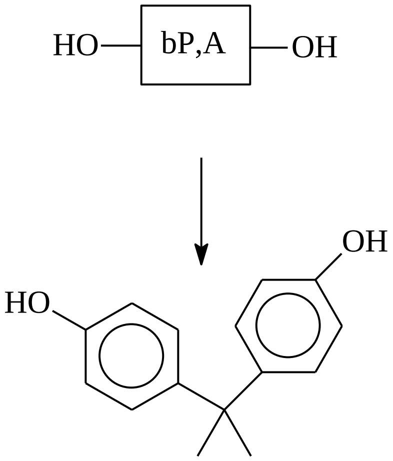
Even in vulcanized rubber, the number of cross-linking bonds is usually small in comparison with polymer units. On the other hand, monomers with three or more points of comedian produces polymers that extend in two and three dimensions rather than having a linear arrangements as in simple polymers such as polyethylene. These extensively cross-linked polymers are often very hard. **Bakelite** is one example: it is a resin (a highly viscose polymer glass) derived from reaction of phenol and formaldehyde.



Bakalite

Epoxy resins

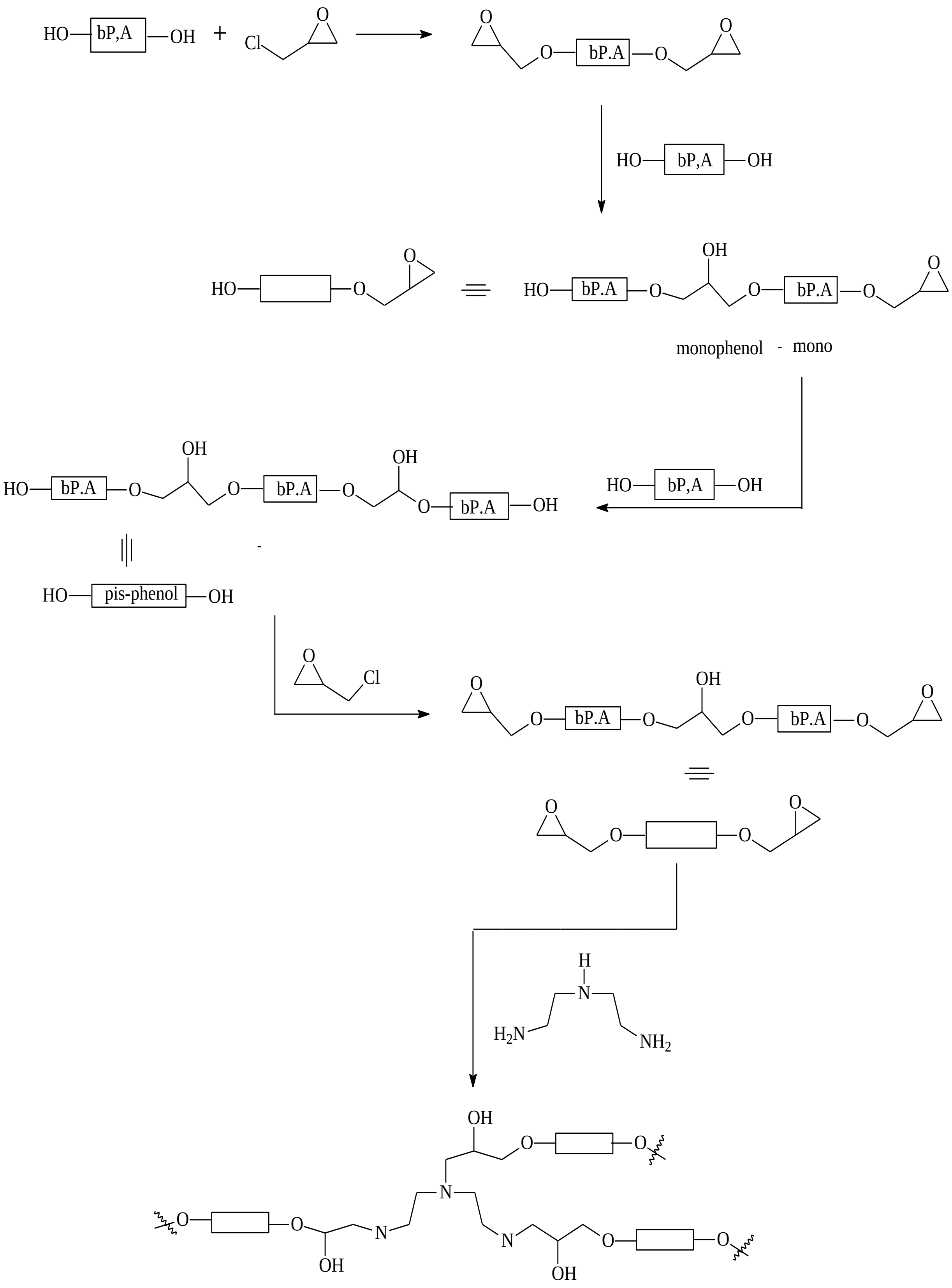
Epoxy resins constitute another important class of cross-linked polymers that have many applications as structural materials. Includes in this class are the commonly used epoxy glues, many laboratory bench tops are made of epoxy resin and microelectronic chips are encapsulated in this material. Because such resins are expensive, a filter is added in the same way that sand and small stones are added to cement to make convert. (for microchips the filter is silicon dust). The chemistry of epoxy resins is straight formed but the structures are complex; for their reason, block diagrams are often used to represent structures such as bisphenol as.



Bisphenol - A

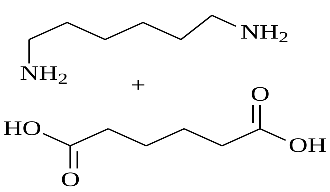
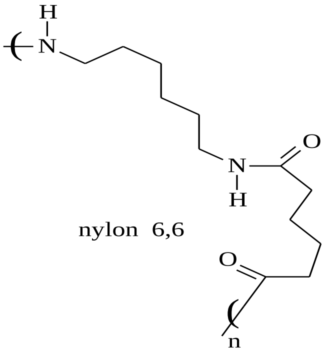
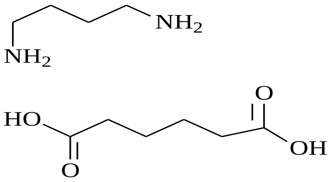
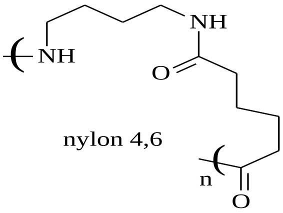
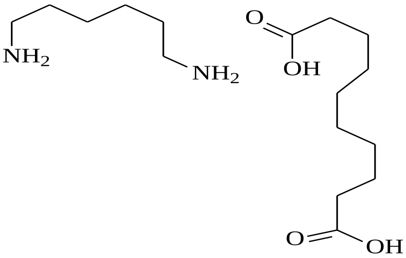
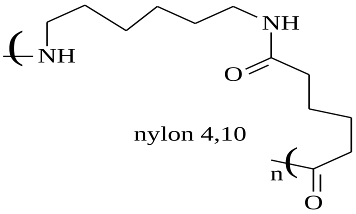
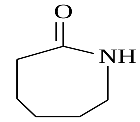
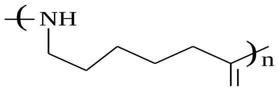
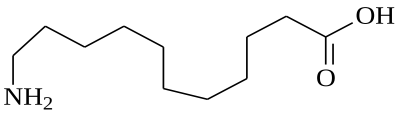
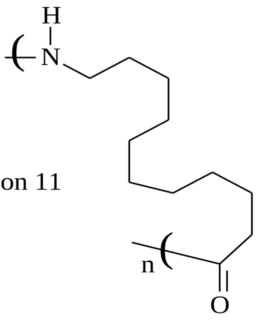
Reaction of bisphenol **A** with epichlorohydrine results in formation of a bis-epoxide: this in when reaction with additional bisphenol **A** in one to one ration, forming first a simple 1:2 adduct. This epoxy alcohol then reacts either with more PPA to form a diol or with more bis-epoxide to form larger bisepoxide. These reactions non tinue, ultimately forming a mixture of short polymers composed of diols, epoxy alcohols, and bis-epoxides. This mixtures is still fluid and is clear, nearly odorless component of two part epoxy glues. This reaction of this complex mixture of linear polymer with a triamin, the fishy smelling component, leads to the opening of terminal epoxides and the formation of three dimentionaly linked not work that is much more rigid than the original resin.

Example of gallery with epoxy resin


HO—bP,A—OH
+
Cl
O
bP.A
HO—bP,A—OH
HO
OH
monophenol - mono
HO—bP,A—OH
HO—pis-phenol—OH
Cl
H
N
H_2N
NH_2
N
OH

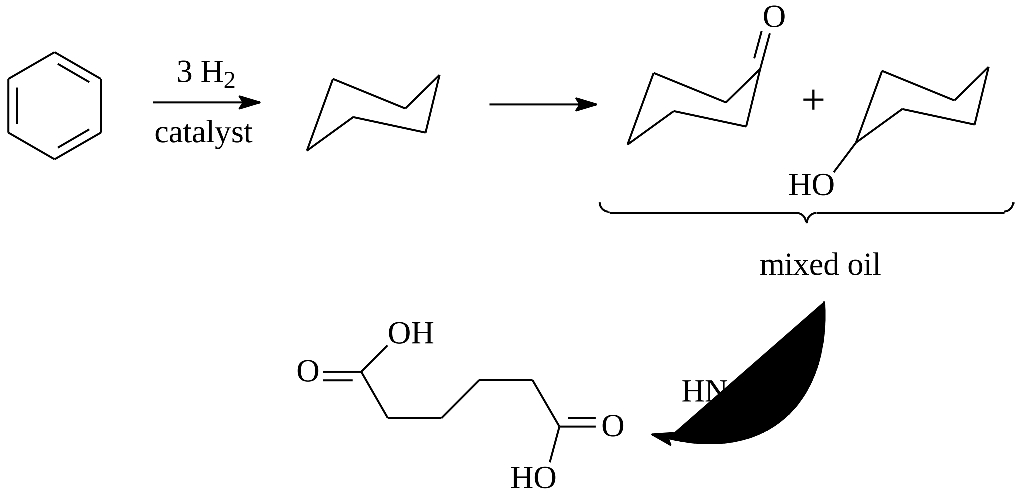
The Nylon Story

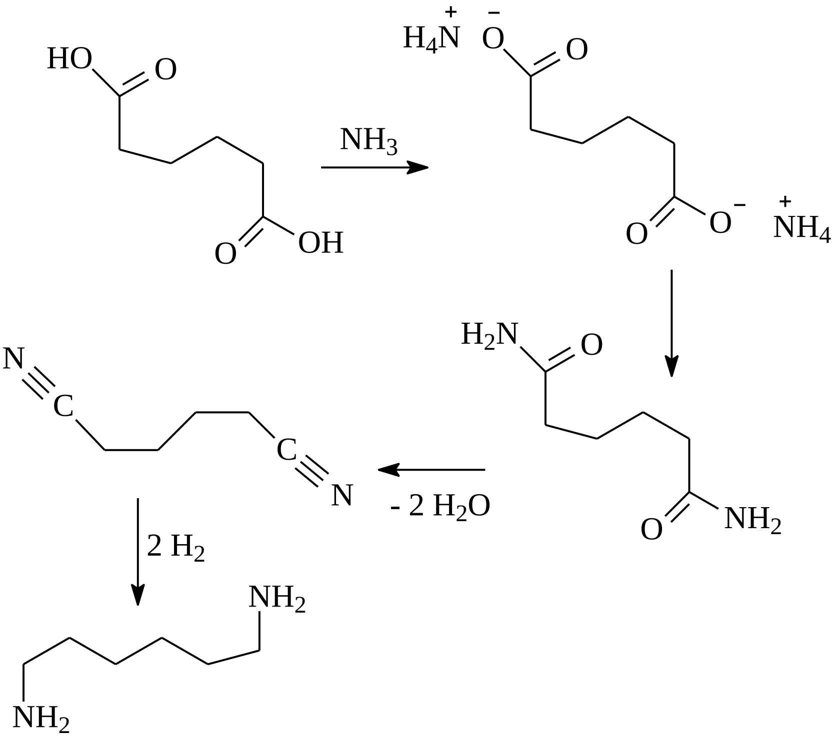
1- In 1928 DuPont asked prof. Carothers to do also basic research on petrochemicals in direction of polymers.
2- He selected condensation polymerization as a direction for his work
3- Initially he investigated condensing diesters with diols but removal of water from reaction proved a tidous process in industry and his discoveries in this area could not be scaled up.
4- He shifted to condensation of diamines with diacids.
5- Several types of polyamides were obtained.

