Alicyclic Chemistry

3rd Year Students – Chemistry Group

Faculty of Education

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Dr./ Ibrahim Abdul-Motaleb Mousa

SOUTH VALLY UNIVERSITY

FACULTY OF SCIENCE

INTRODUCTION TO THE CHEMISTRY OF ALICYCLIC COMPOUNDS

By

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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.

Author
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Contents

Unit one

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 students ability to solve synthetic problems in alicyclic chemistry.

We shall 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

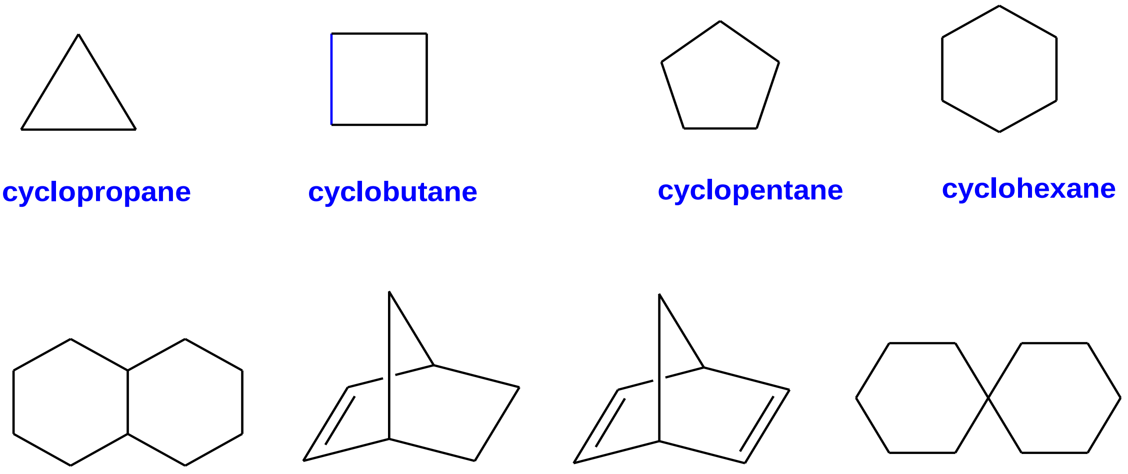
1.1 Introduction

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).

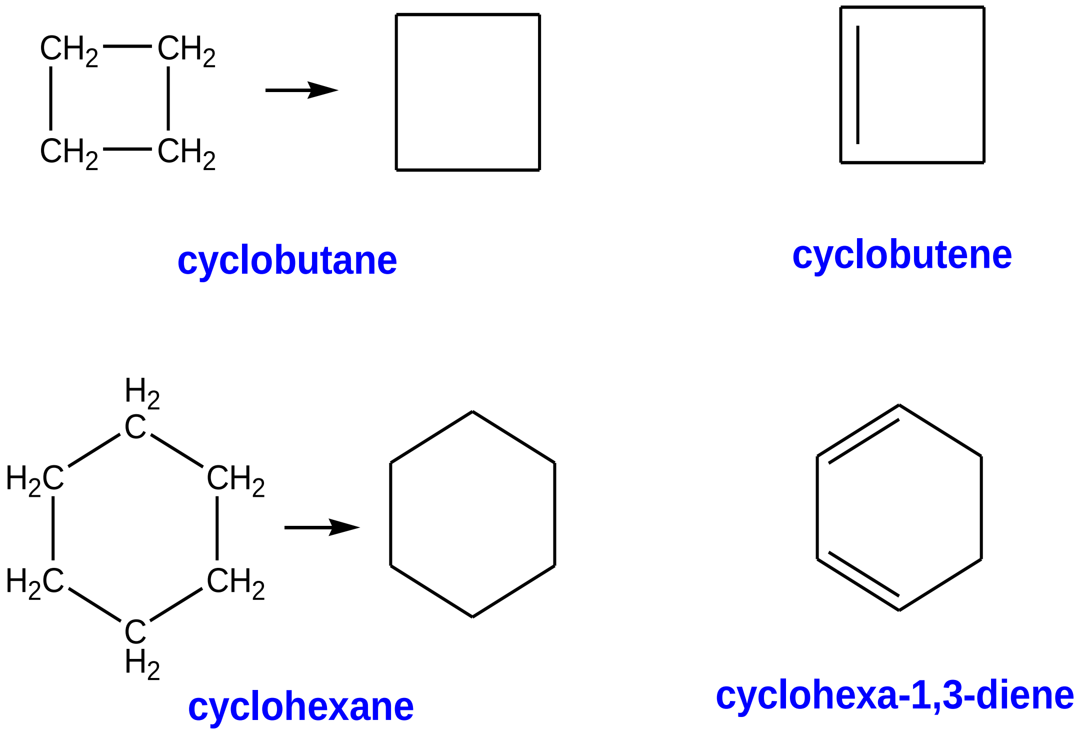
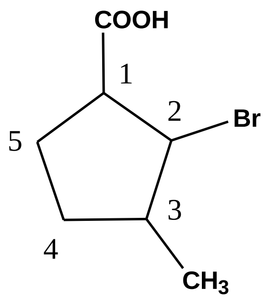
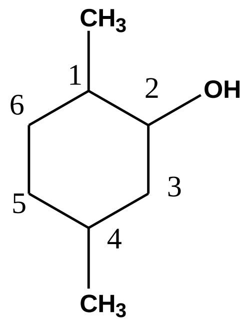


Fig. 1.2

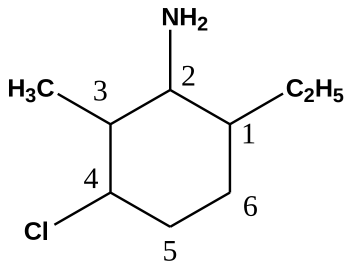
When a monocyclic hydrocarbon has a long and complex side chain, the open chain is named according to the I.U.P.A.C system, and the ring is regarded as a substituent, see examples in (Fig. 1.3).



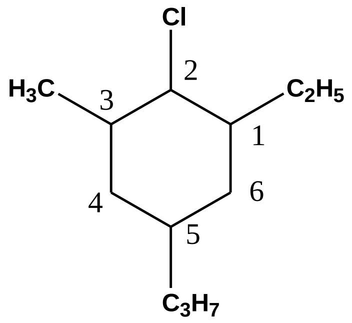
2-bromo-3-methyl-cyclopentanecarboxylic acid



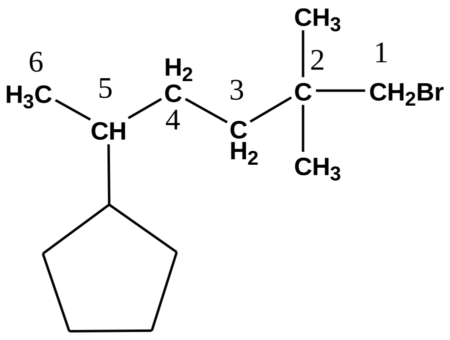
1,4-dimethyl-2-cyclohexanol



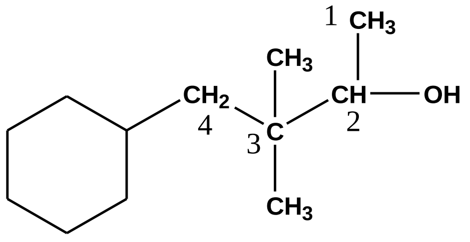
4-chloro-1-ethyl-3-methyl-2-cyclohexylamine



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



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



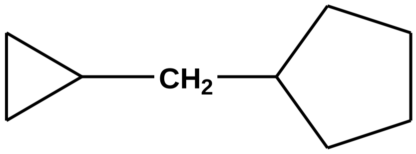
4-cyclohexyl-3,3-dimethyl-2-butanol

Fig. 1.3

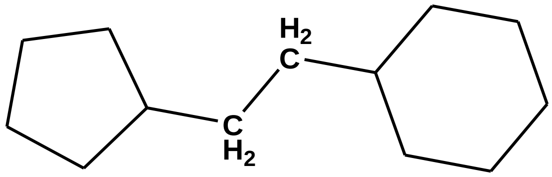
B- Bicyclic system:

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;

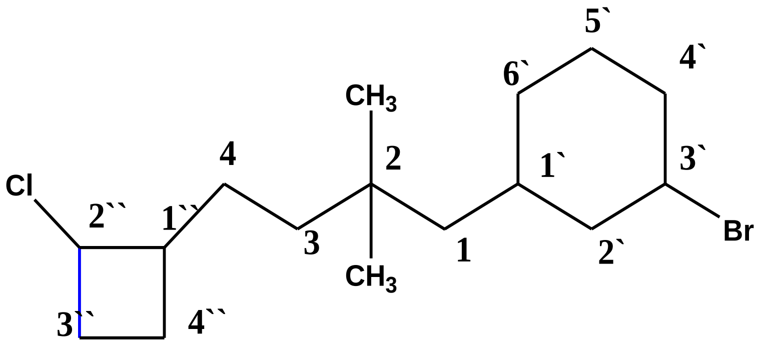


cyclopropylcyclopentylmethane

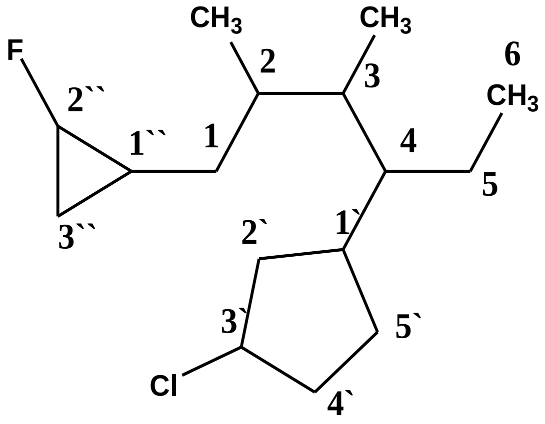


cyclopentylcyclohexylethane

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

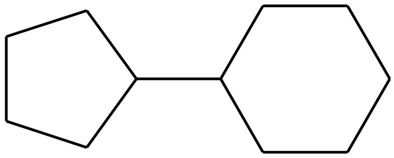


2,3-dimethyl-4-(3`-chlorocyclopentyl)-1-(2``-flourocyclopropyl)-hexane

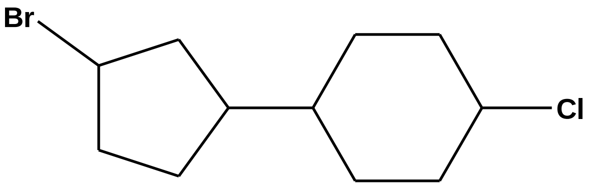
Fig. 1.4

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.,



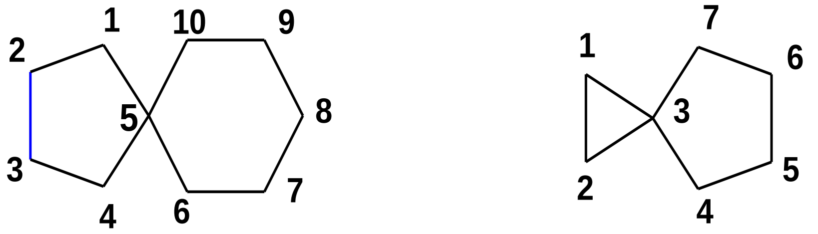
cyclopentyl-cyclohexane



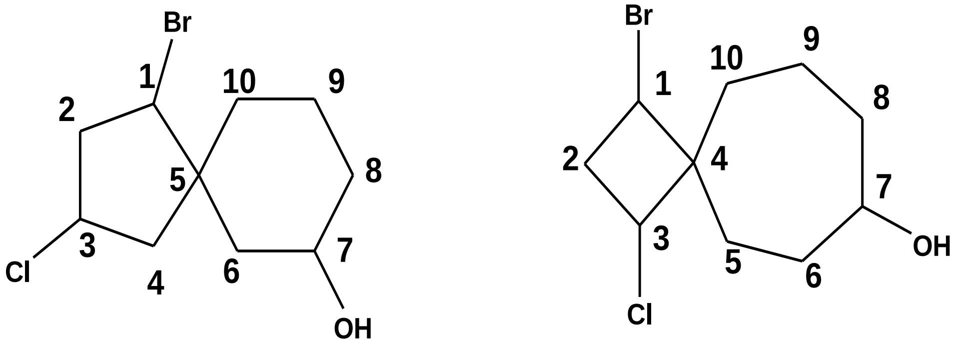
1-(3`-bromocyclopentyl)-4-chloro-cyclohexane

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

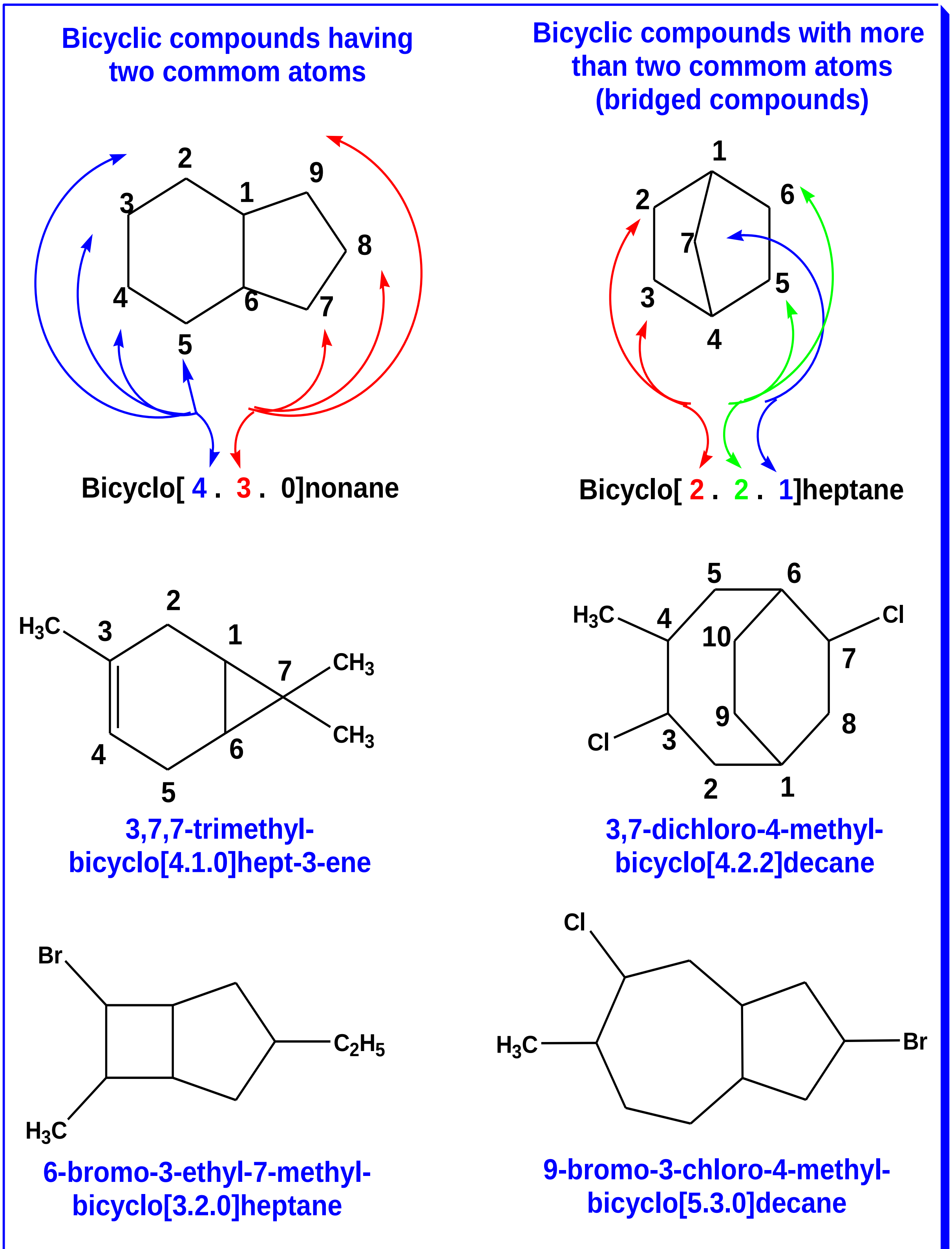


1-Bromo-3-chloro-spiro[4.5]decan-7-ol 1-Bromo-3-chloro-spiro[3.6]decan-7-ol

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

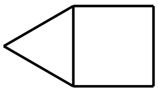
9-bromo-3-chloro-4-methyl-bicyclo[5.3.0]decane

Fig. 1.6

Quizzes:

1. Sign the correct name for each of the following compounds:

a-

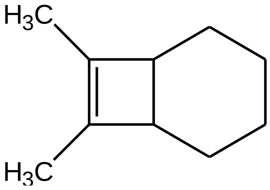


○ i)bicyclo[3.2.0]pentane

○ ii) bicyclo[2.1.0]pentane

○ iii)bicycle[2.1.1]pentane

b-

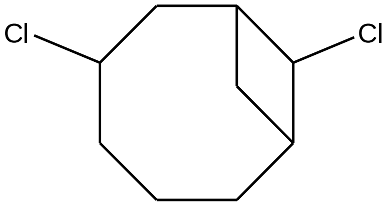


○ i) 2,3-dimethyl-bicyclo[4.2.0]oct-7-ene

○ ii) 7,8-dimethyl-bicyclo[4.2.1]oct-2-ene

○ iii) 7,8-dimethyl-bicyclo[4.2.0]oct-7-ene

c-



○ i) 3,8-dichloro-bicyclo[5.1.1]nonane

○ ii) 3,7-dichloro-bicyclo[5.2.1]nonane

○ iii) 1,4-dichloro-bicyclo[5.1.0]nonane

The solution;

1- a (ii), b (iii), c (i).

Unit 1

Lesson 2: General properties of alicyclic compounds

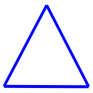
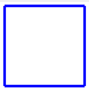
2.1 Occurrence and physical properties

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).

S	Name	Formula	Melting point ^{o}C	Boiling point ^{o}C	Density g/cm^3
1.	**Cyclopropane**		**-126.6**	**-34.4**	**0.72**
2.	**Cyclobutane**		**-91**	**12.5**	**0.703**

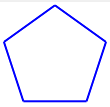
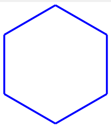
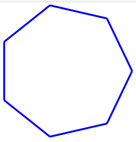
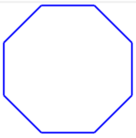
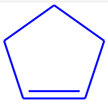
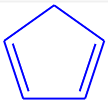
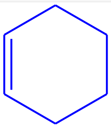
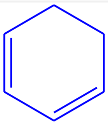
3.	**Cyclopentane**		**-93.3**	**49.5**	**0.751**
4.	**Cyclohexane**		**6.5**	**81.4**	**0.779**
5.	**Cycloheptane**		**-12**	**118.1**	**0.809**
6.	**Cyclo octane**		**14.3**	**148**	**0.835**
7.	**Cyclopentene**		**-93.3**	**44.2**	**0.772**
8.	**1,3-cyclopentadiene**		**-8.5**	**42.5**	**0.802**
9.	**Cyclohexene**		**-103.7**	**83**	**0.810**
10.	**1,3-cyclohexadiene**		**-98**	**80.5**	**0.84**

Table 2.1

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):

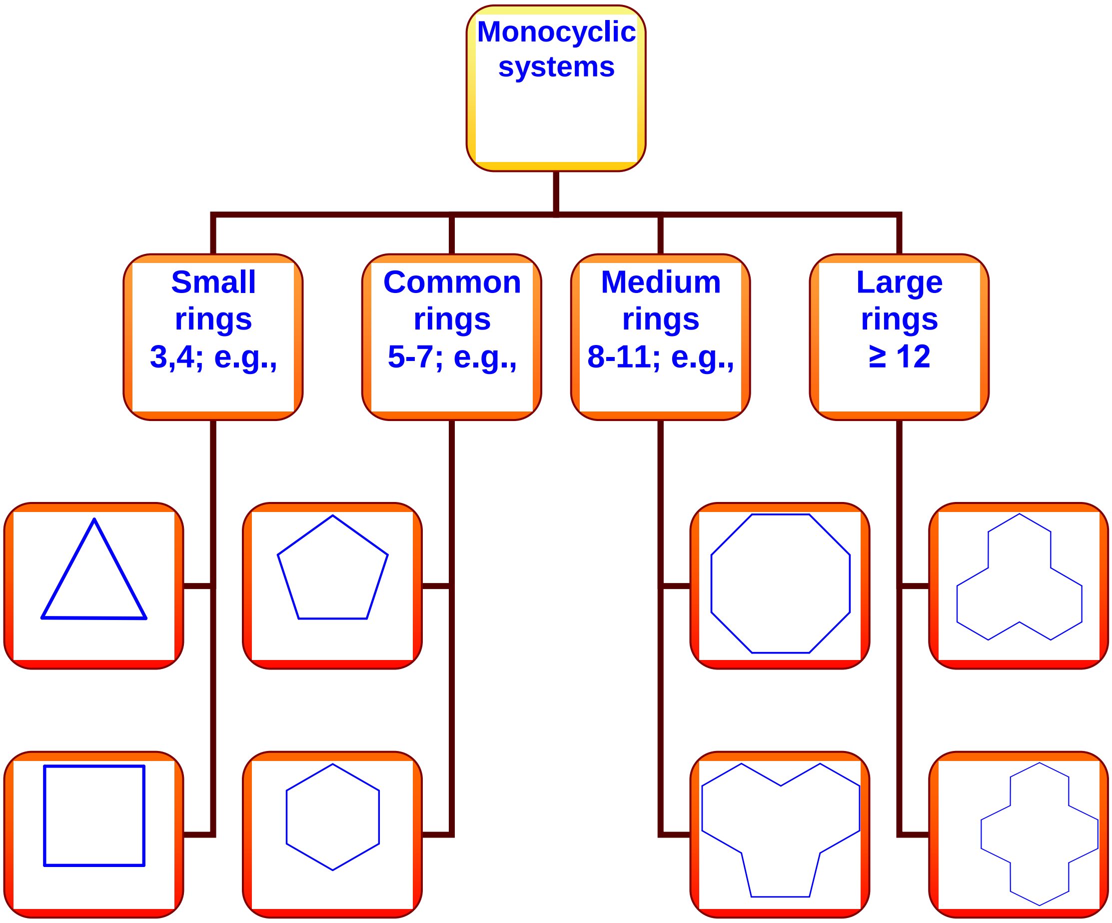


Diagram 2.2

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`

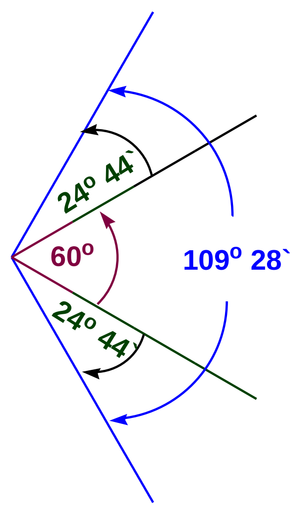


Fig. 2.3

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

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**	**60^{o}**	**24^{o} 44`**	**697**	**120**

2.	**4**	**90^{o}**	**9^{o} 44`**	**685**	**112**
3.	**5**	**108^{o}**	**0^{o} 44`**	**664**	**35**
4.	**6**	**120^{o}**	**-5^{o} 16`**	**659**	**12**
5.	**7**	**128^{o} 34`**	**-9^{o} 33`**	**662**	**35**
6.	**8-11**	**135^{o}-147^{o} 16`**	**-12^{o} 46`-- $18^{o}$ 54`**	**661-665**	**32-88**

Table 2.4

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.

Quizzes:

1. True or False

a- Cyclohexane occur in terpenes.

○ a) true

○ b) false

b- Cyclopentane can be classified as one of the medium rings.

○ a) true

○ b) false

c- Baeyer assumed that all the rings are planar.

○ a) true

○ b) false

d- The strain in cyclobutane according Baeyer calculations equal to -9^{o} 33`.

○ a) true

○ b) false

The solution;

1- a (false), b (false), c (true), d (false).

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):

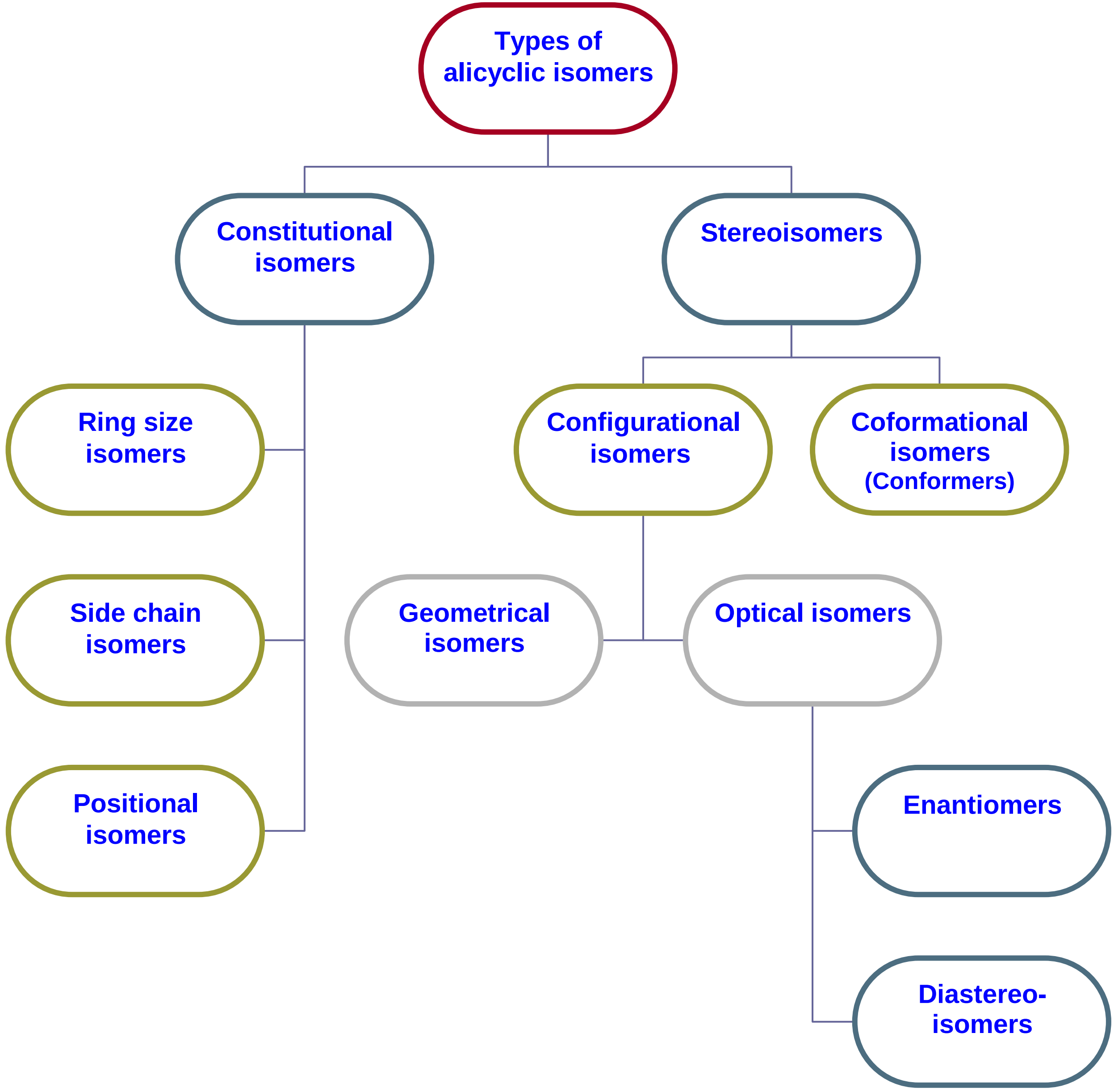


Diagram 3.1

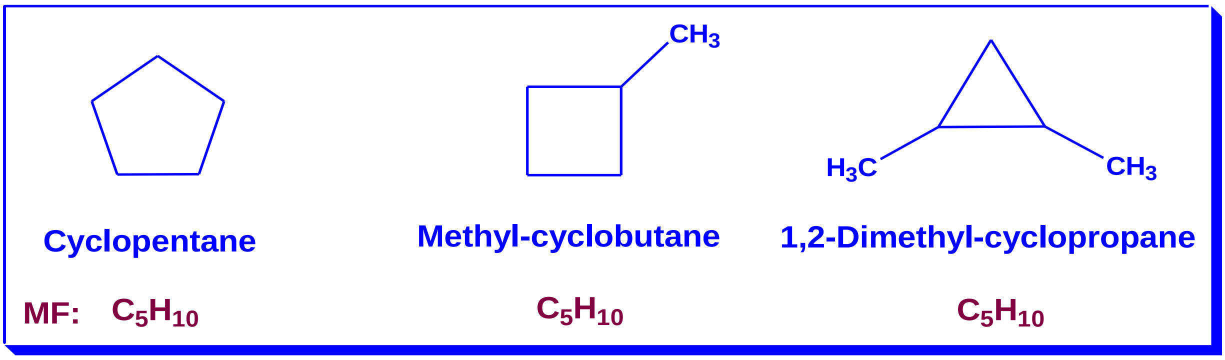
3.2 Constitutional isomers:

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:

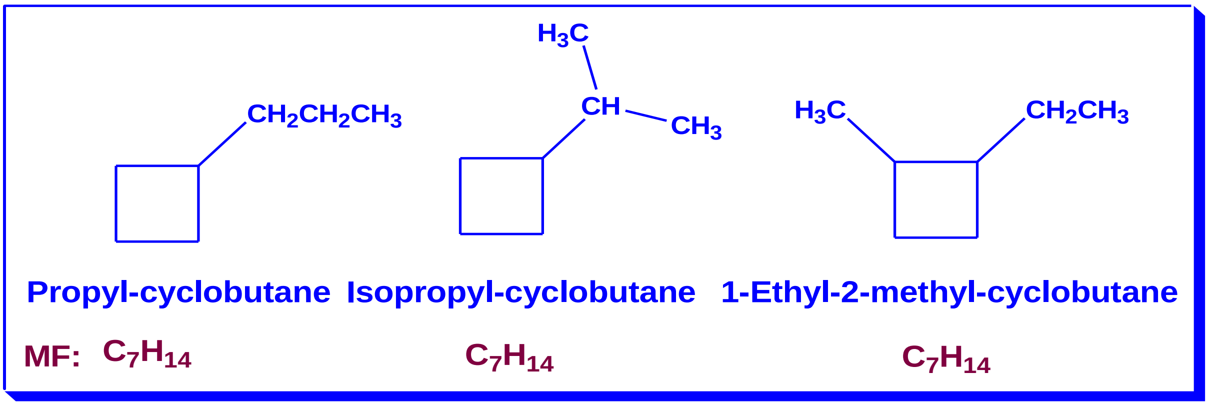
Ring size isomers are compounds have the same molecular formula but differ in the ring size, e.g.,



Cyclopentane	Methyl-cyclobutane	1,2-Dimethyl-cyclopropane
MF: C_5H_{10}	C_5H_{10}	C_5H_{10}

II- Side chain isomers:

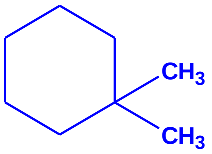
Side chain isomers are compounds have the same molecular formula but differ in the side chain structure, e.g.,



Propyl-cyclobutane	Isopropyl-cyclobutane	1-Ethyl-2-methyl-cyclobutane
MF: C_7H_{14}	C_7H_{14}	C_7H_{14}

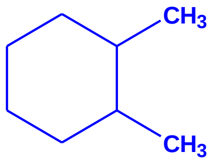
III- Positional isomers:

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



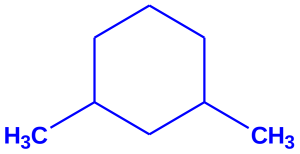
1,1-Dimethyl-cyclohexane

MF: C_8H_{16}



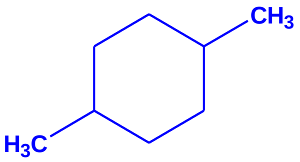
1,2-Dimethyl-cyclohexane

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.

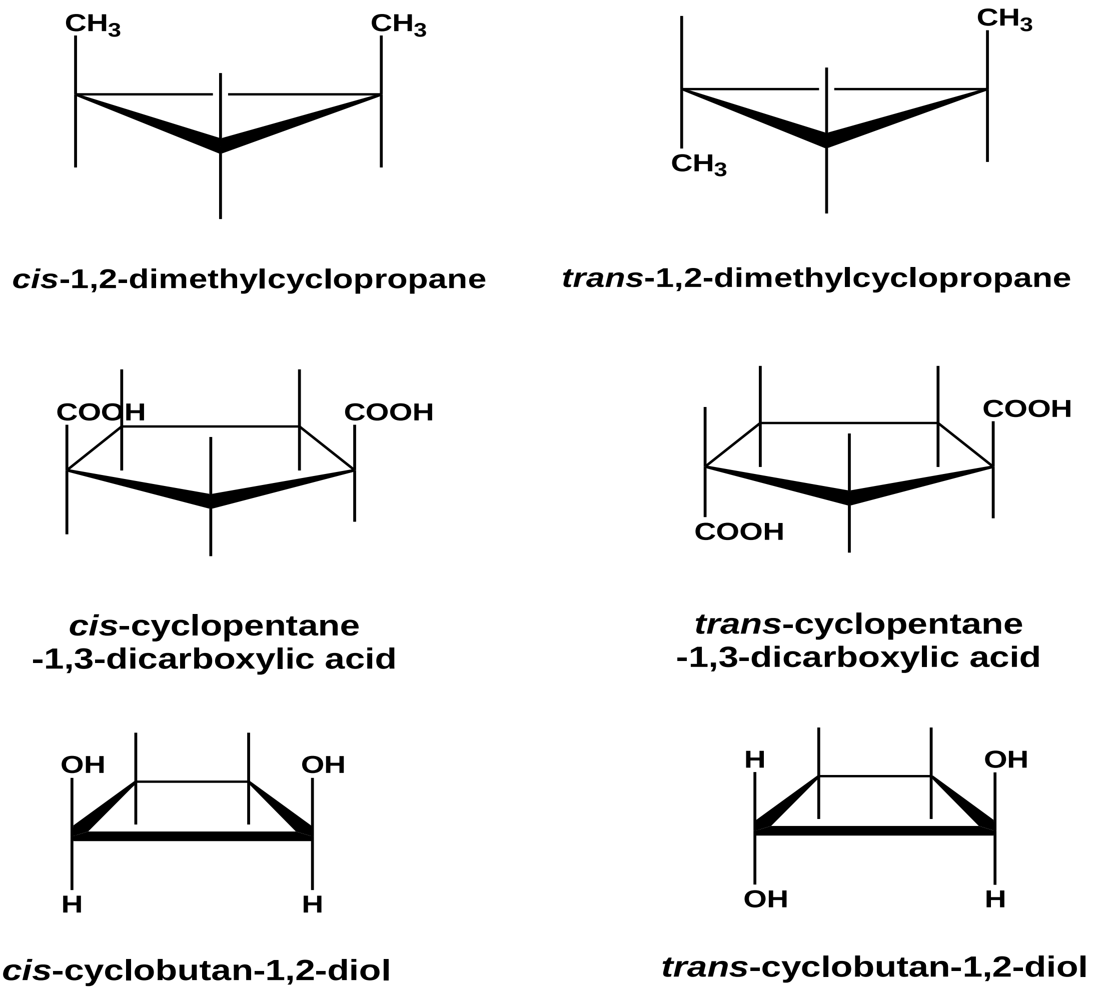
Stereoisomer can be divided into two categories configurational and conformational isomers.

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.

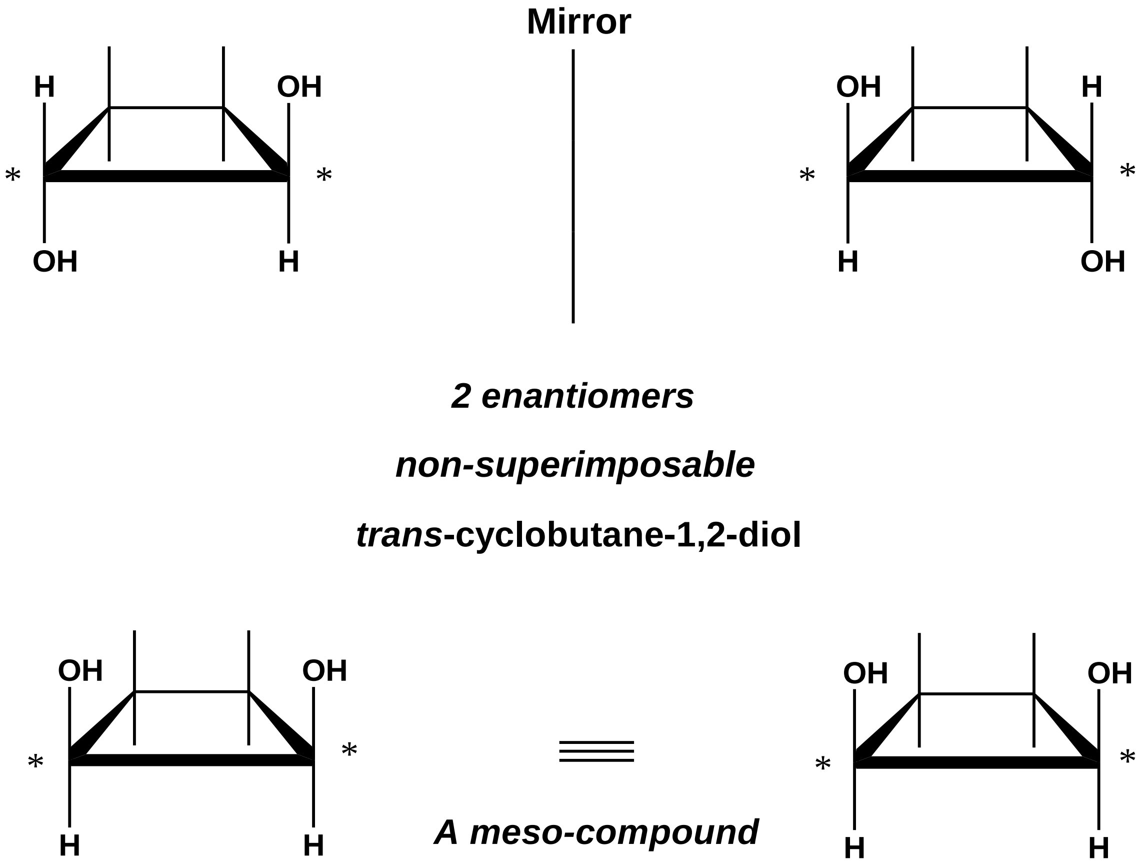
IV- Meso-form:

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

Quizzes:

1. True or False

a- The cis- trans- forms in a cyclic form are geometrical isomers.

○ a) true

○ b) false

b- When identical groups are on the same side of the ring, the isomer is known as the ***trans***-form.

○ a) true

○ b) false

c- **Side chain isomers:** are compounds have the same molecular formula but differ in the relative arrangement of the substituents connected to the ring.

○ a) true

○ b) false

d- The chirality refers to objects which are related as non–superimposable mirror images.

○ a) true

○ b) false

The solution;

1- a (true), b (false), c (false), d (true).

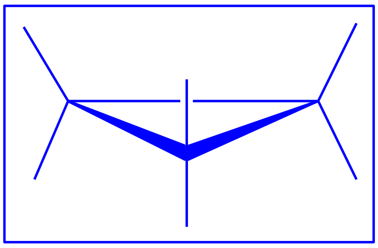
Unit 1

Lesson 4: Conformations of cycloalkanes

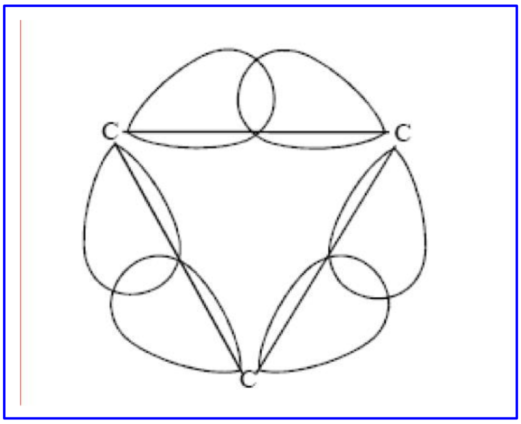
4.1 Geometrical shape of the rings

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}.



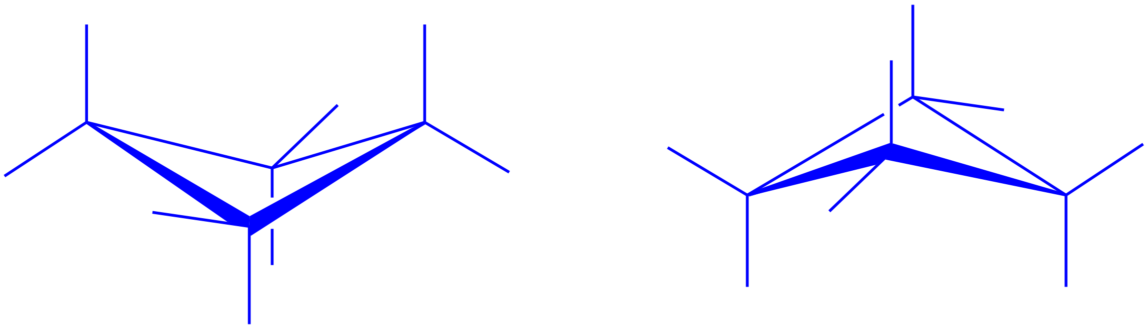
Propane molecule



Banana-bond of cyclopropane

Fig. 4.1

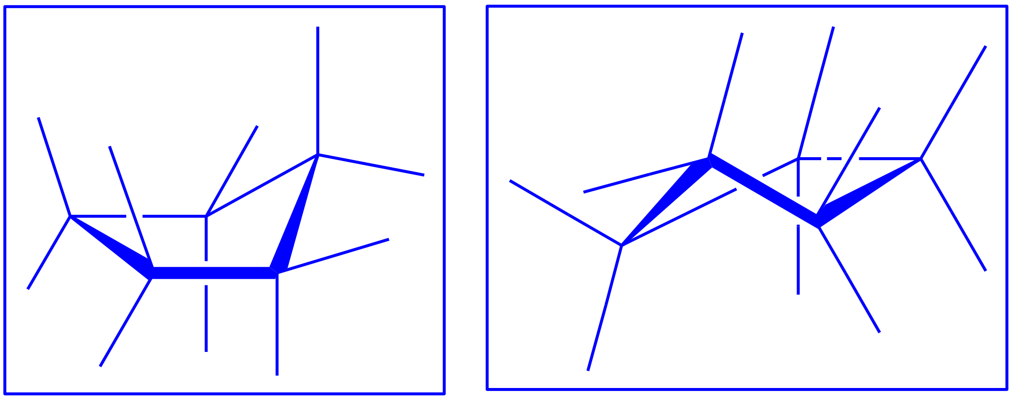
B- Cyclobutane: (Flat bond angles will be = 90^{O}) is puckered, even through the puckered causes more-strained bond angles (Fig. 4.2).