monomer(s)	**Polymer**	**Properties**
	 nylon 6,6	**Tm = 265 ºC** **Eq H_2O = 8%**
	 nylon 4,6	**Tm = 283-319 ºC** **Eq H_2O > 8%**
	 nylon 4,10	**Tm = 225 ºC** **Eq H_2O = 3 %**
	 nylon 6	**Tm = 230 ºC** **Eq H_2O = 11 %**
	 nylon 11	**Tm = 188 ºC** **Eq H_2O = 2 %**

6- Synthesis of Adepic acid and hexamethylenediamine

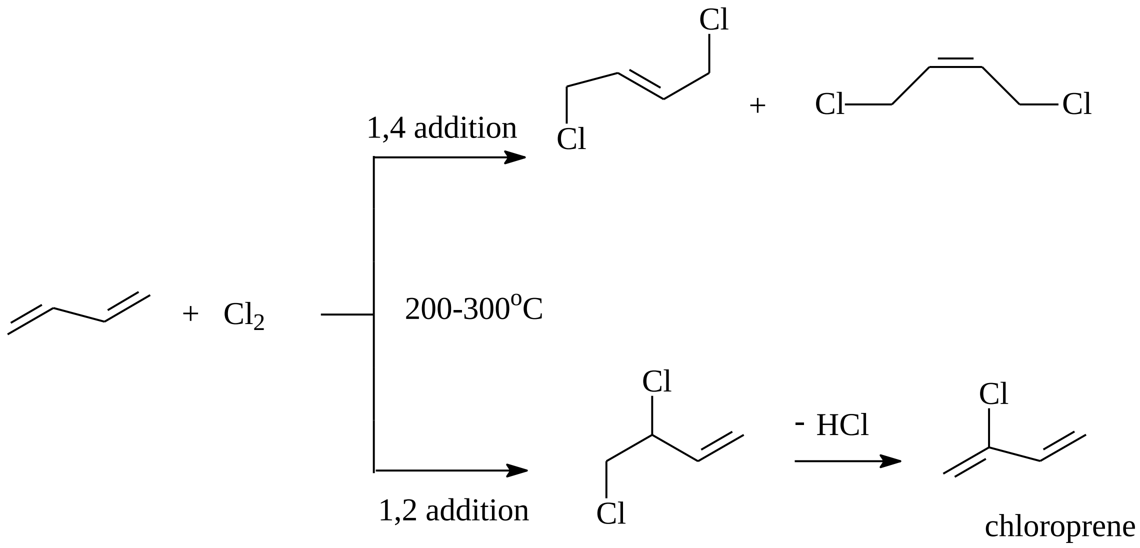
Three steps from benzene to adipic acid



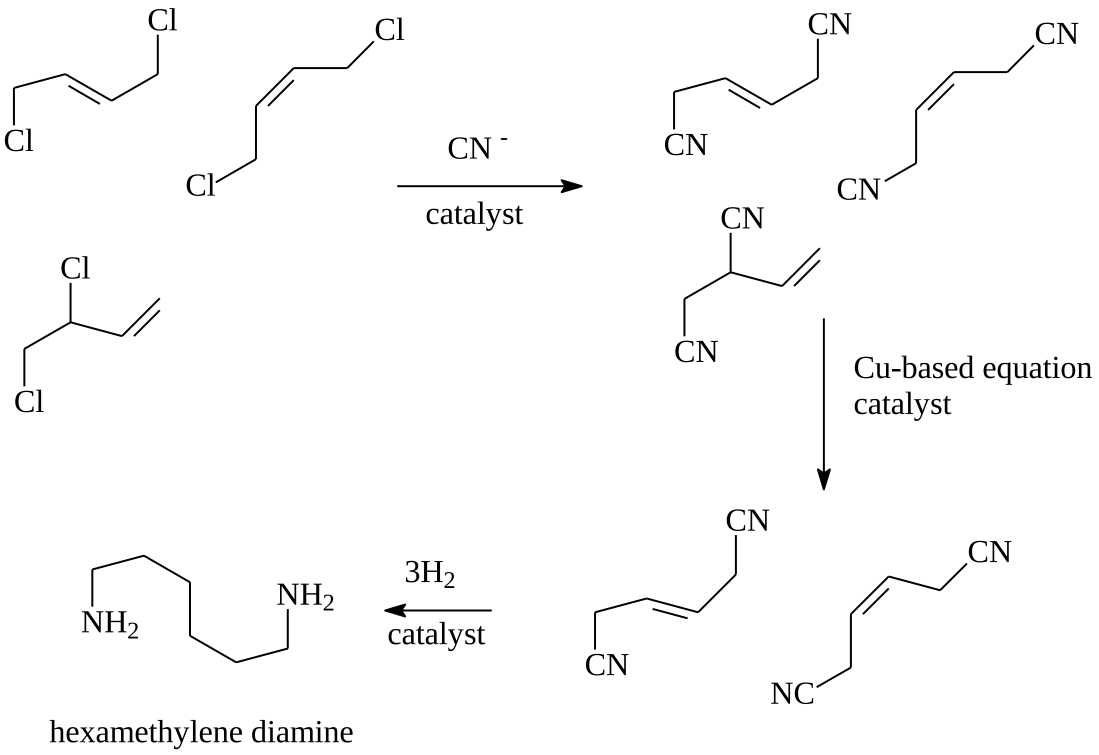


This is expensive and multistageouses

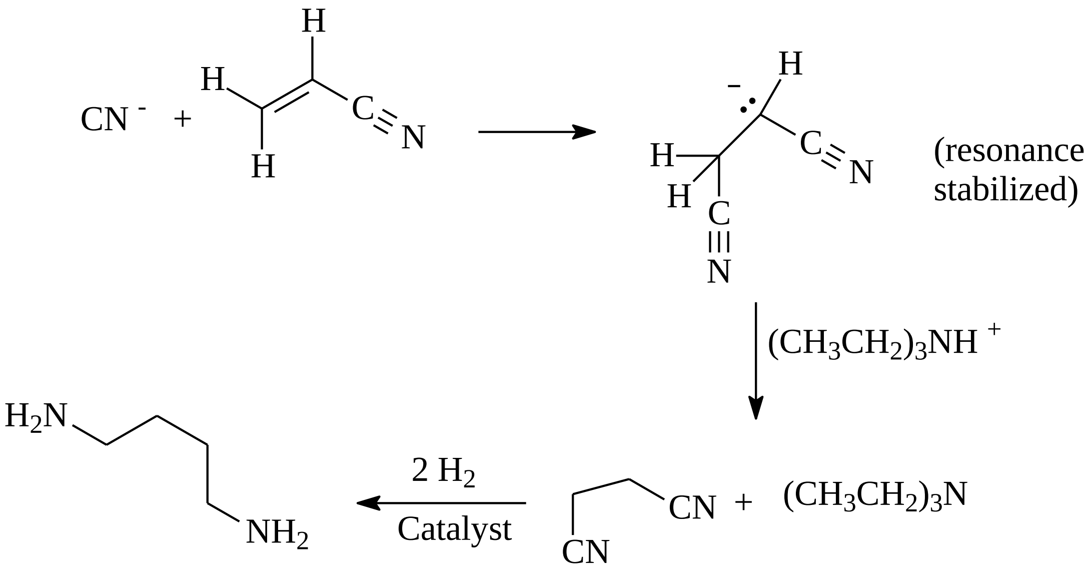
7- Other routes to hexamethylenediamine were thus investigated.



How

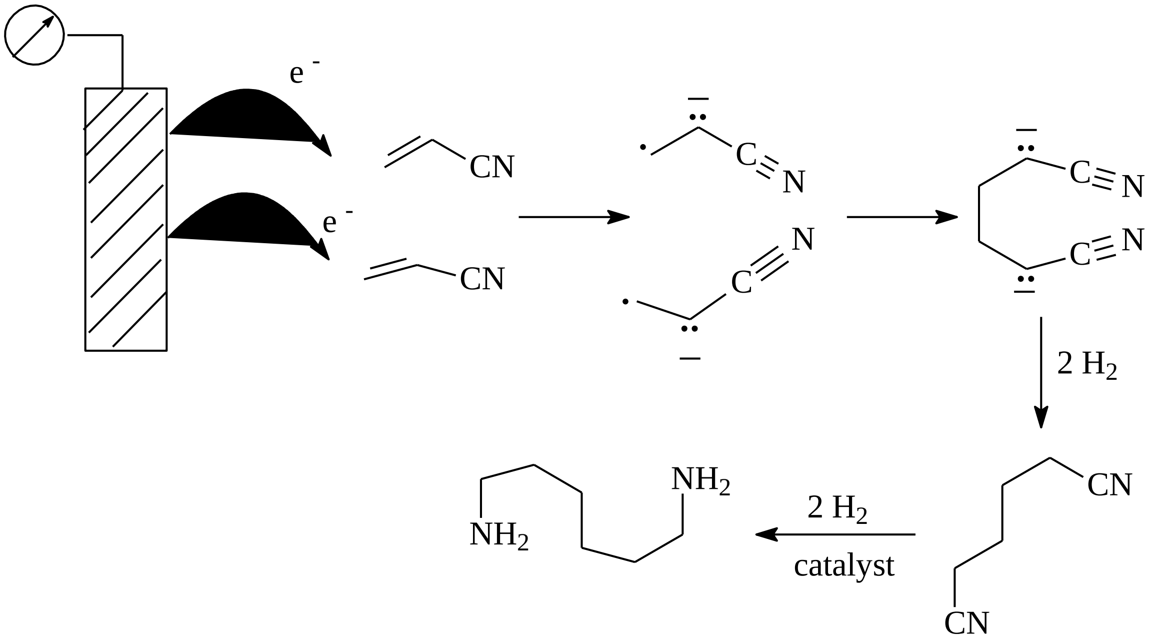


8- Other source to diamines were considered. Successful synthesis of tetramethylenediamine afforded nylon 4, 6.



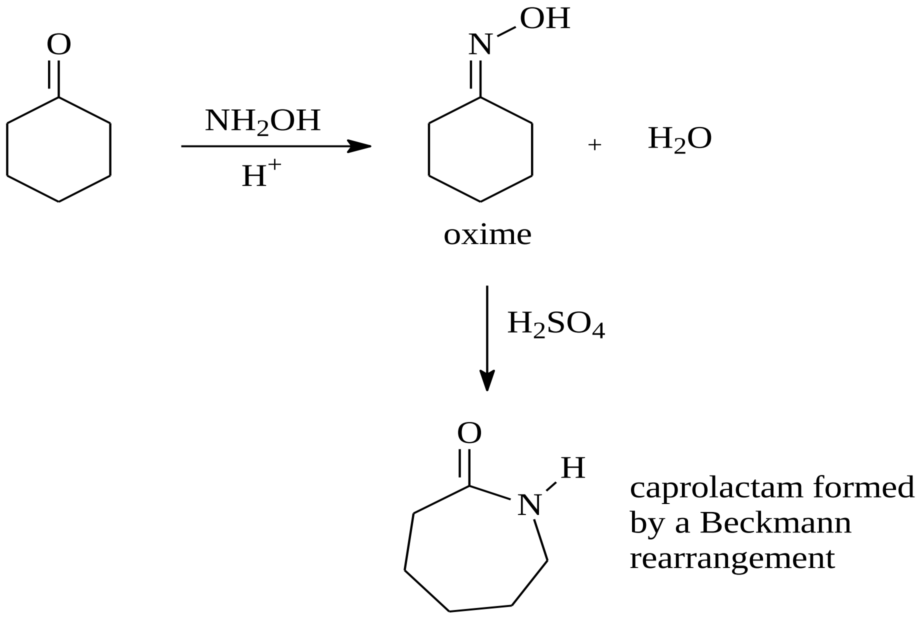
tetramethylene
diamine
reacts with adipic acid to produce nylon 4,6

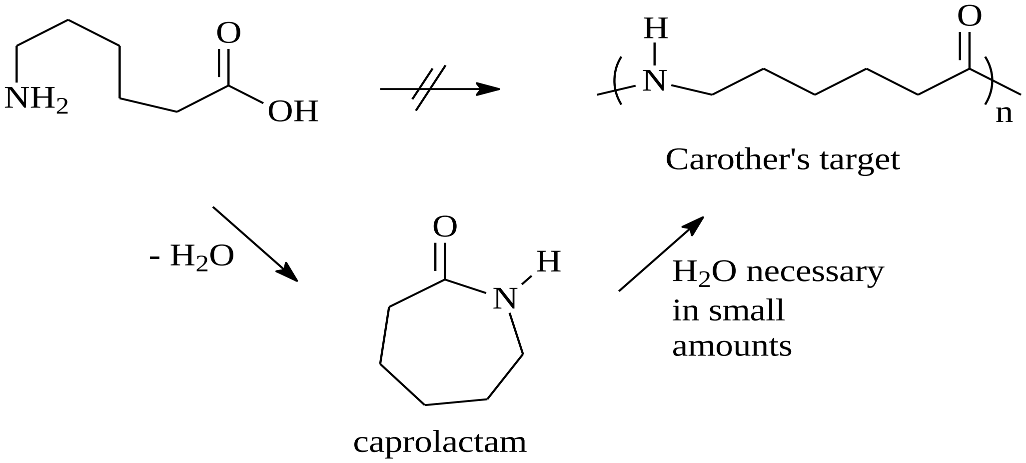
9- Monsanto process (Dr. Emanuel Baizer).



10- **Purity of both monomers is essential to get long chains as impurity can stop chain growth. This is achieved by crystallization and in this way both nylons 6,6 and could be produced Nylon made from single monomer.**

Nylon 6





Reference :-

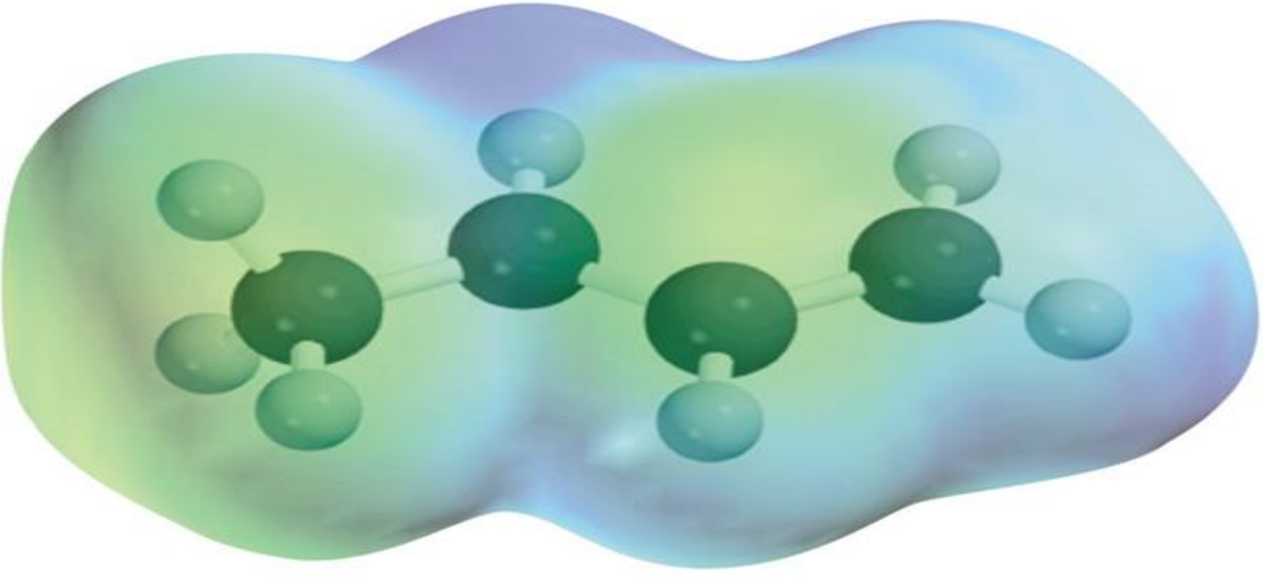
1- An Introduction to Polymer Chemistry (book)
2-some publication of prof.M.H.Elnagdi
3-polymer chemistry (springerlink)

Dienes

Dr. Hemat Mohamed Dardeer
3rd year students (chemistry group)
Faculty of Education
2022/2023

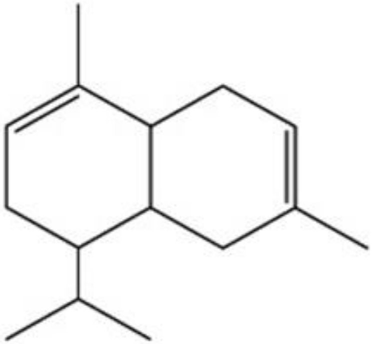
Contents

Reactions of Dienes
Ultraviolet and Visible Spectroscopy

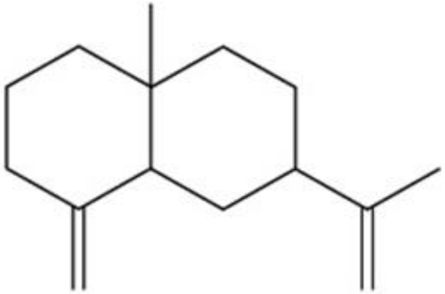


$$\mathrm{CH_3{-}\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}H_2}$$

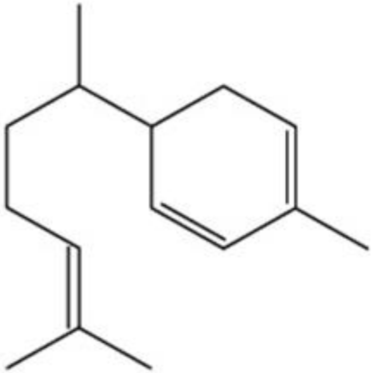
- Hydrocarbon containing
- two double bonds: diene
- three double bonds: triene
- four double bonds: tetraene
- many double bonds: polyene



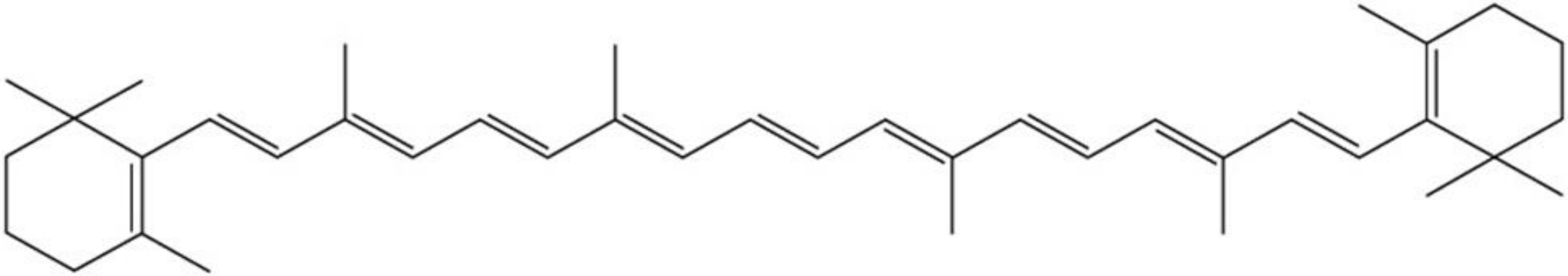
α-cadinene
oil of citronella
a diene



β-selinene
oil of celery
a diene



zingiberene
oil of ginger
a triene



β-carotene
a polyene

Different Kinds of Dienes

$\mathrm{CH_3CH{=}CH{-}CH{=}CHCH_3}$

a conjugated diene

$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2}$

an isolated diene

$\mathrm{CH_3{-}CH{=}C{=}CH{-}CH_3}$

a cumulated diene

an allene

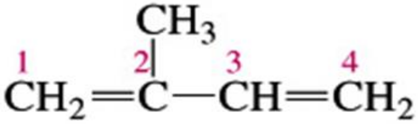
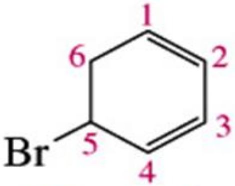
Nomenclature of Alkenes with More than One Functional Group

- 1. Identify the longest continuous chain containing
- both double bonds

- 2. Give the double bonds the lowest possible number

- 3. The numbers indicating the double bonds are cited
- either before the name of the parent compound or
- before the suffix

- 4. Substituents are cited in alphabetical order

	$CH_2{=}C{=}CH_2$	 $\overset{1}{CH_2}{=}\overset{CH_3}{\overset{|}{\overset{2}{C}}}{-}\overset{3}{CH}{=}\overset{4}{CH_2}$	
systematic:	propadiene	2-methyl-1,3-butadiene	5-bromo-1,3-cyclohexadiene
common:	allene	isoprene	

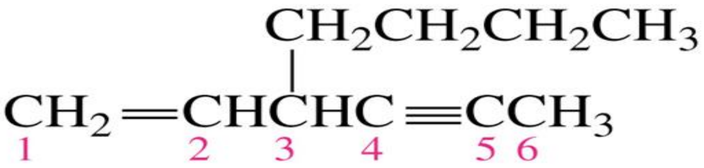
When the double bonds are a double bond and a triple bond

$\overset{7}{CH_3}\overset{6}{CH}=\overset{5}{CH}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{C}\equiv\overset{1}{CH}$