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).

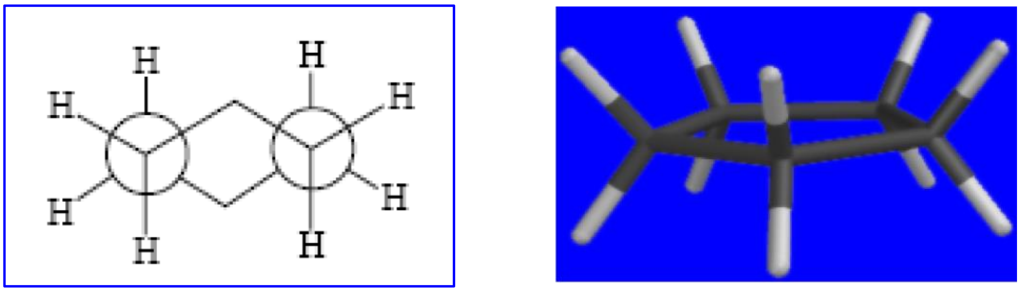


Envelop-form **Half chair-form**

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

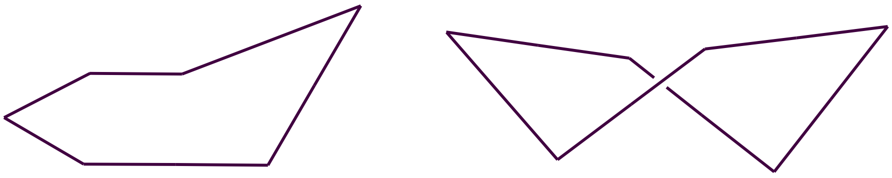
Fig. 4.4

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

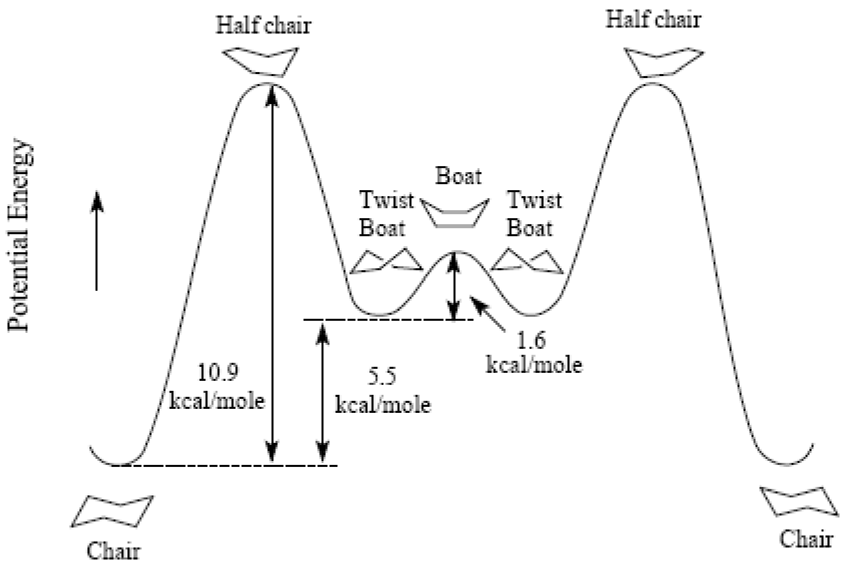


The half-chair form of cyclohexane

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).

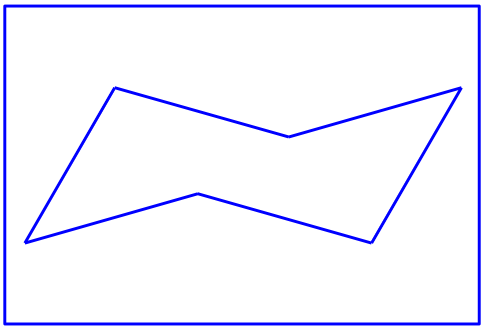


The energy diagram for the ring inversion of cyclohexane.

Diagram 4.6

From the above diagram, it can be conclude 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

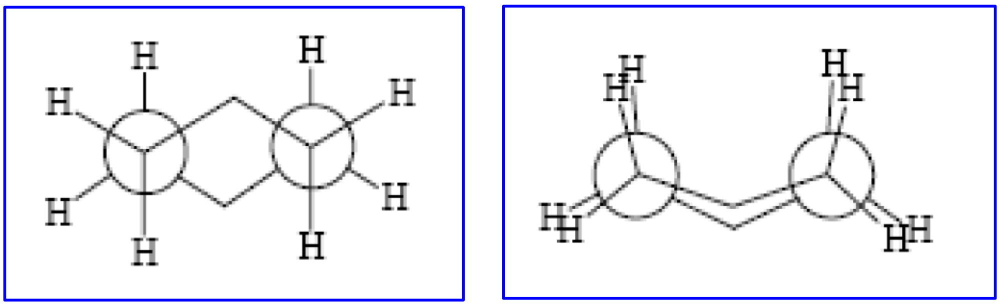
The stability of the chair-form is due to the following reasons:

(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).

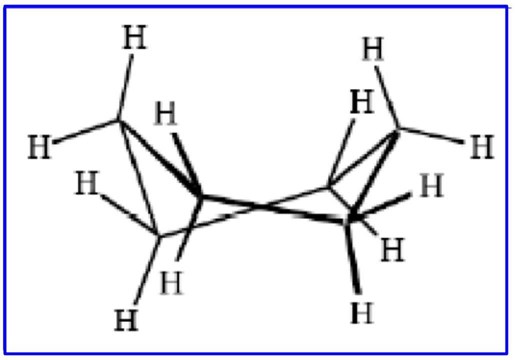


Newman projection of the chair-form

Newman projection of the boat-form

Fig. 4.8

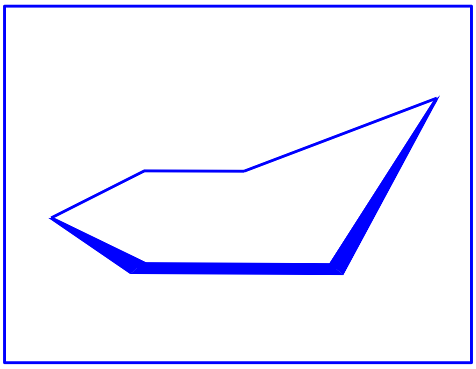
3- A third conformation of cyclohexane is the twist-boat (Fig. 4.9), there is a relieving in this form minimizes the torsional strain and make the twist-boat is lower in energy than the boat-conformation.



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).

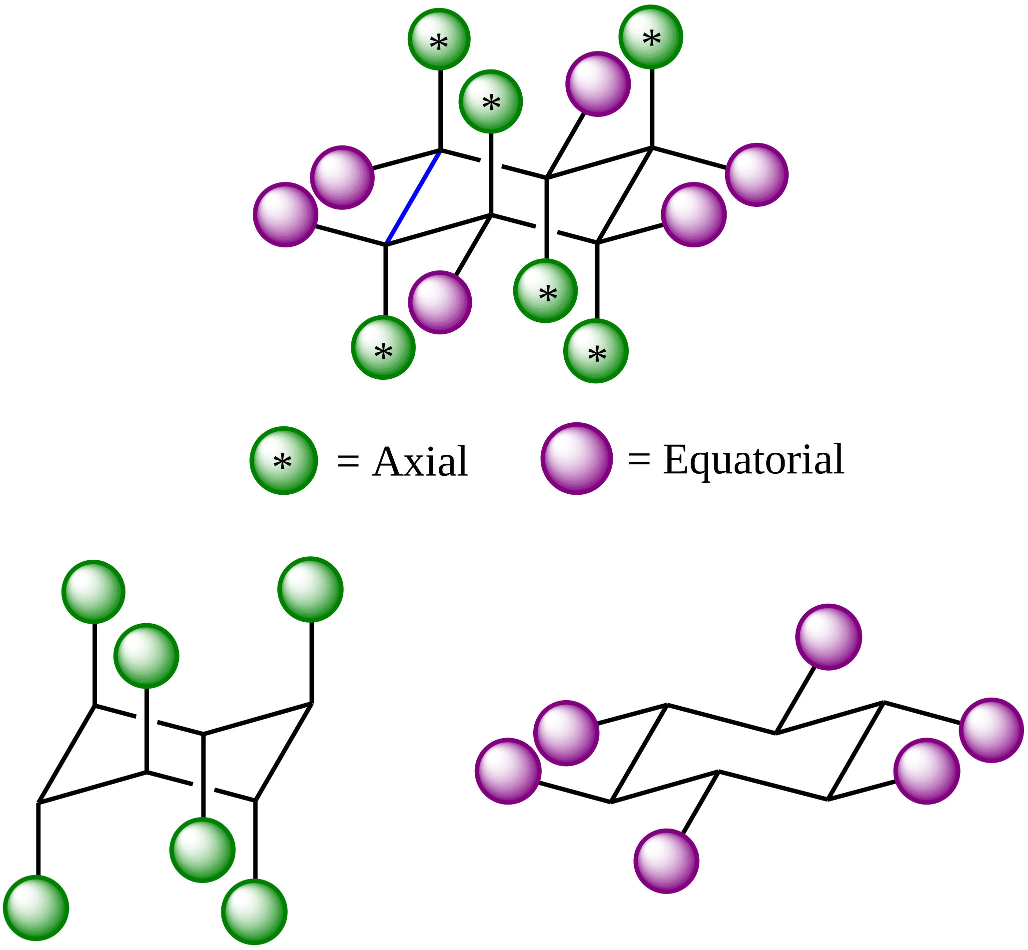


The half-chair form of cyclohexane

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).



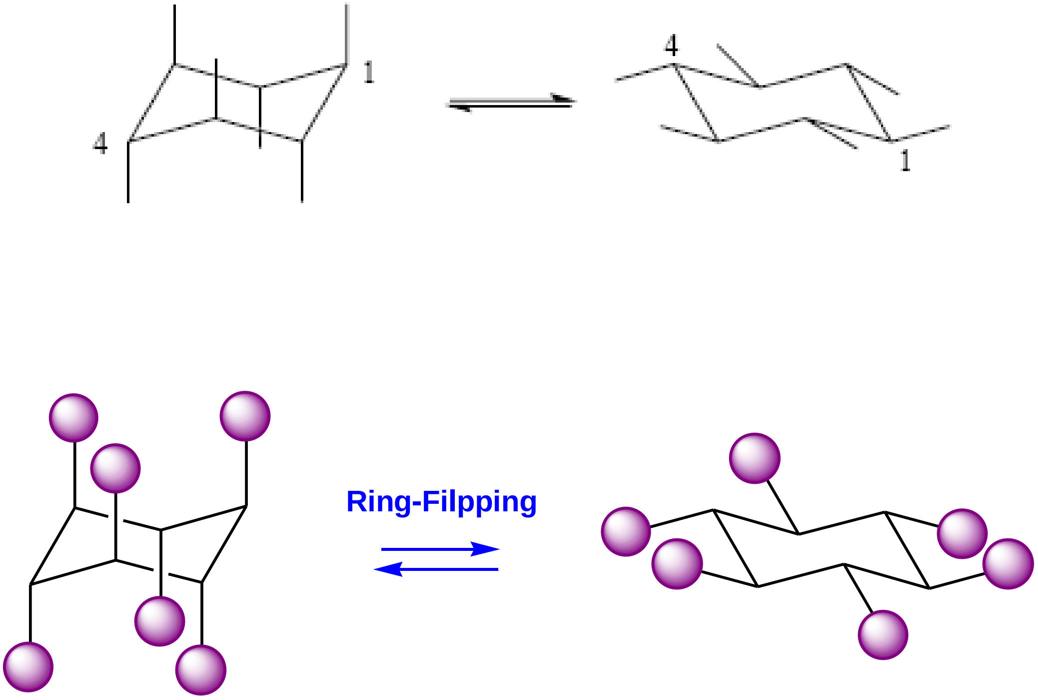
Axial hydrogens of cyclohexane

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.

Quizzes:

1. True or False

a- Cyclobutane ring is a flat.

○ a) true

○ b) false

b- Cyclopropane must be planar.

○ a) true

○ b) false

2- Multiple Choice Questions

I. The hydrogen atoms in the chair-form of cyclohexane are:

○ a) Eclipsed.

○ b) Staggered.

○ c) Gauche-staggered.

○ d) All of the above.

II. Ring flipping: is a chair-chair interconversion, in which,

○ a) The axial substituents become axial.

○ b) The equatorial substituents become axial.

○ c) The axial substituents become equatorial.

○ d) b and c.

The Solution;

1- a (false), b (true).

2- I (b), II (d).

The Summary of Unit 1

- **Alicyclic compounds** are organic compounds that is both aliphatic and cyclic.
- **Different types of Alicyclic compounds:**

1- Monocyclic compounds.
2- Bicyclic compounds with isolated rings separated by a chain of carbons.
3- Bicyclic compounds with rings connected by singly carbon-carbon bond.
4- Bicyclic compounds with rings having one common atom (Spirans).
5- Bicyclic compounds with rings having two or more common atoms.

- **Occurrence of some cycloalkanes:**

-3, 4 and 5 membered rings occur in terpenes.
-5 and 6 membered paraffins occur in petroleum (Naphthenes).
-Cyclic acids occur in petroleum (Naphthenic acids).
-Cyclopentene derivatives occur naturally in fatty acids.

- **Physical properties of Alicyclic compounds**

Alicyclic hydrocarbons are:

Light liquids, immiscible with water and miscible in all proportions with the nonpolar solvents

- **Classification of monocyclic system**

- Small rings: 3 and 4 membered rings.
- Common rings: 5-7 membered rings.
- Medium rings: 8-11 membered rings.
- Large rings: ≥ 12 membered rings.

- **Baeyer's strain theory; Baeyer assumed that:**

- All the rings are planar.

- Any deviation from the normal angle causes a strain within a molecule.

- The greater deviation from the normal angle, the greater strain.

- The most stable molecule which has the least strain.

- The strain in the molecule can be calculated.

- **Constitutional isomers** are isomers that differ because their atoms are connected in a different order.
- **Types of constitutional isomers of Alicyclic compounds:**

  Ring size isomers.

  Side chain isomers

  Position isomers
- **Stereoisomers** are isomers that have same formula and connectivity but differ in the position of the atoms in space.
- **Configurational isomers** are divided into two types**:**

  i- Geometrical or cis-trans isomers.

  ii- Optical isomers.
- **Optical Activity** is the ability of some compounds to rotate plane polarized light.
- **Chirality** that refers to objects which are related as non–superimposable mirror images.
- **Chiral carbon atom** is a carbon atom attached to four different atoms or groups.
- **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.
- **Diastereoisomers** stereoisomers that are not mirror images.
- Racemic mixture: is an equimolar mixture (1:1) of two enantiomers.

- **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.
- **Cyclopropane:** The bond in it named "Banana-Bond".
- **Banana-Bond** is a bond that occupies an intermediate position between the ordinary σ- and π-bonds.
- **Cyclobutane** also puckered, the puckered causes more-strained bond angles.
- **Cyclopentane** has near-optimal bond angle (109O28`) and also is slightly puckered, the hydrogen atoms attached to the ring carbons are staggered as in envelop and half-chair conformers**.**
- **Cyclohexane** can be exists in a number of flexible forms as chair, half-chair, boat, and twist-boat.
- **The chair-form** is the most stable conformation of cyclohexane and the least stable one is the half-chair form.
- **The chair conformation of cyclohexane has two distinct types of carbon—hydrogen bonds:** axial and equatorial.
- **Ring flipping** is a chair-chair interconversion, in which, the equatorial substituents become axial, and the axial substituents become equatorial.
- **Monosubstituted-cyclohexanes** exist in two conformations, one in which the Methyl group is axial and one in which it is equatorial. The axial conformer is less stable than the equatorial conformer. This is due to the 1,3-diaxial interactions.

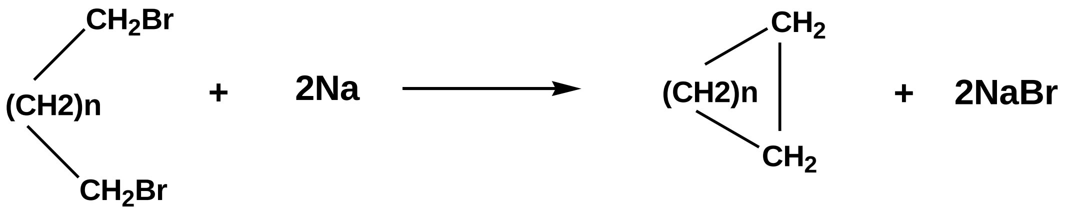
Unit 2

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).

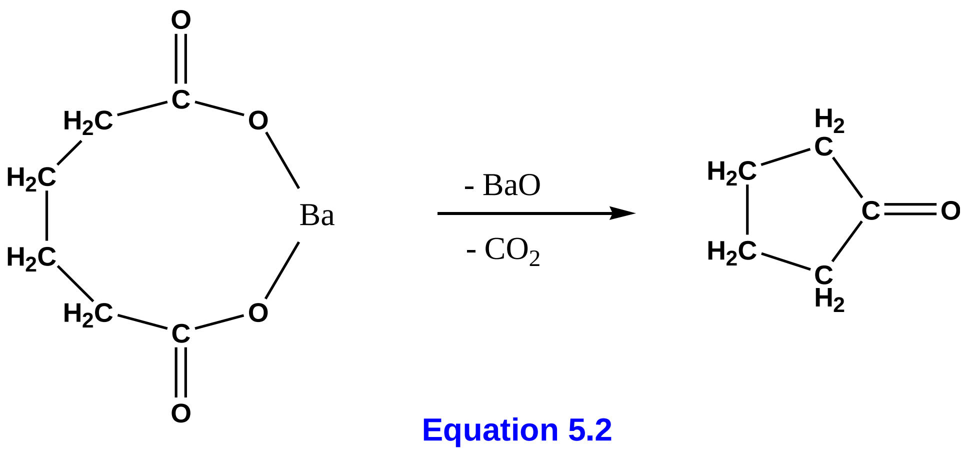


n = 1-6

Equation 5.1

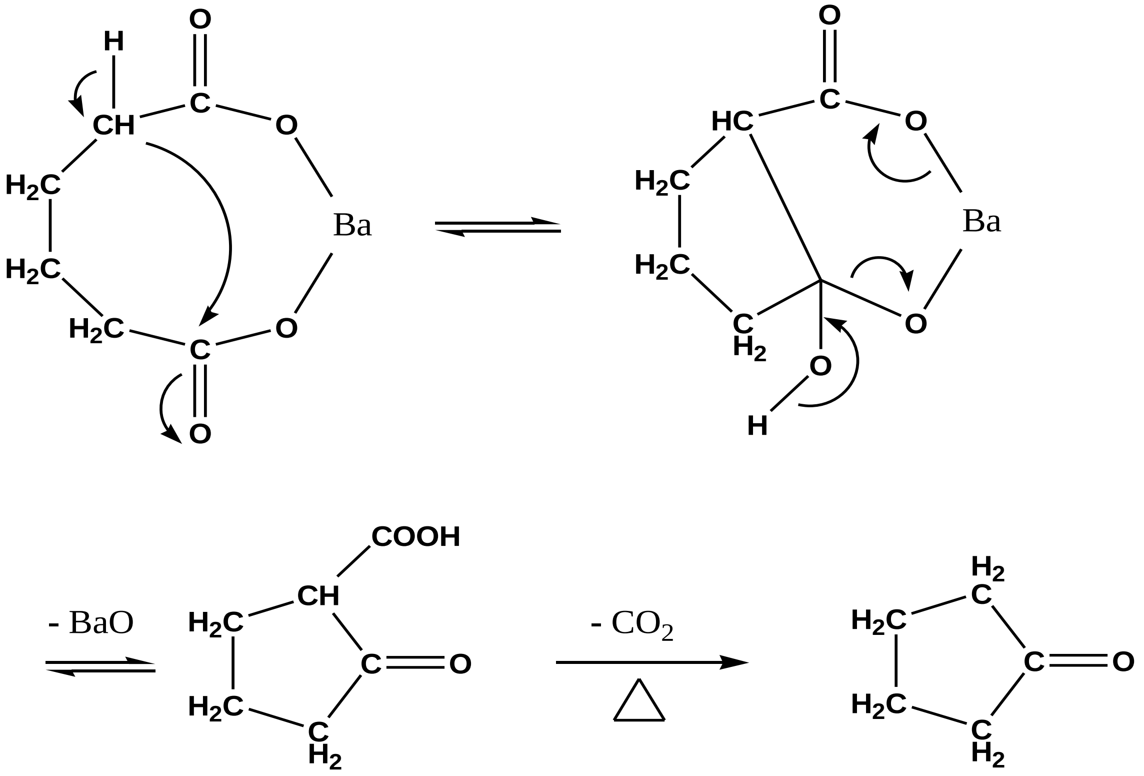
2. Pyrolysis of the salts of dibasic acid:

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).



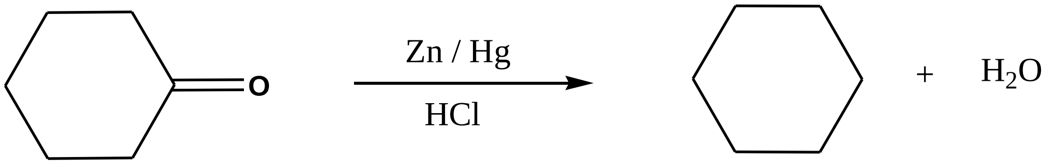
Equation 5.2

The reaction mechanism;



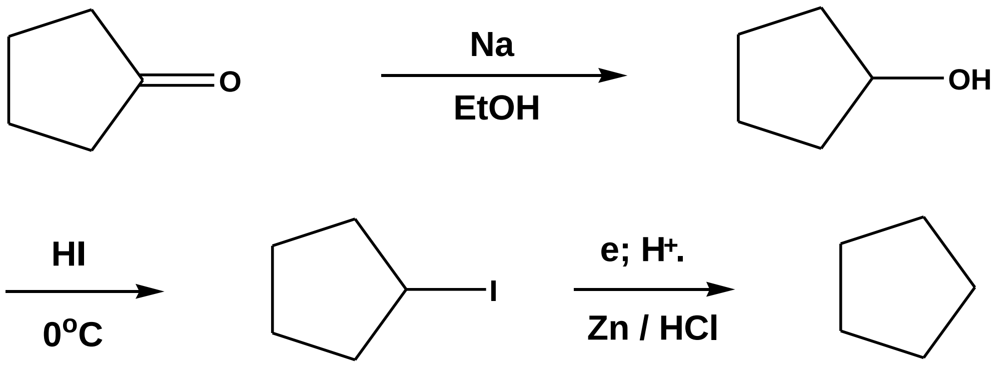
3. Reduction of cyclic ketones:

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

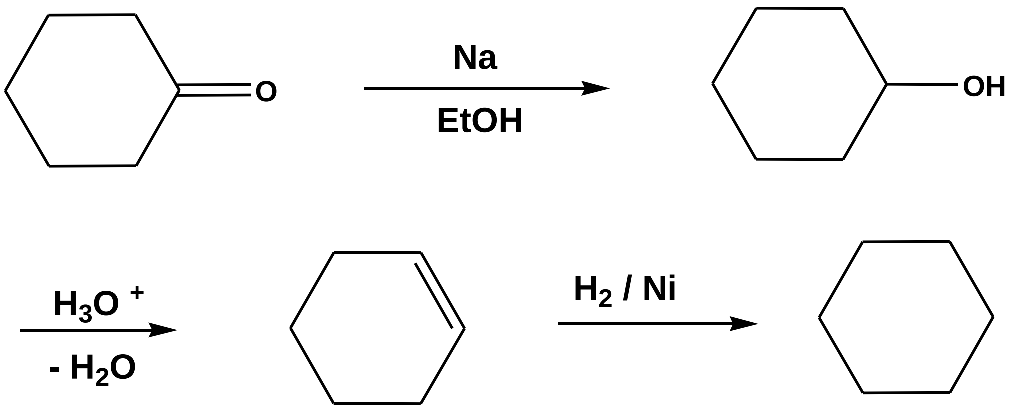


Equation 5.3

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



Equation 5.4



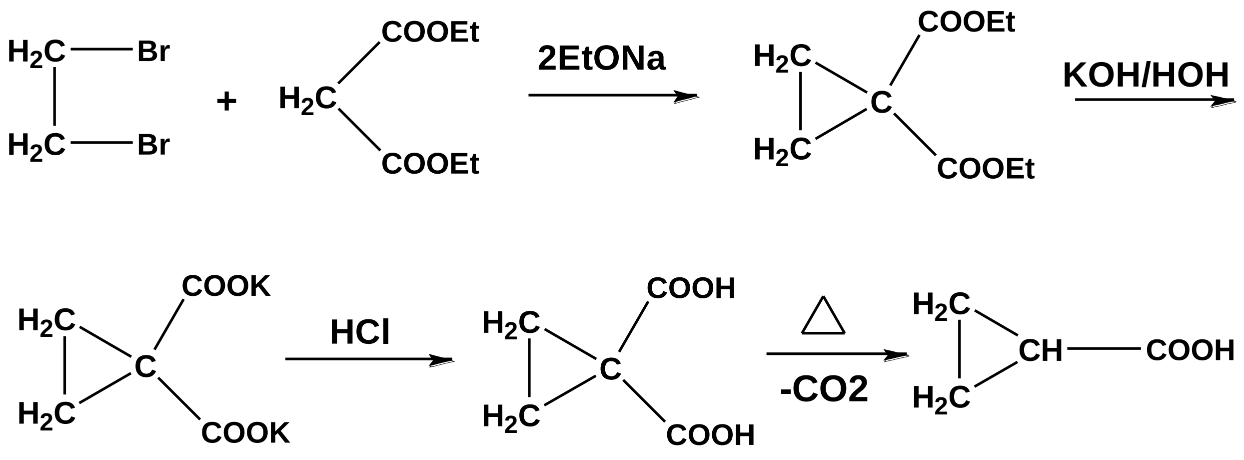
Equation 5.5

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.

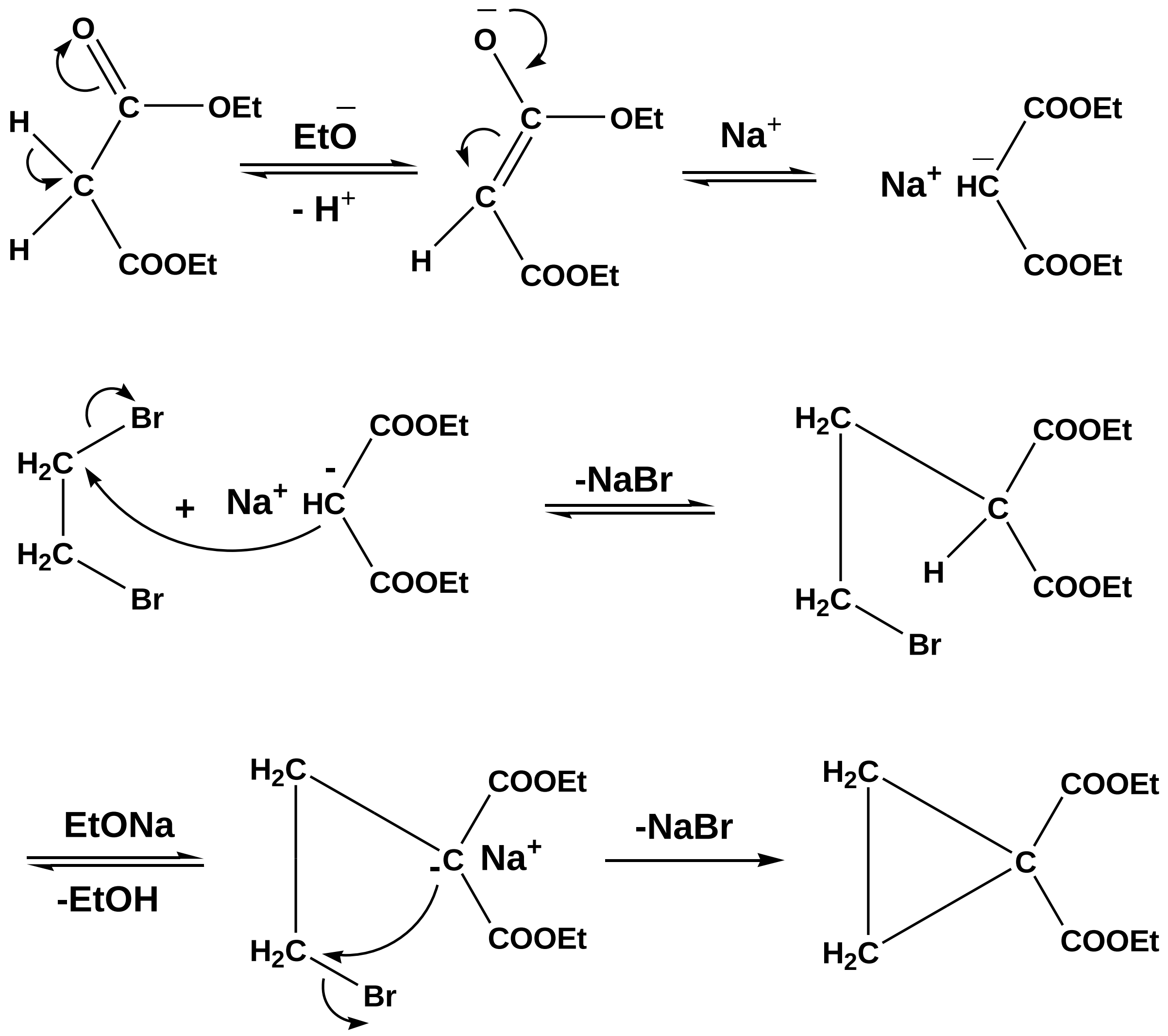
I- Condensation with malonic ester:

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).



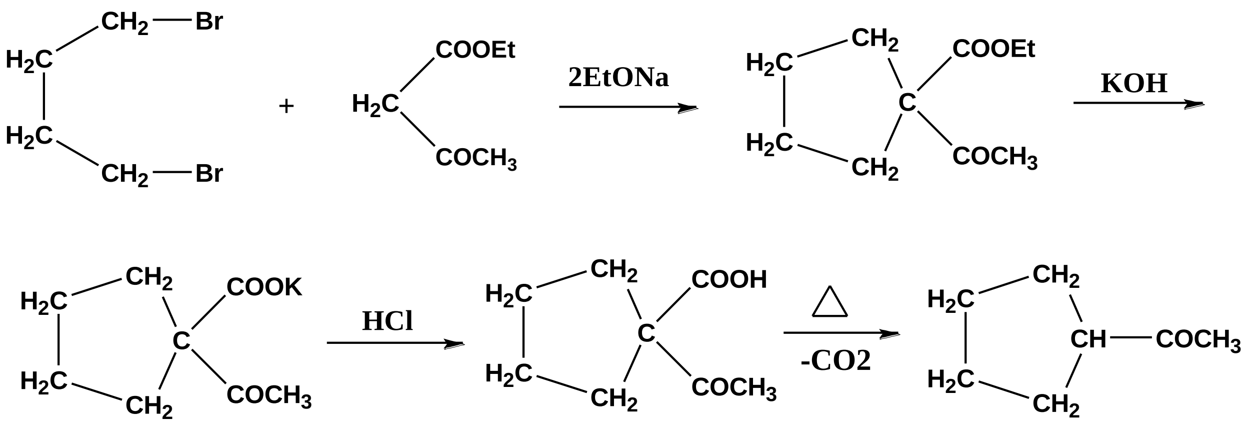
Equation 5.6

The reaction mechanism;



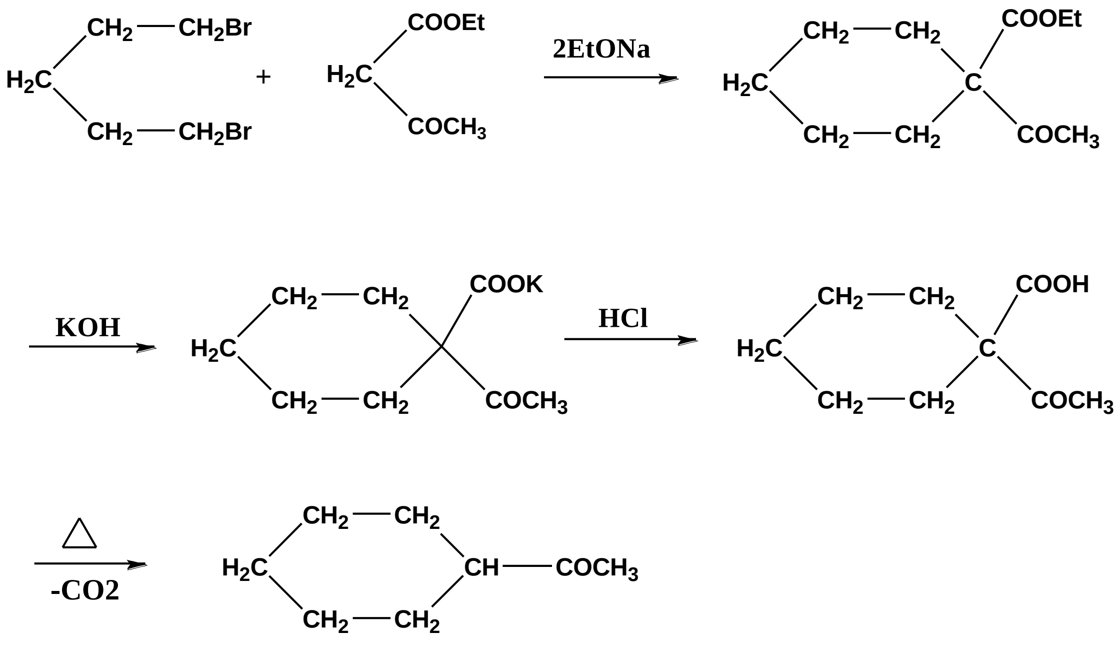
I- Condensation with ethylacetoacetate:

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



cyclopentylmethylketone

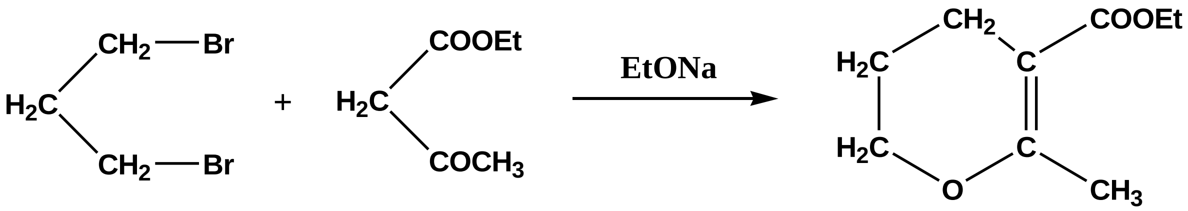
Equation 5.7



cyclohexylmethylketone

Equation 5.8

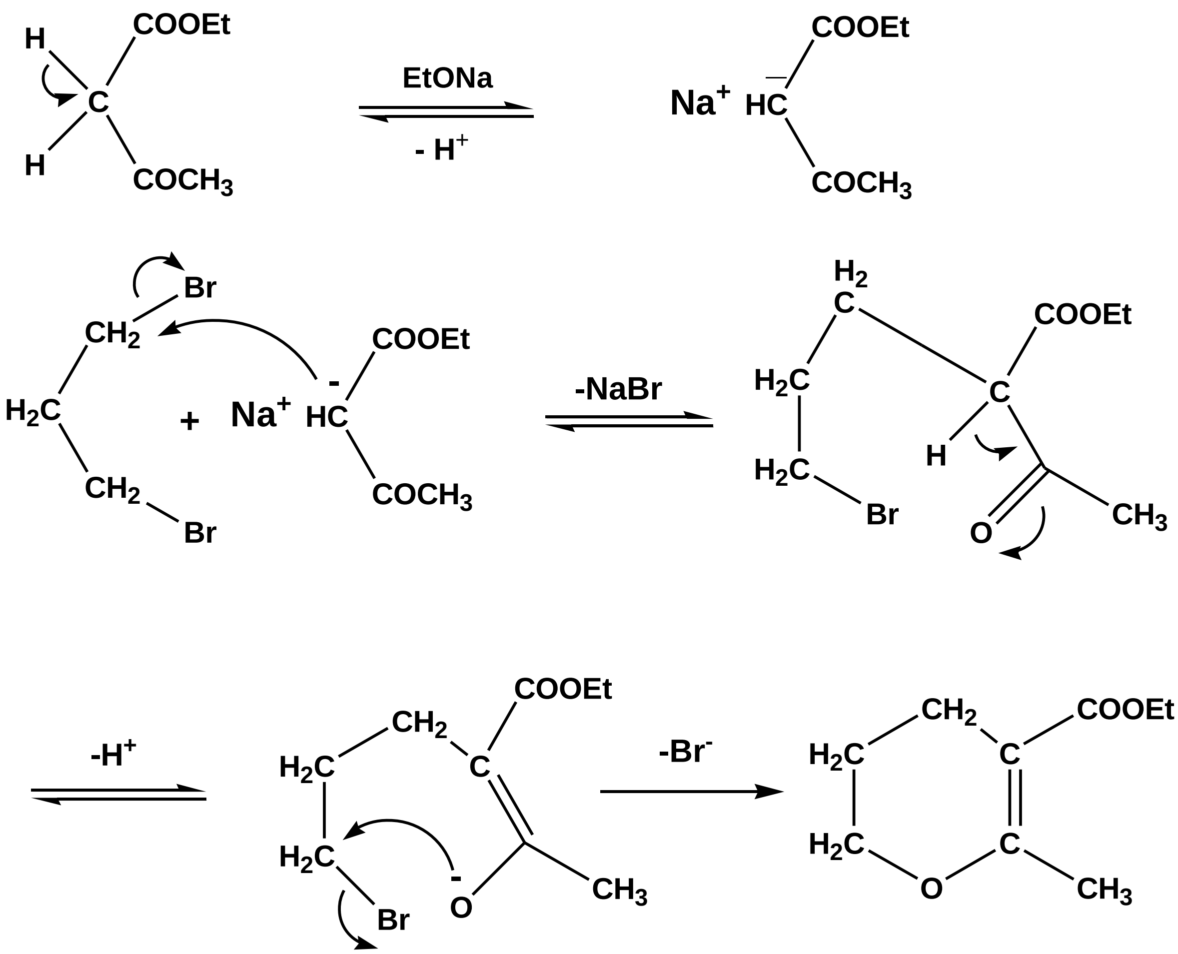
All attempts to prepare a four-membered ring result in the formation of a dihydropyran derivative (Equations 5.9).