5-hepten-1-yne
not **2-hepten-6-yne**
because 1 < 2

$\overset{1}{CH_2}=\overset{2}{CH}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{C}\equiv\overset{6}{C}\overset{7}{CH_3}$

1-hepten-5-yne
not **6-hepten-2-yne**
because 1 < 2



$\underset{1}{CH_2}=\underset{2}{CH}\underset{3}{\overset{CH_2CH_2CH_2CH_3}{\overset{|}{C}}}H\underset{4}{C}\equiv\underset{5}{C}\underset{6}{CH_3}$

3-butyl-1-hexen-4-yne

the longest continuous chain has eight carbons, but the 8-carbon chain does not contain both functional groups; therefore, the compound is named as a hexenyne because the longest continuous chain containing both functional groups has six carbons

If there is a tie, the double bond gets the lowest number

$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}{\equiv}\overset{5}{C}\overset{6}{C}H_3$

2-hexen-4-yne

***not* 4-hexen-2-yne**

$H\overset{6}{C}{\equiv}\overset{5}{C}\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$

1-hexen-5-yne

***not* 5-hexen-1-yne**

A chain is numbered to give the lowest number to the functional group with the highest priority

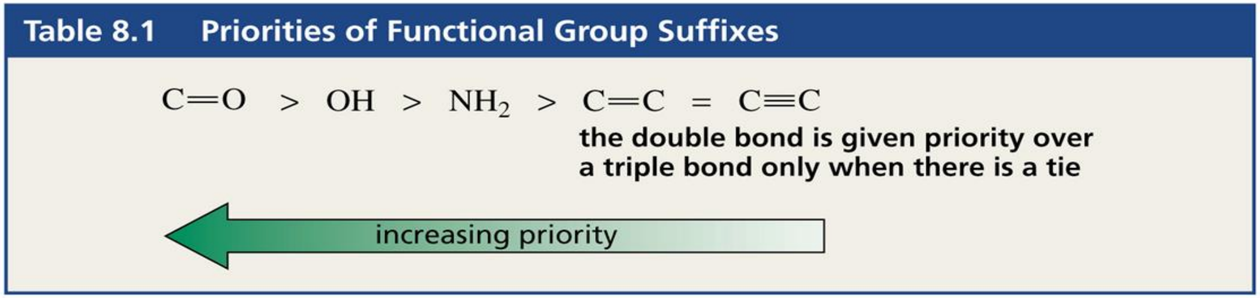


Table 8.1 Priorities of Functional Group Suffixes

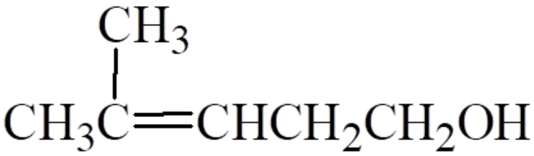
$\mathrm{C{=}O} > \mathrm{OH} > \mathrm{NH_2} > \mathrm{C{=}C} = \mathrm{C{\equiv}C}$

the double bond is given priority over a triple bond only when there is a tie

increasing priority

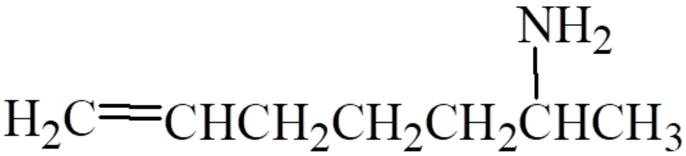
$H_2C{=}CHCH_2OH$

2-propen-1-ol



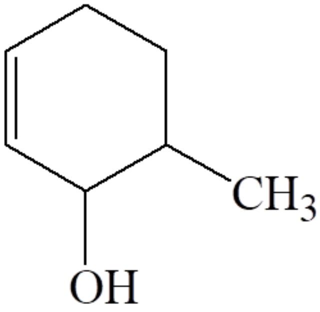
$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2OH$

4-methyl-3-penten-1-ol

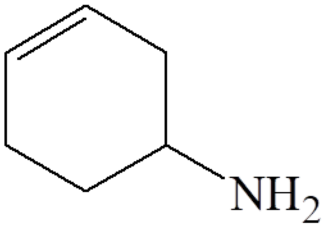


$H_2C{=}CHCH_2CH_2CH_2\overset{NH_2}{\overset{|}{C}}HCH_3$

6-hepten-2-amine



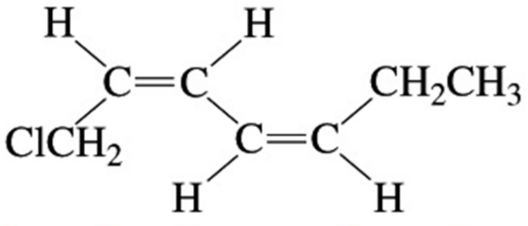
6-methyl-2-cyclohexanol



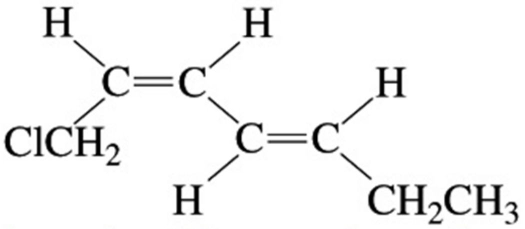
3-cyclohexenamine

Configurational Isomers of Dienes

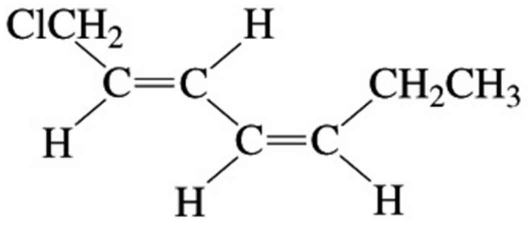
The *Z* isomer has the high-priority groups on the same side



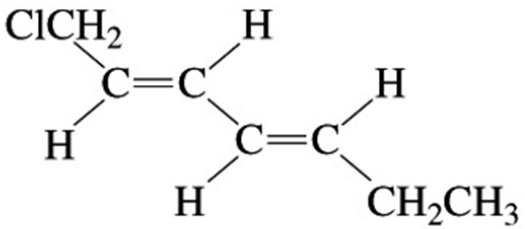
(2*Z*,4*Z*)-1-chloro-2,4-heptadiene



(2*Z*,4*E*)-1-chloro-2,4-heptadiene



(2*E*,4*Z*)-1-chloro-2,4-heptadiene



(2*E*,4*E*)-1-chloro-2,4-heptadiene

Stability of Dienes

relative stabilities of dienes

conjugated diene > isolated diene > cumulated diene

$CH_3CH{=}C{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -70.5$ kcal/mol (-295 kJ/mol)

2,3-pentadiene

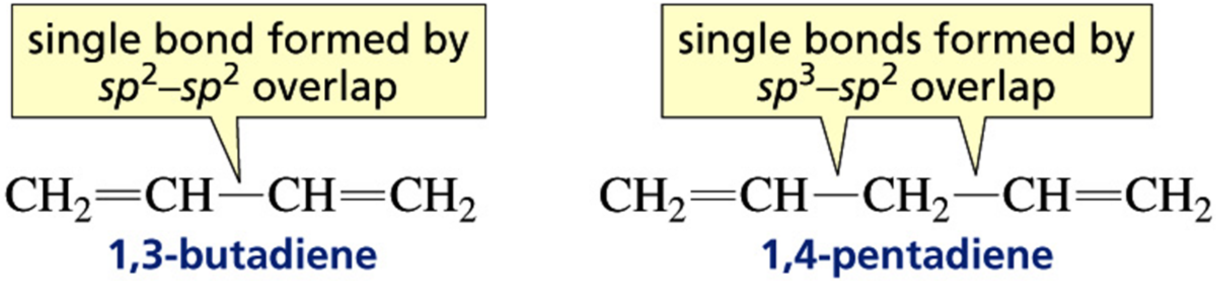
$CH_2{=}CHCH_2CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -60.2$ kcal/mol (-252 kJ/mol)

1,4-pentadiene

$CH_2{=}CHCH{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -54.1$ kcal/mol (-226 kJ/mol)

1,3-pentadiene

Why is conjugated diene more stable than isolated diene?



$CH_2{=}CH{-}CH{=}CH_2$

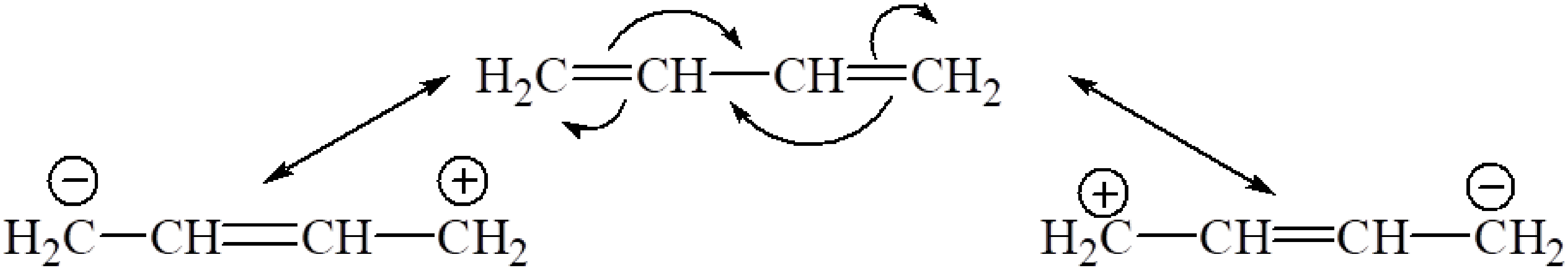
1,3-butadiene

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

1,4-pentadiene

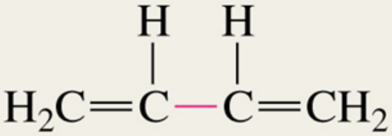
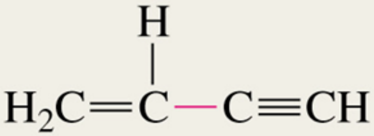
The closer the electrons are to the nucleus, the shorter and stronger is the bond

Electron Delocalization Stabilizes a Conjugated Diene

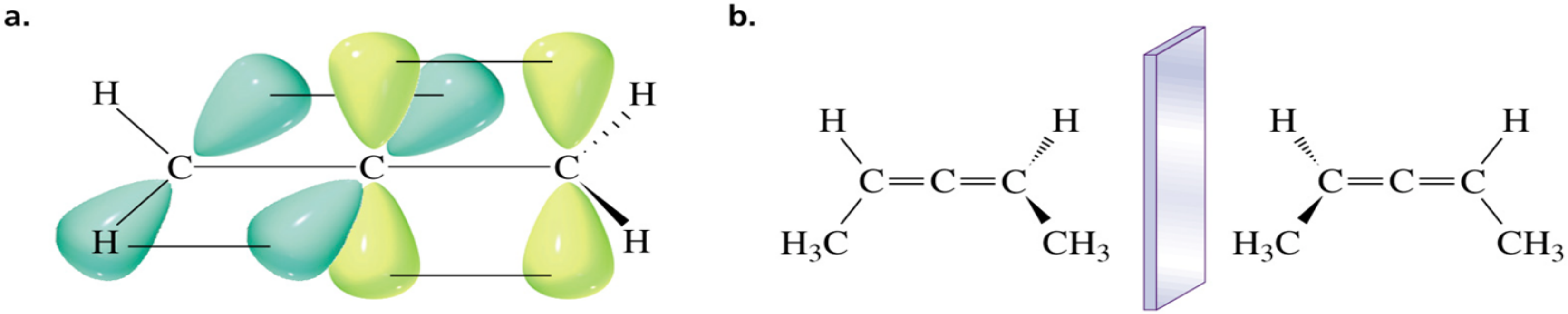


resonance hybrid

Table 8.2 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation

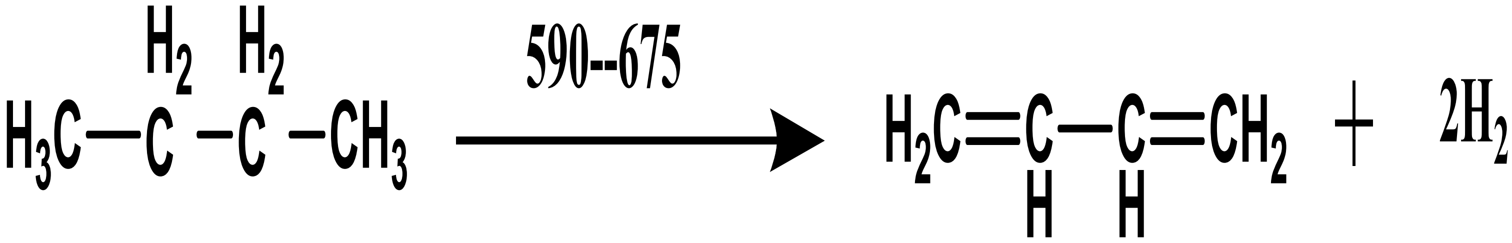
Compound	Hybridization	Bond length (Å)
H_3C-CH_3	sp^3–sp^3	1.54
 $H_3C-\overset{H}{\overset{\vert}{C}}=CH_2$	sp^3–sp^2	1.50
 $H_2C=\overset{H}{\overset{\vert}{C}}-\overset{H}{\overset{\vert}{C}}=CH_2$	sp^2–sp^2	1.47
$H_3C-C\equiv CH$	sp^3–sp	1.46
 $H_2C=\overset{H}{\overset{\vert}{C}}-C\equiv CH$	sp^2–sp	1.43
$HC\equiv C-C\equiv CH$	sp–sp	1.37

A cumulated diene is less stable than an isolated diene



Preparation of Dienes

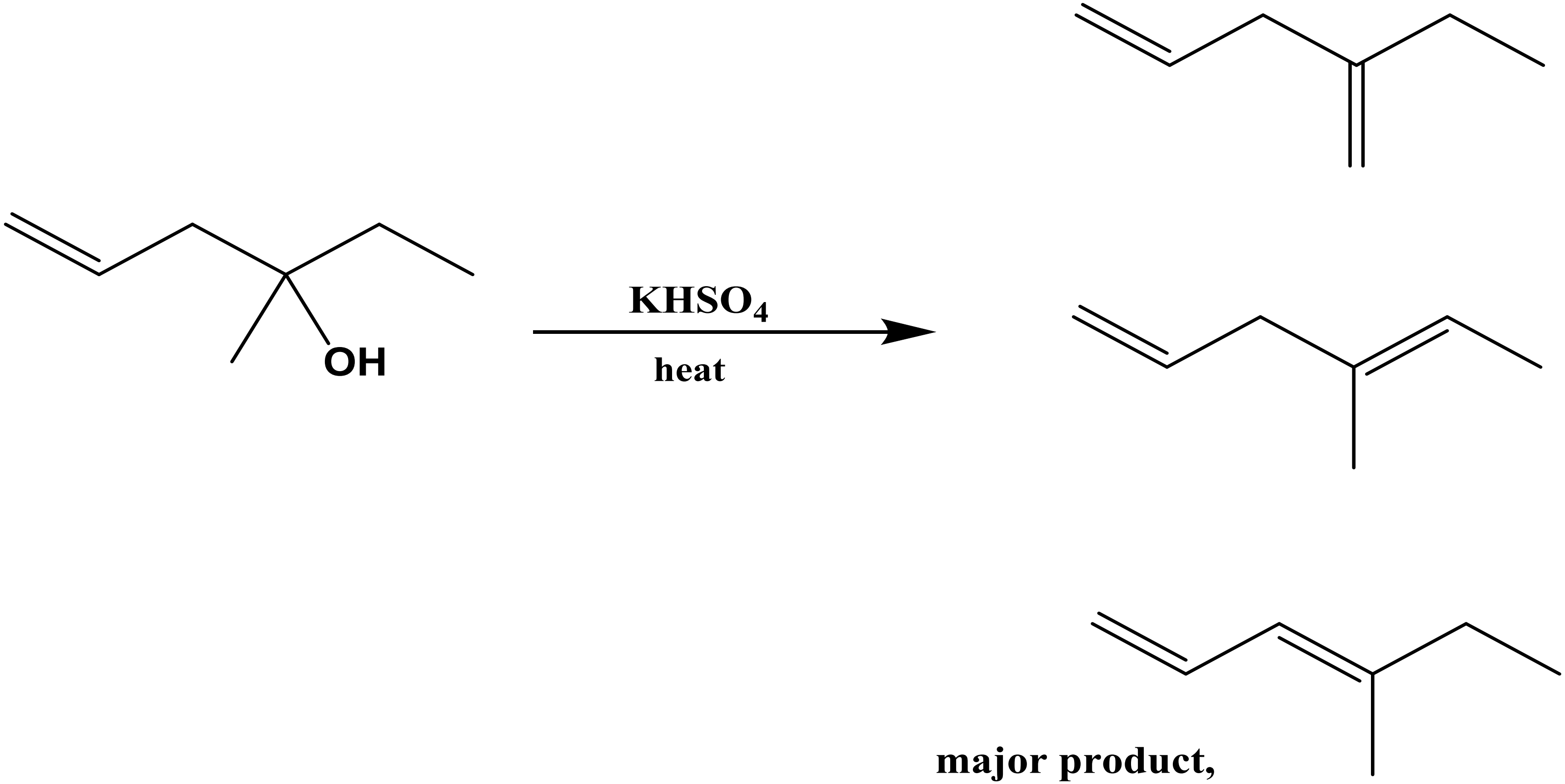
1,3-butadiene



$$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-CH_3 \xrightarrow{590\text{--}675} H_2C=\underset{H}{C}-\underset{H}{C}=CH_2 + 2H_2$$

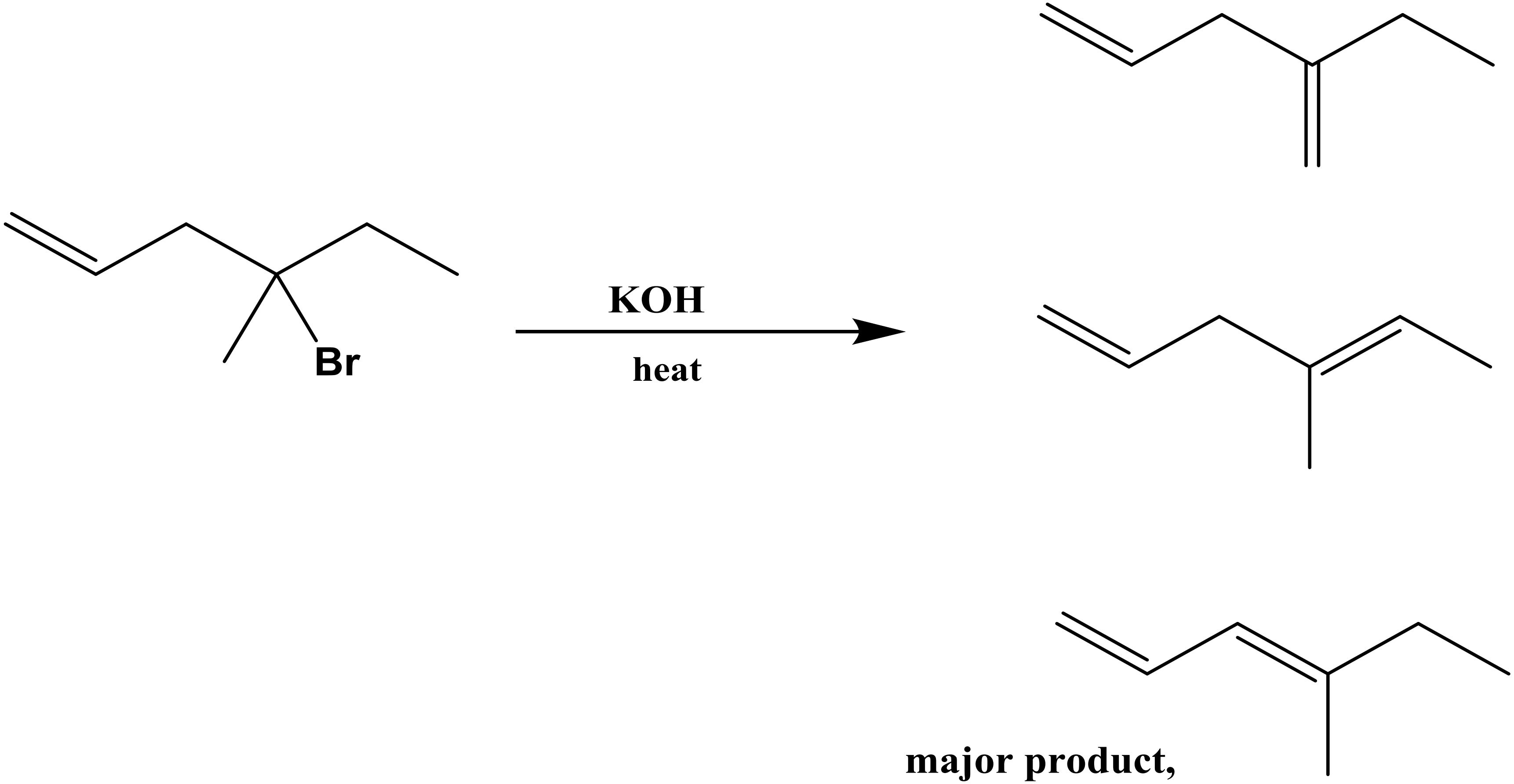
More than 4 billion pounds of 1,3-butadiene prepared by this method in U.S. each year used to prepare synthetic rubber.