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

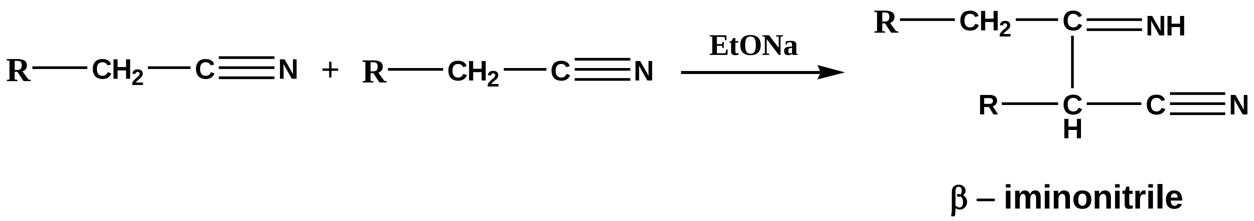
Equation 5.9

The reaction mechanism;



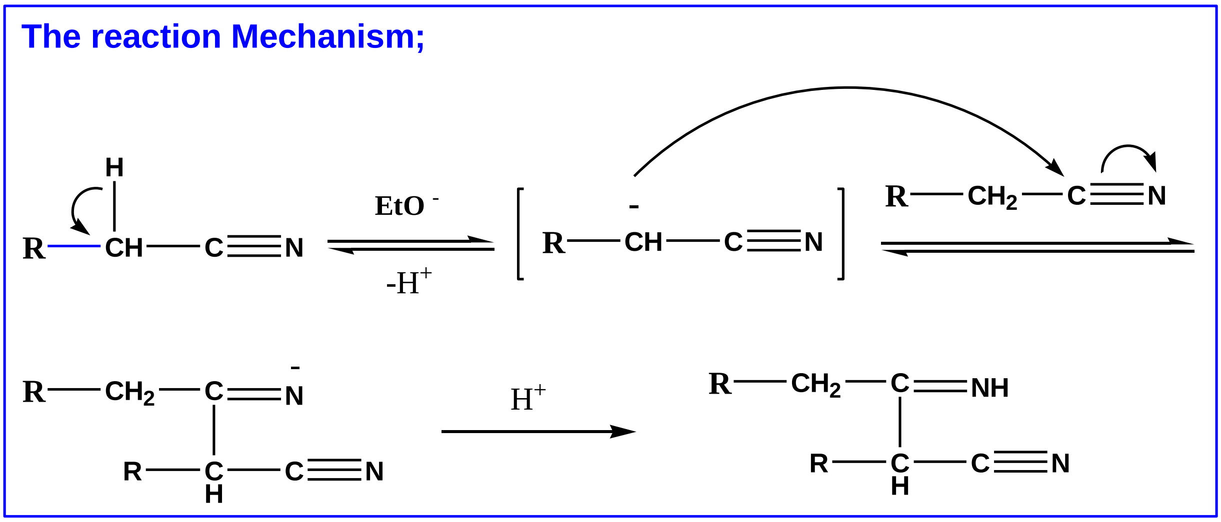
5. Ziegler-Thorpe reaction:

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

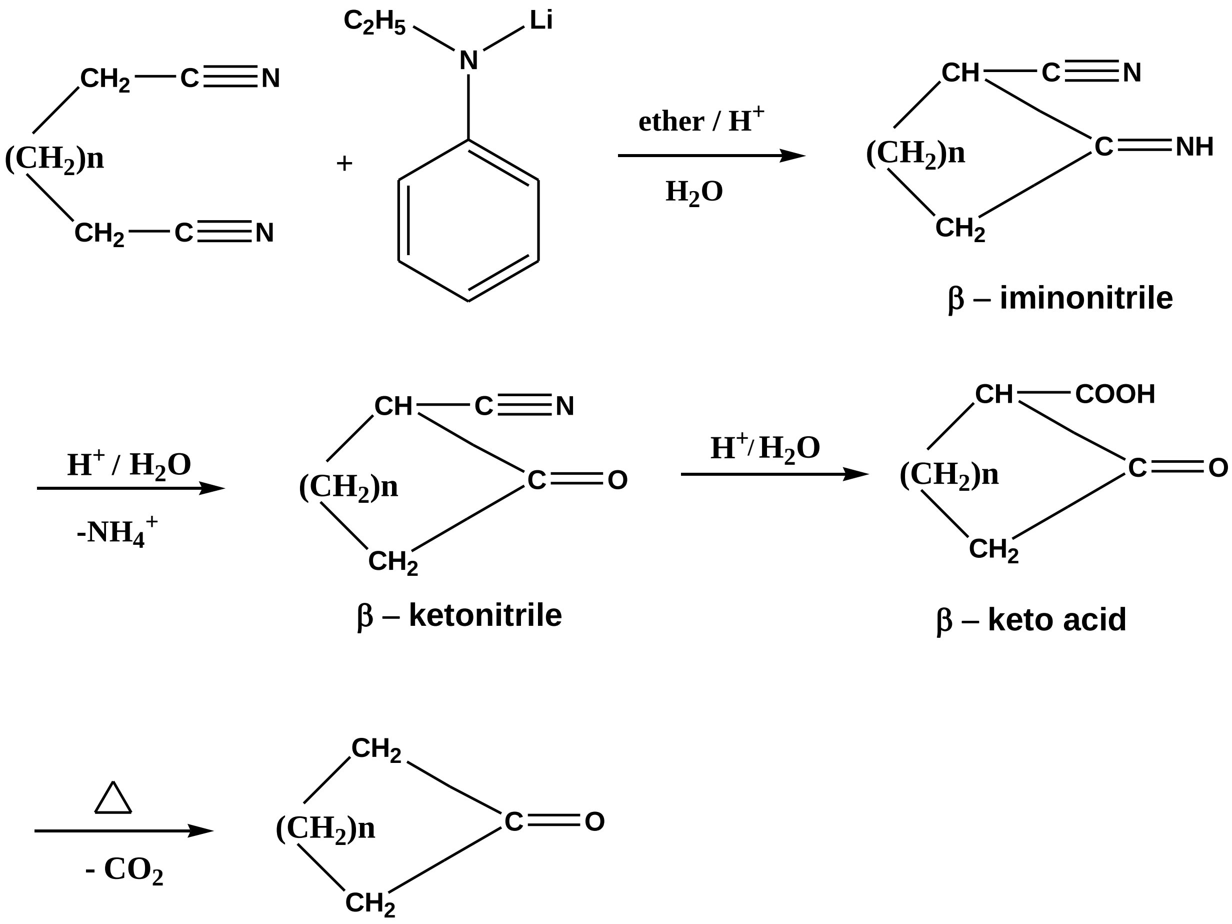


Equation 5.10

The Mechanism of this reaction shown as follows:



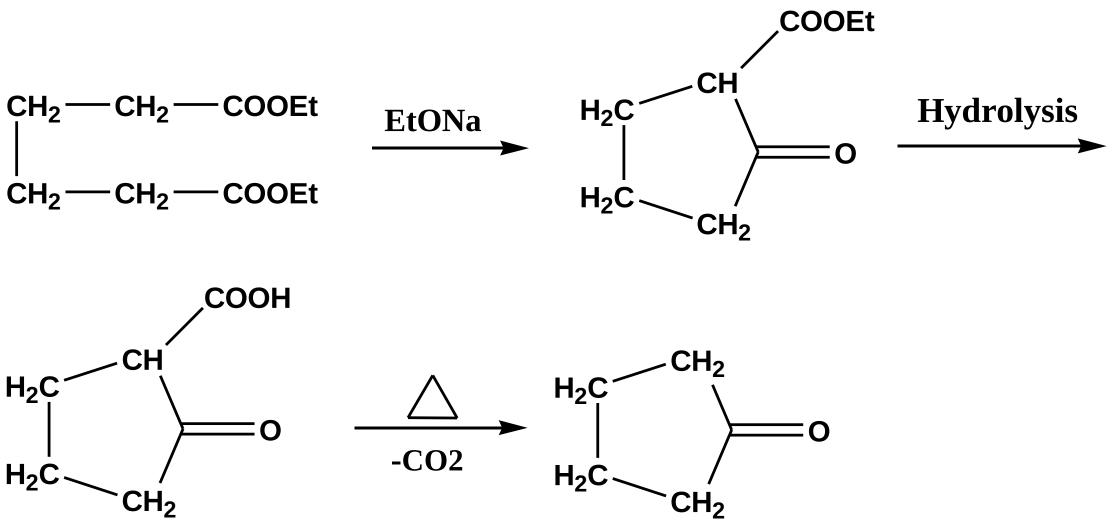
Ziegler used **Thorpe** reaction to yield a **cyclic iminonitrile** using Lithium n-ethylaniline as a basic catalyst, then the product hydrolyzed with aqueous acid to yield the **cyclic ketonitrile**. Boiling the later with aqueous acid converts the nitrile group to a carboxylic acid to yield **β-ketoacid**,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



Equation 5.11

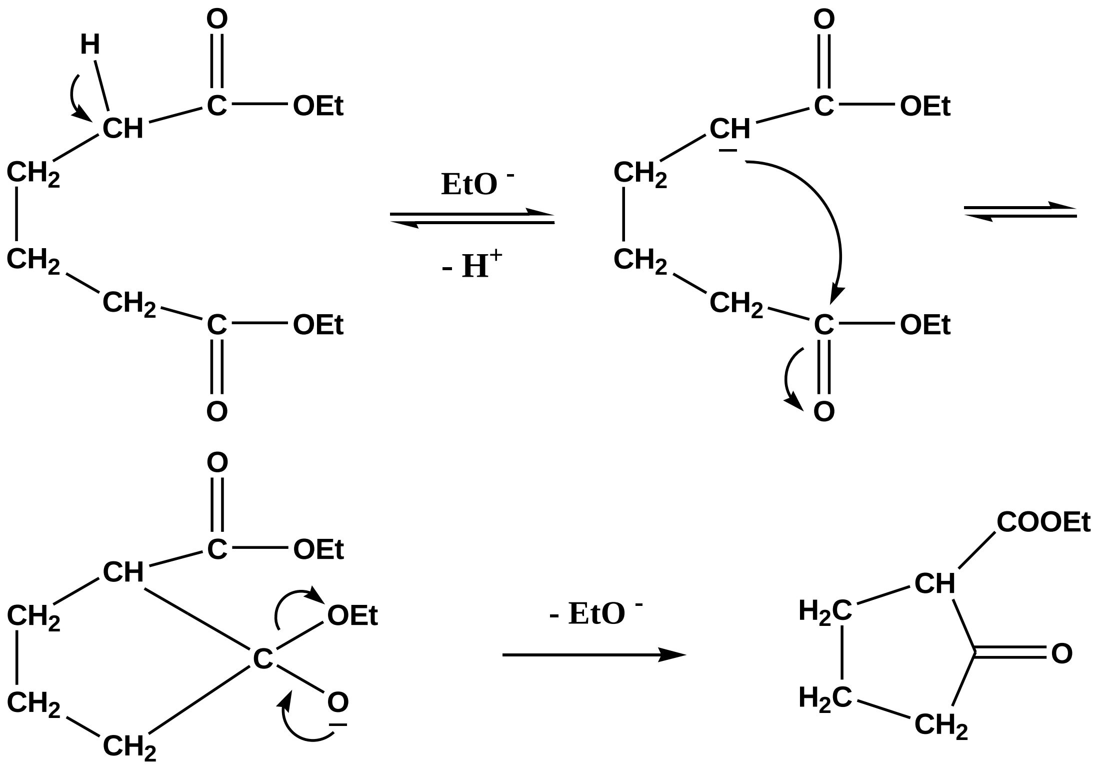
6. Dieckmann condensation:

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).

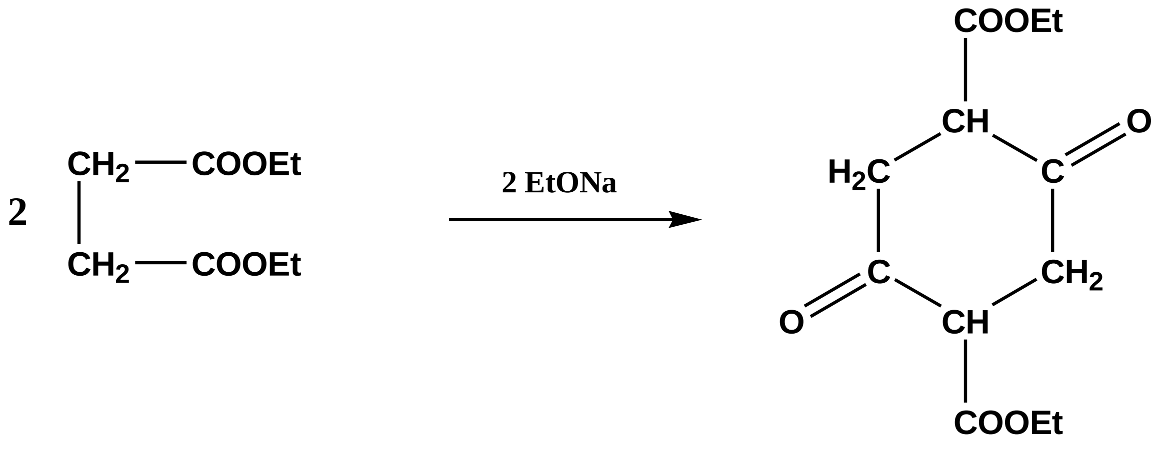


Equation 6.1

The reaction mechanism;



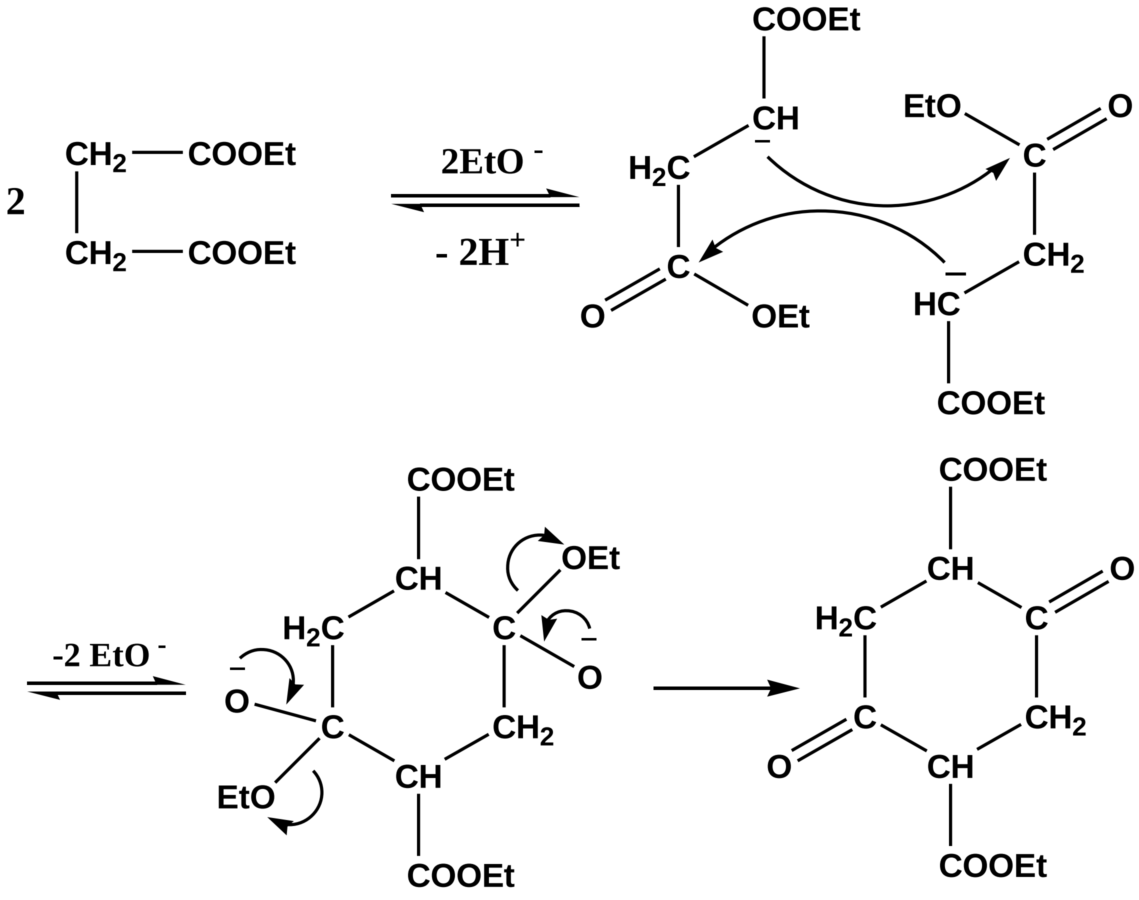
Esters lower than adipic ester may form cyclic products through the intermolecular condensation and cyclization, e. g., treatment of ethyl succinate in presence of sodium ethoxide forms succinosuccinic ester (cycohexane-2,5-dione-1,4-carboxylic ester) (Equation 6.2).



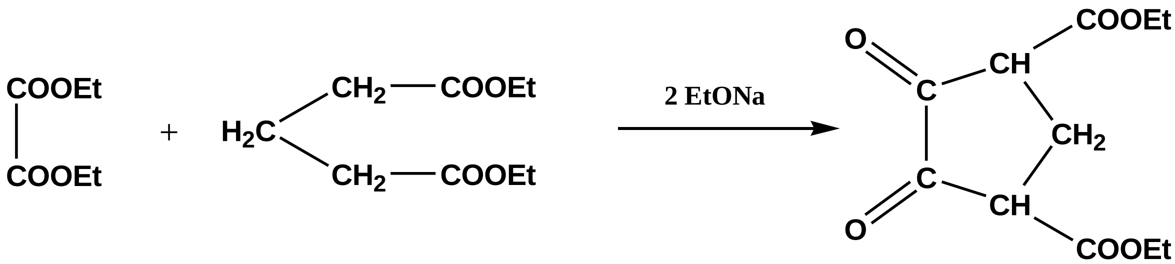
succino-succinic ester

Equation 6.2

The reaction mechanism;



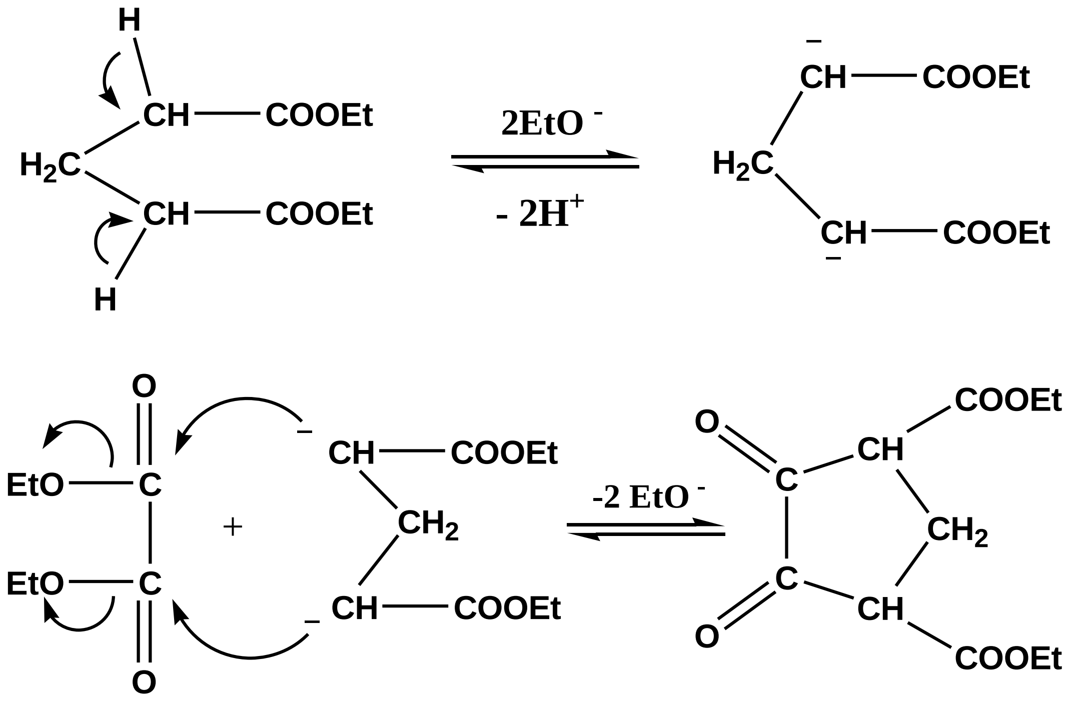
Also, five-membered ring cycloalkanes may be obtained through the intermolecular condensation between two different esters, such as, ethyl oxalate and ethyl glutarate (Equation 6.3).



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

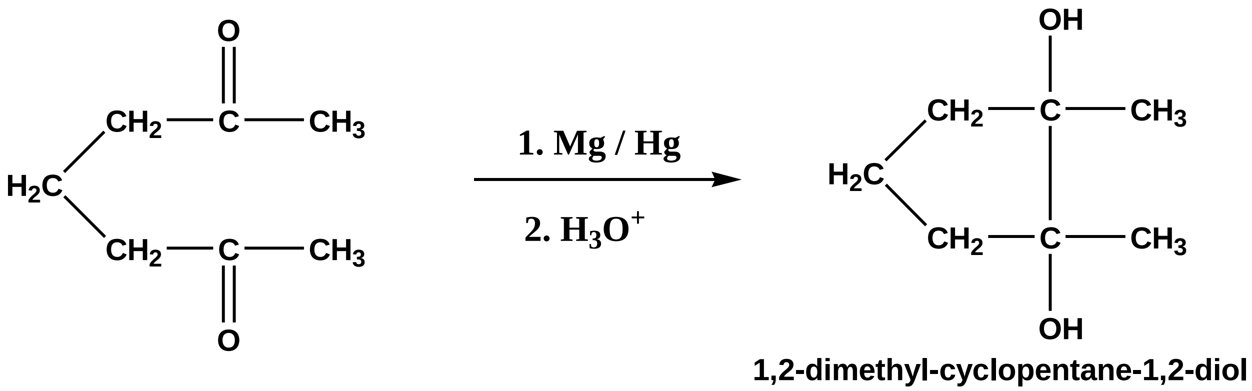
Equation 6.3

The reaction mechanism;



7. Reduction of diketones:

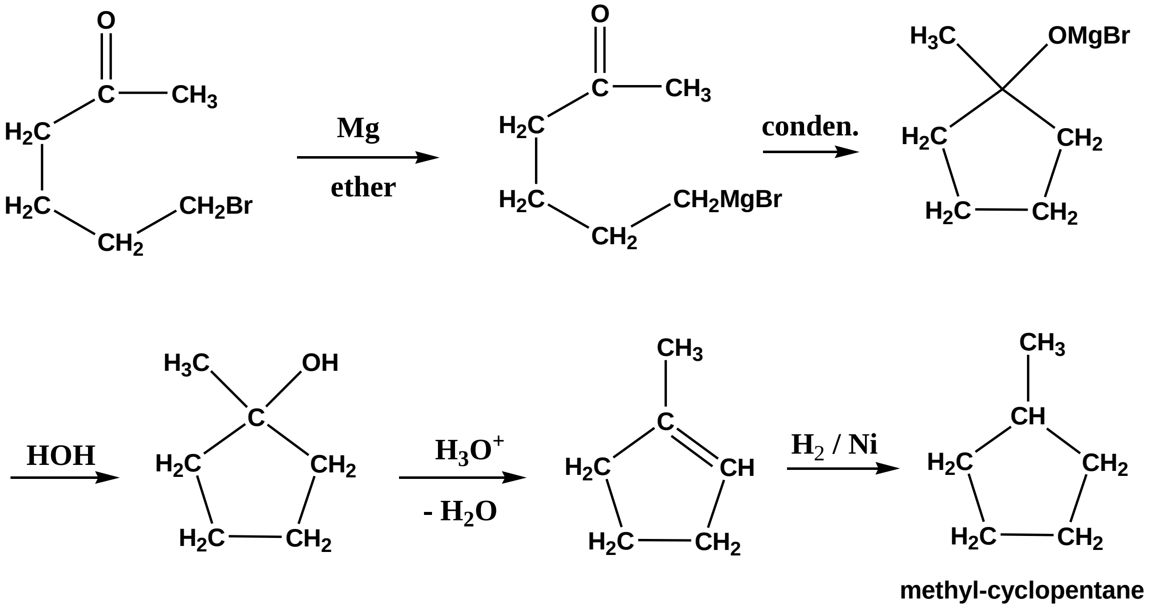
Five- or six-membered ring can be obtained through an intramolecular cyclization of certain diketones with magnesium amalgam, e. g., reduction of heptane-2,6-dione to form 1,2-dimethylcyclopentane-1,2-diol (Equation 6.4).



Equation 6.4

8. The Grignard method:

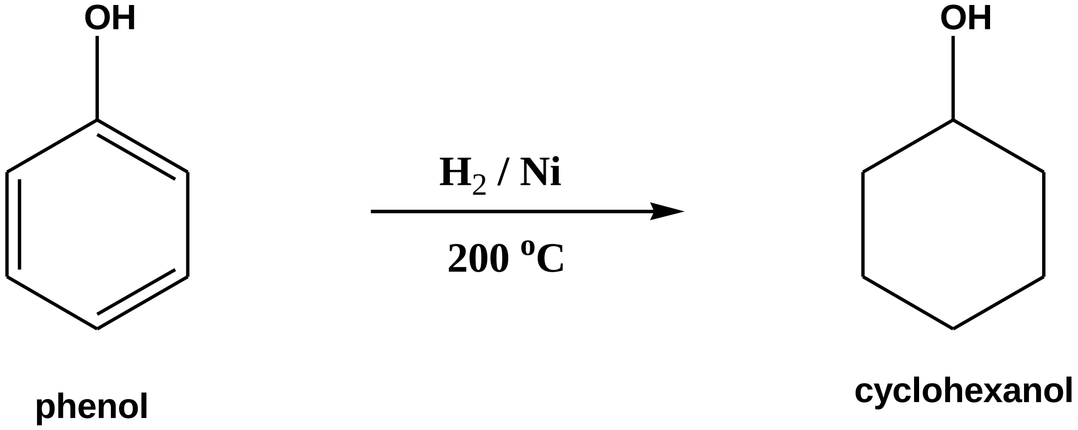
Certain halogen compounds react with magnesium which condenses internally to give cycloalkane derivatives, e. g., 6-bromo-2-hexanone reacts with **Mg** to give 1-methylcyclopentanol, which up on hydrolysis then reduction gives methylcyclopentane (Equation 6.5).



Equation 5.6

9. Reduction of benzene and its derivatives:

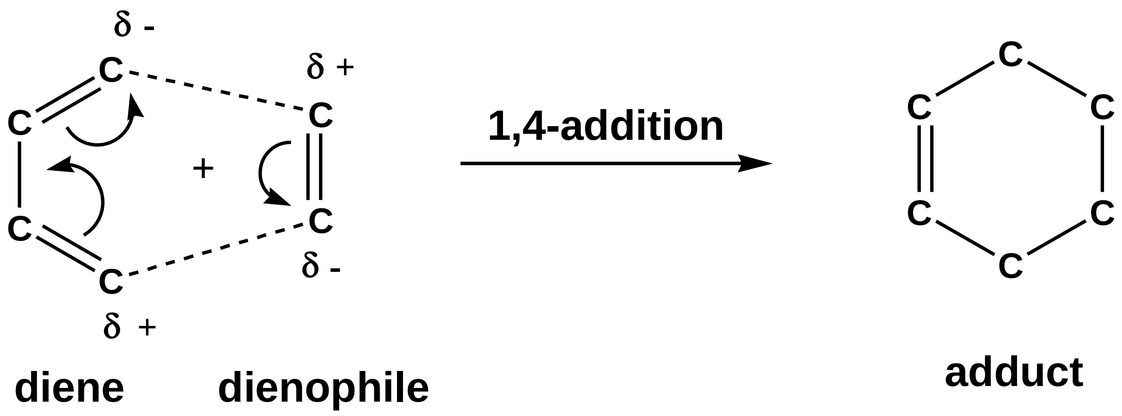
Catalytic reduction under pressure using nickel converted benzene or its derivatives into the corresponding six-membered cycloalkanes (Equation 6.6).



Equation 6.6

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

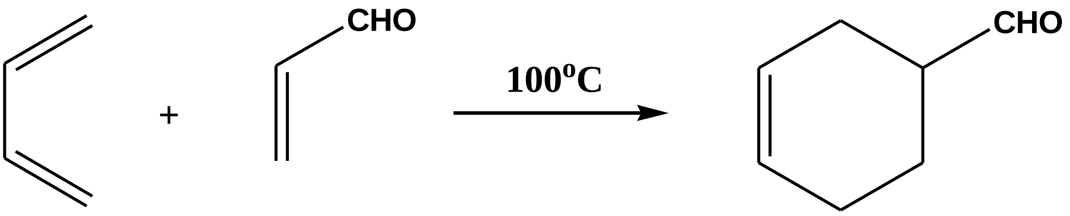
Diels-Alder reaction is an addition reaction between the diene (a compound containing conjugated double bonds) and the dienophile (unsaturated hydrocarbon) to yield a product known as the adduct. The adduct is usually a six-membered ring, the addition taking place in the 1,4-positions. In general terms,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



Equation 6.7

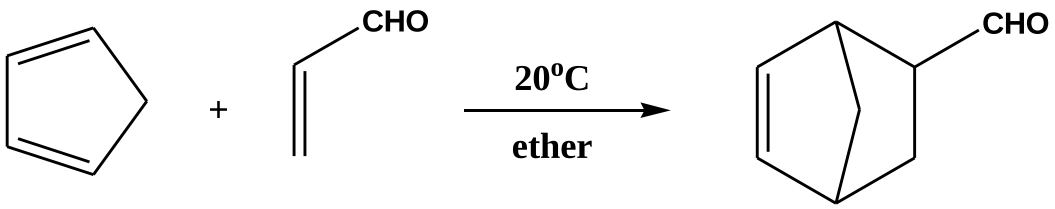
The diene may be of various types: acyclic, cyclic, semicyclic, bicyclic,

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



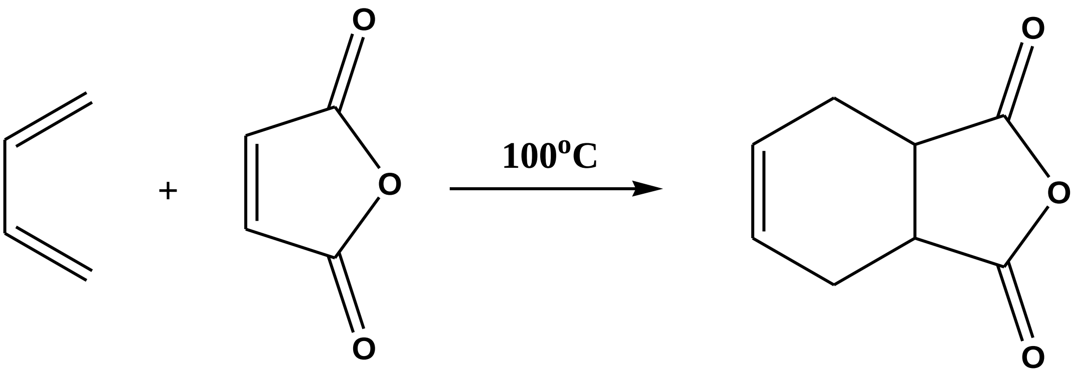
3-cyclohexene-carbaldehyde

Equation 6.8



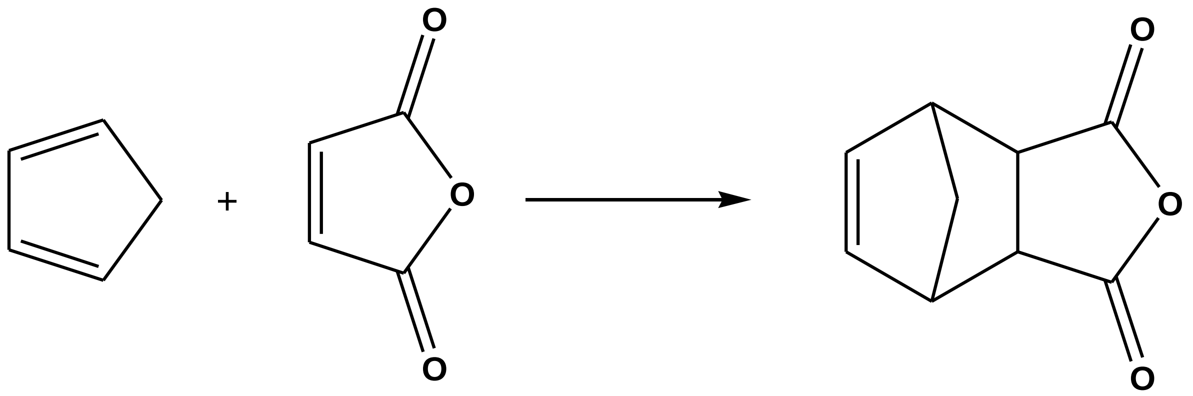
bicyclo[2.2.1]hept-5-ene-
2-carbaldehyde

Equation 6.9

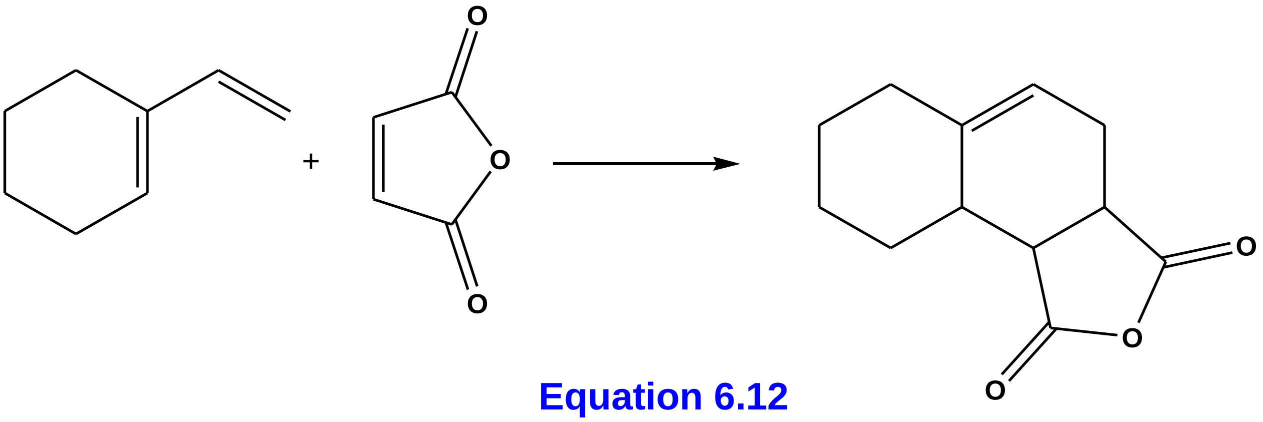


tetrahydrophthalic anhydride

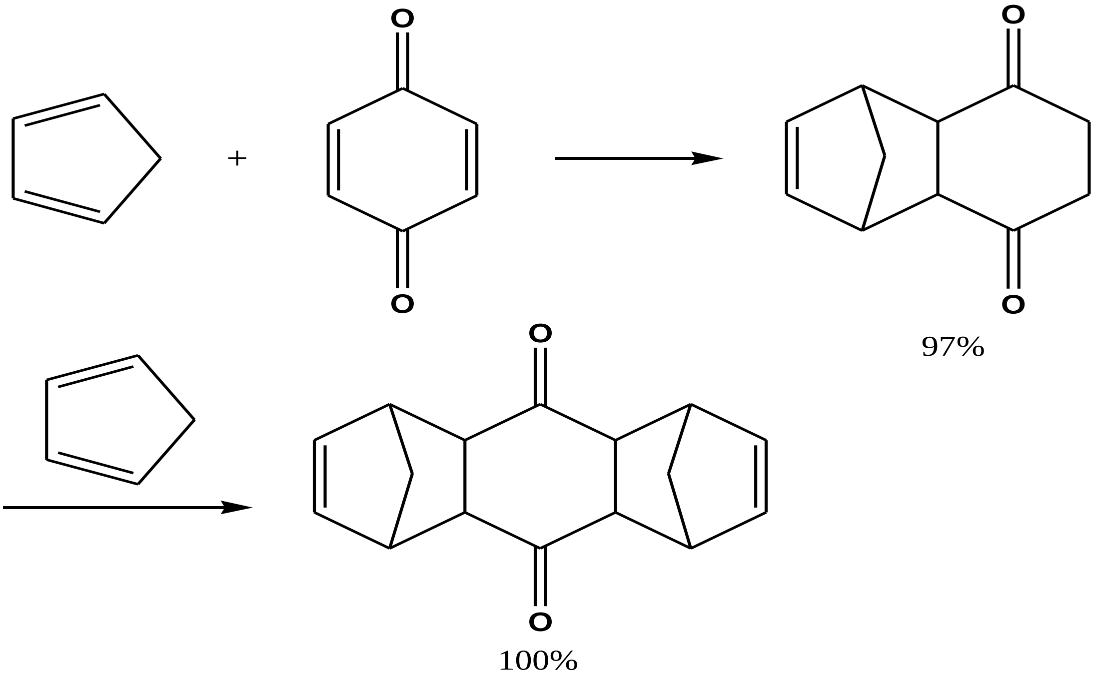
Equation 6.10



Equation 6.11

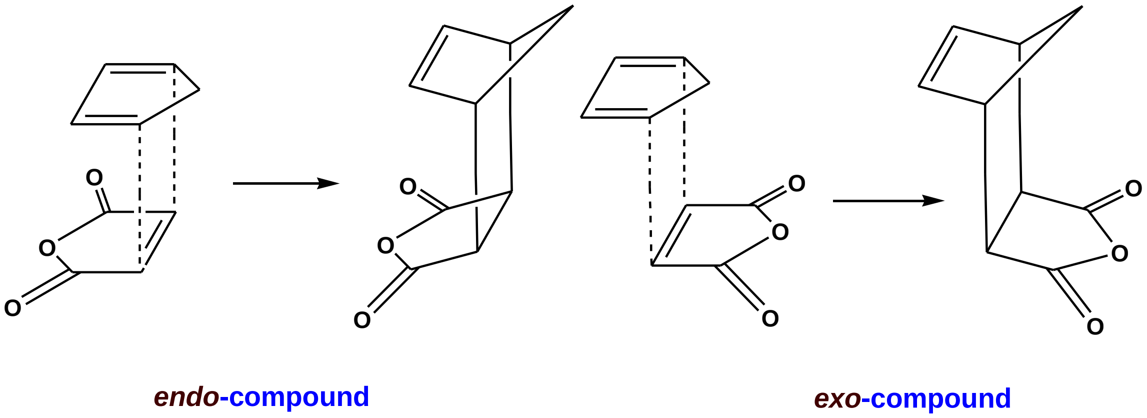


Equation 6.12



Equation 6.13

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



cis-addition

Fig. 6.14

Quizzes:

1. True or False

a- In Perkin's methods, it can be easily prepare 4-membered ring using ethyl acetoacetate.

○ 1)true

○ 2) false

b- **Thorpe** used **Ziegler** reaction to yield **cyclic iminonitriles**.

○ 1)true

○ 2) false

c- Dieckmann condensation is an intramolecular reaction.

○ 1)true

○ 2) false

d- Reduction of diketones is an intermolecular cyclization.

○ 1)true

○ 2) false

e- The *endo*-compound is thermodynamically controlled, while the *exo*-compound is kinetically controlled.

○ 1)true

○ 2) false

2- Multiple Choice Questions

a- A cyclic ketone is formed, when:

○ 1) The potassium or copper salts of a dicarboxylic acid are distilled.

○ 2) The sodium or boron salts of a dicarboxylic acid are distilled.

○ 3) The calcium or barium salts of a dicarboxylic acid are distilled.

○ 4) The lithium or magnesium salts of a dicarboxylic acid are distilled.

b- The diene may be of various types:

○ 1) Benzene ring.

○ 2) Semicyclic,

○ 3) Bicyclic.

○ 4) 2 and 3.

The Solution;

1- a (false), b (false), c(true), d (false), e (false).

2- a (3), b (4).

The Summary of Unit 2

General methods for the preparation of alicyclic compounds

- **Freund method** is a reaction of alkyl dihalide with sodium to gives the corresponding cycloalkane.
- **Pyrolysis of the salts of dibasic acid** by heating of barium salts of a dicarboxylic acid gives cyclic ketones.
- **Reduction of cyclic ketones:** Cyclic ketones may be reduced to the corresponding cycloalkanes.
- **Perkin's methods:** condensation of alkyl dihalide with either malonic ester or ethylacetoacetate in presence of a base gives the corresponding cyclic ester.
- **Ziegler-Thorpe reaction** is a base catalyzed condensation of dinitrile molecules to yield a cyclic β-iminonitrile.
- **Dieckmann condensation** is an intramolecular Claisen condensation of diester molecules when treated with sodium ethoxide.
- **Reduction of diketones:** Certain diketones undergo intramolecular cyclization with magnesium amalgam to afford five- or six-membered rings.
- **The Grignard method:** Certain halogen compounds react with magnesium, then condense to give the cycloalkane derivatives.
- **Reduction of benzene and its derivatives:** Catalytic reduction under pressure using nickel converted benzene or its derivatives into the corresponding six-membered cycloalkanes.
- **Diels-Alder reaction:** Diels-Alder reaction is an addition reaction between the diene and the dienophile to yield an adduct. The adduct is usually a six-membered ring.

Unit 3

Lesson 6: Cyclopropane and its derivatives

6.1 Physical properties of cyclopropane: b.p.= -34°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.

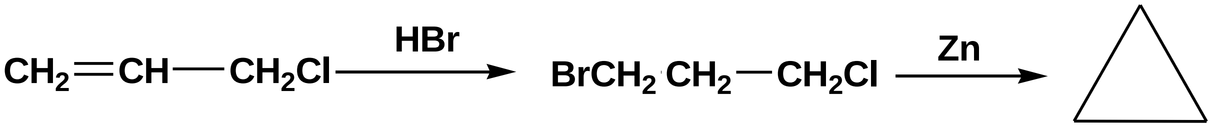
6.2 Chemical properties:

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

I- Methods of preparation:

1. Gustavson method:

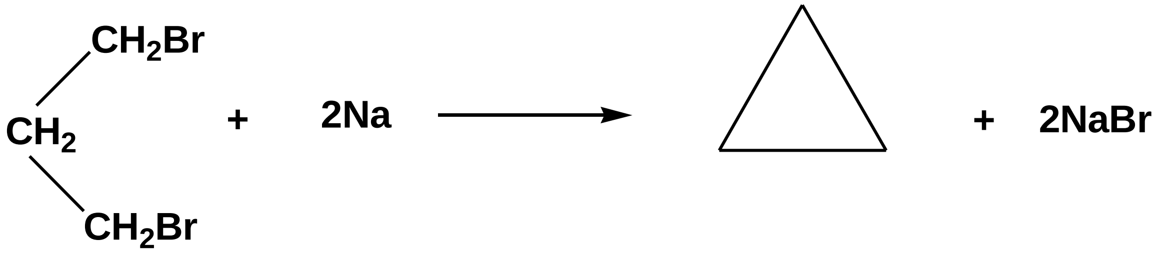
Cyclopropane is produced on an industrial scale by the action of zinc on 1,3-chlorobromo-propane, which prepared by addition of HBr to allylchloride (Equation 6.1).



Equation 6.1

2. Freund method:

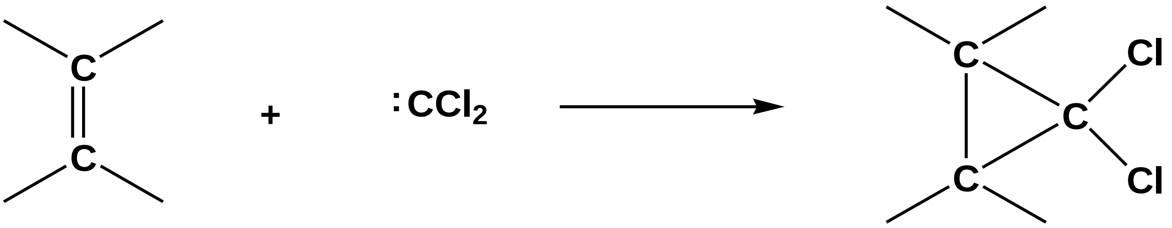
Treatment of 1,3-dibromopropane with metallic sodium gives the cyclopropane (Equation 6.2).



Equation 6.2

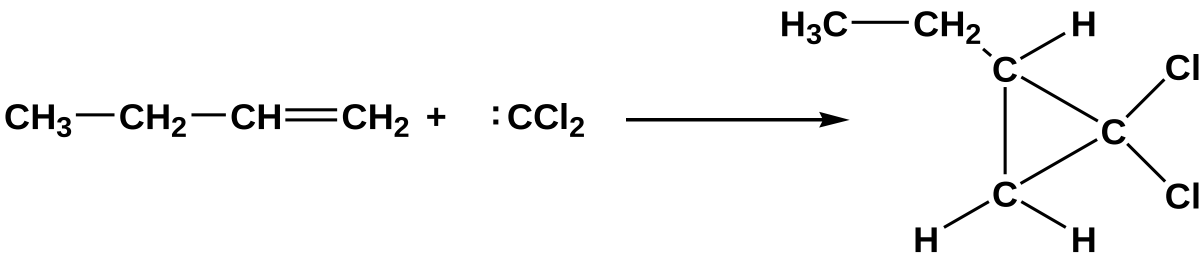
3. Action of carbenes on unsaturated compounds:

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

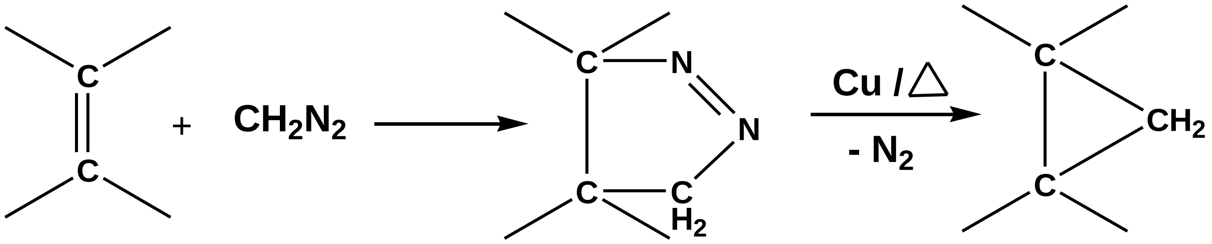
For example (Equation 6.4).