Dehydration of alcohols



major product,
80% yield

Dehydrohalogenation of alkyl halides



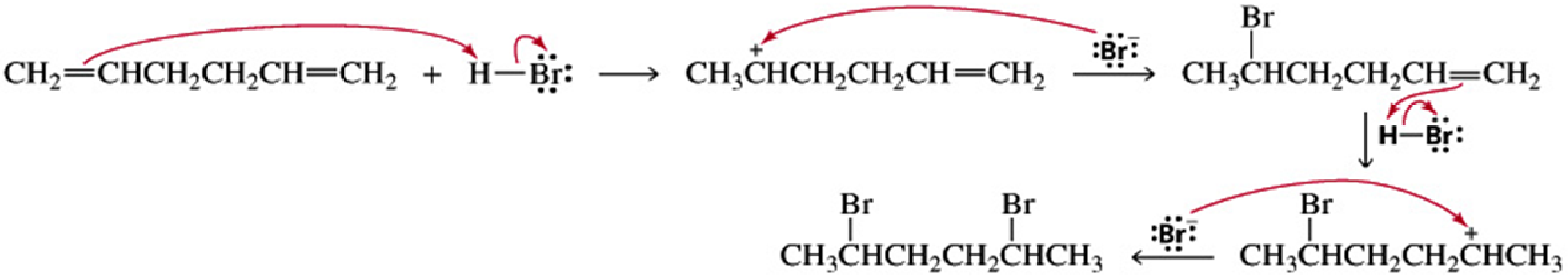
major product,
78% yield

Electrophilic Addition Reactions of Dienes

Electrophilic Addition Reactions of Isolated Dienes

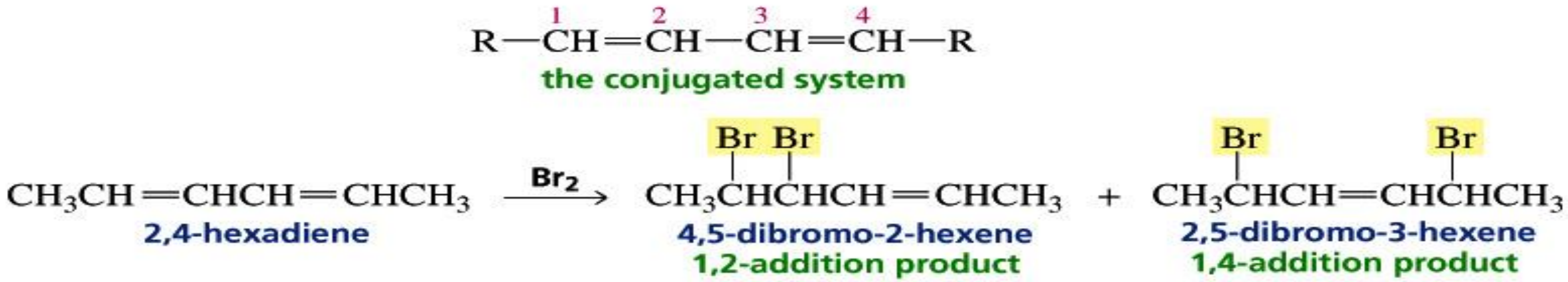
$$\underset{\text{1,5-hexadiene}}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + \underset{\text{excess}}{HBr} \longrightarrow CH_3\underset{\underset{Br}{|}}{CH}CH_2CH_2\underset{\underset{Br}{|}}{CH}CH_3$$

mechanism for the reaction of 1,5-hexadiene with excess HBr



Addition can occur at only one of the double bonds when 1 mole of HBr is available

Electrophilic Addition Reactions of Conjugated Dienes



$$R-\overset{1}{C}H=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-R$$

the conjugated system

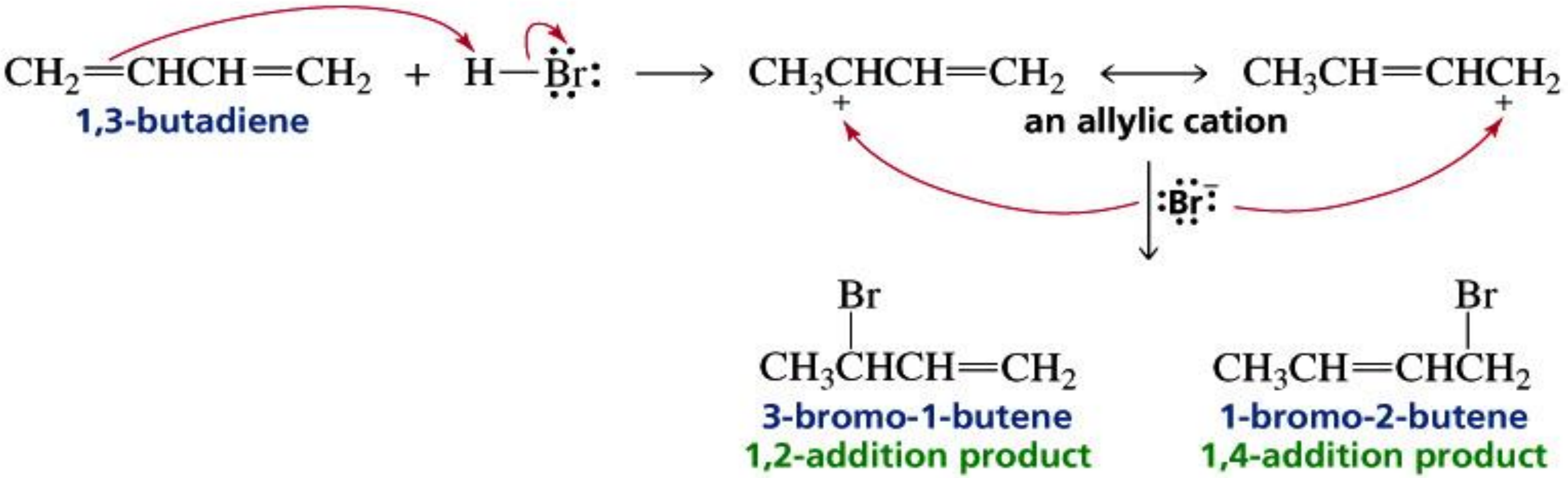
$$CH_3CH=CHCH=CHCH_3 \xrightarrow{Br_2} CH_3\overset{Br}{C}H\overset{Br}{C}HCH=CHCH_3 + CH_3\overset{Br}{C}HCH=CH\overset{Br}{C}HCH_3$$

2,4-hexadiene

4,5-dibromo-2-hexene
1,2-addition product

2,5-dibromo-3-hexene
1,4-addition product

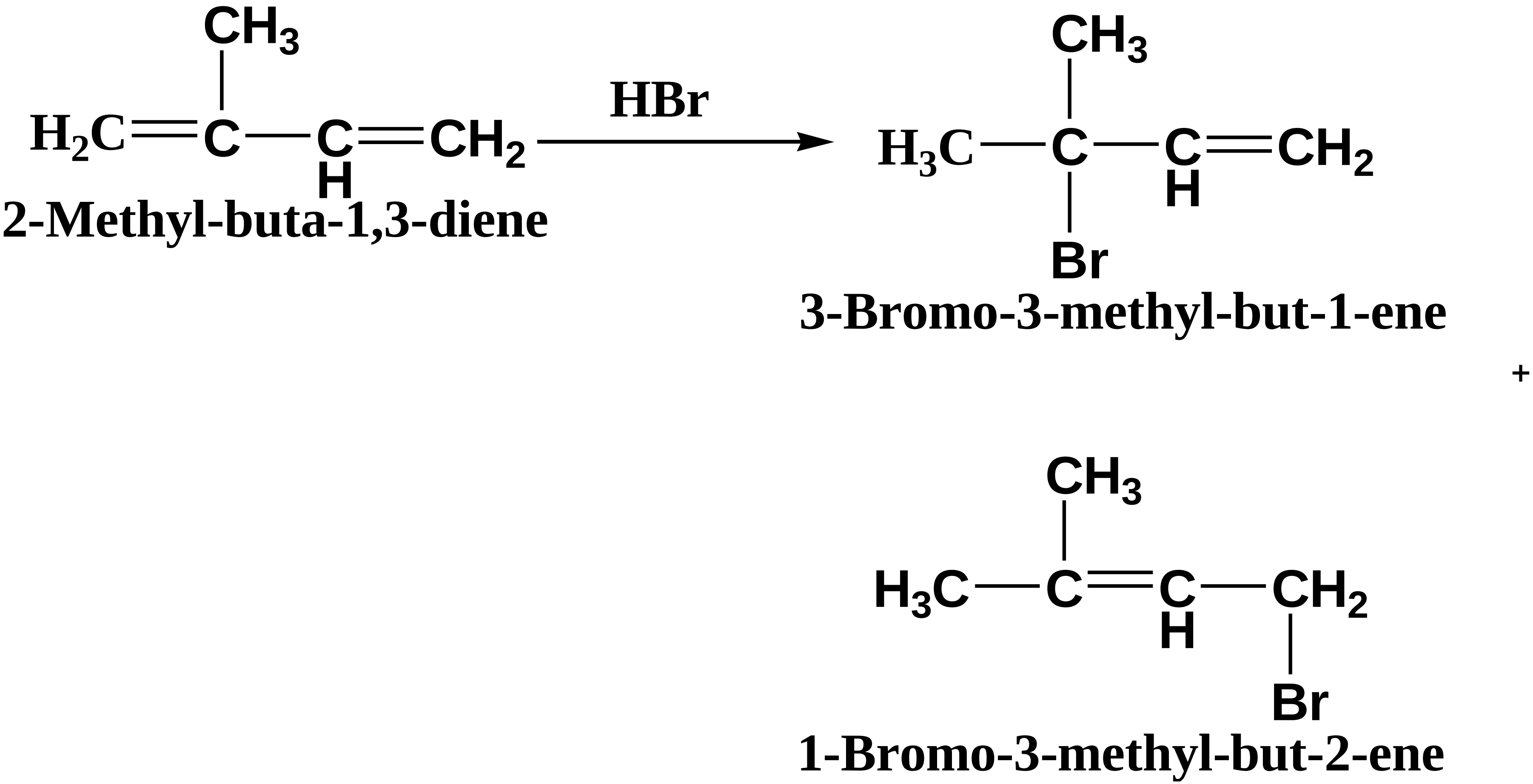
mechanism for the reaction of 1,3-butadiene with HBr



$$CH_2{=}CHCH{=}CH_2 + H{-}Br \longrightarrow CH_3\overset{+}{C}HCH{=}CH_2 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}H_2$$

$$\xrightarrow{Br^-} CH_3CH(Br)CH{=}CH_2 + CH_3CH{=}CHCH_2Br$$

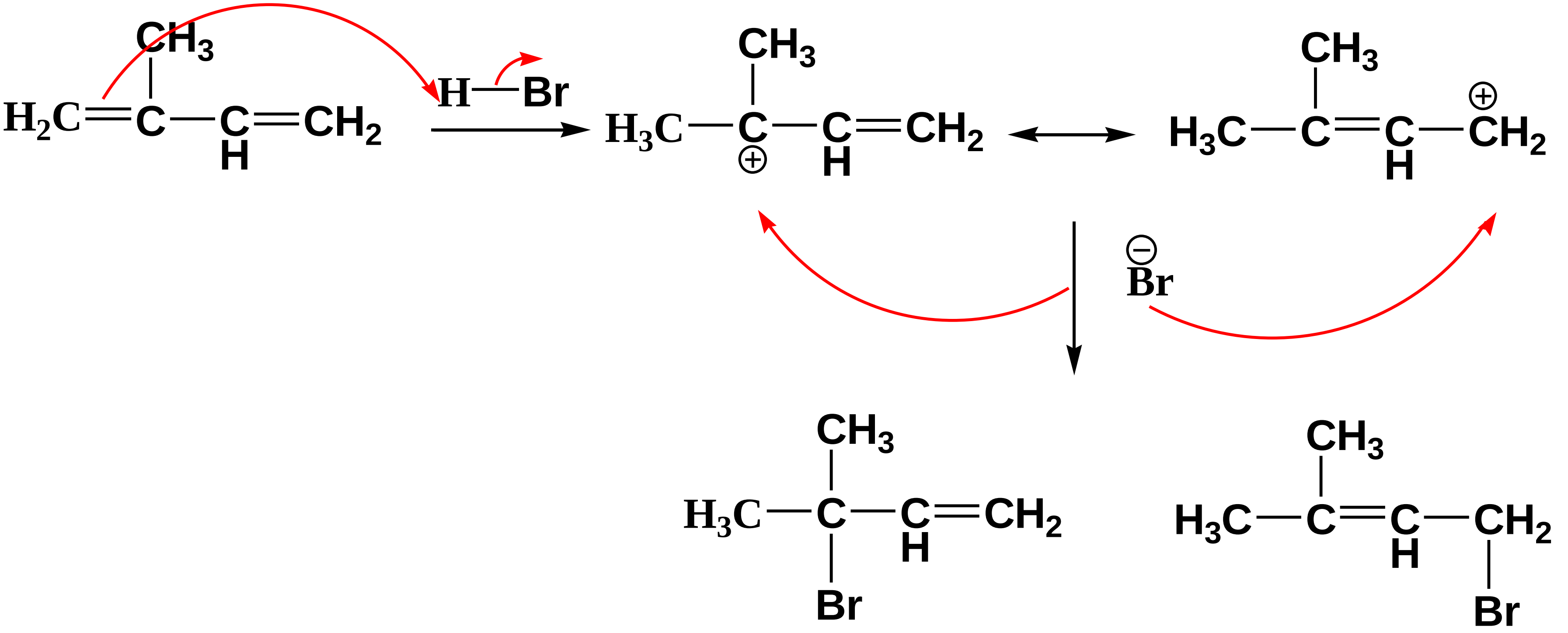
A conjugated diene undergoes both 1,2- and 1,4-addition



2-Methyl-buta-1,3-diene

3-Bromo-3-methyl-but-1-ene

1-Bromo-3-methyl-but-2-ene



1,2 addition

1,4 addition

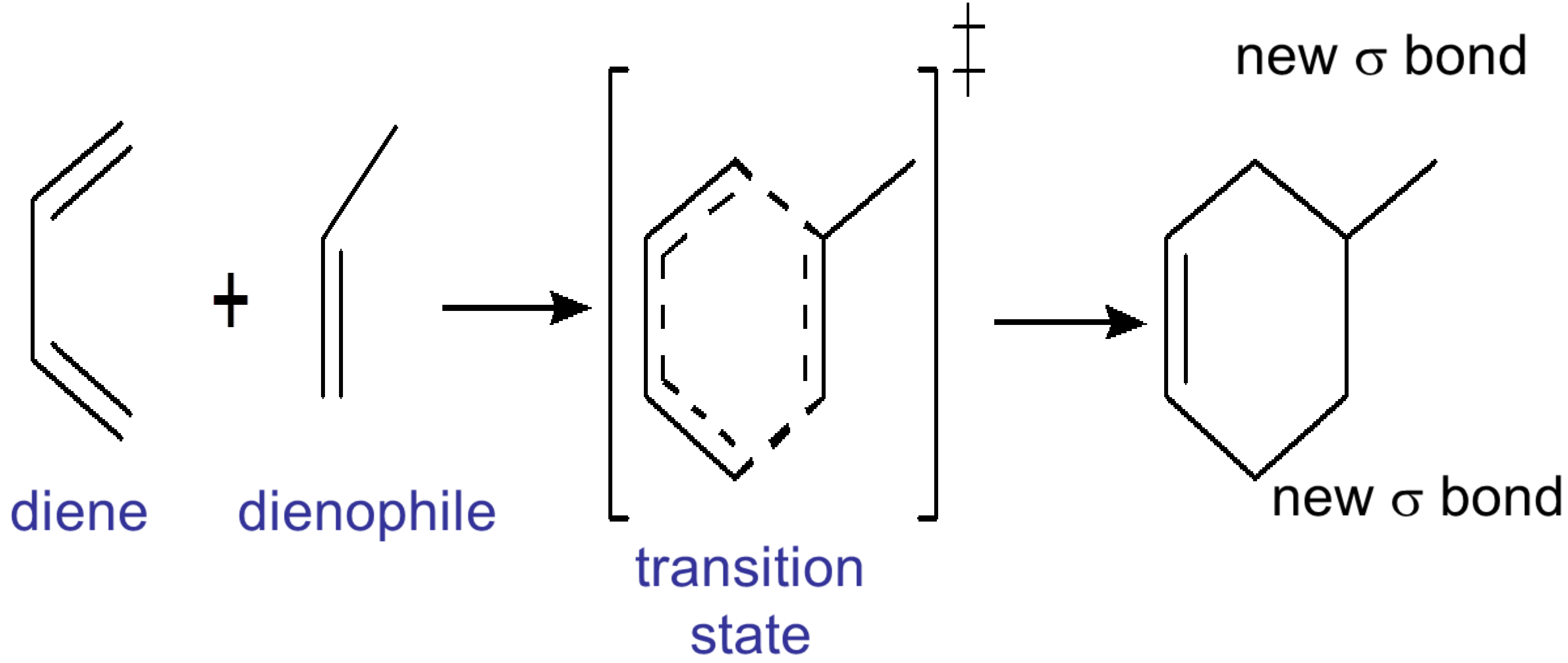
Thermodynamic Versus Kinetic Control

- The thermodynamic product is the most stable product
- The thermodynamic product predominates when the
- reaction is reversible (thermodynamic control)
- The kinetic product is the product that is formed most
- rapidly
- The kinetic product predominates when the reaction is
- irreversible (kinetic control)

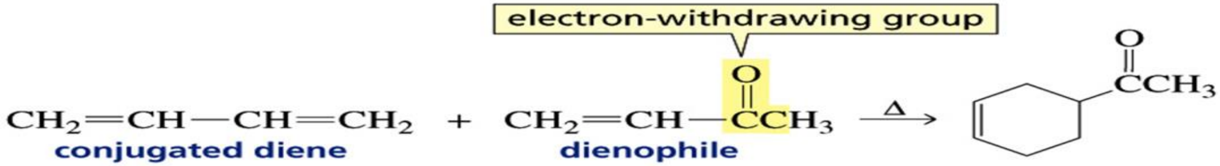
The Diels–Alder Reaction:
A 1,4-Addition Reaction

- It is organic chemical reaction
- cycloaddition reaction
- Between conjugated diene (4) and alkenes (2) called dienophile

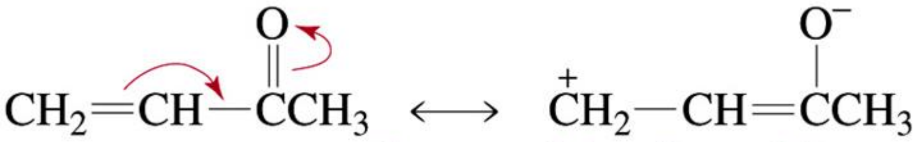
The Diels–Alder reaction is a pericyclic reaction; a [4+2] cycloaddition reaction



The reactivity of the dienophile is increased if one or more electron-withdrawing groups are attached to its *sp*^{2} carbons

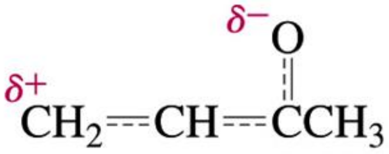


$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{\Delta}$



$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}CH_3 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{O^-}{\overset{|}{C}}CH_3$

resonance contributors of the dienophile

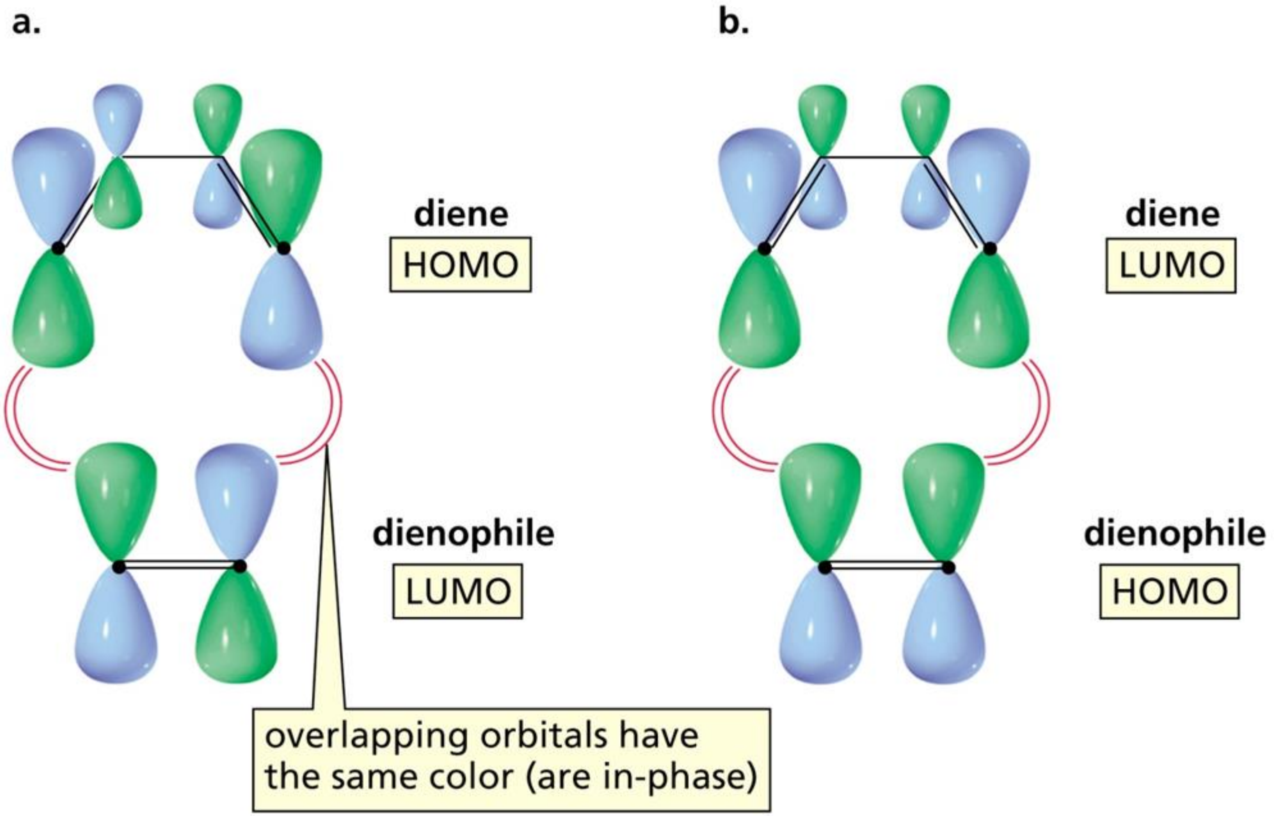


$\overset{\delta+}{C}H_2 \cdots CH \cdots \overset{\delta- O}{\overset{\vdots}{C}}CH_3$