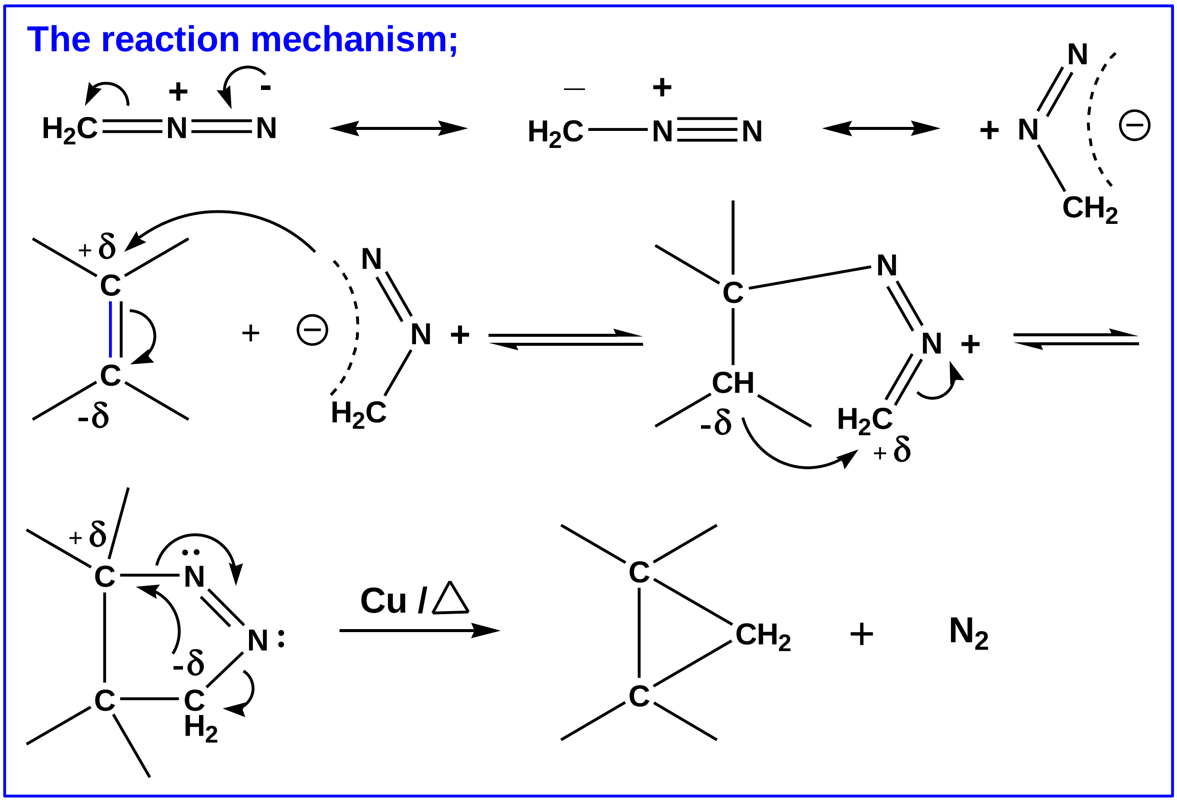
Equation 6.4

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).

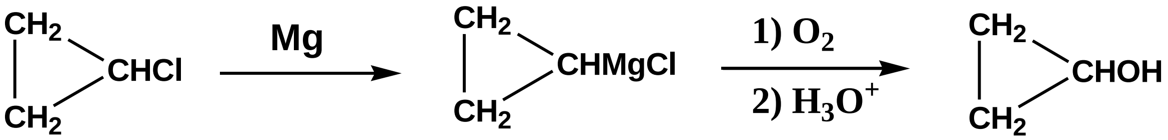


Equation 6.5



5. Synthesis of cyclopropanol:

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

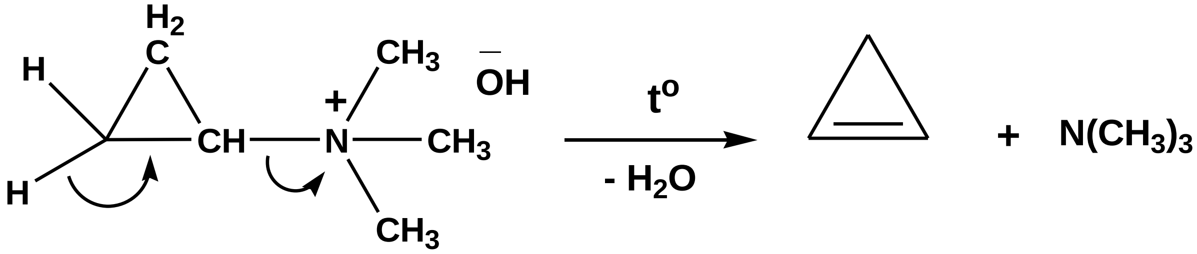


Equation 6.6

6. Synthesis of cyclopropenes:

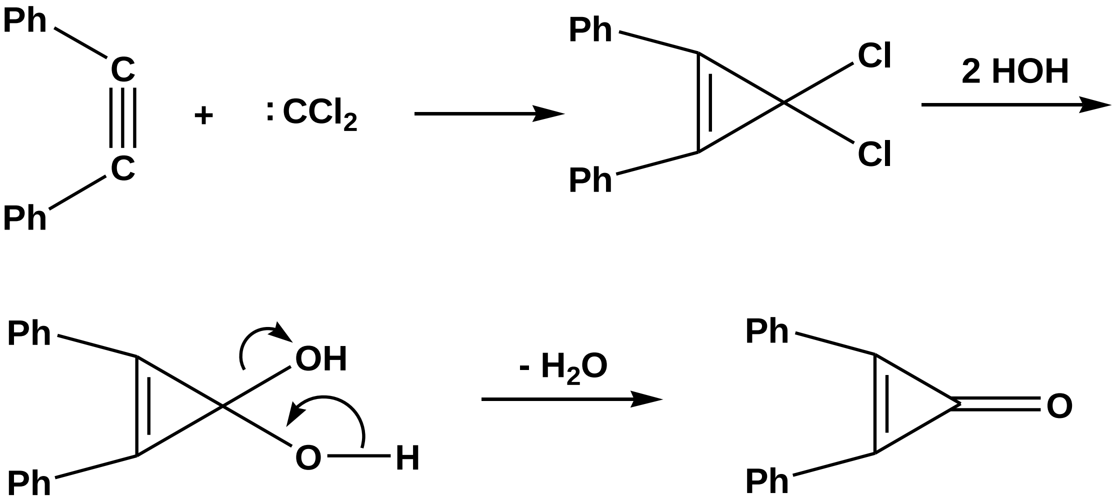
Two methods described the preparation of cyclopropene and cyclopropenenone as follows:

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



Equation 6.7

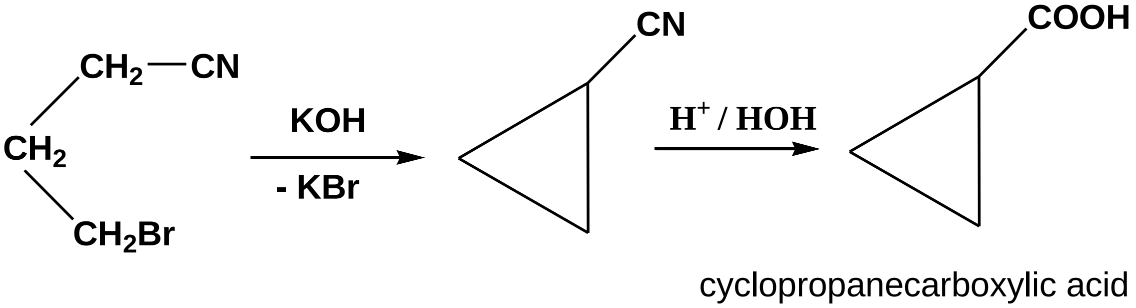
ii- Action of carbenes on acetylenes (Equation 6.8).



Equation 6.8

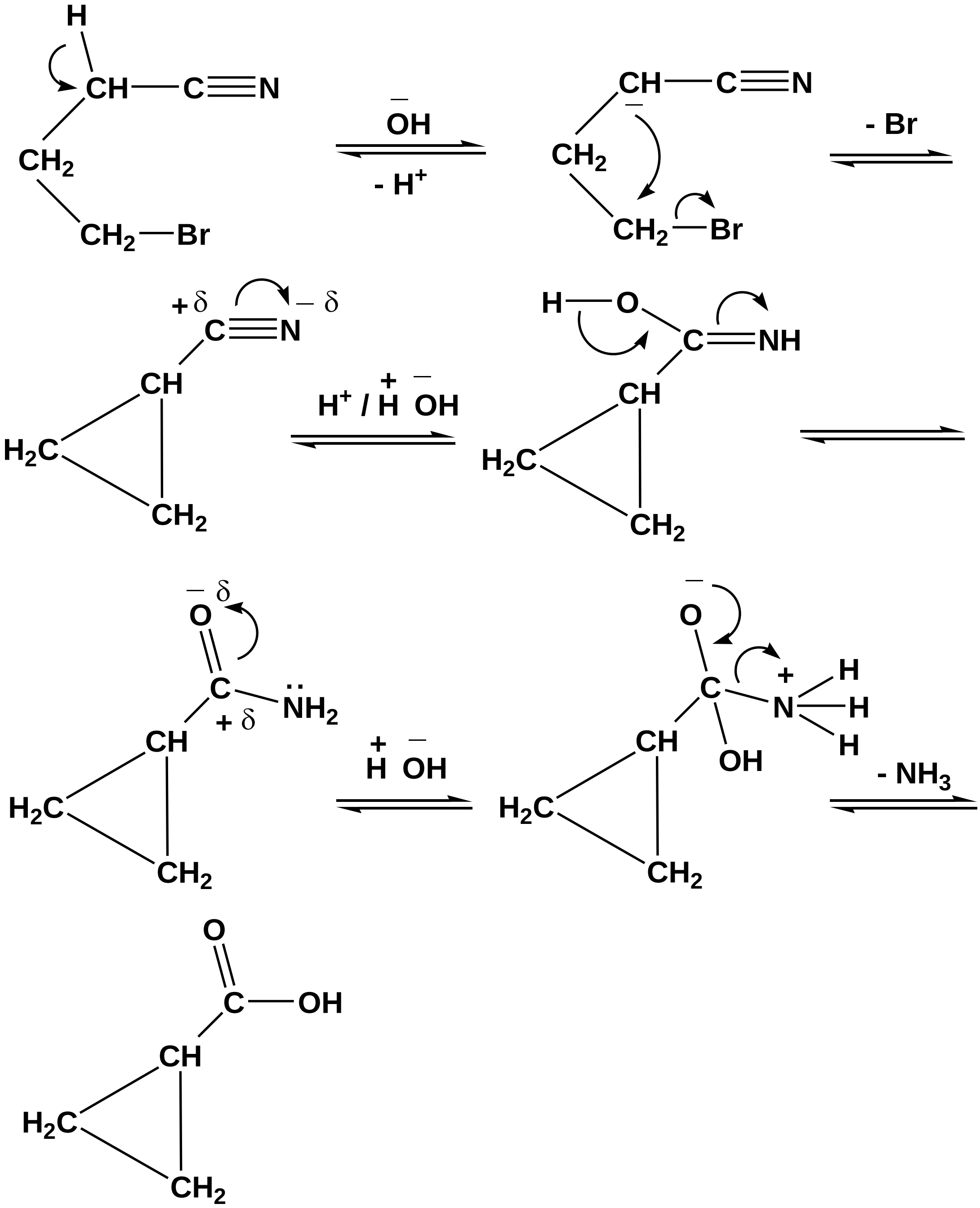
7. Synthesis of cyclopropanecarboxylic acid:

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



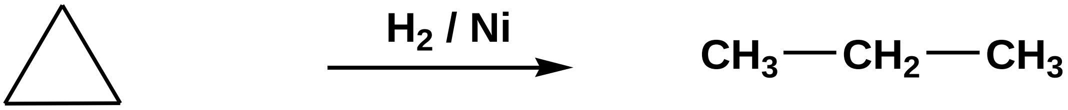
Equation 6.9

Mechanism;



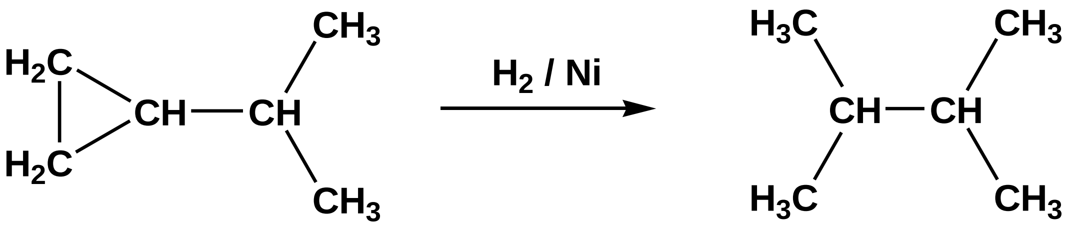
II- Chemical reactions of cyclopropane and its derivatives:

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).



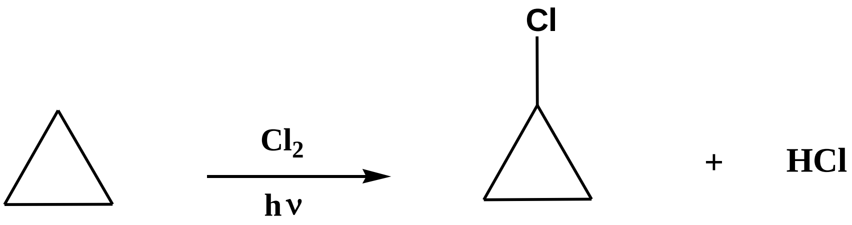
2,3-dimethyl-butane

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).

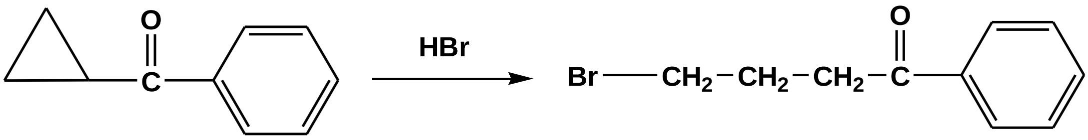


Equation 6.13

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

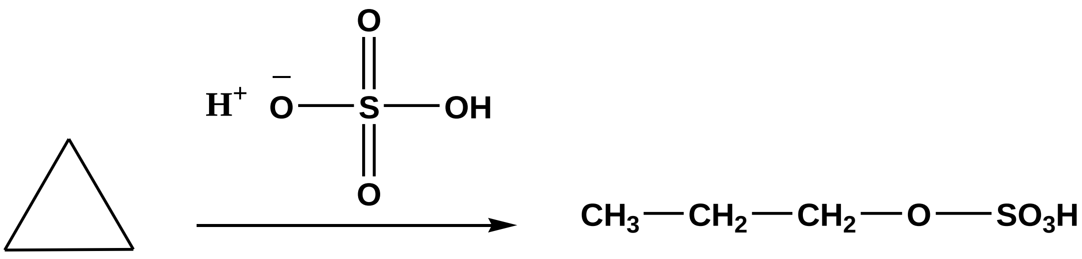
Equation 6.14

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

Quizzes:

1. True or False

a- Addition of diazomethane to the double bonds gives directly the cyclopropane derivatives.

○ 1)true

○ 2) false

b- Hydrogenation of propane gives cyclopropane.

○ 1)true

○ 2) false

2- Multiple Choice Questions

a- Chlorination of cyclopropane gives:

○ 1) Propane.

○ 2) Chloropropane.

○ 3) Chlorocyclopropane.

○ 4) 1,3-dichloropropane.

The Solution;

1- a (false), b (false)

2- a (3).

Unit 3

Lesson 7: Cyclobutane and its derivatives

7.1 Physical properties of cyclobutane: C_4H_8, b.p.= 12.5°C, 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.

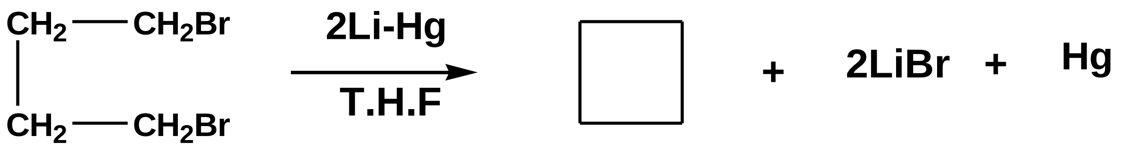
7.2 Chemical properties:

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

I- Methods of preparation:

1. Connor and Wilson reaction (1967):

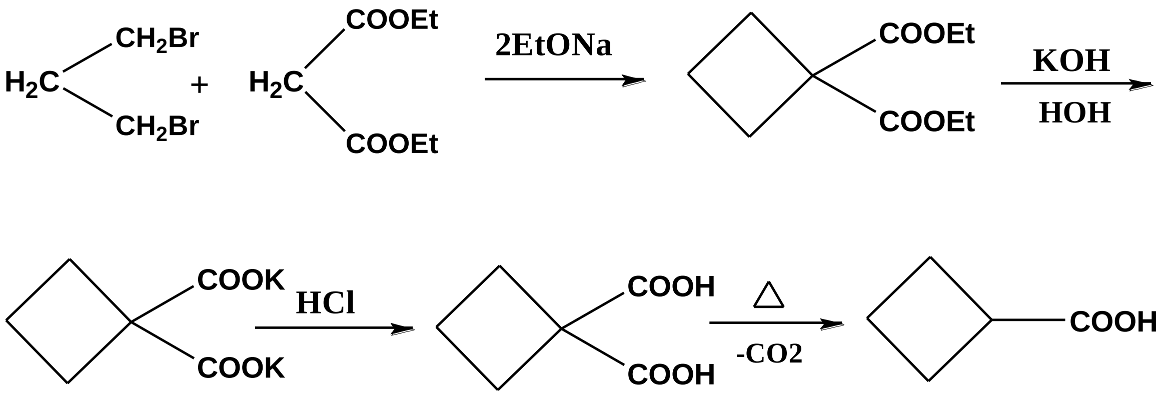
When 1,4-dibromobutane reacted with lithium amalgam in tetrahydrofuran, cyclobutane in a good yield was obtained (Equation 7.1).



Equation 7.1

2- Perkin's reaction:

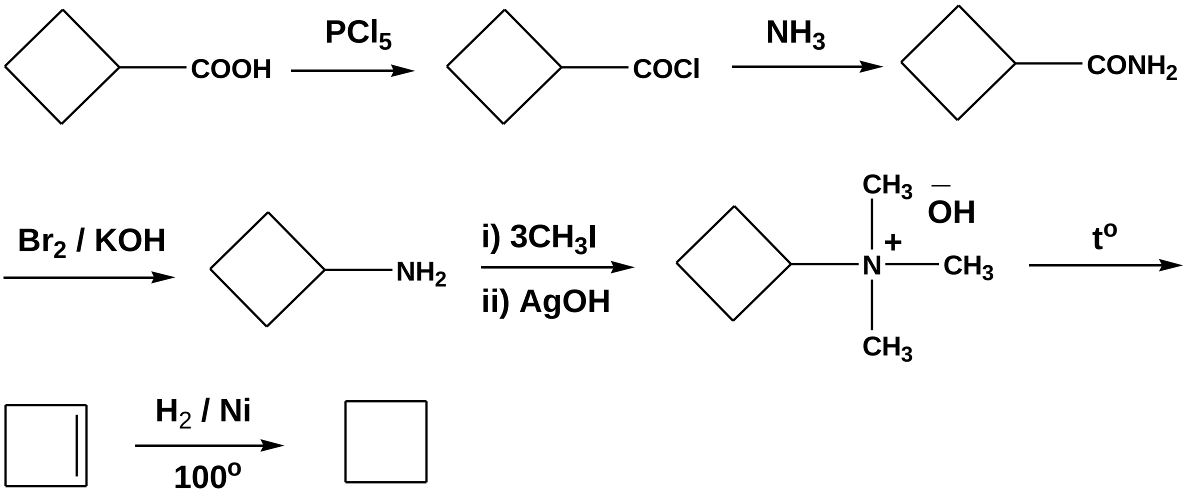
1,3-dibromobutane reacts with diethyl malonate in presence of sodium ethoxide to give cyclobutane dicarboxylic esters, which converts to cyclobutanecarboxylic acid (Equation 7.2).



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).



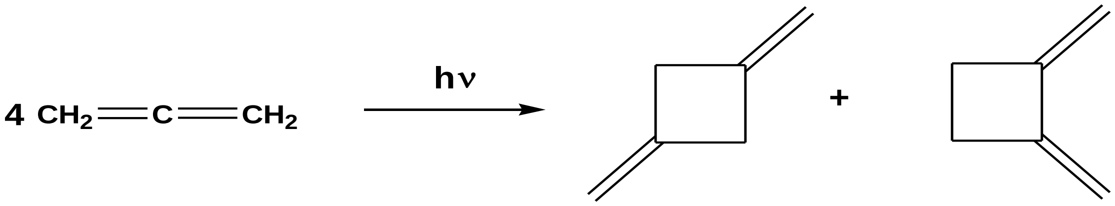
Equation 7.3

4- By photochemical reactions:

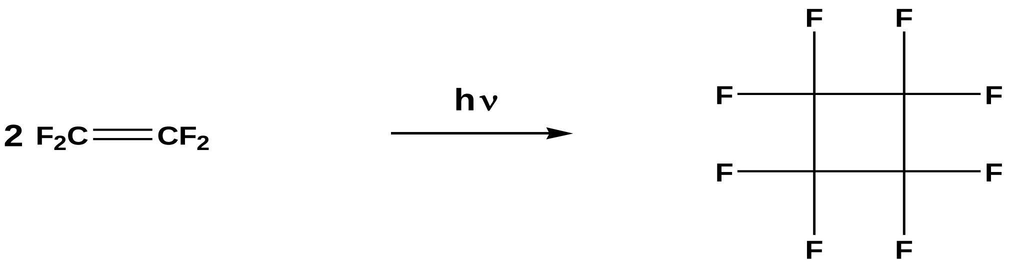
Cyclobutane or its derivatives can be prepared photochemically according to the following methods:

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).

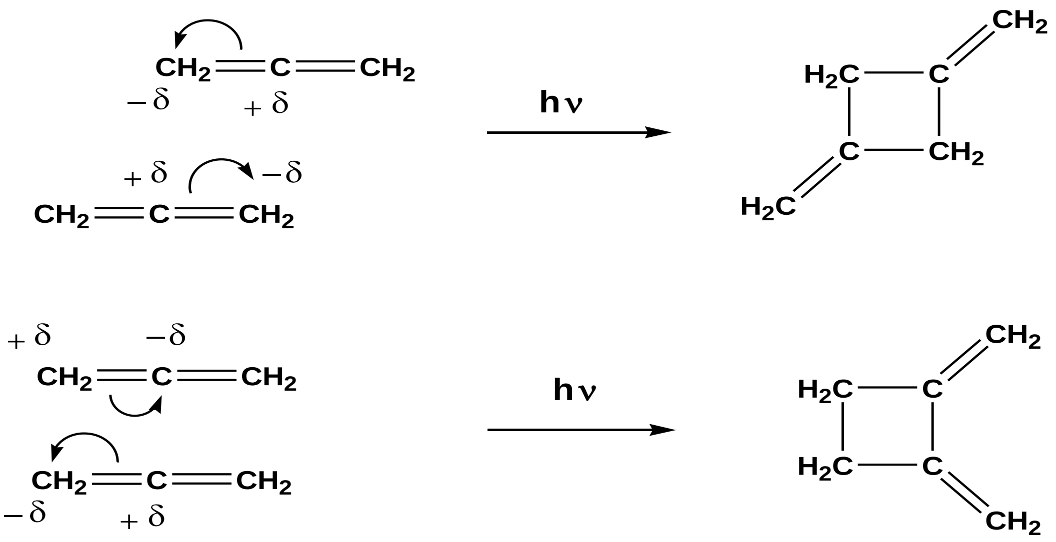


Equation 7.4



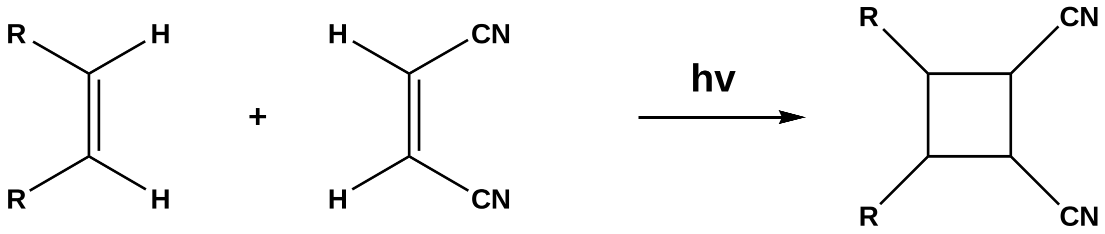
Equation 7.5

The reaction Mechanism;

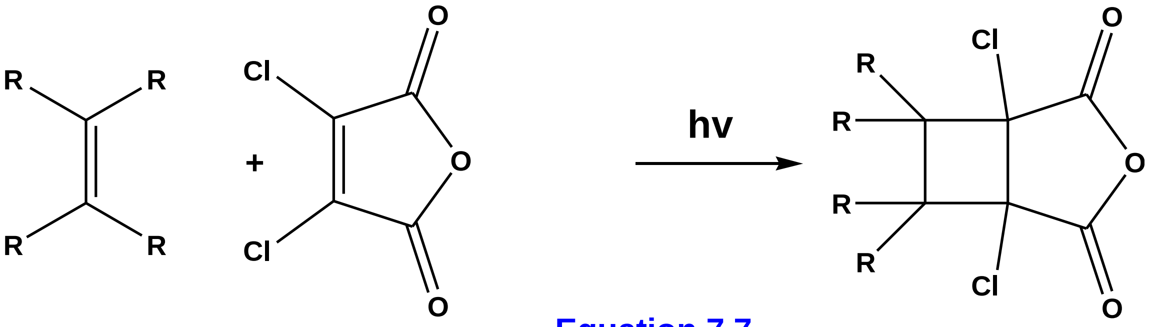


b- Olefin- Olefin addition:

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).



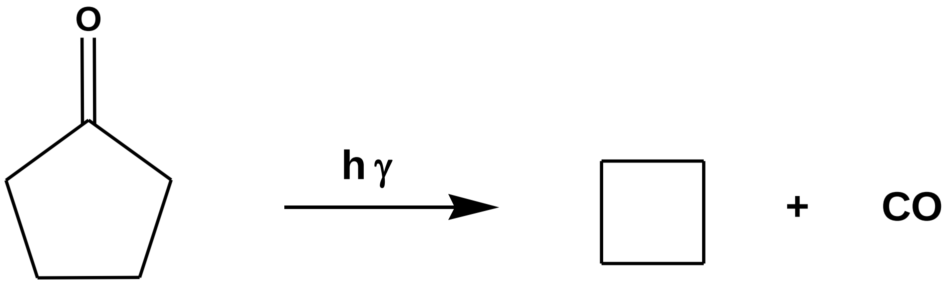
Equation 7.6



Equation 7.7

c- Proteolysis of cyclopentanone:

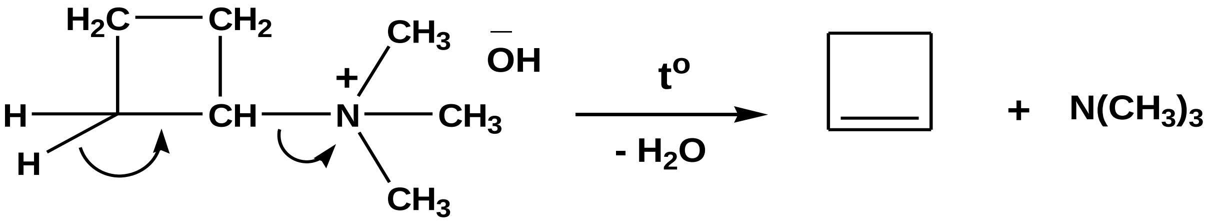
cyclobutane and carbon monoxide are the products of the proteolysis of cyclopentanone (Equation 7.8).



Equation 7.8

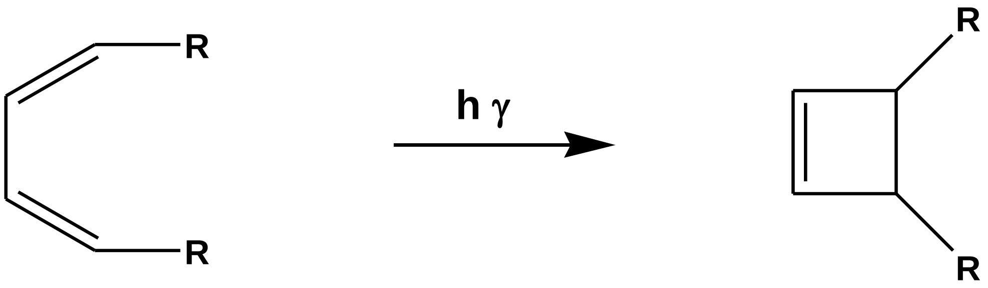
5- Preparation of cyclobutenes:

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).

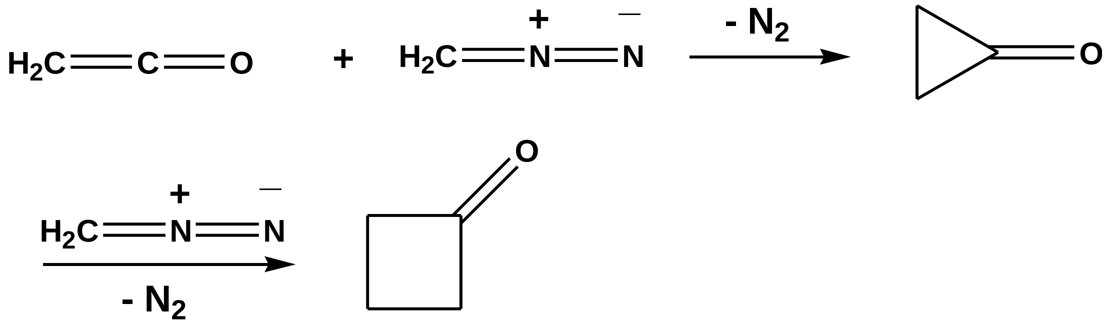


Equation 7.10

6- Carbonyl compounds of cyclobutane:

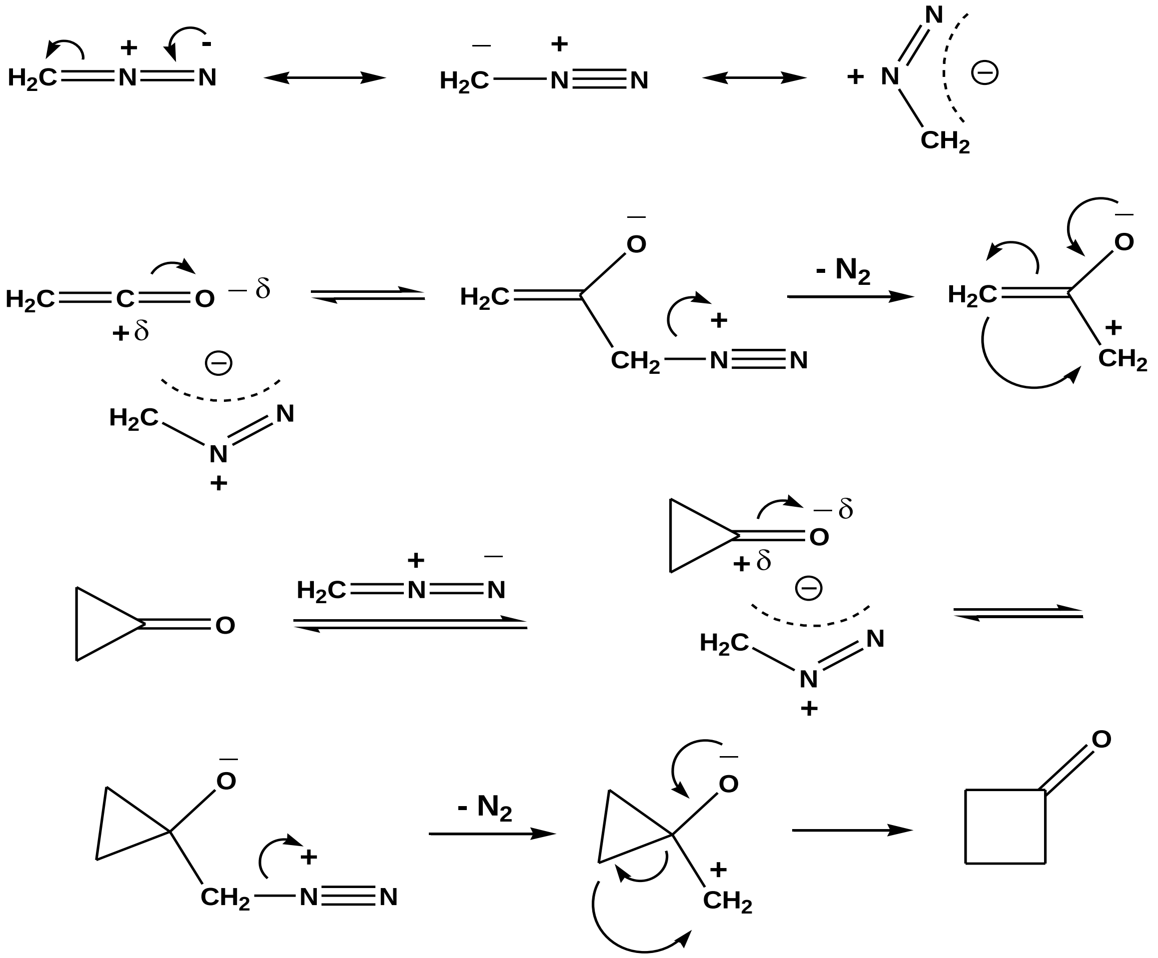
a- Cyclobutanone:

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



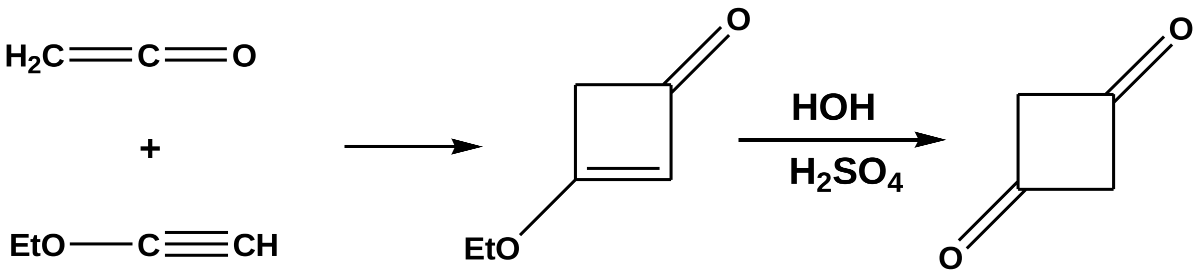
Equation 7.11

The reaction mechanism;



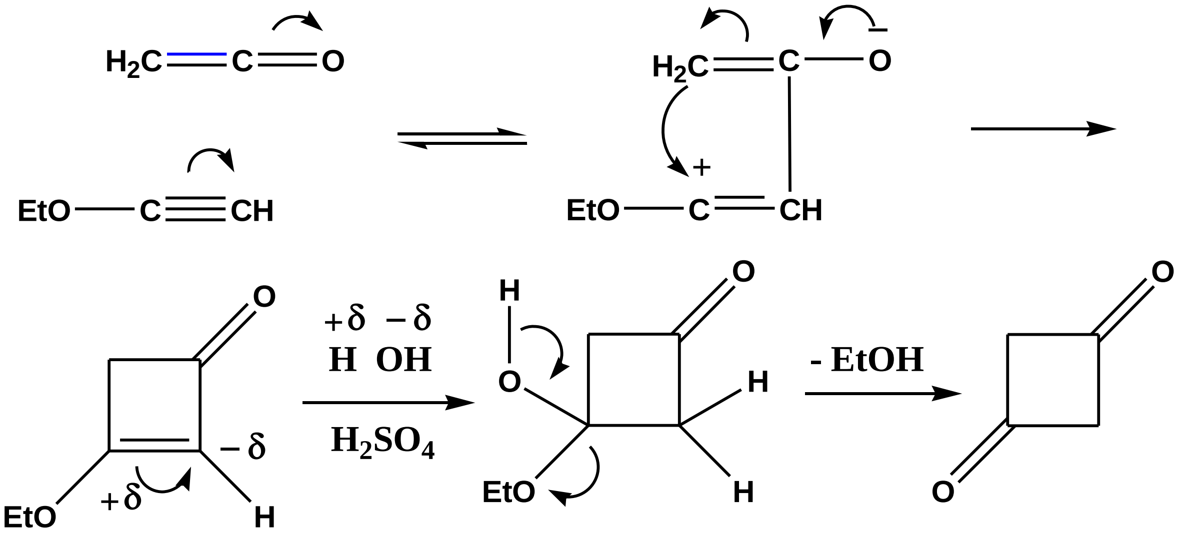
b- Cyclobutanedione:

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



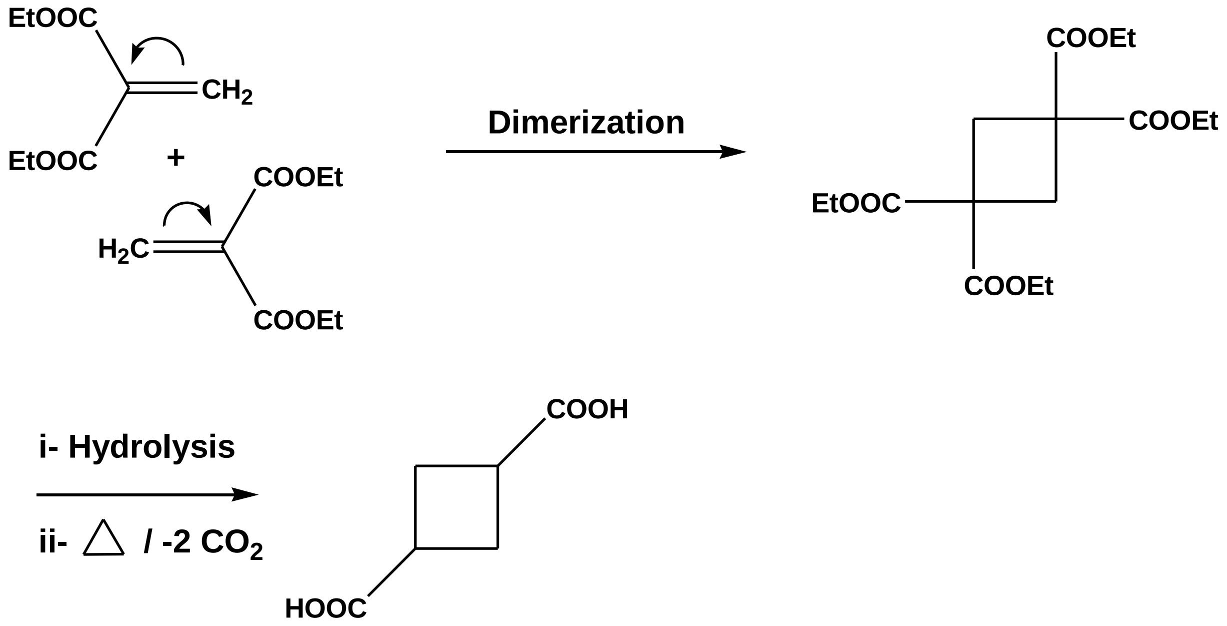
Equation 7.12

The reaction mechanism;



7- Cyclobutanecarboxylic acids:

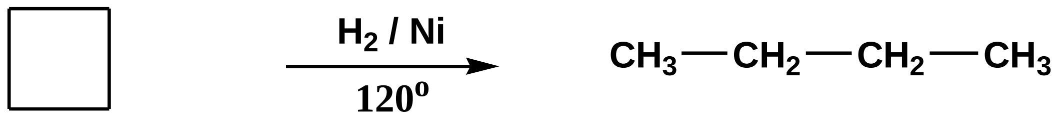
Cyclobutane-1,3-dicarboxylic acid as an example was prepared by the dimerization of 2-methylene-malonic acid diethyl ester (Equation 7.13).



Equation 7.13

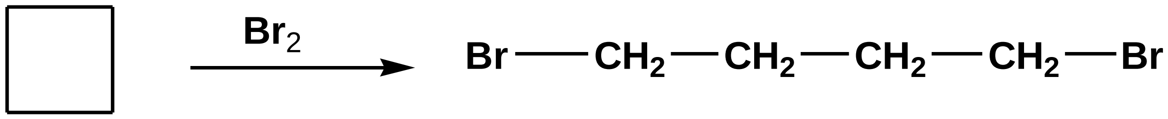
II- Chemical reactions of cyclobutane and its derivatives:

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



Equation 7.14

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

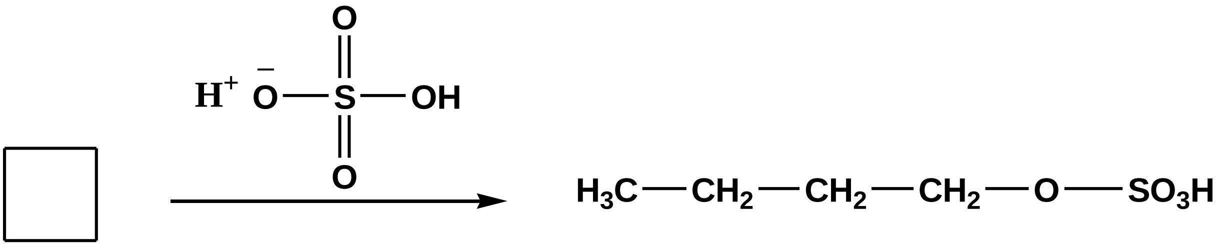


Equation 7.15

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

Quizzes:

1. True or False

a- The decarboxylation of cyclobutanecarboxylic acid does not lead to the cyclobutane.

○ 1)true

○ 2) false

b- Diazomethane reacts with ketene to give only cyclopropanone.

○ 1)true

○ 2) false

c- Irradiation of 1,3-dienes by ultraviolet rays affords 1,3-cyclobutadiene derivatives**.**

○ 1)true

○ 2) false

2- Multiple Choice Questions

a- Proteolysis of cyclopentanone gives:

○ 1) Cyclopentane.

○ 2) Cyclobutane.

○ 3) Cyclopropane.

○ 4) Pentane.

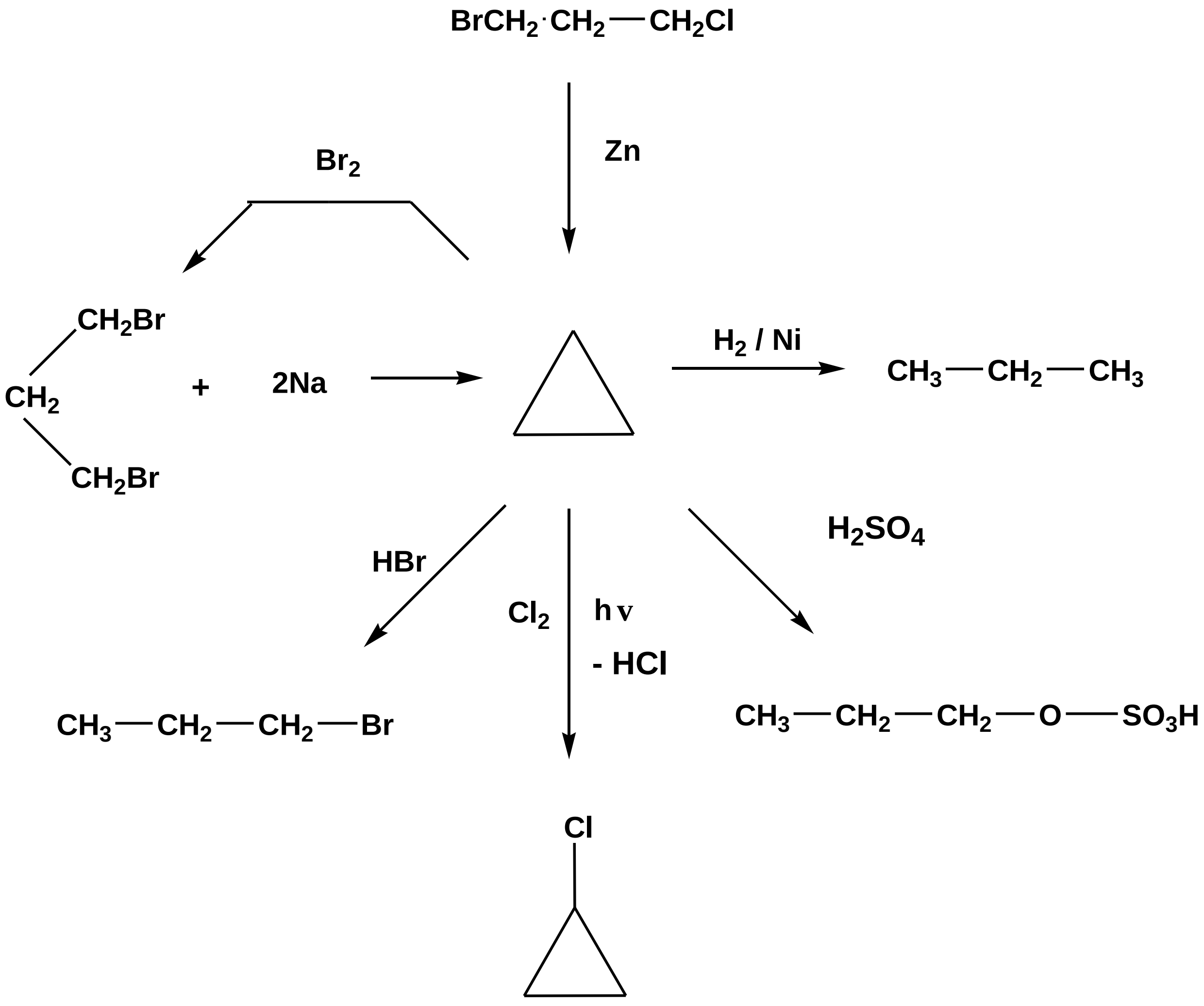
The Solution;

1- a (true), b (false), c (false).

2- a (1).

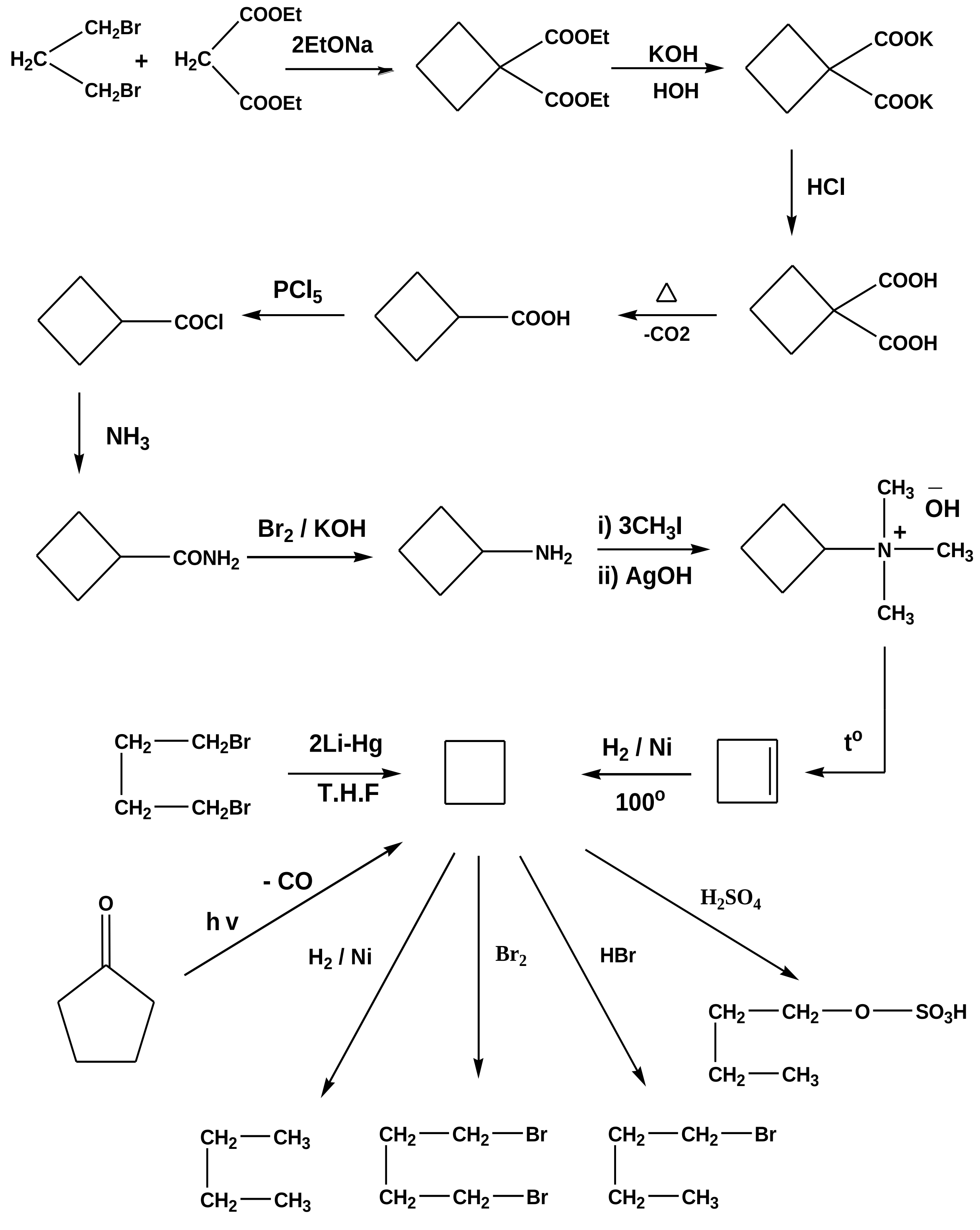
The Summary of Unit 3

The preparation and the reactions of cyclopropane can be summarized in the scheme 1:



Scheme 1

The preparation and the reactions of cyclobutane can be summarized in the scheme 2:



Scheme 2

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.

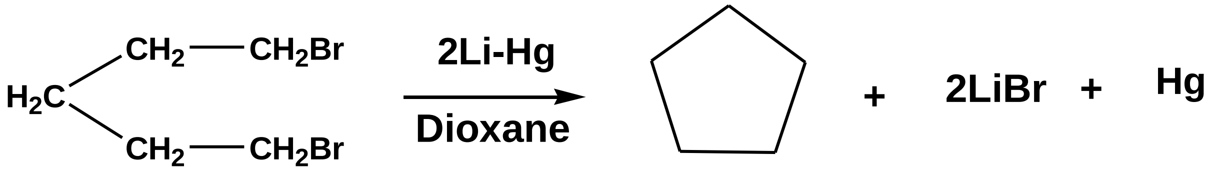
8.2 Chemical properties:

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

I- Methods of preparation:

1. Connor and Wilson reaction:

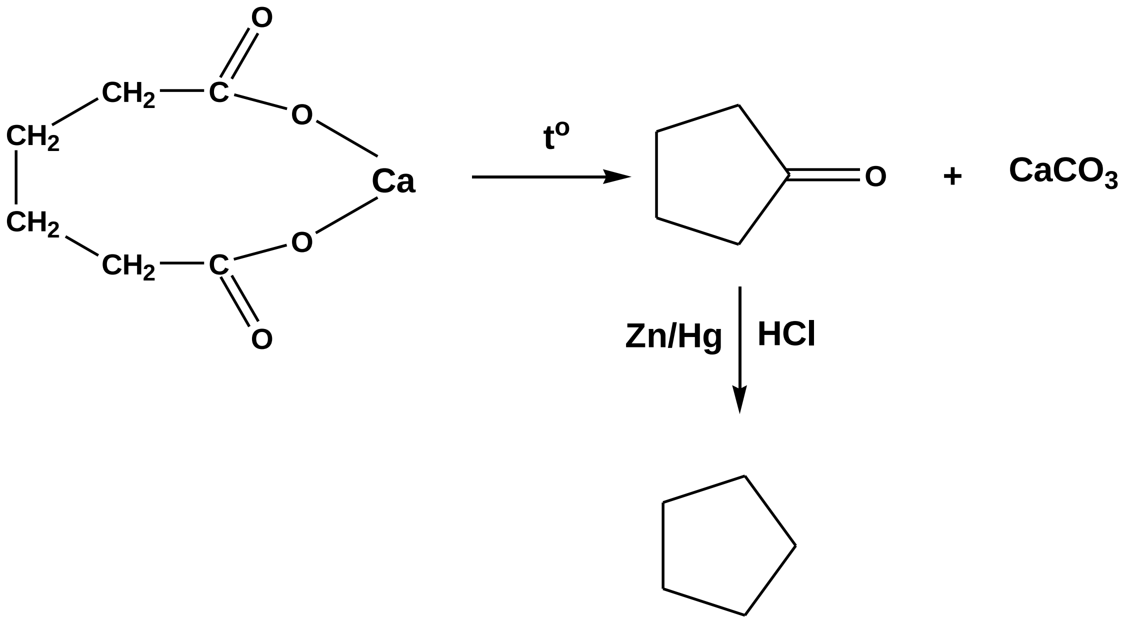
Action of lithium amalgam on a dioxane solution of 1,5-dibromopentane can give cyclopentane in 75% yield (Equation 8.1).



Equation 8.1

2. Pyrolysis of calcium salt of adipic acid:

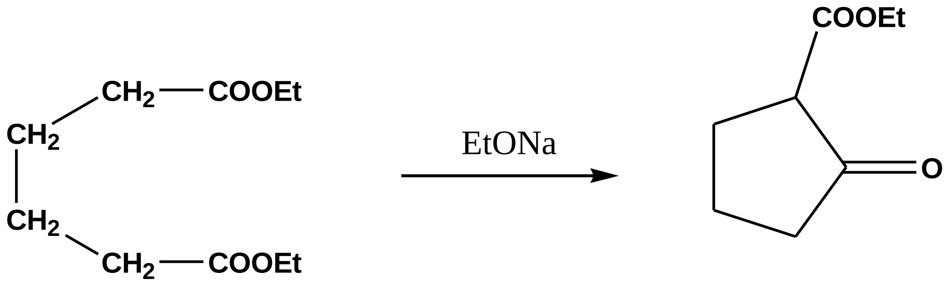
This method can be used to synthesize cyclopentanone with good yield under pyrolysis of the calcium adipate. Cyclopentanone may be converted into cyclopentane by means of the Clemmenson reduction (Equation 8.2).



Equation 8.2

3. Dieckmann condensation:

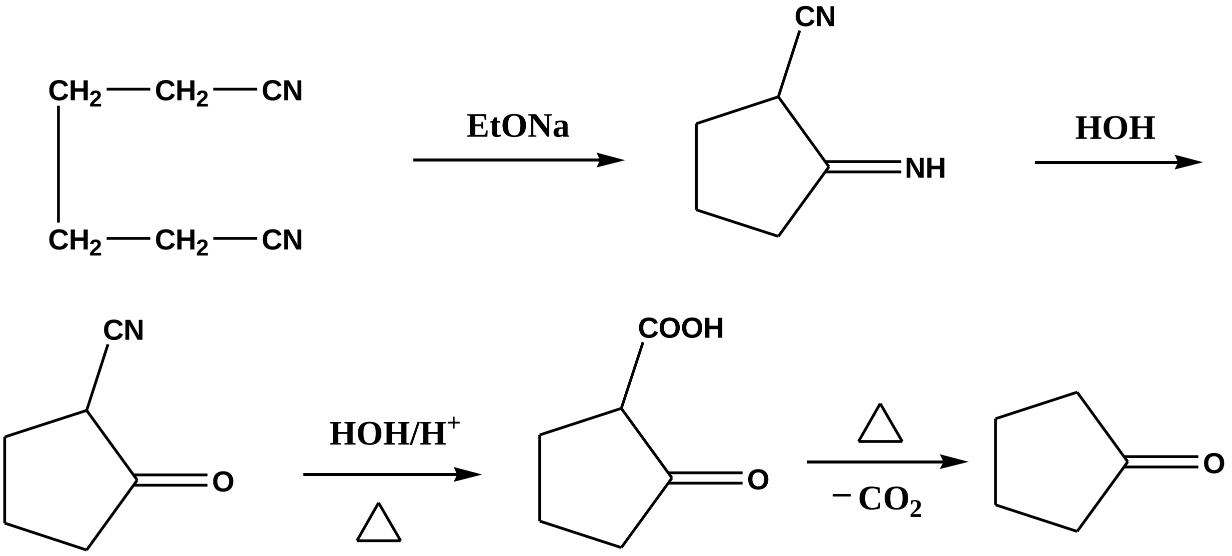
Treatment of diethyl adipate with excess of sodium ethoxide can give 2-cyclopentanonecarboxylic acid ethyl ester (Equation 8.3).



Equation 8.3

4. Ziegler-Thorpe reaction:

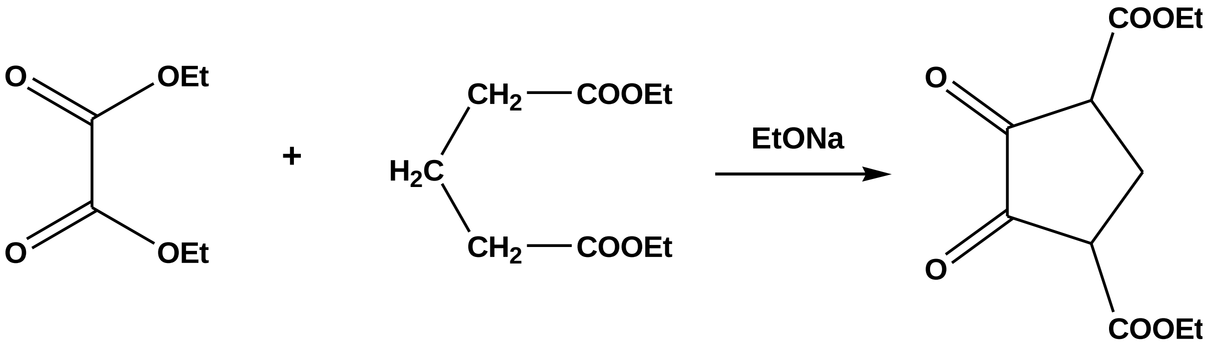
Condensation of hexanedinitrile in presence of sodium ethoxide gives 2-cyclopentanonecarbonitrile, which up-on hydrolysis affords 2-cyclopentanonecarboxylic acid. Decarboxylation of the later gives cyclopentanone (Equation 8.4).



Equation 8.4

5. Condensation of oxalic ester with glutatric ester:

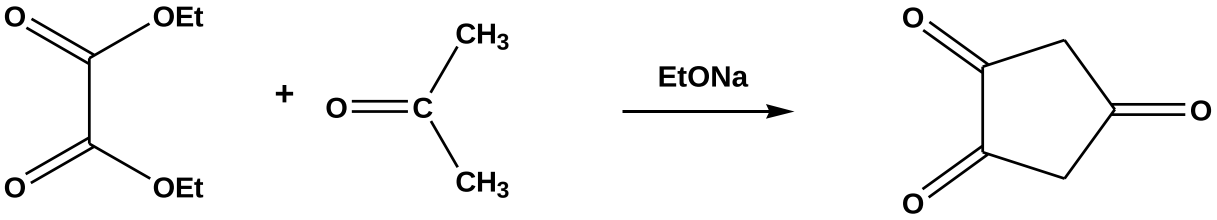
Treatment of ethyl oxalate with ethyl glutrate in presence of sodium ethoxide gives cyclopentan-4,5-dione-1,3-dicarboxylic acid diethyl ester (Equation 8.5).



Equation 8.5

6. Condensation of oxalic ester with acetone:

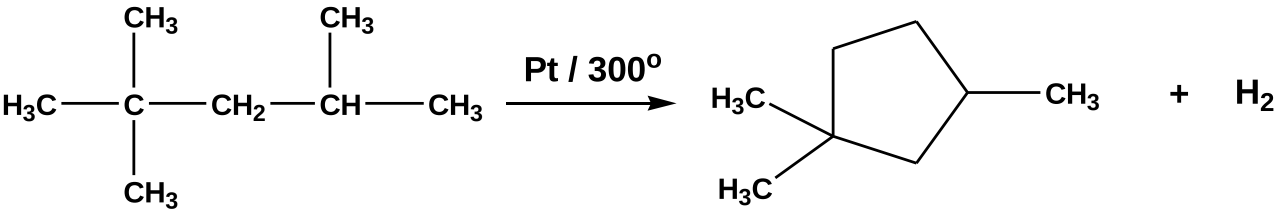
Treatment of acetone with ethyl oxalate in presence of sodium ethoxide gives cyclopentane-1,2,4-trione (Equation 8.6).



Equation 8.6

7. Dehydrocyclization of hydrocarbon chains:

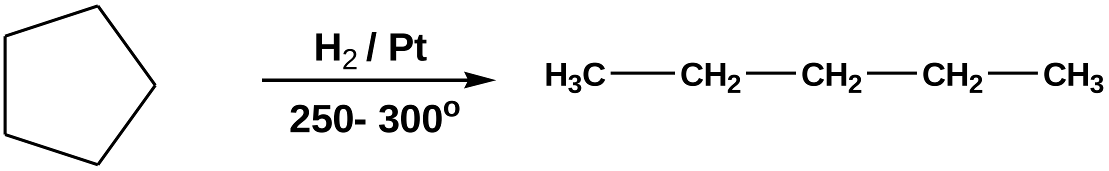
When a five carbon atoms chain contains a quaternary carbon atom is passed over a platinium catalyst at 300 °C, cyclopentane derivative was obtained (Equation 8.7).



Equation 8.7

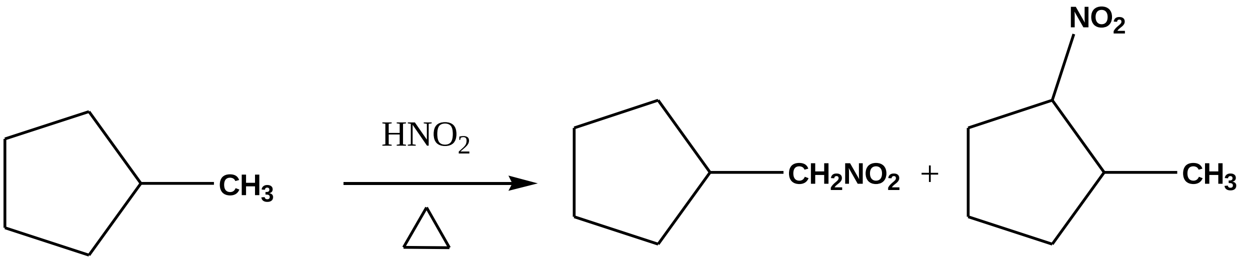
II- Chemical reactions of cyclopentane and its derivatives:

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



Equation 8.8

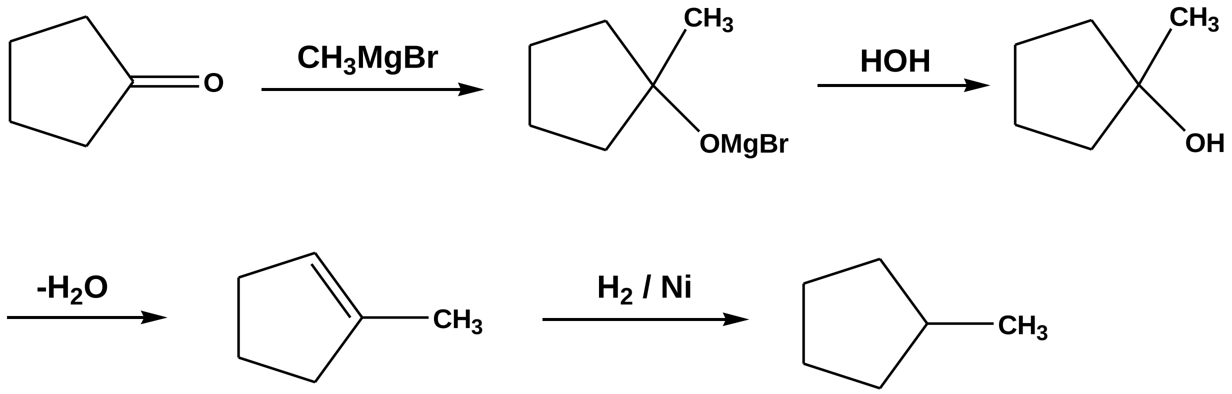
2. Nitration: cyclopentane and its derivatives can be nitrated, e. g., nitration of methylcyclopentane yields two products (Equation 9.9).



Equation 8.9

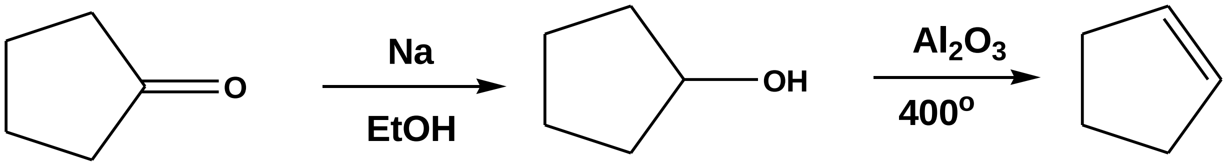
3. Cyclopentanone:

a- Grignard reaction: treatment of cyclopentanone with Grignard reagent (CH_3MgBr) followed by hydrolysis gives 1-methyl-cyclopentanol. The later lose a molecule of water to give 1-methyl-cyclopentene, which on hydrogenation gives methylcyclopentane (Equation 8.10).



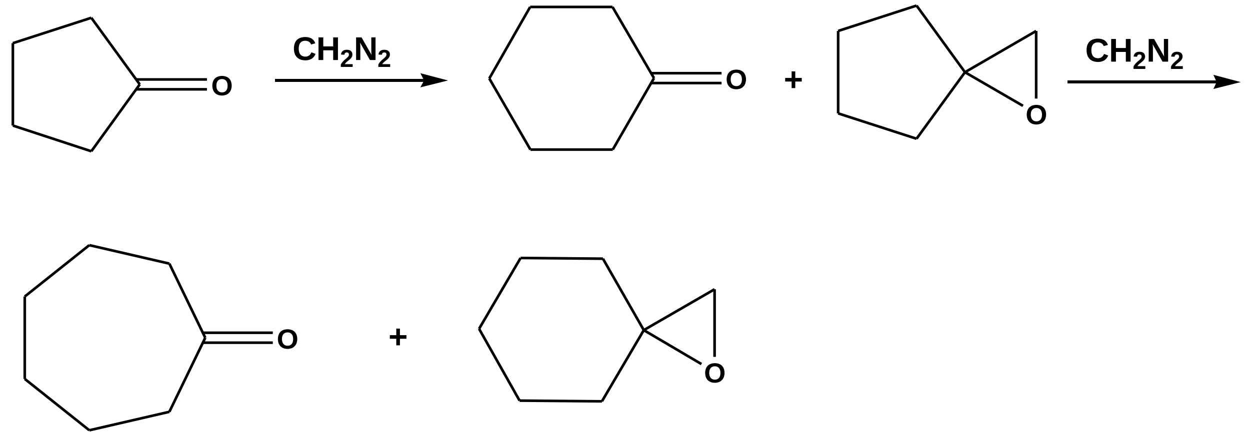
Equation 8.10

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



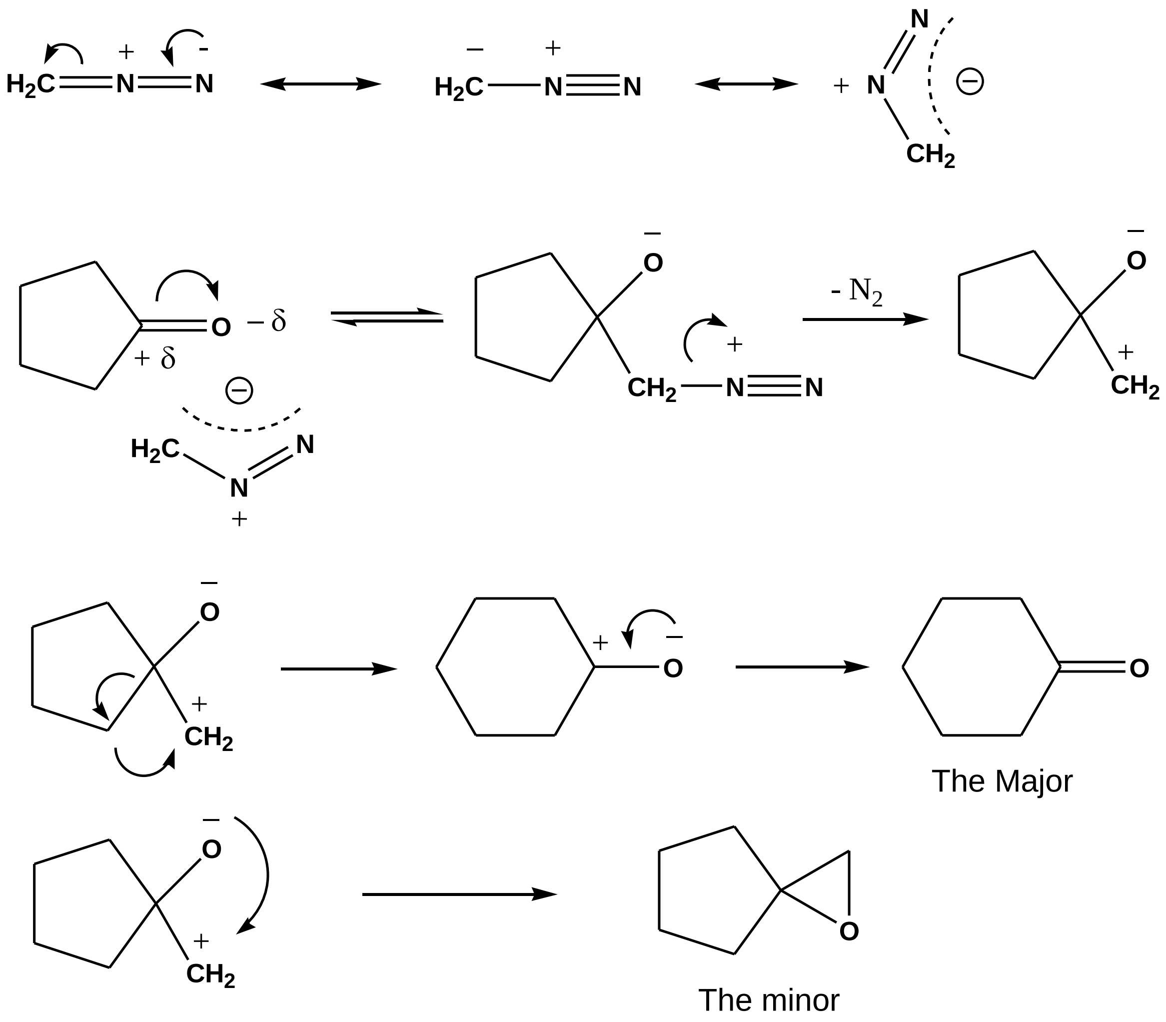
Equation 8.11

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



Equation 8.12

The reaction mechanism;



4. Cyclopentadiene:

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

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

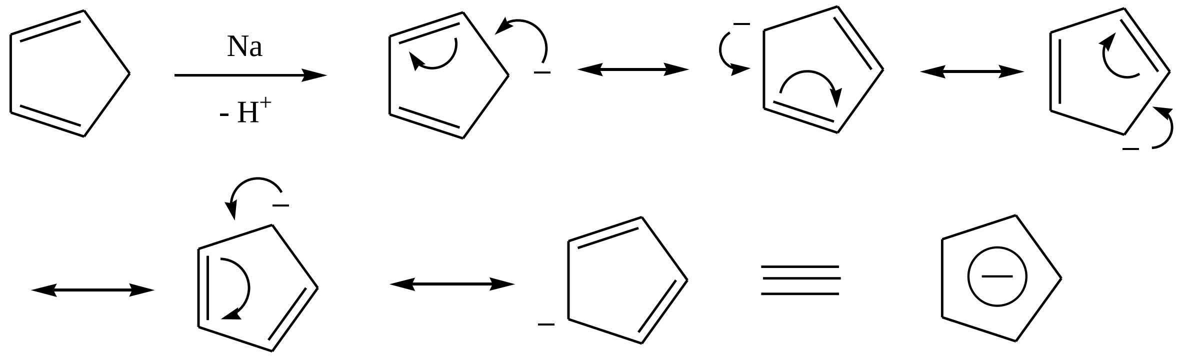
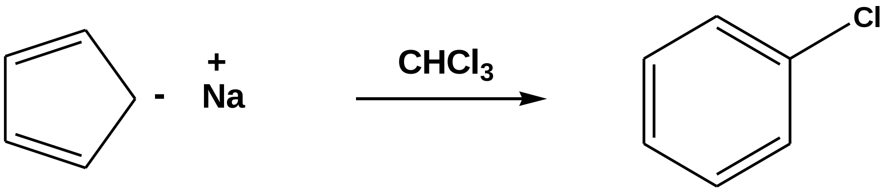


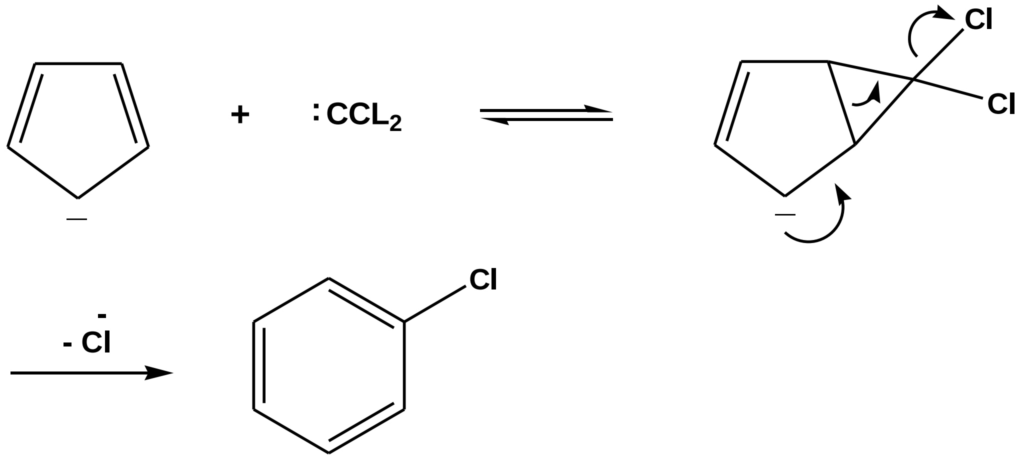
Figure 8.13

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

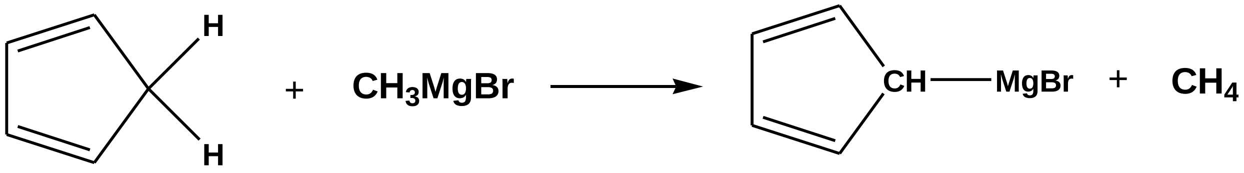


Equation 8.14

The reaction mechanism;

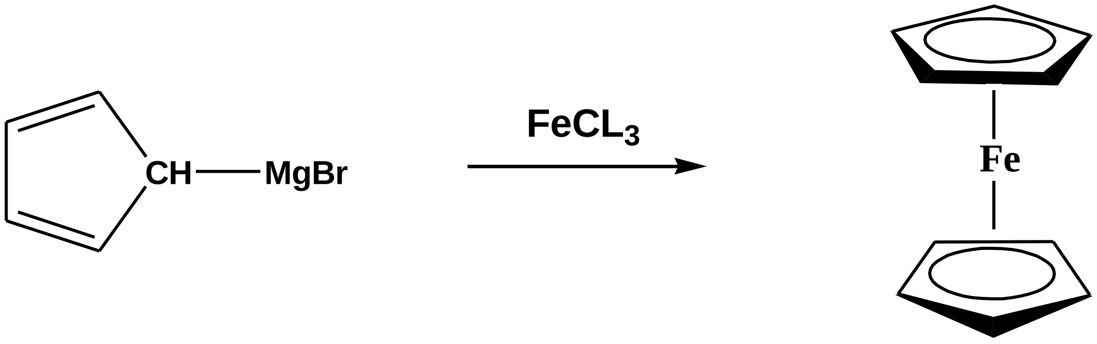


b- Grignard reaction: cyclopentadiene reacts with Grignard reagents to form cyclopentadienyl magnesium halide and the corresponding hydrocarbon (Equation 8.15).



Equation 8.15

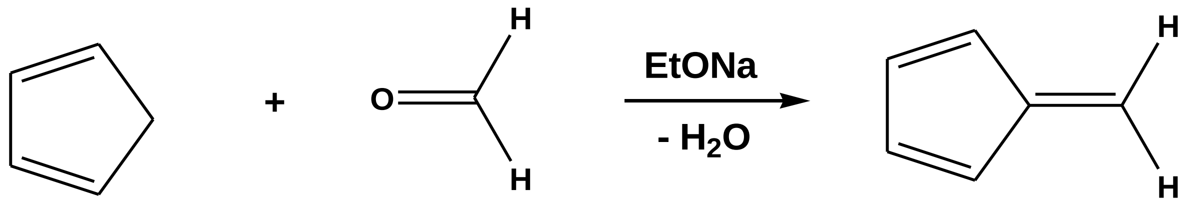
When cyclopentadienyl magnesium bromide reacts with ferric chloride, dicyclopentadienyl iron was isolated. This iron (Fe II) complex was named *ferrocene* by Woodward *et al* (Equation 8.16).



Ferrocene

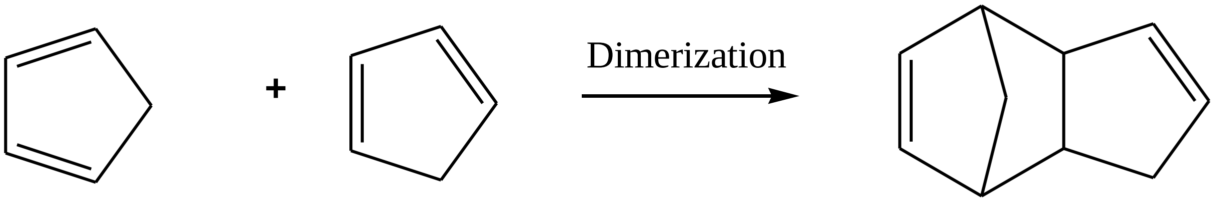
Equation 8.16

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



Equation 8.17

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



Equation 8.18

Quizzes:

1. True or False

a- Cyclopentadiene condenses with aldehydes to afford *fluvenes*.

○ 1)true

○ 2) false

b- Treatment of cyclopentadiene with sodium gives the *ferrocene*.

○ 1)true

○ 2) false

c- Cyclopentadiene dimerizes into dicyclopentadiene.

○ 1)true

○ 2) false

2- Multiple Choice Questions

a- Sodium cyclopentadienyl reacts with chloroform to give:

○ 1) Benzene.

○ 2) Cyclopentadiene.

○ 3) Chlorobenzene.

○ 4) pentane.

The Solution;

1- a (true), b (false), c (true).

2- a (3).

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.

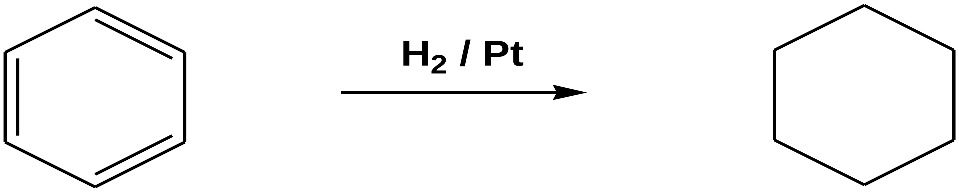
9.2 Chemical properties:

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

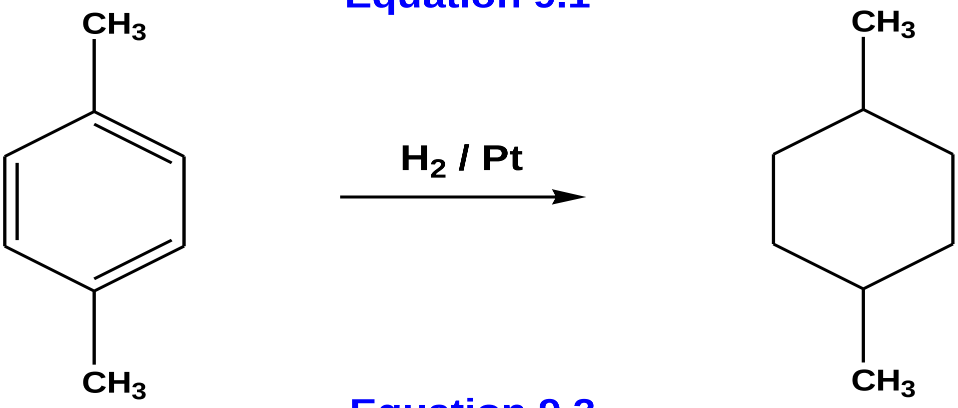
I- Methods of preparation:

1. Hydrogenation of benzene and its derivatives:

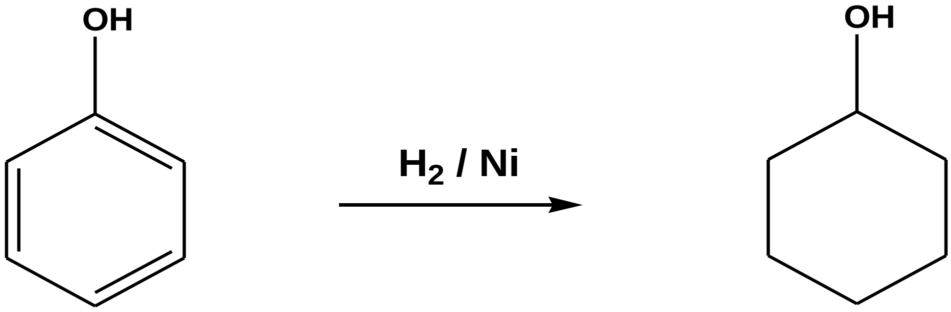
Cyclohexane is prepared commercially by catalytic hydrogenation of benzene. Certain derivatives of cyclohexane are mainly prepared by catalytic hydrogenation of certain aromatic compounds over platinum or nickel (Equations 9.1- 9.4).



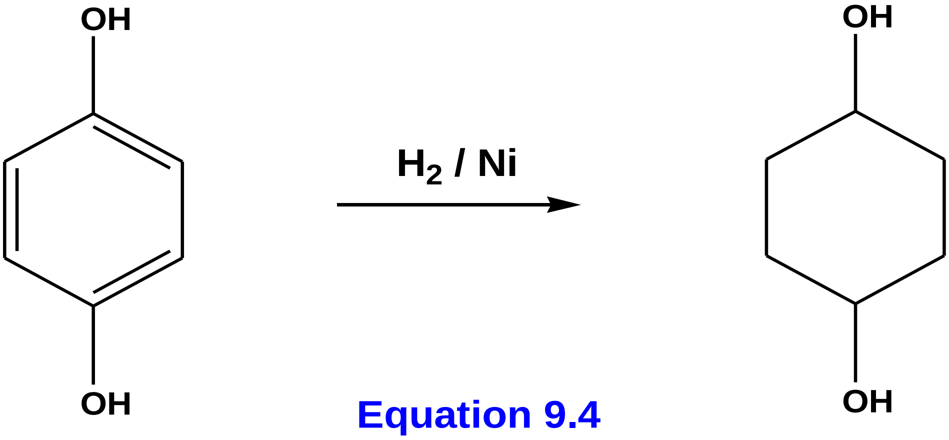
Equation 9.1



Equation 9.2



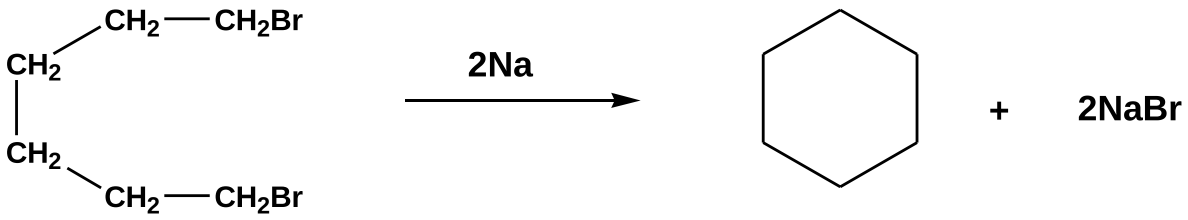
Equation 9.3



Equation 9.4

2- Freund reaction:

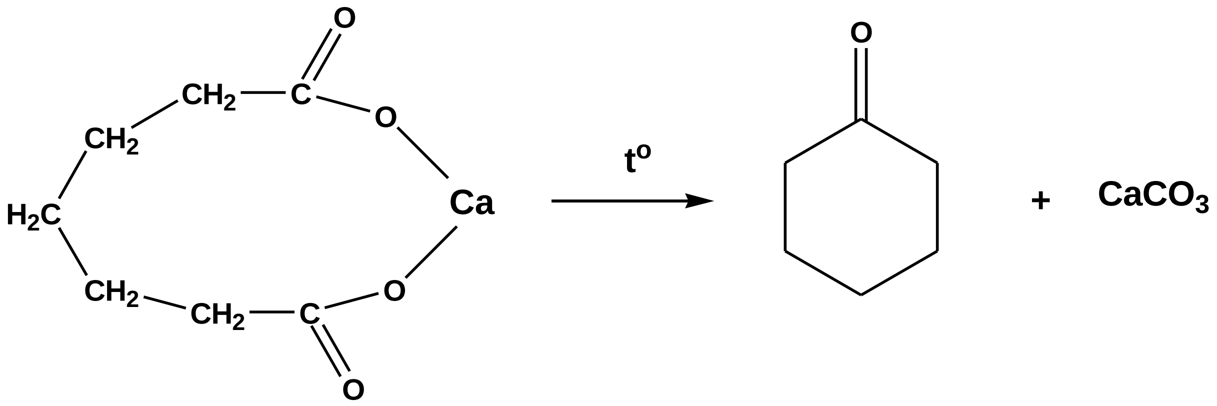
Treatment of 1,6-dibromohexane with a metal like sodium or zinc gives cyclohexane (Equation 9.5).