resonance hybrid

A Molecular Orbital Description of the Diels–Alder Reaction

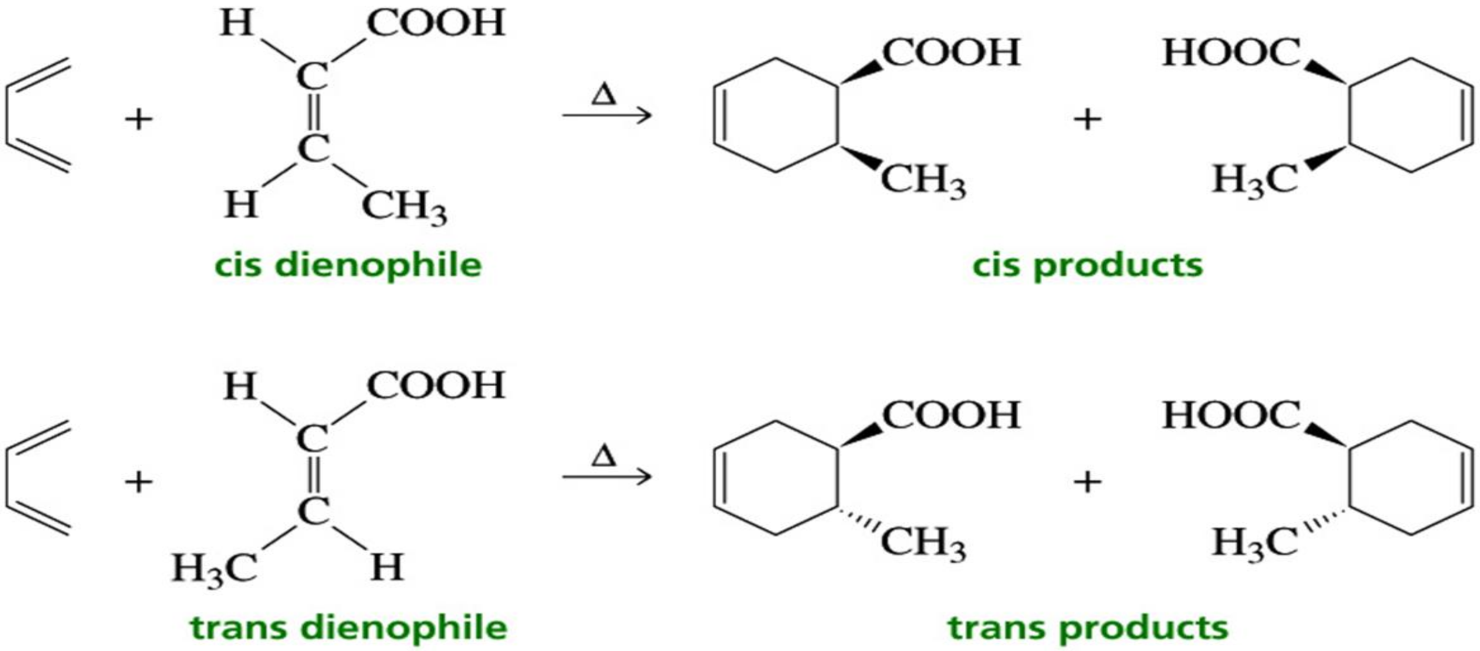
Let’s focus on the HOMO and the LUMO of the reactants



overlapping orbitals have the same color (are in-phase)

Stereochemistry of the Diels–Alder Reaction

The reaction is a syn addition

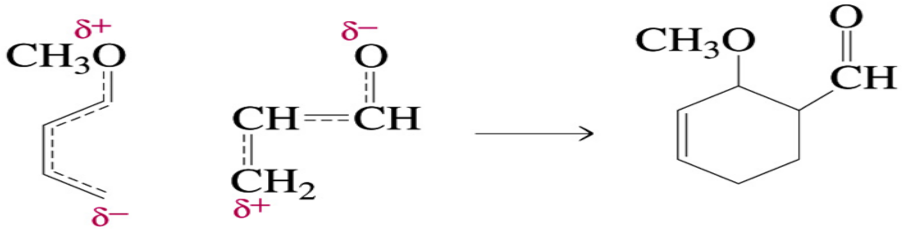


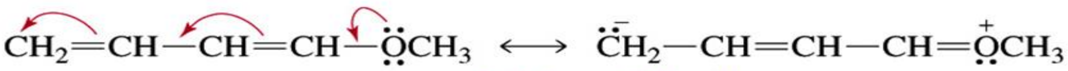
- The Diels–Alder reaction is stereospecific
- The configuration of the reactants is maintained
- The reaction is concerted

Predicting the reaction products

1. Consider the alignment of the reactants

2. Consider the charge distribution in each of the reactants





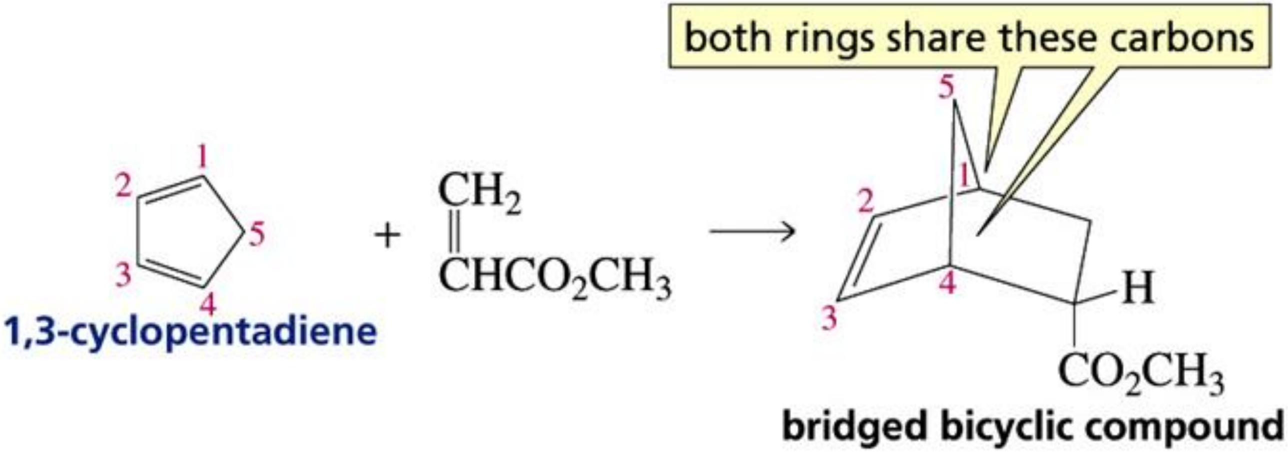
$CH_2{=}CH{-}CH{=}CH{-}\ddot{\underset{\cdot\cdot}{O}}CH_3 \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}CH{=}CH{-}CH{=}\overset{+}{\underset{\cdot\cdot}{O}}CH_3$

resonance contributors of the diene

$CH_2{=}CH{-}\overset{\overset{:\ddot{O}}{\|}}{CH} \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{\overset{:\ddot{O}:^{-}}{|}}{CH}$

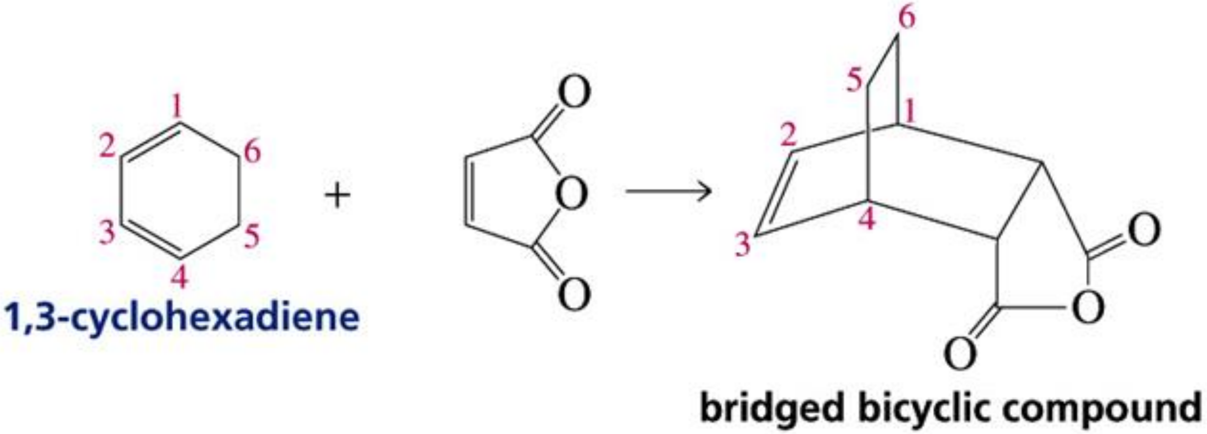
resonance contributors of the dienophile

Only the cis conformation can participate in a Diels–Alder reaction


both rings share these carbons

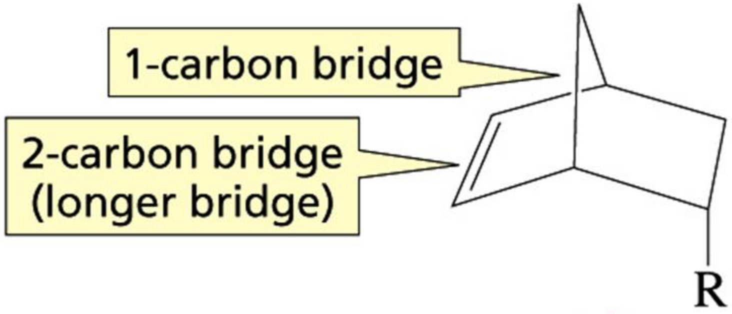
1,3-cyclopentadiene

bridged bicyclic compound

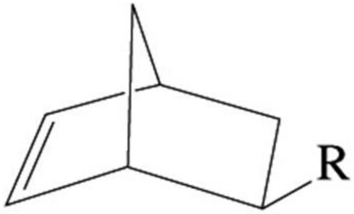

1,3-cyclohexadiene

bridged bicyclic compound

Two Possible Configurations of Bridged Bicyclic Compounds

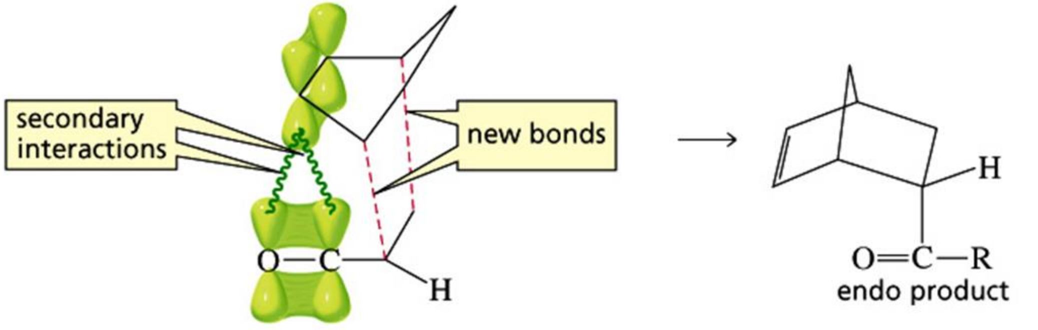


endo

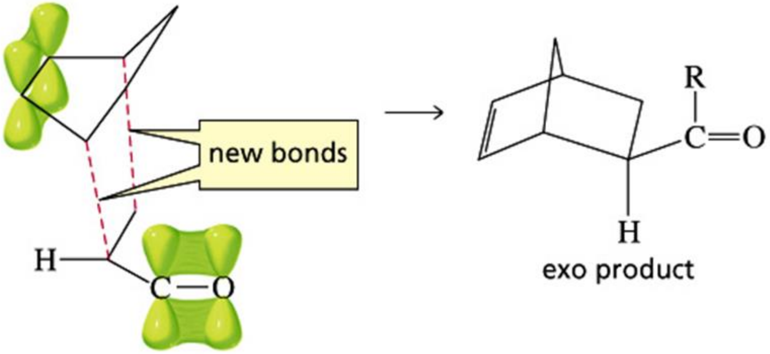


exo

Secondary orbital overlap favors the endo product formation



secondary orbital overlap
in the endo transition state



no secondary orbital
overlap in the exo transition state

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