Equation 9.5

3. Pyrolysis of calcium salt of pimelic acid:

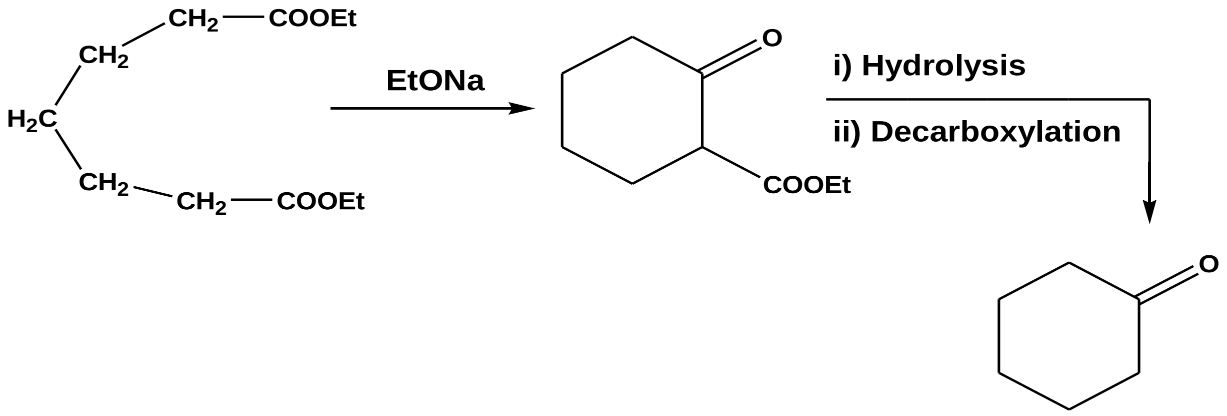
Cyclohexanone can be obtained under the pyrolysis of calcium pimelate (Equation 9.6).



Equation 9.6

4. Dieckmann condensation:

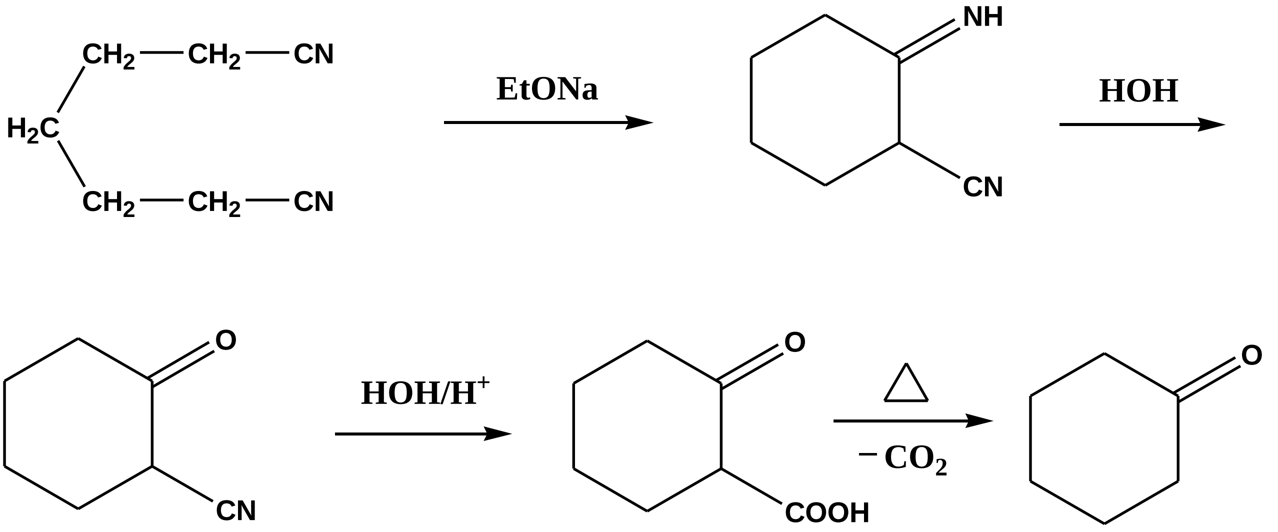
Treatment of diethyl pimelate with sodium ethoxide can give 2-cyclohexanonecarboxylic acid ethyl ester, which upon hydrolysis and decarboxylation turns to cyclohexanone (Equation 9.7).



Equation 9.7

5. Ziegler-Thorpe reaction:

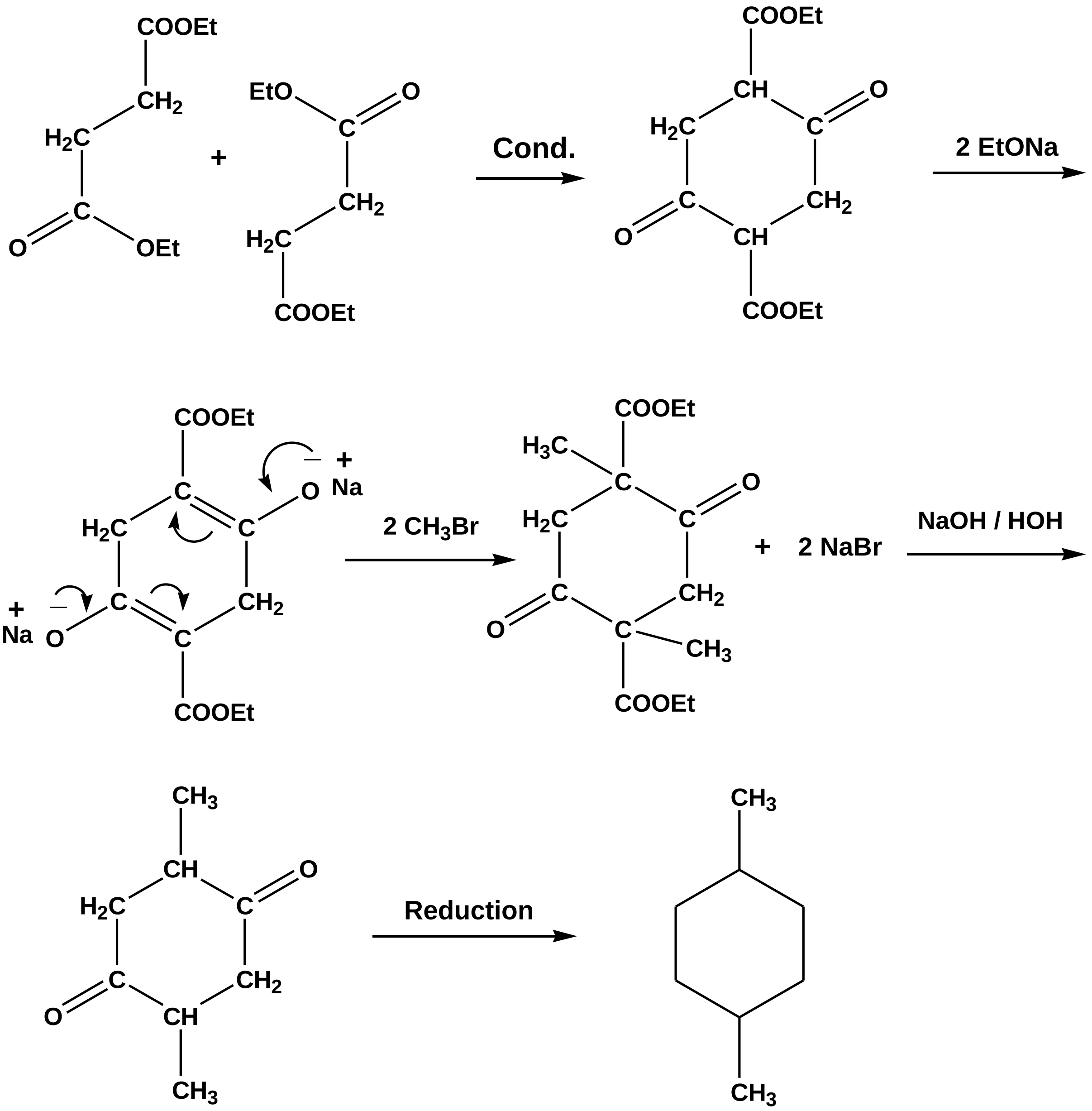
When heptanedinitrile treated with sodium ethoxide followed by hydrolysis affords 2-cyclohexanonecarbonitrile. After hydrolysis and decarboxylation of the later, cyclohexanone was obtained (Equation 9.8).



Equation 9.8

6. Ester condensation of succinic ester:

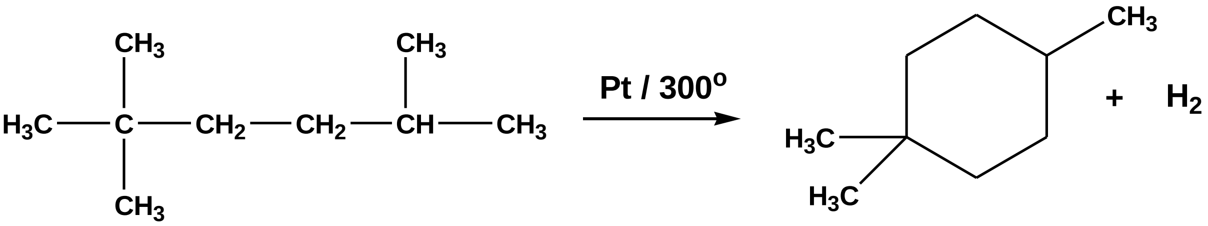
Condensation of two molecules of diethylsuccinate in presence of sodium ethoxide gives succinosuccinic ester. The sodium salt of the later was treated with alkyl halide followed by saponification and then finally Clemmenson reduction to afford 1,4-disubstituted-cyclohexane (Equation 9.9).



Equation 9.9

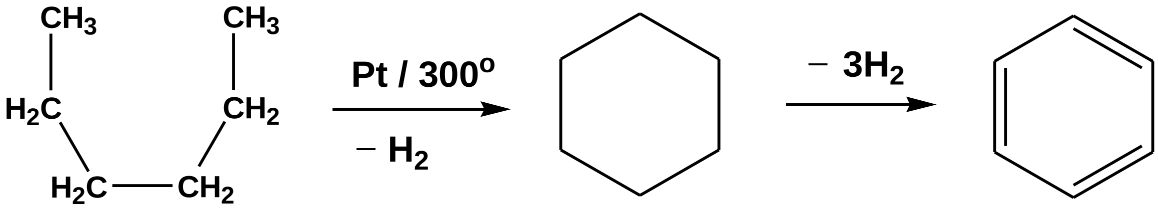
7. Dehydrocyclization of hydrocarbon chains:

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



Equation 9.10

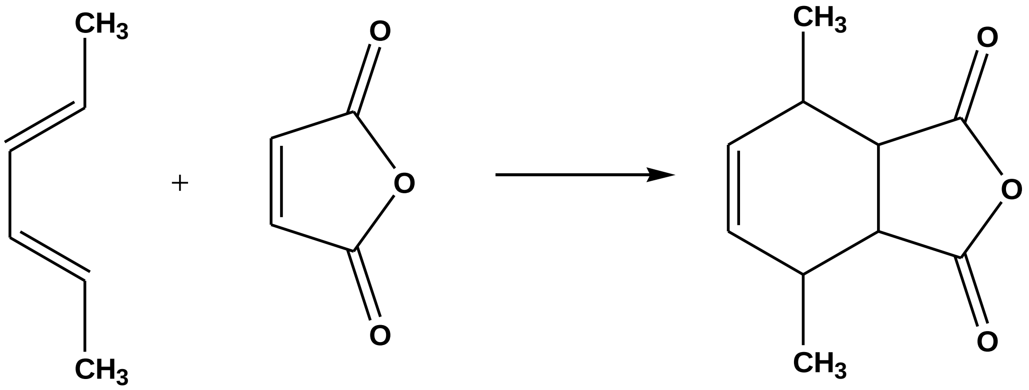
Absence of a quaternary carbon atom in the carbon chain makes the produced cyclohexane dehydrogenated to benzene (Equation 9.11).



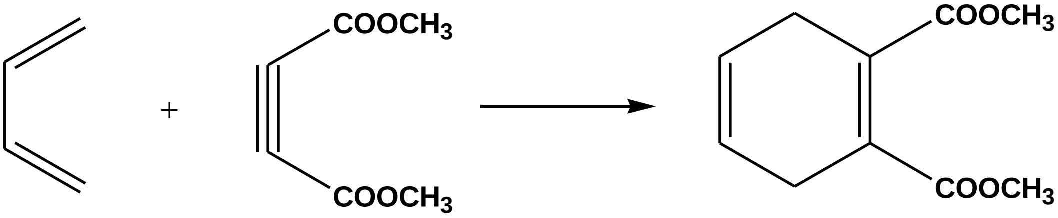
Equation 9.11

8. Diels-Alder reaction:

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



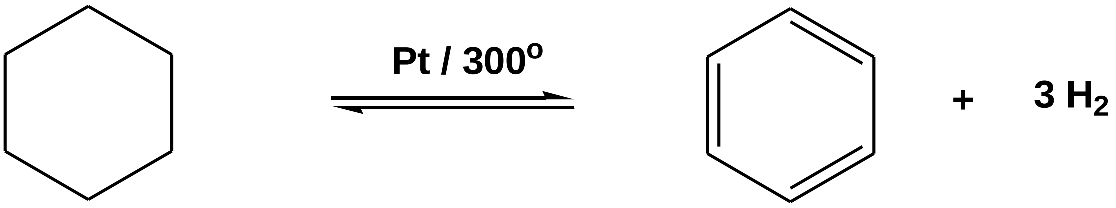
Equation 9.12



Equation 9.13

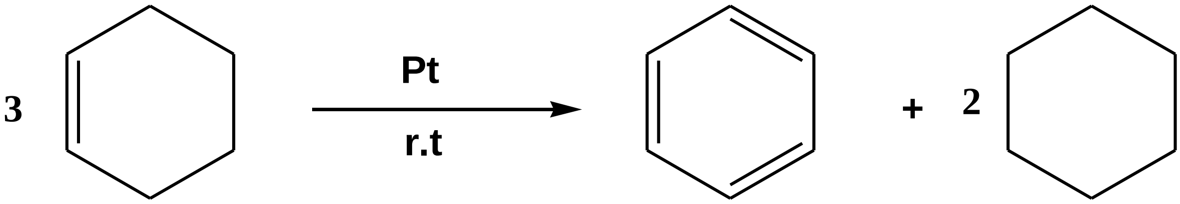
II- Chemical reactions of cyclohexane and its derivatives:

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



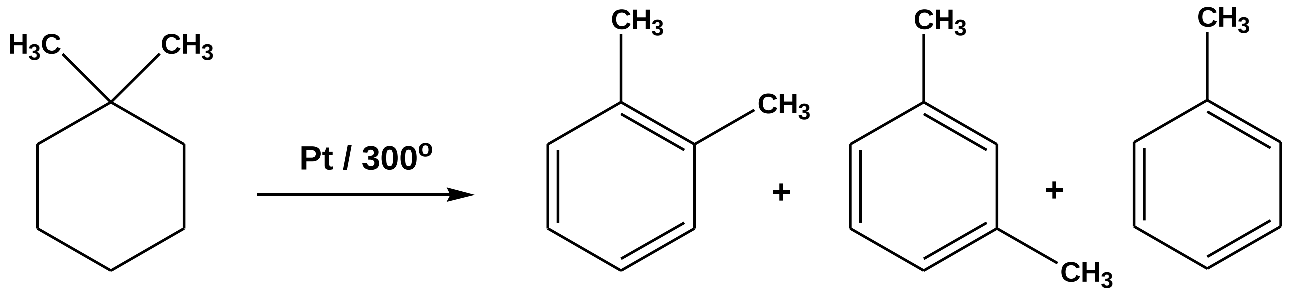
Equation 9.14

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).



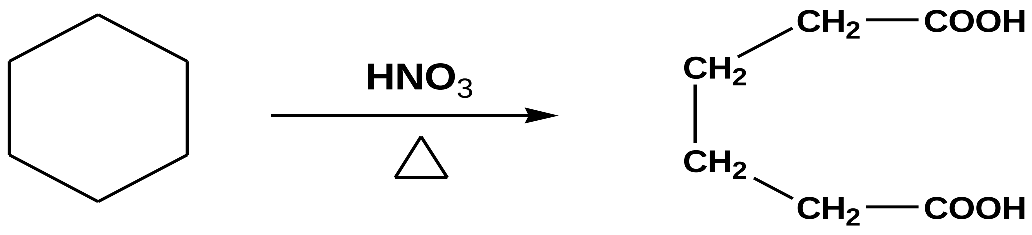
Equation 9.15

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

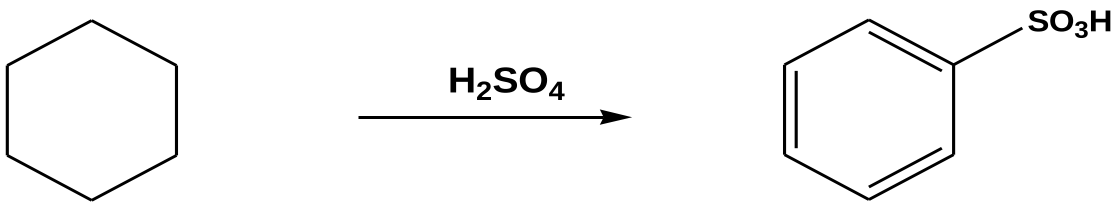
2. Nitration: in hot concentrated nitric acid, cyclohexane can be oxidized to adipic acid (Equation 9.17).



Adipic acid

Equation 9.17

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

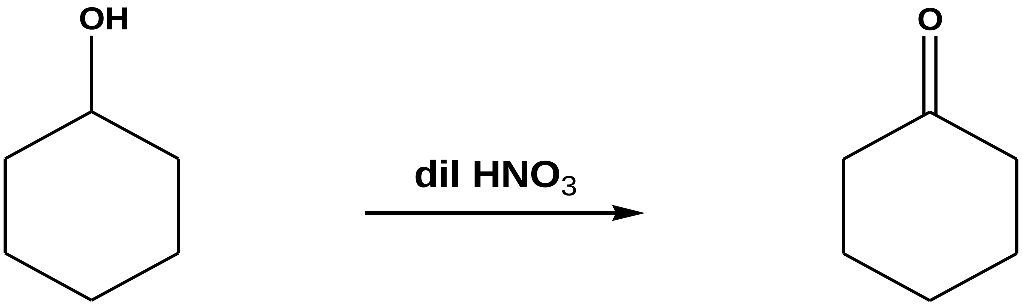


Benzenesulphonic acid

Equation 9.18

4. Cyclohexanol:

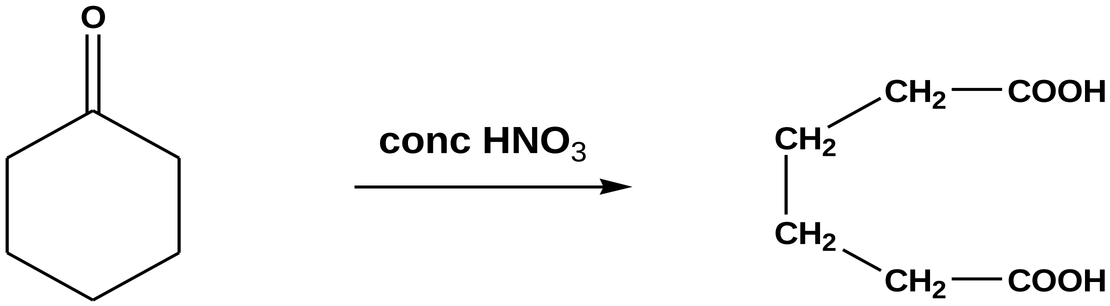
Cyclohexanol is converted by oxidation with dilute nitric acid into cyclohexanone (Equation 9.19).



Equation 9.19

5. Cyclohexanone:

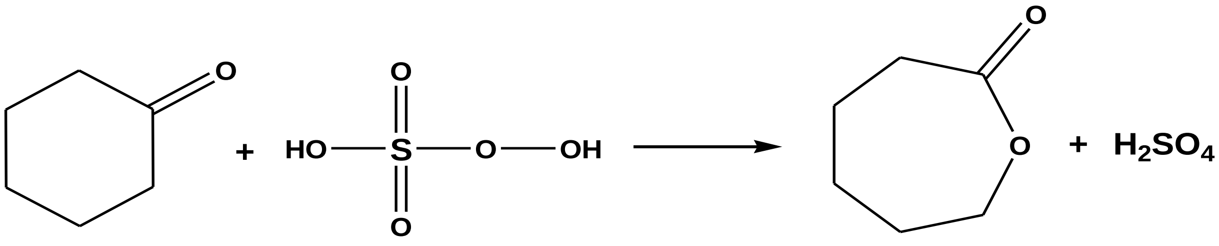
a- Oxidation with nitric acid: The vigorous oxidation of cyclohexanone with *conc* nitric acid produces adipic acid (Equation 9.20).



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).

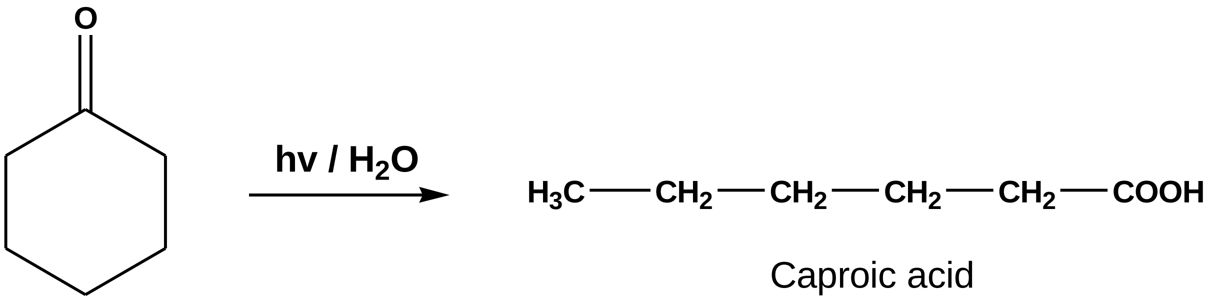


Permonosulphuric acid

Caprolactone

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

Quizzes:

1. True or False

a- Hydrogenation of benzene gives cyclohexadiene.

○ 1) true

○ 2) false

b- Nitration of cyclohexane gives nitrocyclohexane.

○ 1) true

○ 2) false

c- Cyclohexanone gives hexanoic acid under the influence of light in presence of water.

○ 2) false

2- Multiple Choice Questions

a- Cyclohexanone oxidized by Caro's acid to give:

○ 1) Caproic acid.

○ 2) Adipic acid.

○ 3) Succinosuccinic ester.

○ 4) Caprolactone.

The Solution;

1- a (false), b (false), c (true).

2- a (4).

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.

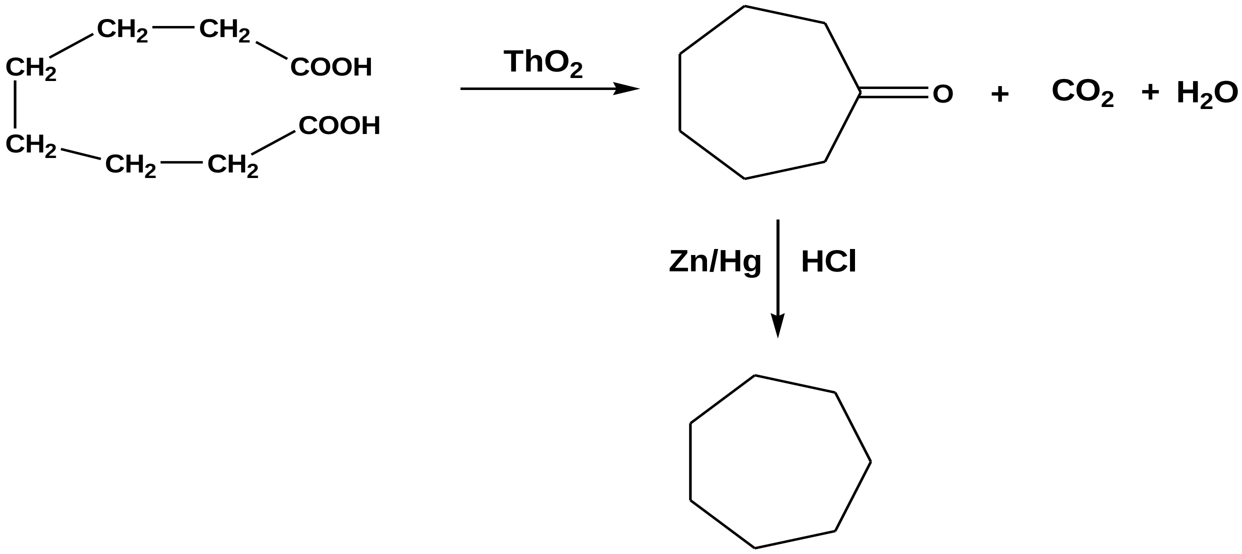
10.2 Chemical properties:

I- Methods of preparation:

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

1. Pyrolysis of dibasic acids:

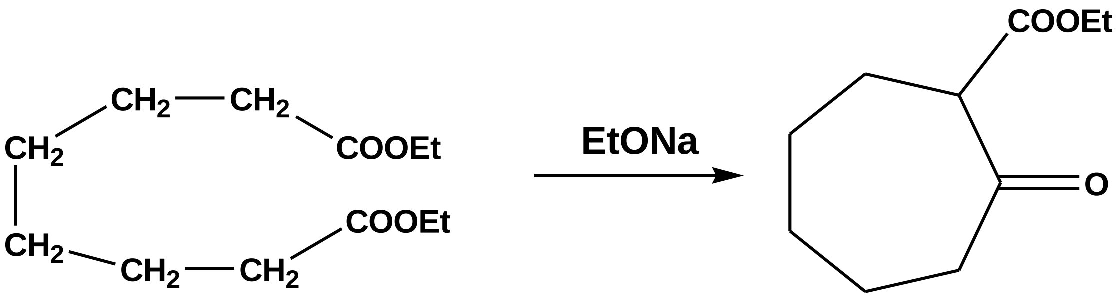
Pyrolysis of suberic acid over **ThO_2** gives cycloheptanone, which turns to cycloheptane by Clemmenson reduction (Equation 10.1).



Equation 10.1

2. Dieckmann condensation:

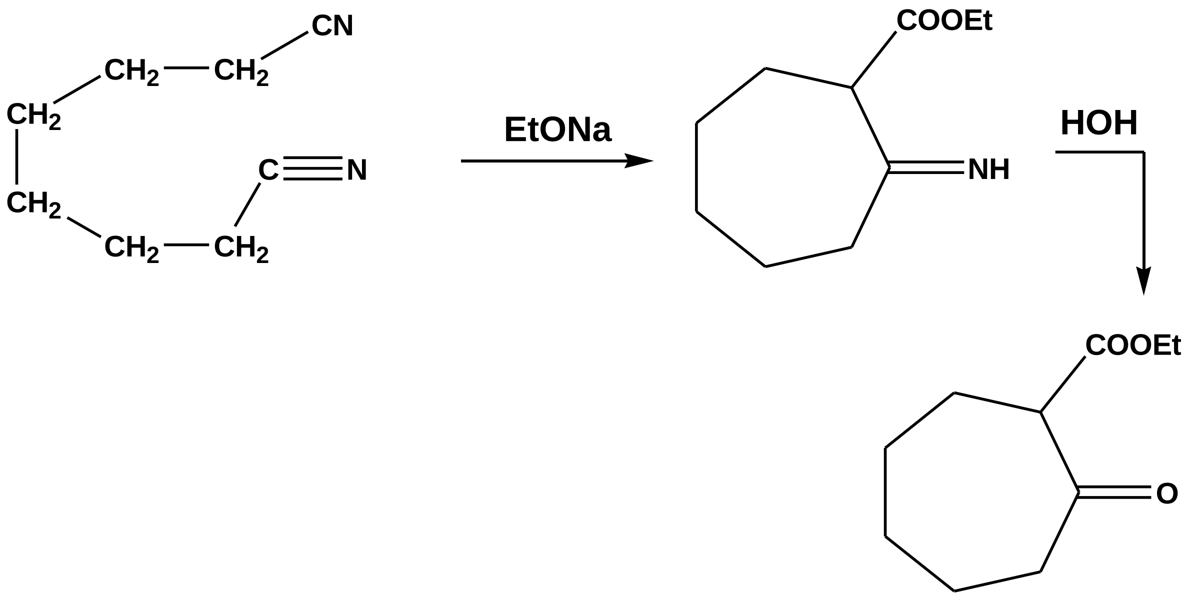
Ester condensation of octanedioic acid diethyl ester in a basic medium (sodium ethoxide) affords 2-cycloheptanonecarboxylic acid ethyl ester (Equation 10.2).



Equation 10.2

3. Thorpe reaction:

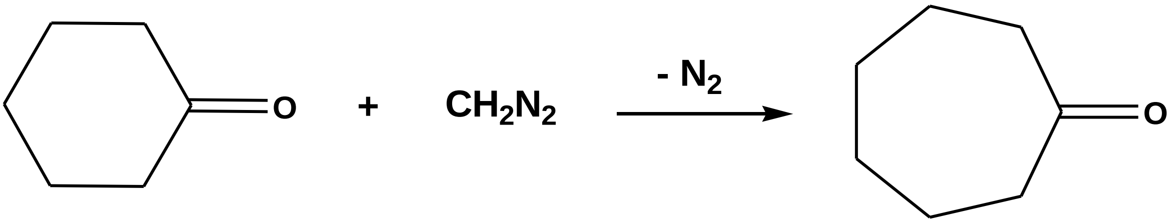
Condensation of octanedinitrile in presence of sodium ethoxide followed by hydrolysis affords 2-cycloheptanonecarbonitrile (Equation 10.3).



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).



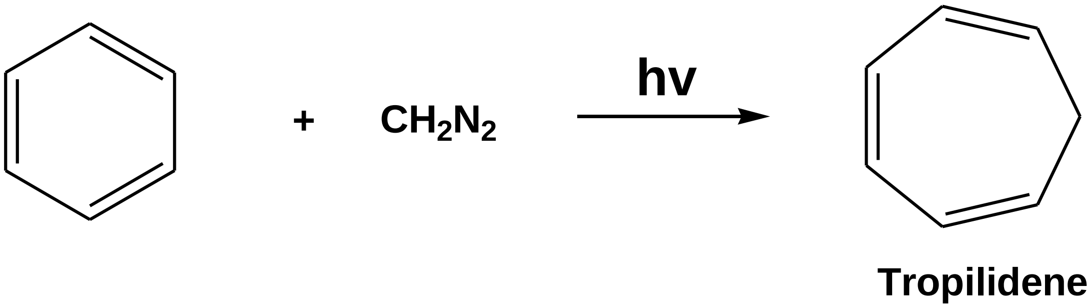
Equation 10.4

5. Synthesis of tropilidene:

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

a- Ring expansion of benzene:

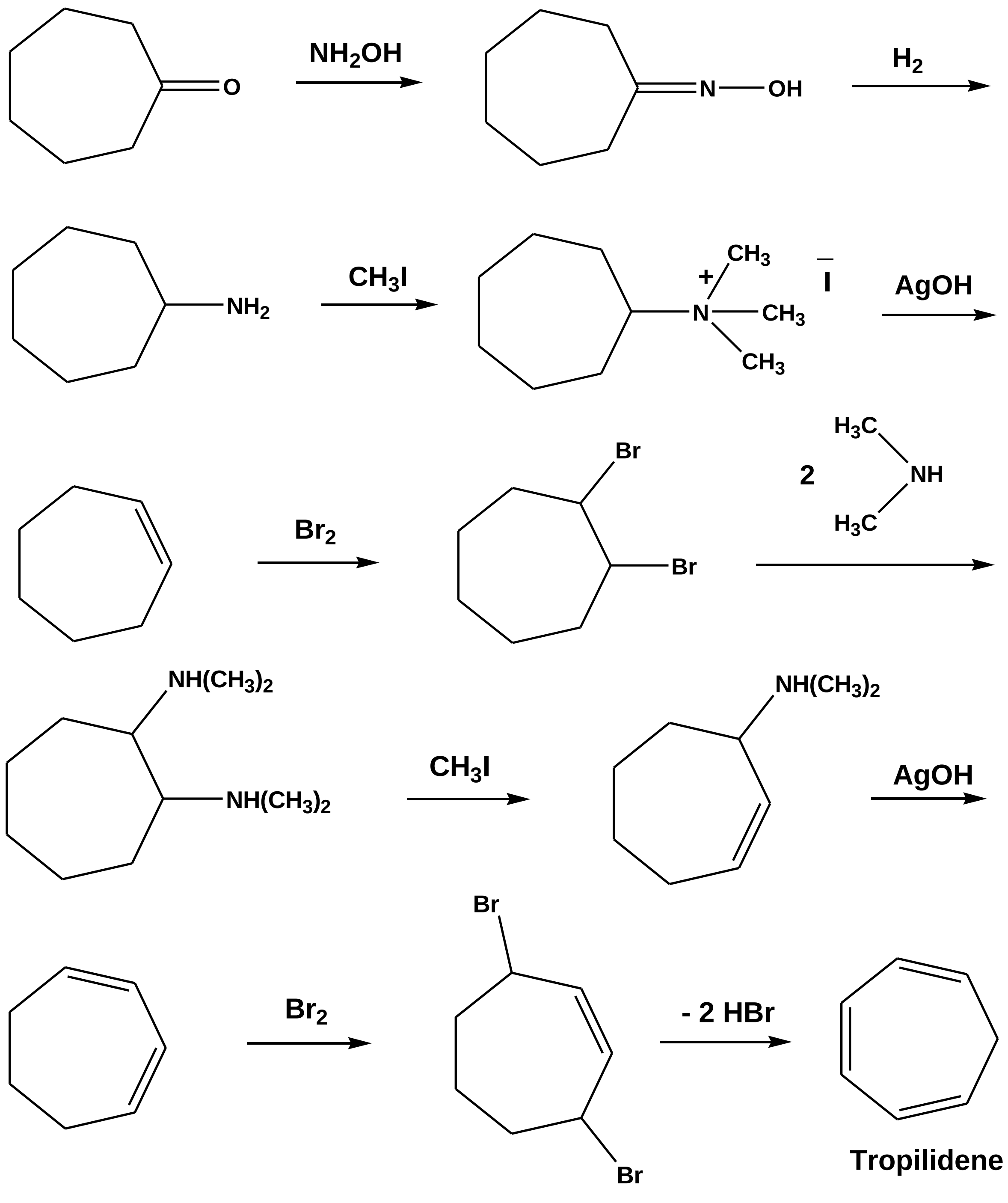
Pyrolysis of diazomethane in presence of benzene undergoes ring expansion to give the tropilidene ring (Equation 10.5).



Equation 10.5

b- From cycloheptanone:

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


O
NH2OH
N
OH
H2
NH2
CH3I
CH3
+
N
CH3
CH3
I
AgOH
Br
Br
Br2
H3C
2
NH
H3C
NH(CH3)2
NH(CH3)2
CH3I
NH(CH3)2
AgOH
Br
Br2
- 2 HBr
Br
Tropilidene

Scheme 10.6

Quizzes:

1. True or False

a- Suberone can be prepared by the action of diazomethane on cyclohexanone.

○ 1) true

○ 2) false

b- Pyrolysis of suberic acid over ThO_2 gives cycloheptanone.

○ 1) true

○ 2) false

c- Condensation of octanedioic acid diethyl ester in a basic medium (sodium affords the cycloheptanone.

○ 1) true

○ 2) false

2- Multiple Choice Questions

a- Pyrolysis of diazomethane in presence of benzene gives:

○ 1) Suberone.

○ 2) Suberic acid.

○ 3) Tropilidene.

○ 4) 1,3-cycloheptadiene.

The Solution;

1- a (true), b (true), c (false).

2- a (3).

Unit 4

Lesson 11: Alicyclic compounds with two or more Rings

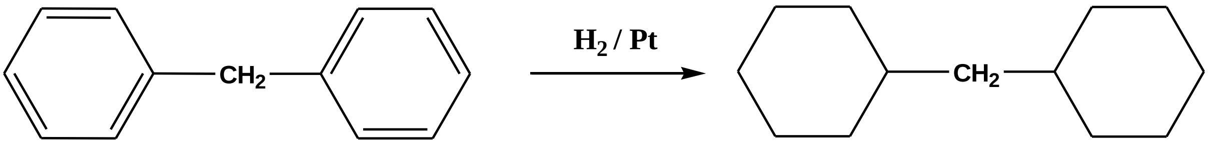
11.1 Bicyclic compounds with isolated rings.

- **Methods of preparation:**

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

1- Hydrogenation:

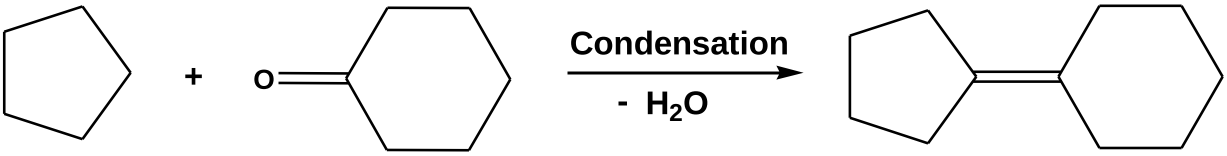
In presence of platinum as a catalyst, hydrogenation of certain aromatic compounds gave the corresponding bicyclic rings (Equation 11.1).



Equation 11.1

2- Condensation of cyclic aldehydes or ketones:

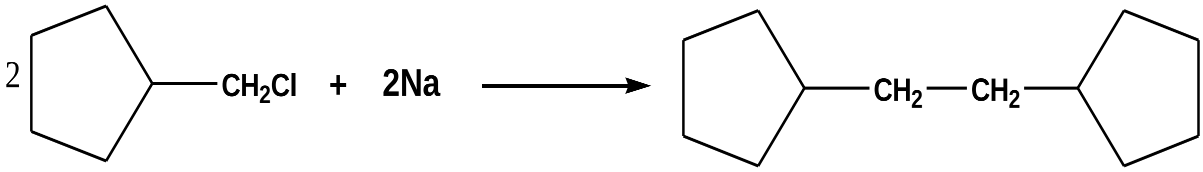
Cyclohexanone and cyclopentane may be condenses to give the cyclopentylidene-cyclohexane (Equation 11.2).



Equation 11.2

3- Wurtz reaction:

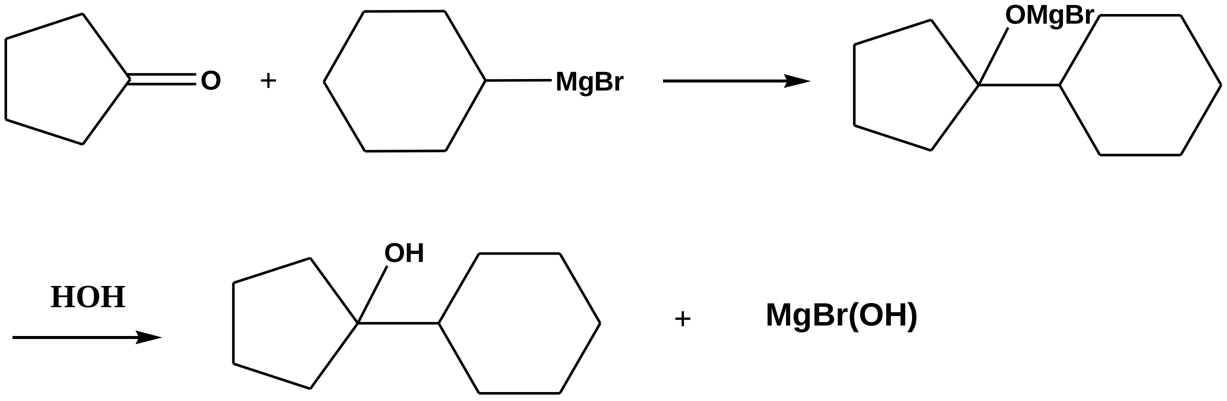
According to Wurtz reaction, the treatment of the chloromethyl-cyclopentane with sodium metal can give 1,2-dicyclopentyl-ethane (Equation 11.3).



Equation 11.3

4- By using organomagnesium compounds:

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

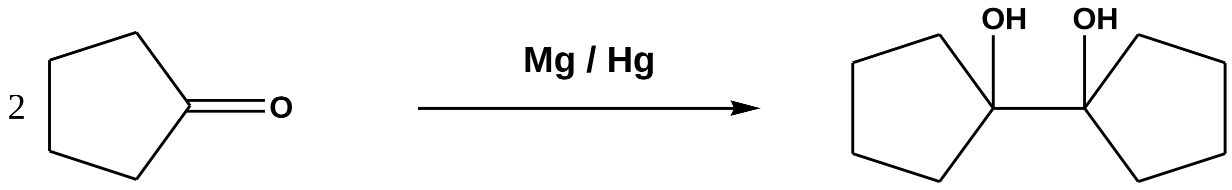


1-cyclohexyl-cyclopentanol

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

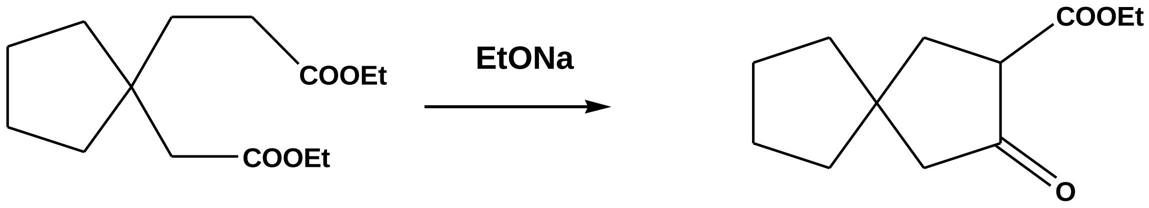
Equation 11.5

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:

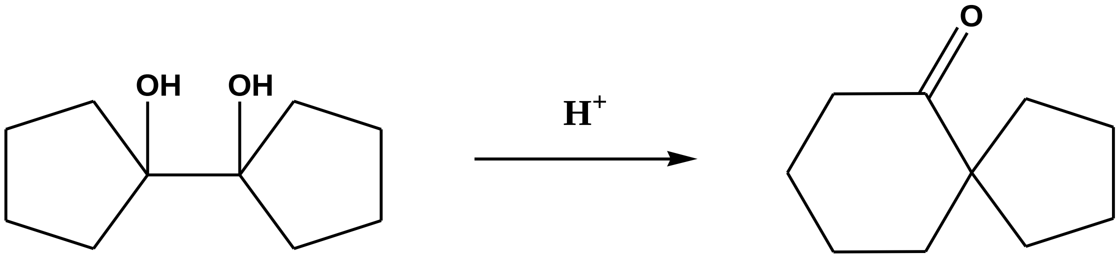
Example 1: (Equation 11.6).



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

Equation 11.6

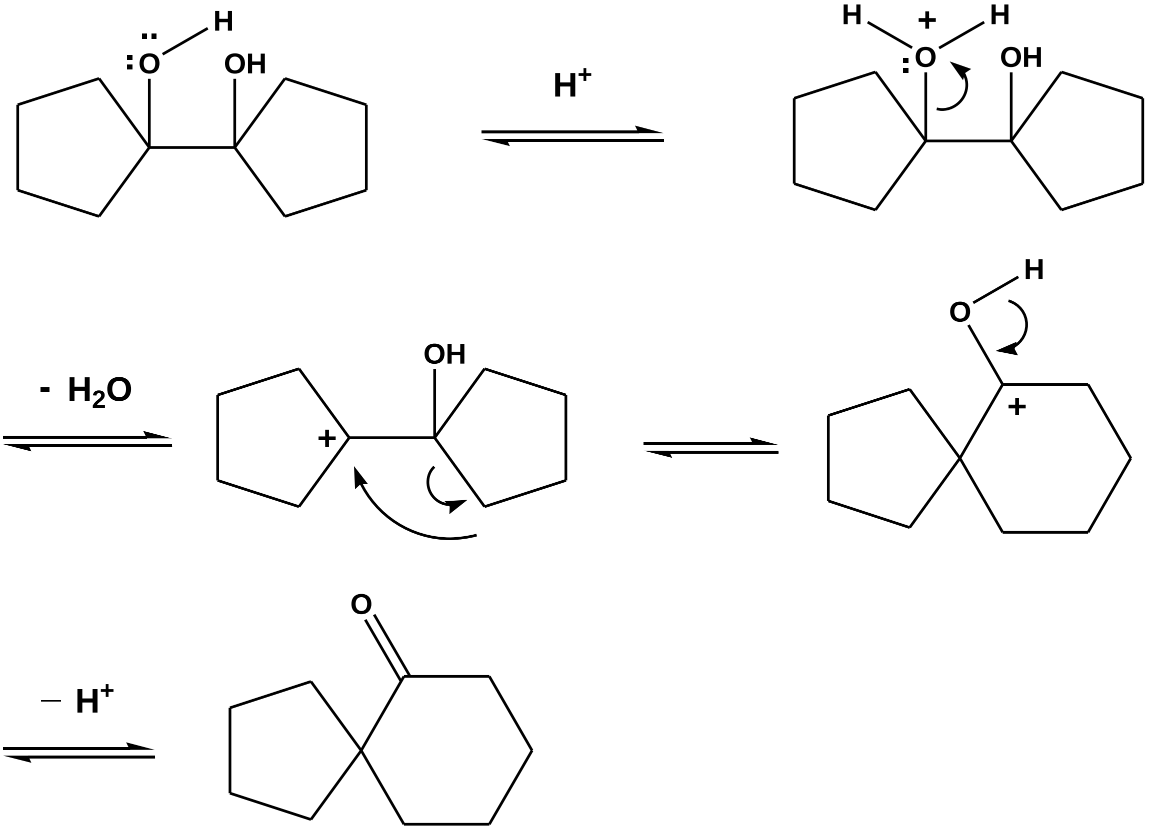
Example 2: Extension of the rings of certain bicyclic compounds (Equation 11.7).



Spiro[4.5]decan-6-one

Equation 11.7

The reaction mechanism;



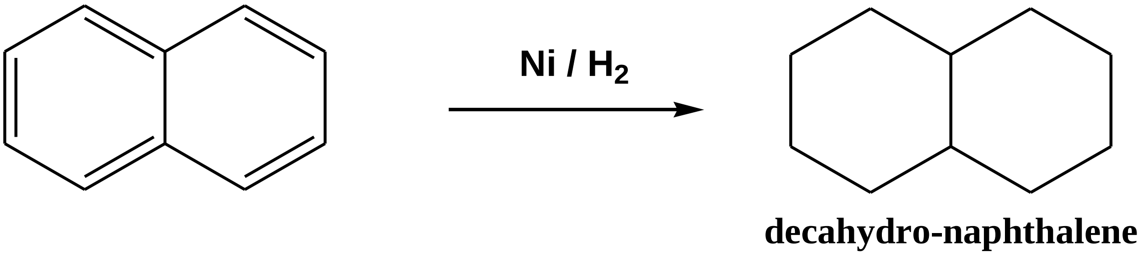
11.3 Alicyclic compounds with fused rings

❖ 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:

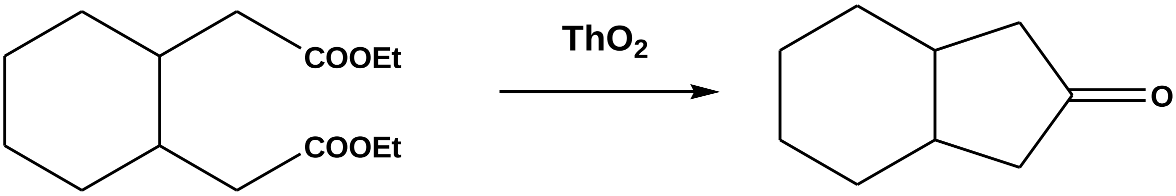
Catalytic hydrogenation of naphthalene, anthracene or phananthrene can give fused rings (Equation 11.8).



Equation 11.8

2- Cyclization of a compound containing one ring:

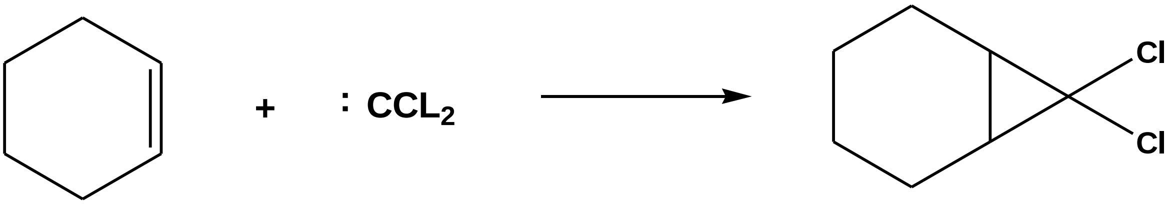
Treatment of 1,2-diethoxycarbonylmethyl-cyclohexane with thorium oxide (**ThO_2**) gives octahydro-inden-2-one (Equation 11.9).



Equation 11.9

3- Addition of carbenes to unsaturated monocyclic compounds:

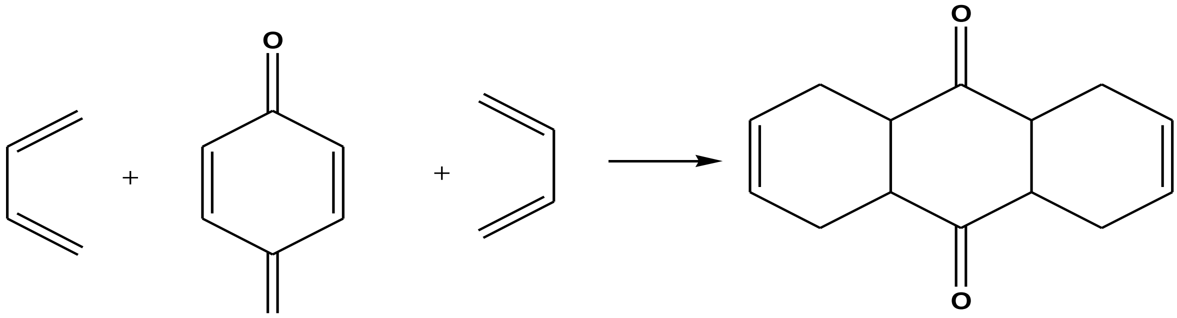
Cyclohexene reacts with carbenes to give bicyclo[4.1.0]heptane (Equation 11.10).



Equation 11.10

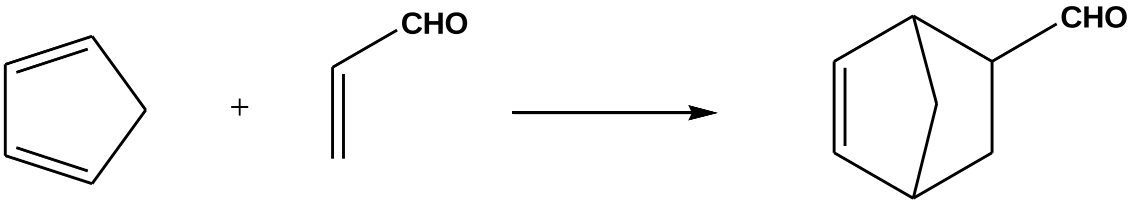
4- Diels-Alder reaction:

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



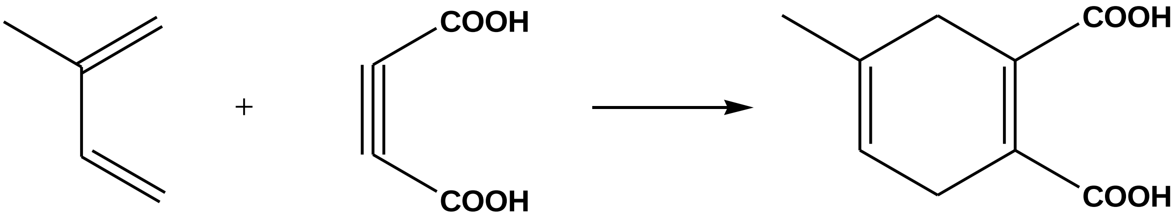
1,4,4a,5,8,8a,9a,10a-octahydroanthraquinone

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

Quizzes:

1. True or False

a- Hydrogenation of naphthalene gives bicyclo[4.4.0]decane.

○ 1)true

○ 2) false

b- Spirans are bicyclic structures in which two rings systems share two carbon atoms.

○ 1)true

○ 2) false

c- Cyclohexene reacts with carbenes to give bicyclo[4.2.0]heptane.

○ 1)true

○ 2) false

2- Multiple Choice Questions

a- Bicyclopentayl-1,1-diol can rearrangements to give:

○ 1) Spiro[4.4]nonane-3-one.

○ 2) Spiro[4.5]decane-6-one.

○ 3) 1-cyclohexyl-cyclopentanol.

○ 4) Octahydro-inden-2-one.

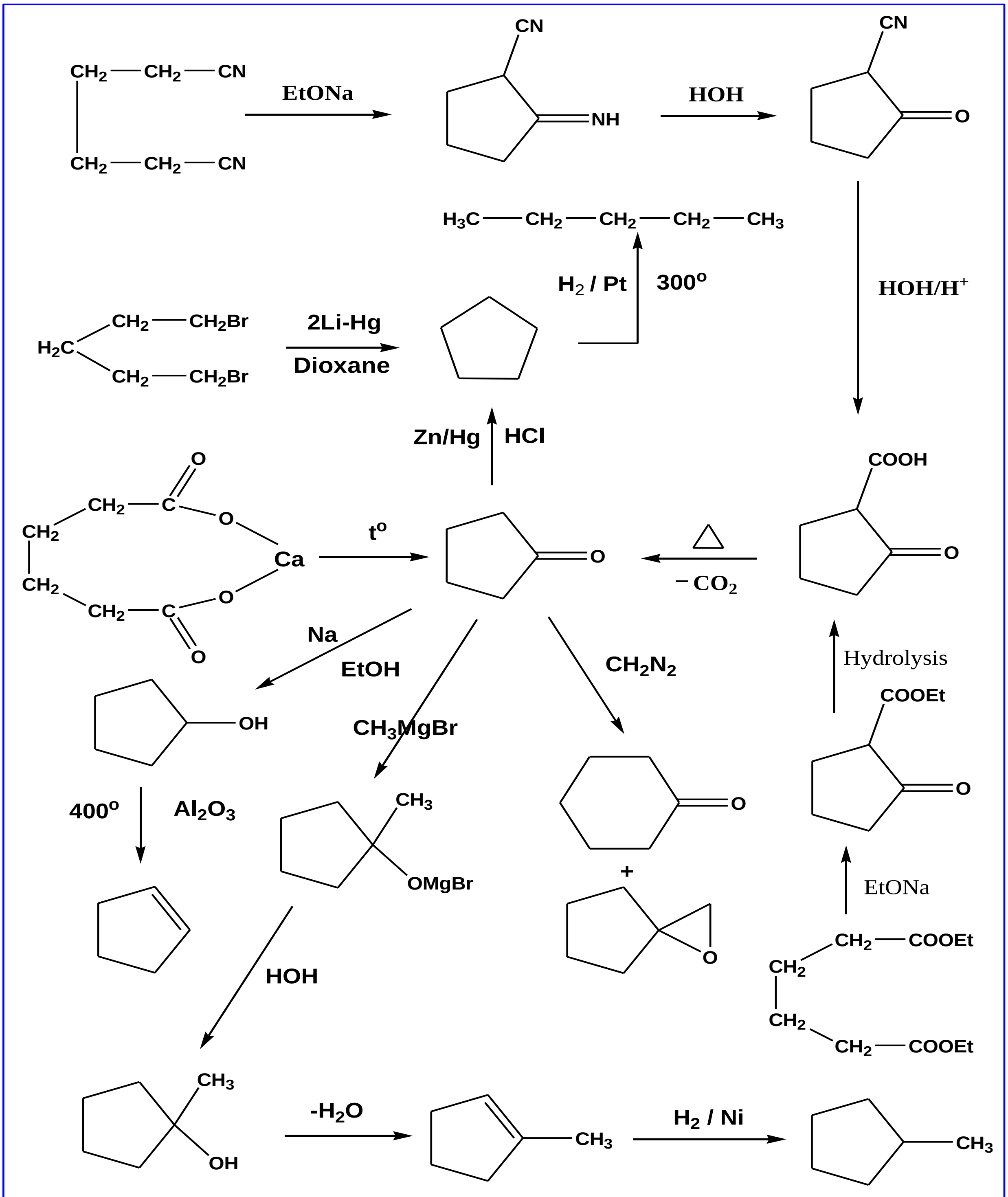
The solution;

1- a (true), b (false), c (false).

2- a (2).

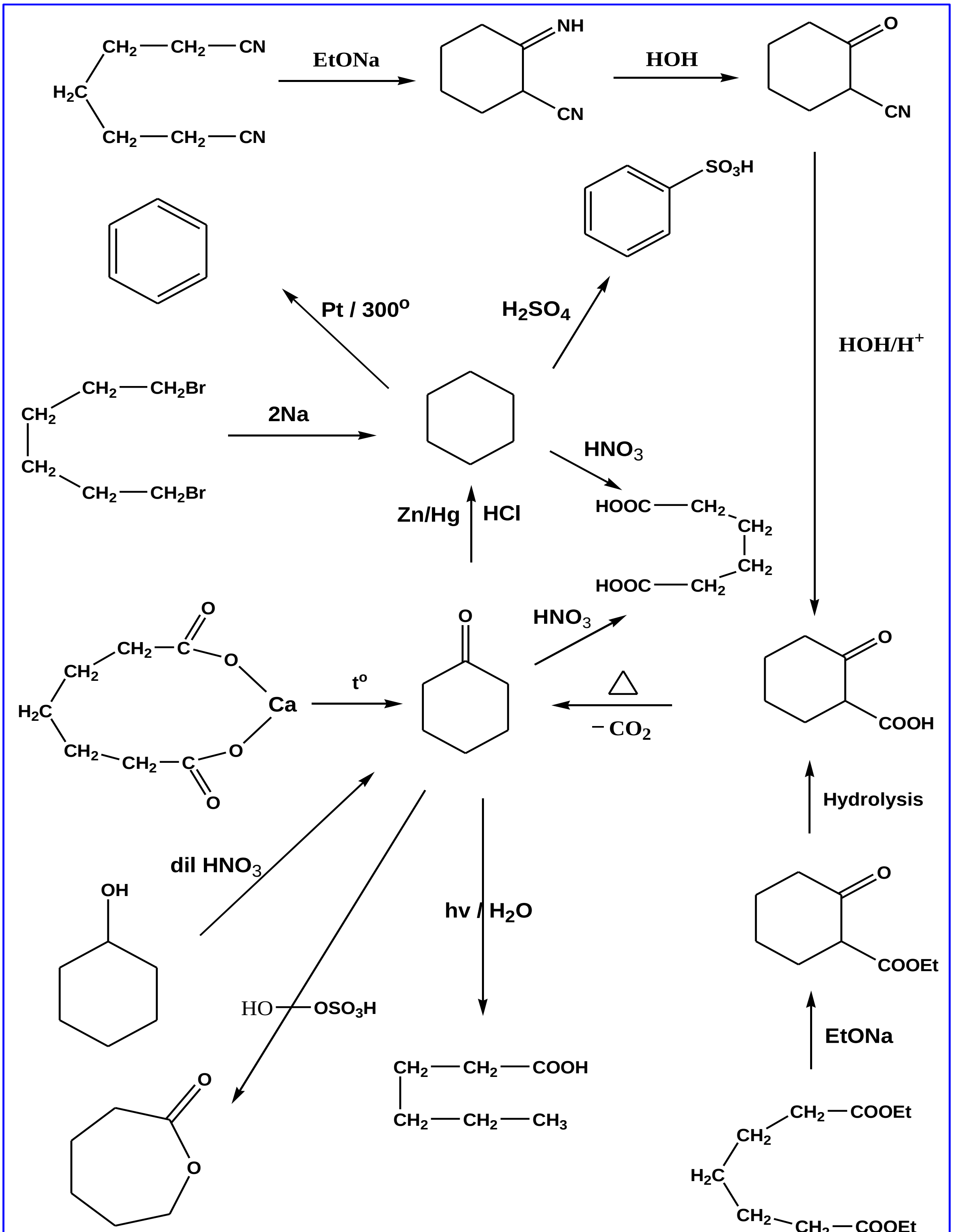
The Summary of Unit 4

The preparation and reactions of cyclopentane can be summarized in the scheme 3:



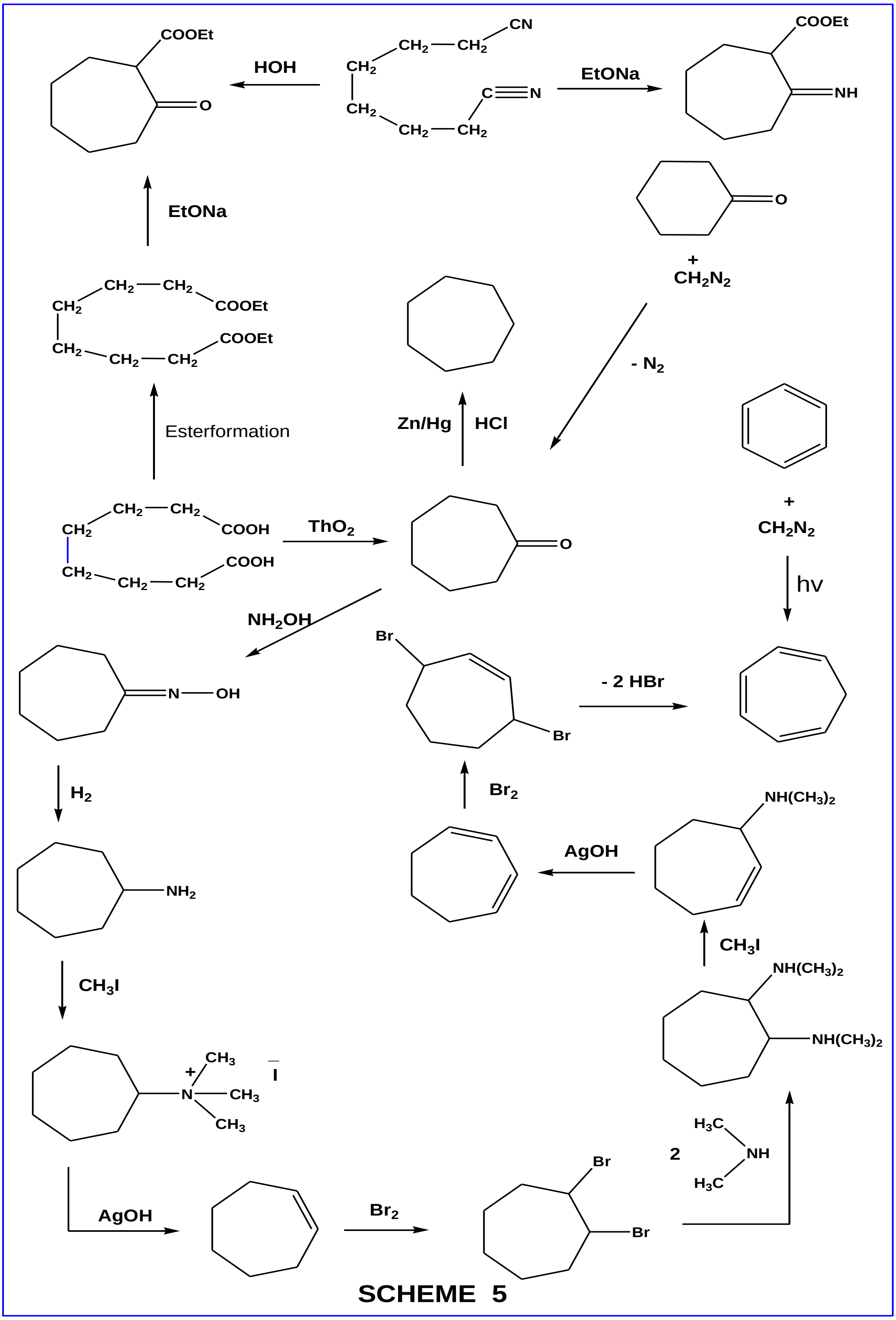
SCHEME 3

The preparation and reactions of cyclohexane can be summarized in the scheme 4:



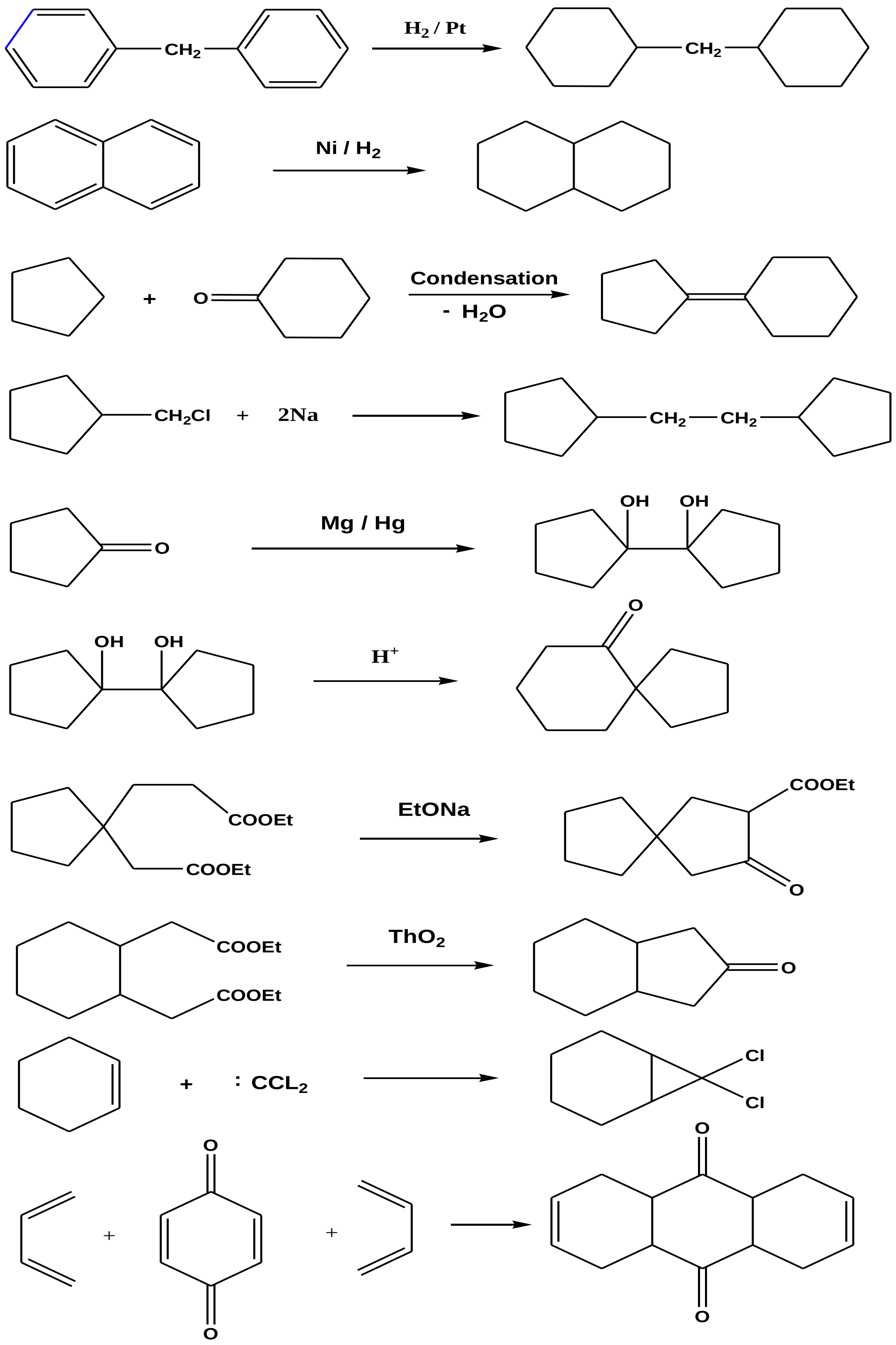
SCHEME 4

The methods used for the preparation of cycloheptane can be summarized in the scheme 5:



SCHEME 5

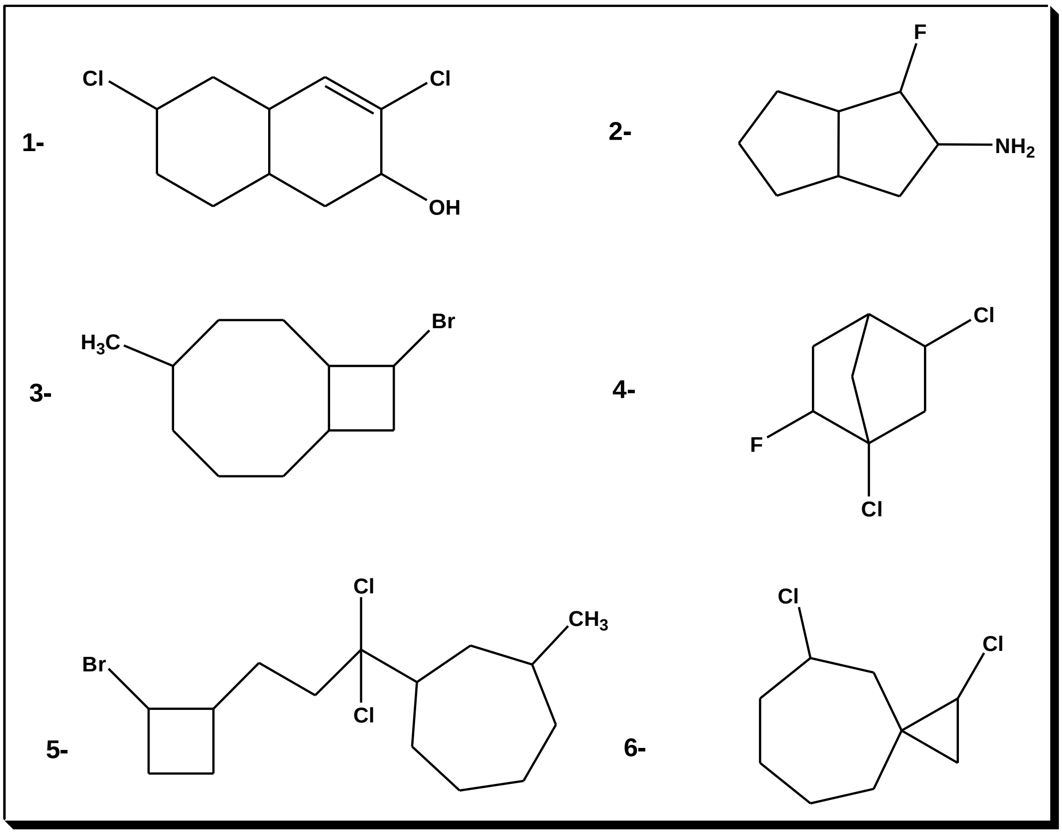
The methods used for the preparation of bicyclic compounds can be summarized in the scheme 6:



SCHEME 6

General problems

Q1. Name each of the following compounds:



Q2. Write shortly on the different types of aliphatic bicyclic compounds.

Q3. Discuss the "Baeyer's strain theory".

Q4. Write briefly on classification of monocyclic system (Give examples).

Q5. Write briefly on:

(i) Reduction of diketones.

(ii) The endo- and the exo-compound in the cycloaddition reactions.

Q6. Write briefly on:

a- Banana-bond of cyclopropane.

b- The stability of the chair-form of cyclohexane.

Q7. Draw the puckered conformations of cyclopropane, cyclobutane, cyclopentane and cyclohexane.

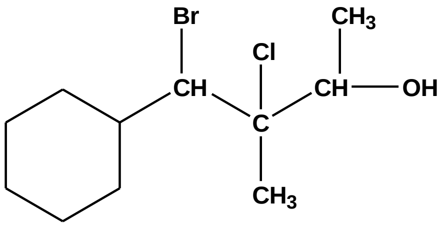
Q8. Write briefly on:

(i) Methods used for the reduction of the cyclic ketones.

(ii) Pyrolysis of the salts of dibasic acid.

Q9. Choose the correct names for the following compounds:

1-

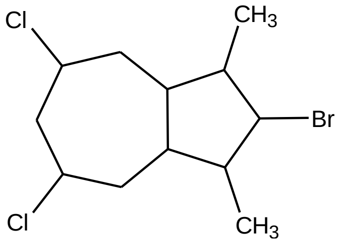


a- 1-bromo-2-chloro-1-cyclohexyl-2-methyl-3-butanol.

b- 4- bromo-3-chloro-4-cyclohexyl-3-methyl-2-butanol.

c- 3- bromo-2-chloro-3-cyclohexyl-1,2-dimethyl-1-propanol

2-

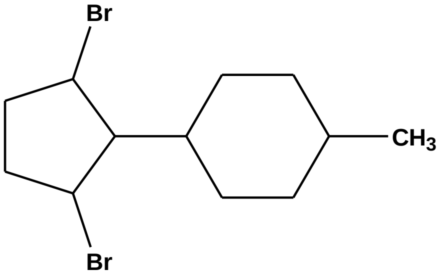


a- 3-bromo-7,9- dichloro-2,4-dimethyl-bicyclo[3.5.0]decane.

b- 3-bromo-7,9- dichloro-2,4-dimethyl-bicyclo[5.3.0]decane.

c- 9-bromo-3,5- dichloro-8,10-dimethyl-bicyclo[5.3.0]decane

3-



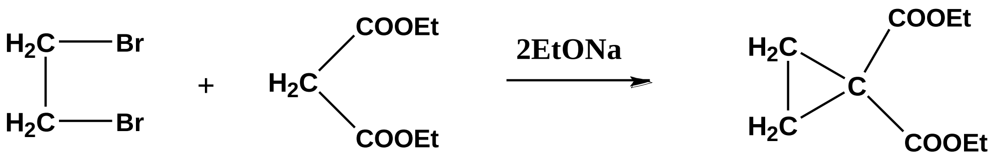
a- 1-(2',5'-dibromo-cyclopentyl)-4-methyl-cyclohexane.

b- 1-(4'-methyl-cyclohexyl)-2,5-dibromo-cyclopentane.

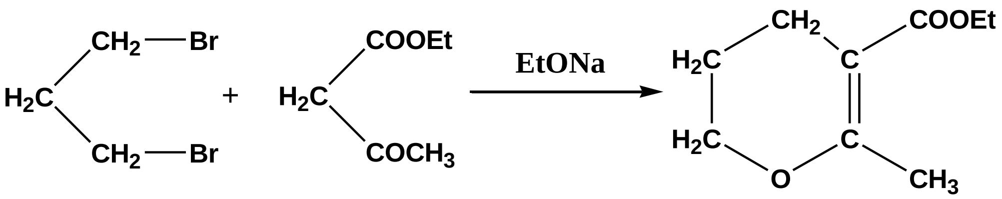
c- 4-(2',5'-dibromo-cyclopentyl)-1-methyl-cyclohexane.

Q9. Write the mechanism of each of the following reactions:

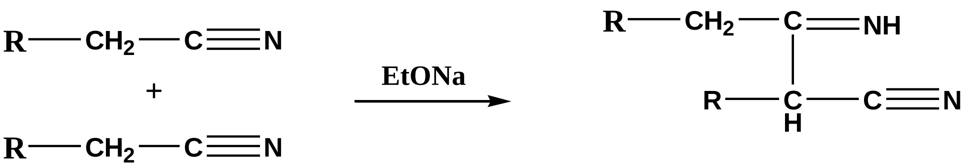
1.



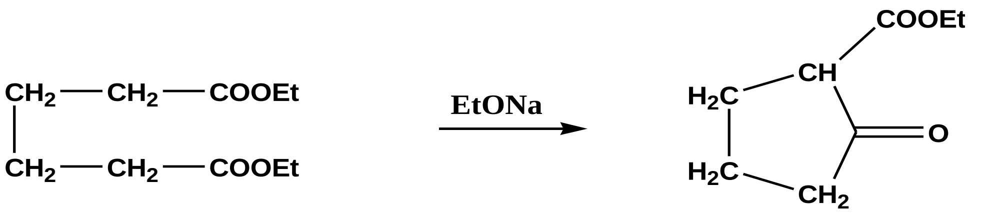
2.



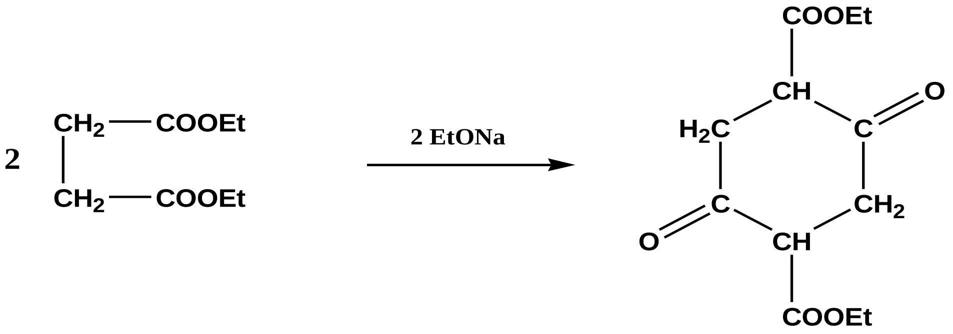
3.



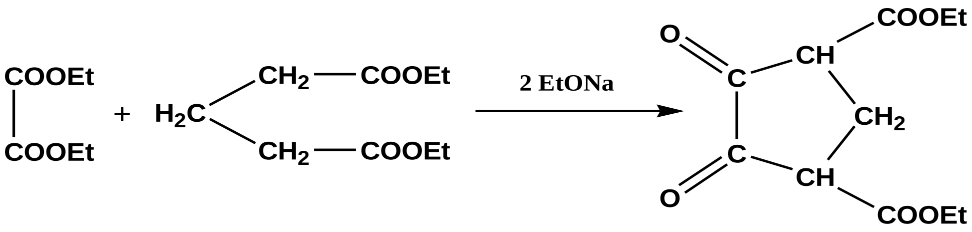
4.


CH2 CH2 COOEt
CH2 CH2 COOEt
EtONa
COOEt
CH
H2C
O
H2C
CH2

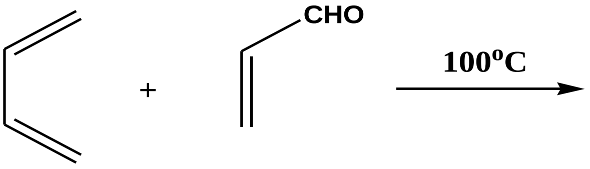
5.


2
CH2 COOEt
CH2 COOEt
2 EtONa
COOEt
CH
O
H2C
C
C
CH2
O
CH
COOEt

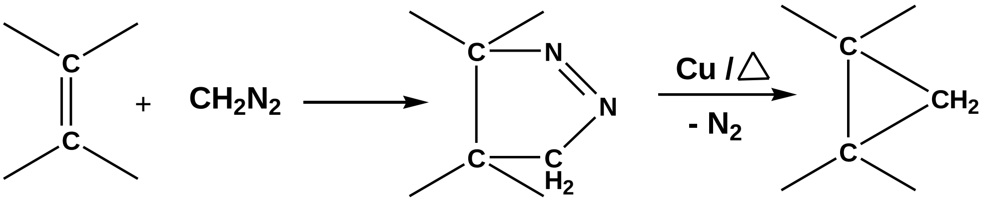
6.


COOEt
COOEt
+
H2C
CH2 COOEt
CH2 COOEt
2 EtONa
O
C
CH
COOEt
CH2
C
CH
O
COOEt

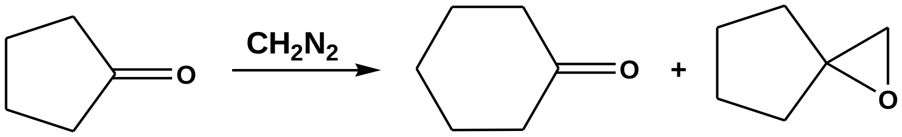
7.


+
CHO
100°C
CHO

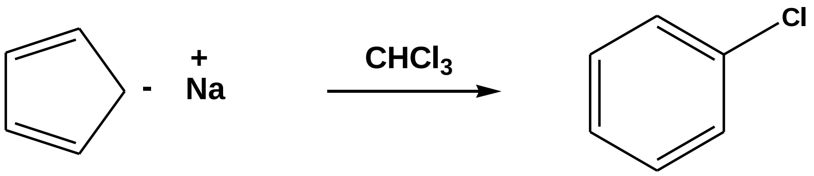
8.


C
C
+
CH2N2
C
N
N
C
C
H2
Cu /△
- N2
C
CH2
C

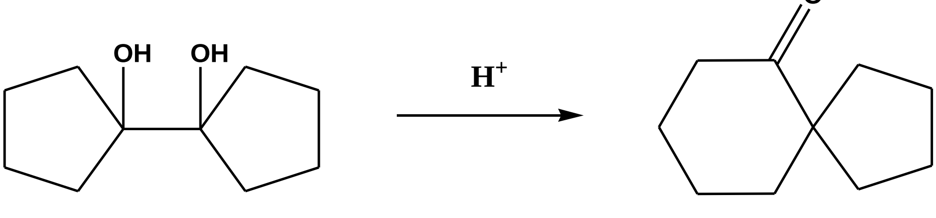
9.


O
CH2N2
O
+
O

10.


-
+
Na
CHCl3
Cl

11.


OH
OH
H+
O

Q10. True or False:

a- The diastereoisomers: Stereoisomers which are mirror images.

○ a) true

○ b) false

b- Molecules with **n** different chiral centers exist in $\mathbf{2^n}$ enantiomeric forms.

○ a) true

○ b) false

c- Optical Activity is the ability of some compounds to rotate plane of light.

○ a) true

○ b) false

d- On treatment of ethylacetoacetate with appropriate alkyldihalide; seven-membered rings can not obtained.

○ a) true

○ b) false

e- By the Clemmensen reduction, the cyclohexanone can be converting to cyclohexane.

○ a) true

○ b) false

f- Addition reactions of carbenes to alkenes lead to the formation of the cyclopropanes

○ a) true

○ b) false

g- Cyclopropane is easy to handle and manufacture.

○ a) true

○ b) false

h- The cyclopentane is a liquid with mp. - 49.5 °C.

○ a) true

○ b) false

i- In absence of hydrogen, cyclohexane can be dehydrogenated to benzene over platinum at 300°C.

○ a) true

○ b) false

The solution;

Q10. a (false), b (true), c (false), d (false), e (true), f (true), g (false), h (false), i (true).

Q11. Multiple Choice Questions:

1- The boat-form of cyclohexane has ……………. bonds in four of its carbon atoms.

○ a) staggered

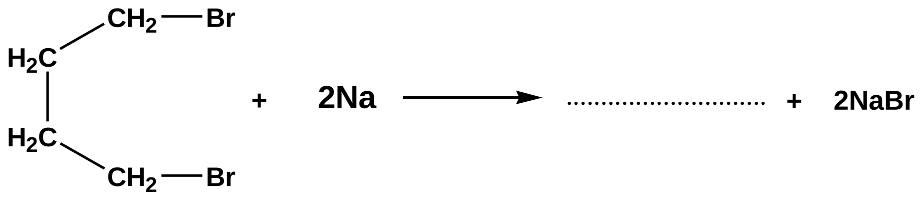
○ b) eclipsed

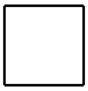
2- The planar conformation of cyclohexane …………….. by torsional strain

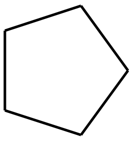
○ a) destabilized

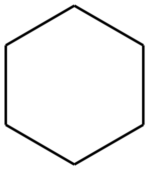
○ b) stabilized

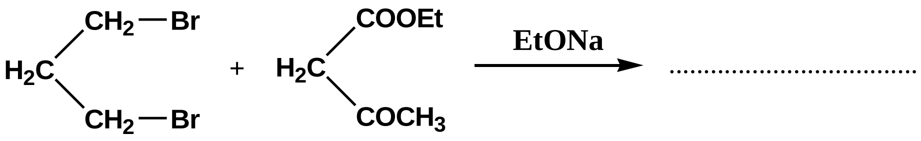
3- Choose the correct product for each equation:

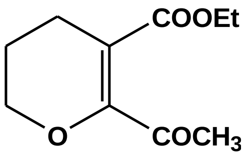


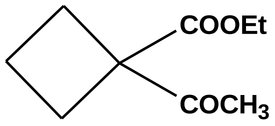
○ a- 

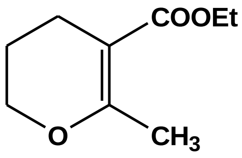
○ b- 

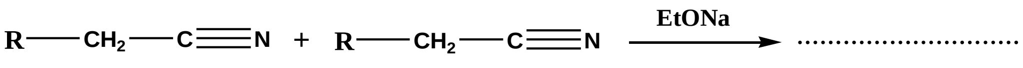
○ c- 

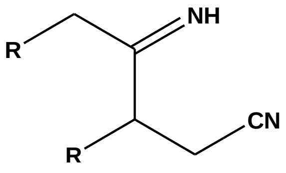


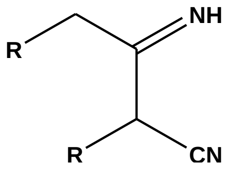
○ a- 

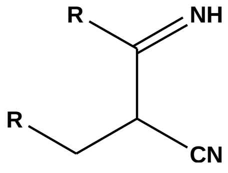
○ b- 

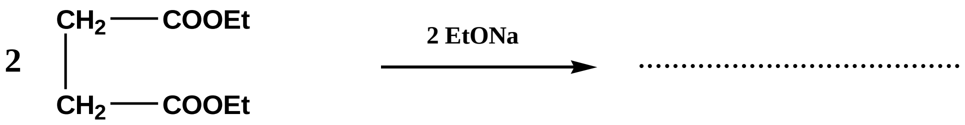
○ c- 

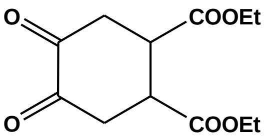


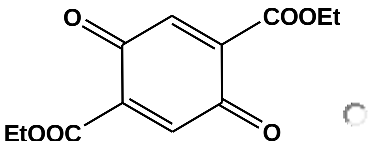
○ a- 

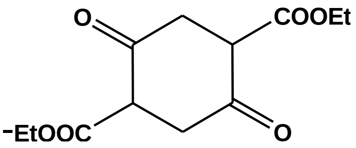
○ b- 

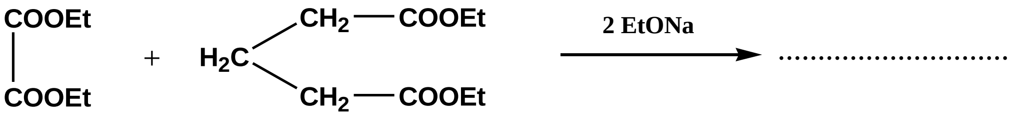
○ c- 

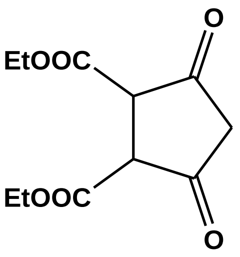

2
CH2
COOEt
CH2
COOEt
2 EtONa
....

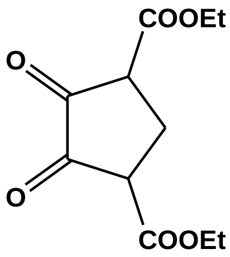
○ a- 
O
O
COOEt
COOEt

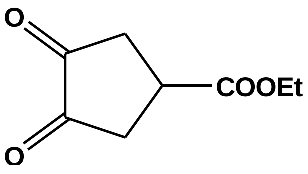
○ b- 
O
COOEt
EtOOC
O

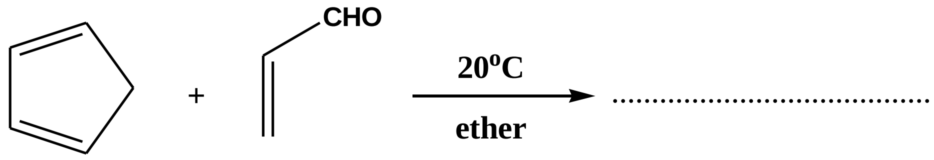
○ C- 
O
COOEt
EtOOC
O

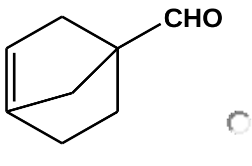

COOEt
COOEt
+
H2C
CH2
COOEt
CH2
COOEt
2 EtONa
....

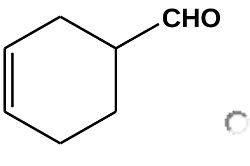
○ a- 
O
EtOOC
EtOOC
O

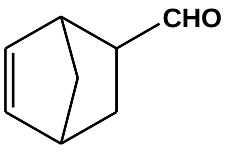
○ b- 
COOEt
O
O
COOEt

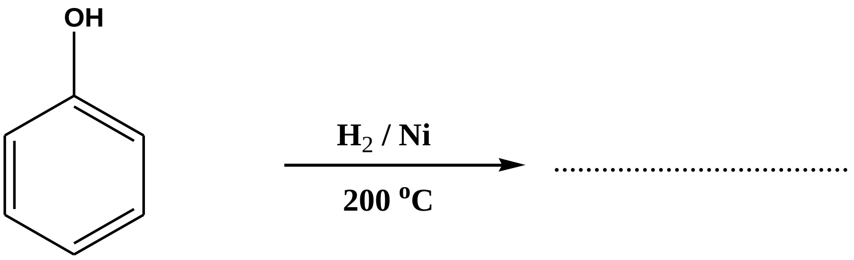
○ c- 
O
COOEt
O

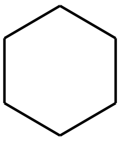

+
CHO
20°C
ether
....

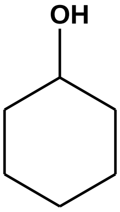
○ a- 
CHO

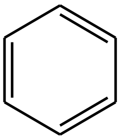
○ b- 
CHO

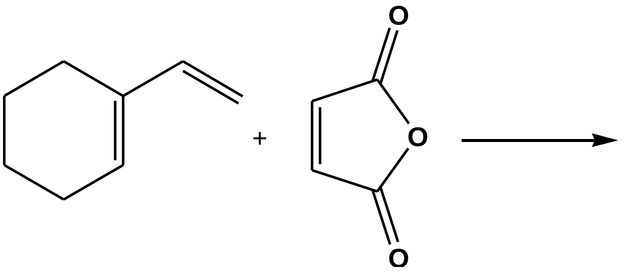
○ c- 
CHO


OH
H2 / Ni
200 °C
....

○ a- 

○ b- 

○ c- 



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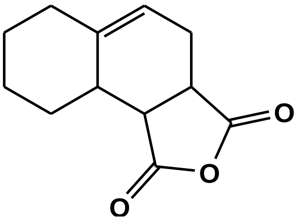
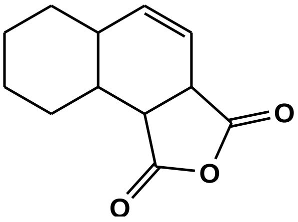
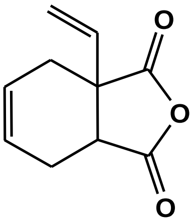
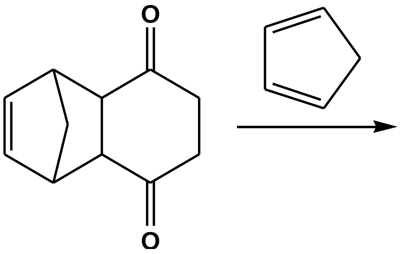
○ a- 

○ b- 

○ c- 



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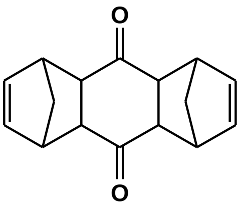
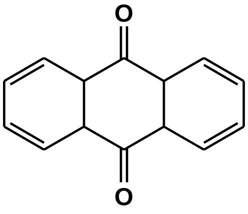
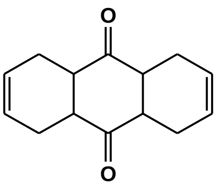
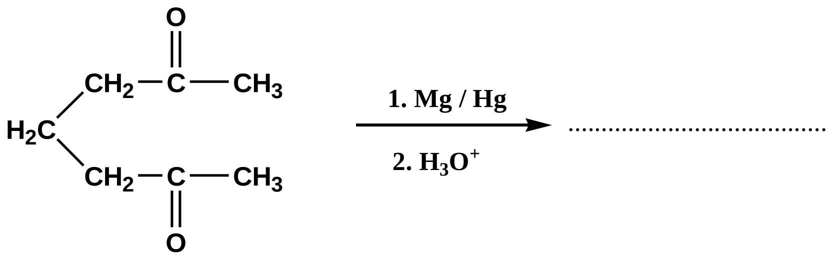
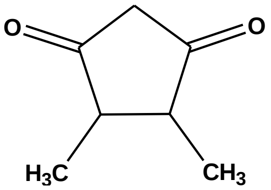
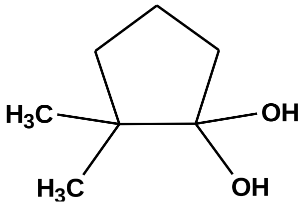
○ a- 

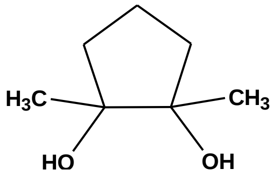
○ b- 

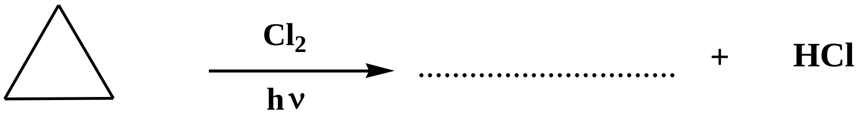
○ c- 

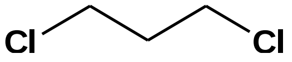


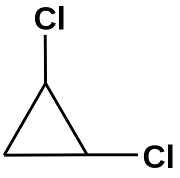
○ a- 

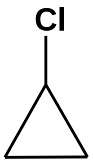
○ b- 

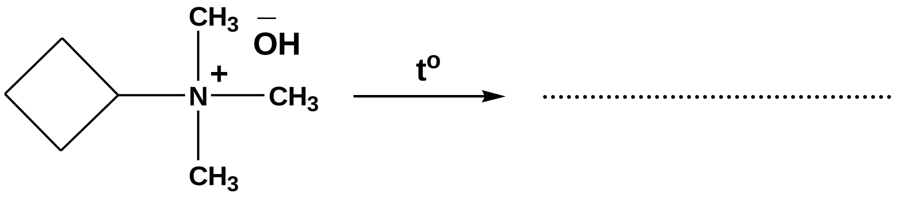
○ c- 

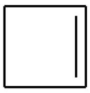


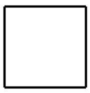
○ a- 

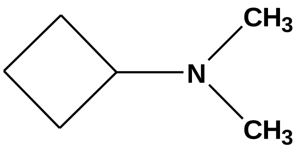
○ b- 

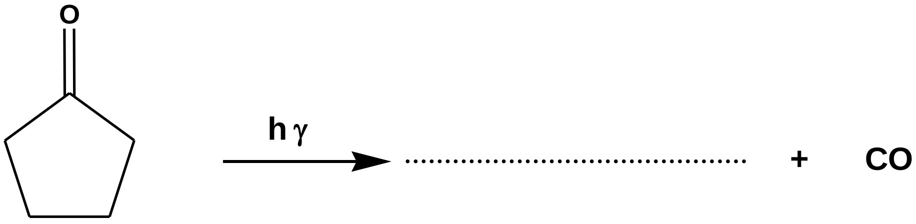
○ c- 

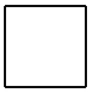


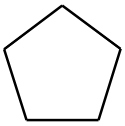
○ a- 

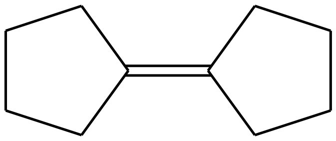
○ b- 

○ c- 

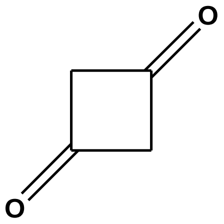


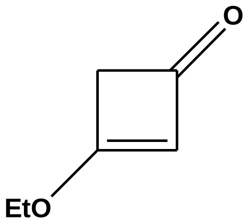
○ a- 

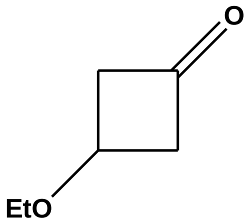
○ b- 

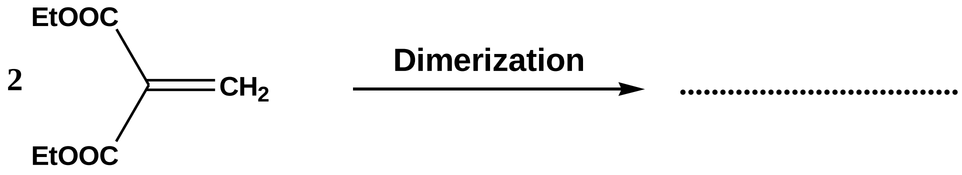
○ c- 

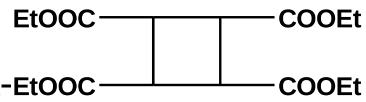
$$H_2C{=}C{=}O \;+\; EtO{-}C{\equiv}CH \xrightarrow{\text{Condensation}} \dots\dots\dots\dots\dots\dots$$

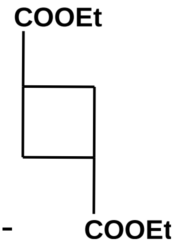
○ a- 

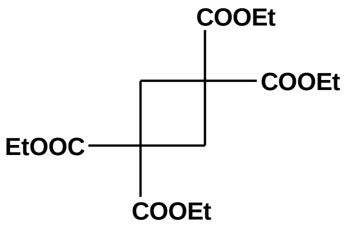
○ b- 

○ c- 

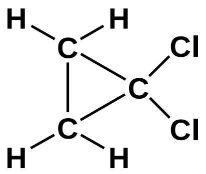


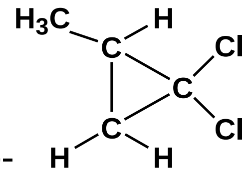
○ a- 

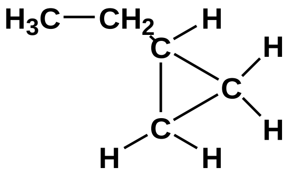
○ b- 

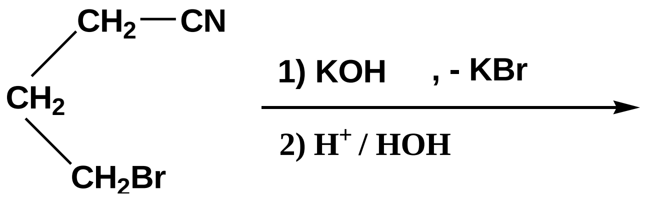
○ c- 

$$CH_3{-}CH_2{-}CH{=}CH_2 \;+\; :CCl_2 \longrightarrow \dots\dots\dots\dots\dots\dots$$

○ a- 

○ b- 

○ c- 



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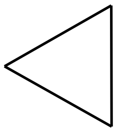
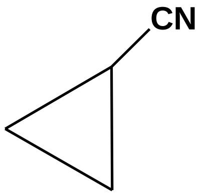
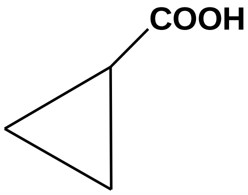
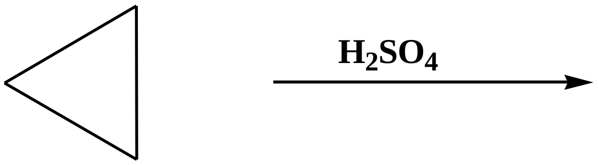
○ a- 

○ b- 

○ c- 



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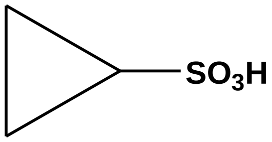
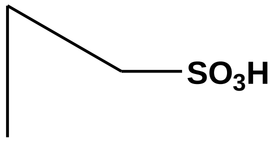
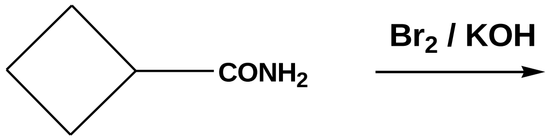
○ a- 

○ b- 

○ c- 



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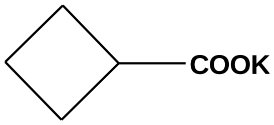
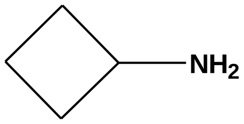
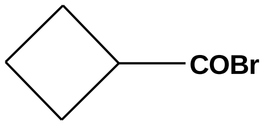
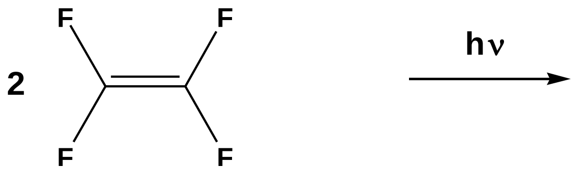
○ a- 

○ b- 

○ c- 



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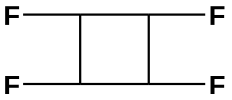
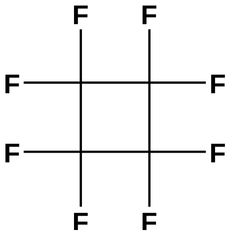
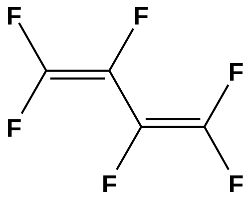
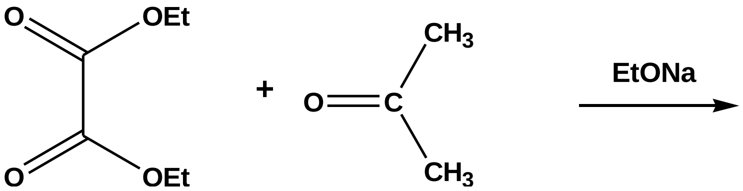
○ a- 

○ b- 

○ c- 



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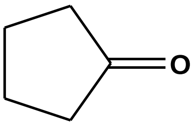
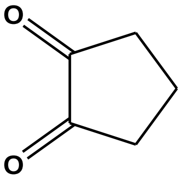
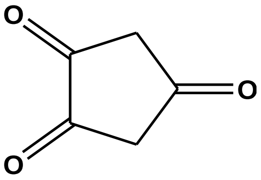
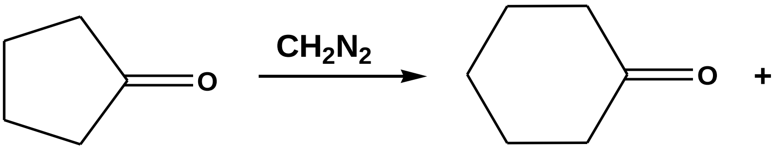
○ a- 

○ b- 

○ c- 



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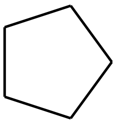
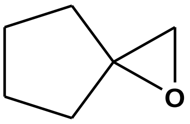
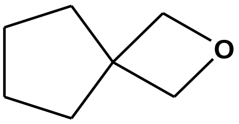
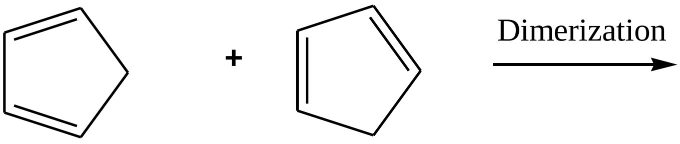
○ a- 

○ b- 

○ c- 



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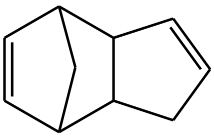
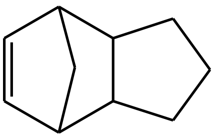
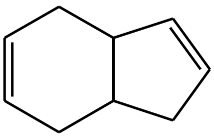
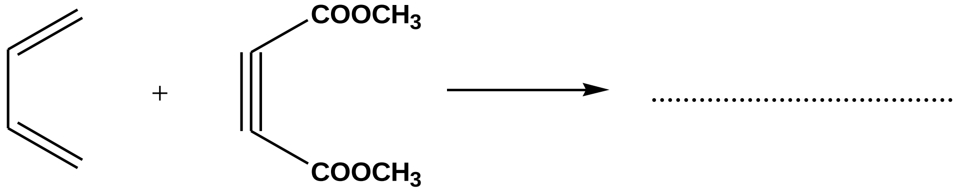
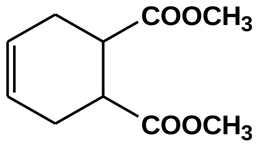
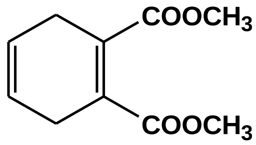
○ a- 

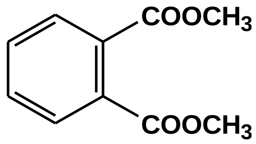
○ b- 

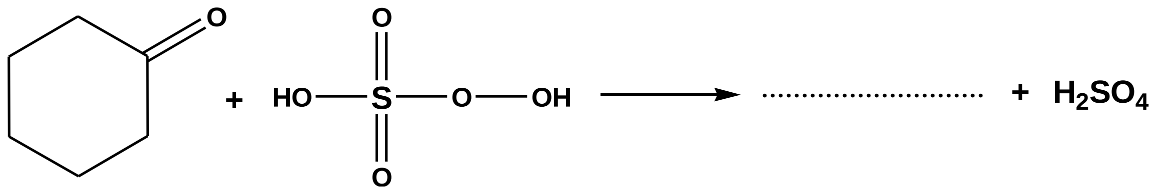
○ c- 

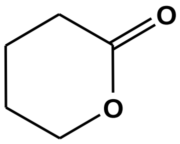

+
COOCH3
COOCH3
....

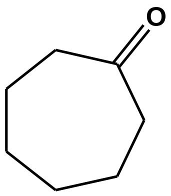
○ a- 
COOCH3
COOCH3

○ b- 
COOCH3
COOCH3

○ c- 
COOCH3
COOCH3


O
+
HO
S
O
OH
O
O
....
+ H2SO4

○ a- 
O
O

○ b- 
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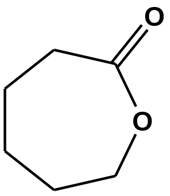
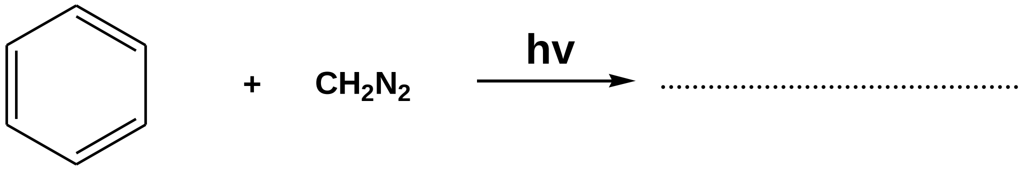
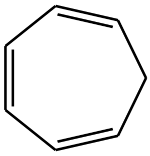
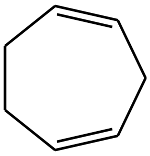
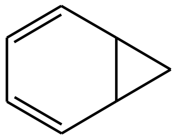
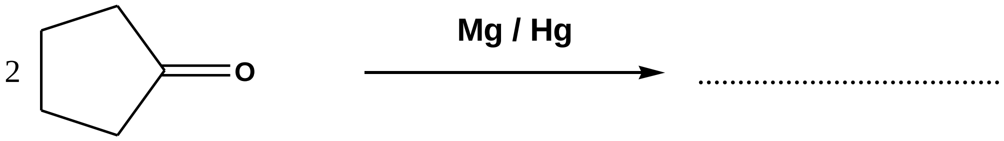
○ c- 
O
O

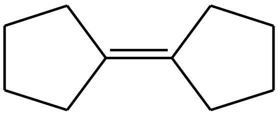

+
CH2N2
hv
....

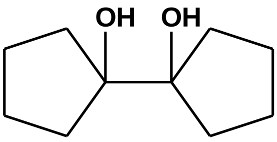
○ a- 

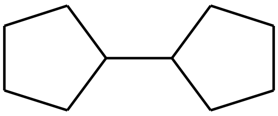
○ b- 

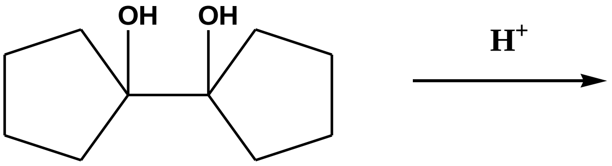
○ c- 


2
O
Mg / Hg
....

○ a- 

○ b- 

○ c- 



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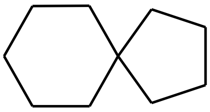
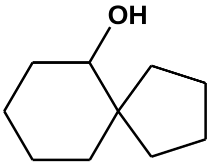
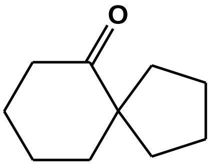
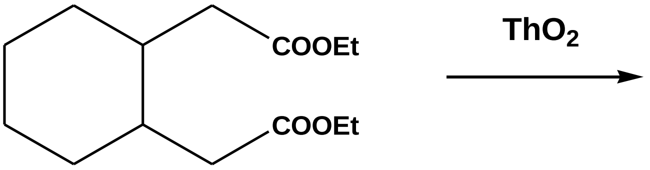
○ a- 

○ b- 

○ c- 



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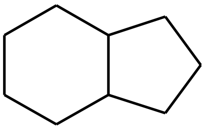
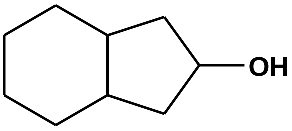
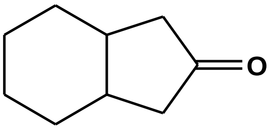
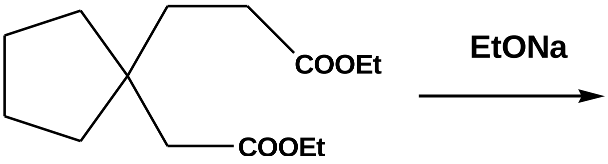
○ a- 

○ b- 

○ c- 



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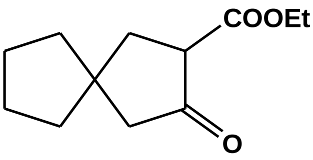
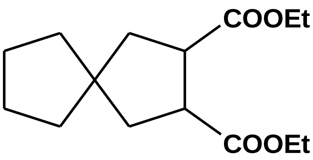
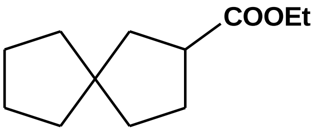
○ a- 

○ b- 

○ c- 

The Solution;

Q11. Multiple Choice Questions

1-b(eclipsed), 2- a (destabilized).

3-Respectively: (a), (c), (b), (c), (b), (c), (b), (a), (a), (c), (c), (a), (a), (b), (c), (c), (c), (b), (b), (b). (c), (b), (a), (b), (c), (a), (b), (c), (c), (a).

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- *Cyclopropylaetylene* Edward G. Corley, Andrew S. Thompson, Martha Huntington Organic Syntheses, Coll. Vol. 10, p.456, 2004; Vol. 77, p.231, 2000. www.orgsynth.org/orgsyn/prep/asp?prep=v77p0231
- Bicyclo[1.1.0]butane Gary M. Lampman and James C. Aumiller Organic Syntheses, Coll. Vol. 6, p.133, 1988; Vol. 51, p.55 (1971) www.orgsynth.org/orgsyn/prep/asp?prep=cv6p0133

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- IUPAC Gold book definition www.answer.com/topic/compendium-of-chemical-terminology
- *Palladium-Catalyzed Ring Enlargement of Aryl-Substituted Methylenecyclopropanes to Cyclobutenes* Min Shi, Le-Ping Liu, and Jie Tang *J. Am. Chem. Soc.*; 2006; 128(23) p. 7430 - 7431; doi:10.1021/ja061749y.
- Cyclohexane@3Dchem ; www.3dchem.com/molecules.asp?ID=176

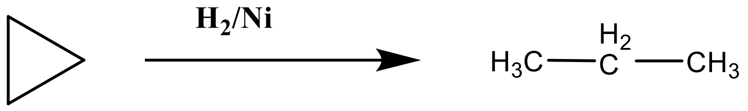
Hyperlinks

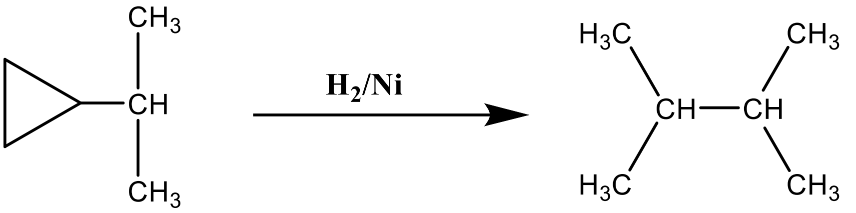
- http://www.answers.com/topic/cycloalkane
- http://www.chem.qmul.ac.uk/iupac/hetero/De.html
- http://people.ok.ubc.ca/wsmcneil/121/conformers.htm
- http://www.usm.maine.edu/~newton/Chy251_253/Lectures/MolecularMotions/MolecularMotions2.html
- http://www.britannica.com/eb/art-84/The-staggered-conformation-of-ethane
- http://people.ok.ubc.ca/wsmcneil/121/conformers.html
- http://www.sparknotes.com/chemistry/organic2/conformations/section1.html
- http://stezlab1.unl.edu/Chem251-2005/PowerPoint/JJSChapter%203.ppt
- http://www.chem.umd.edu/courses/fall05/chem231fribush/pdfs/Chapter%2004.pdf
- http://www.chem.uky.edu/courses/che230/FL/chapter%205.pdf
- http://www.chem.uky.edu/Courses/che230/RBG/lecnotes/J5.pdf

Reactions of Alicyclic compounds:

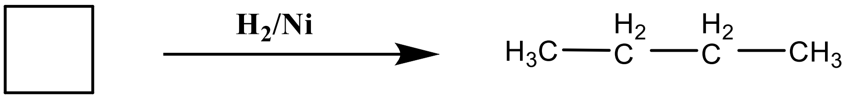
- **Cyclopropane and Cyclobutane:**

1- Hydrogenation:

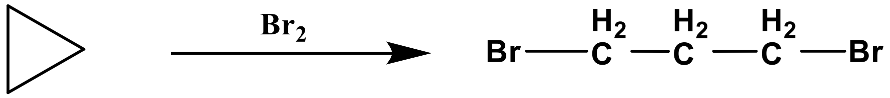


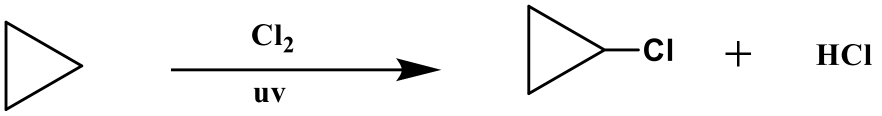


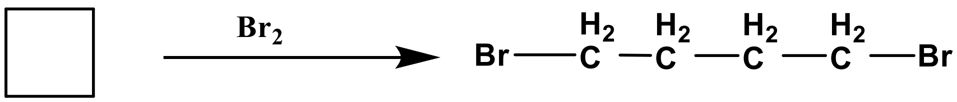
2,3-dimethyl-butane



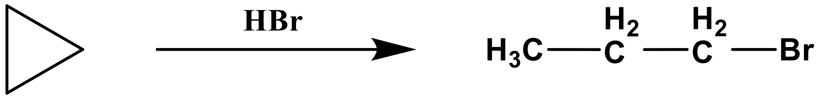
2- Halogenation:

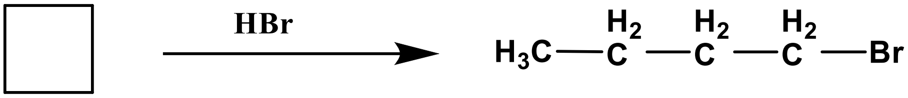




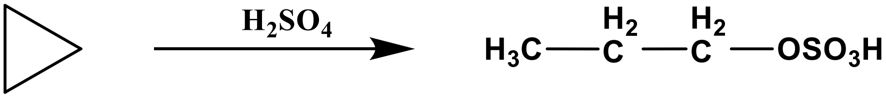


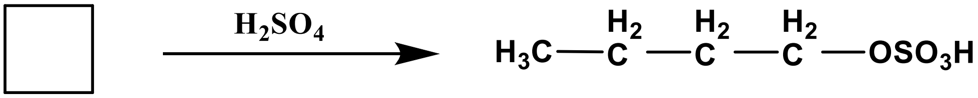
3- Hydrohalogenation:





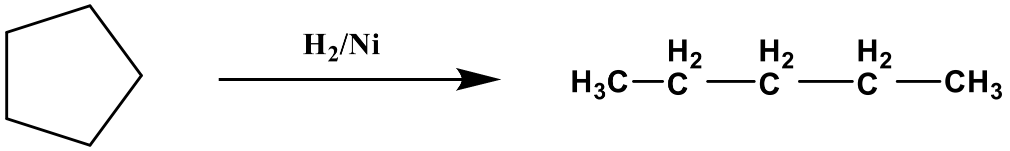
4- Action of conc. H_2SO_4:



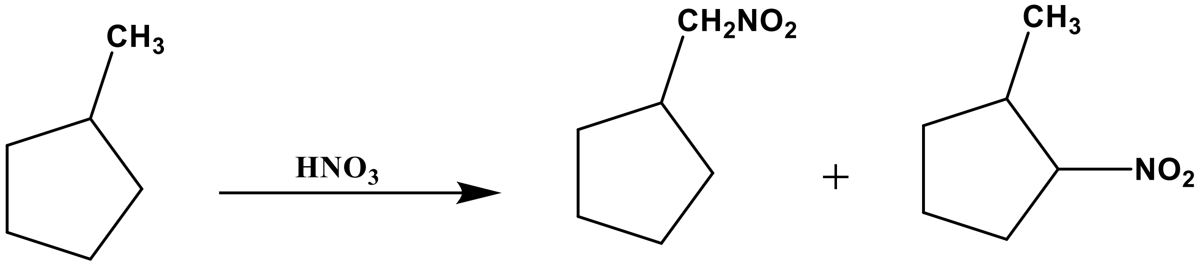


Cyclopentane:

1- Hydrogenation:

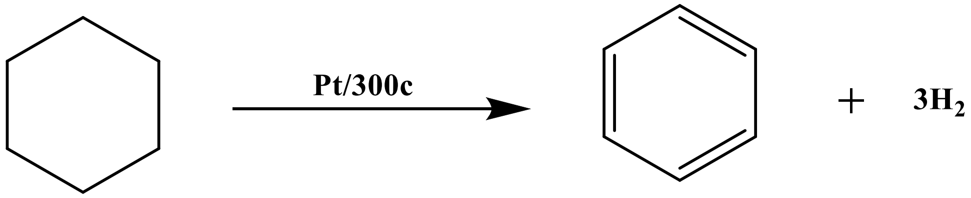


2- Nitration:

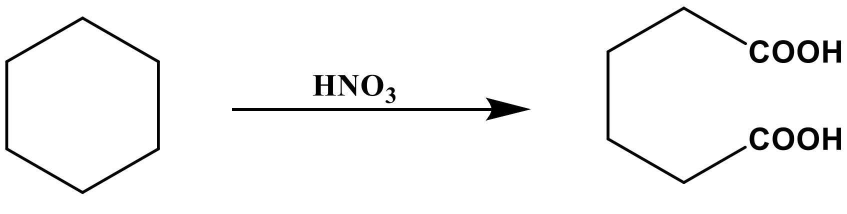


Cyclohexane:

1- Dehydrogenation:



2- Oxidation:



Adipic acid

Introduction to Dienes

Dr. Ibrahim Abdul-Motaleb Mousa

3rd. year students (chemistry group)

Faculty of Education

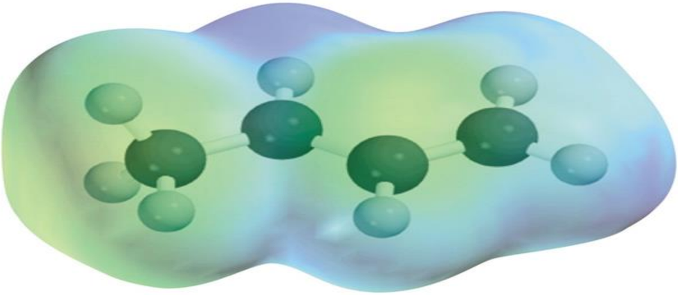
2022/2023

Contents

- **Introduction of Dienes**
- **Types of Dienes**
- **Nomenclature of Dienes**
- **Stability of Dienes**
- **Preparation of Dienes**
- **Electrophilic addition of Dienes**
- **The Diel’s-Alder reaction**

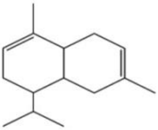
Reactions of Dienes

Ultraviolet and Visible Spectroscopy

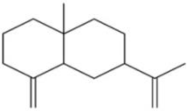


$$\mathrm{CH_3}-\overset{\delta+}{\mathrm{C}}\mathrm{H}=\mathrm{CH}=\overset{\delta+}{\mathrm{C}}\mathrm{H_2}$$

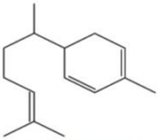
- **Hydrocarbon containing**
- **two double bonds: diene**
- **three double bonds: triene**
- **four double bonds: tetraene**
- **many double bonds: polyene**



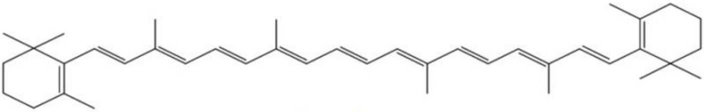
α-cadinene
oil of citronella
a diene



β-selinene
oil of celery
a diene



zingiberene
oil of ginger
a triene



β-carotene
a polyene

Different Kinds of Dienes:

$CH_3CH{=}CH{-}CH{=}CHCH_3$
a conjugated diene

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$
an isolated diene

$CH_3{-}CH{=}C{=}CH{-}CH_3$
a cumulated diene
an allene

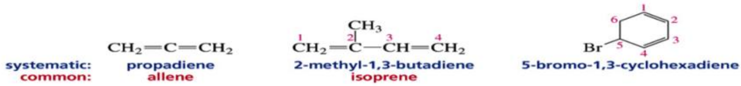
Nomenclature of Alkenes with More than One Functional Group:

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

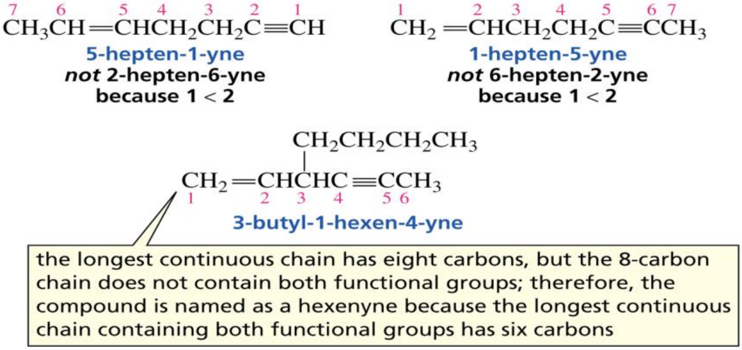
2. Give the double bonds the lowest possible number.

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.



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



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

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

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:

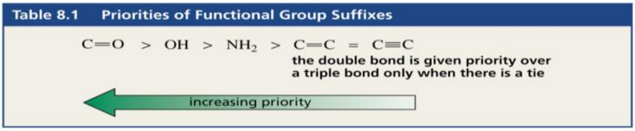


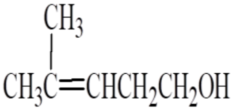
Table 8.1 Priorities of Functional Group Suffixes

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

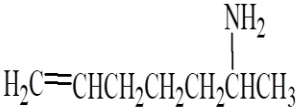
the double bond is given priority over a triple bond only when there is a tie

increasing priority

$H_2C{=}CHCH_2OH$



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

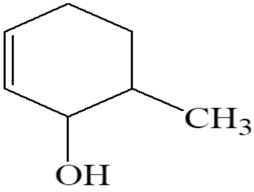


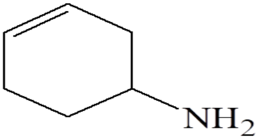
$H_2C{=}CHCH_2CH_2CH_2\overset{NH_2}{\overset{|}{C}}HCH_3$

2-propen-1-ol

6-hepten-2-amine

4-methyl-3-penten-1-ol



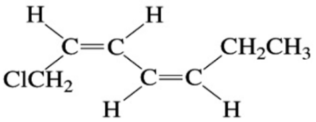


4-methyl-3-penten-1-ol

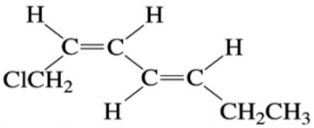
3-cyclohexenamine

Configurational Isomers of Dienes:

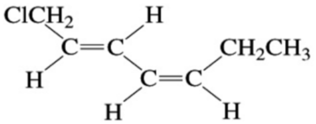
The *Z* isomer has the high-priority groups on the same side



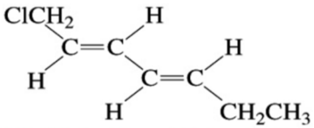
(2*Z*,4*Z*)-1-chloro-2,4-heptadiene



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

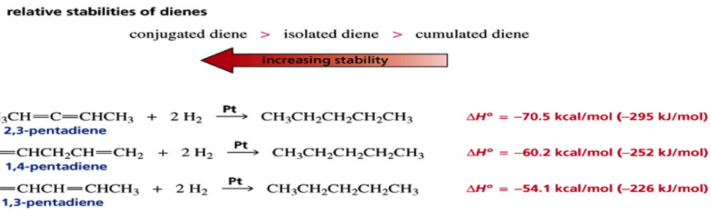


(2*E*,4*Z*)-1-chloro-2,4-heptadiene

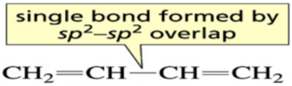


(2*E*,4*E*)-1-chloro-2,4-heptadiene

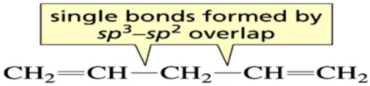
Stability of Dienes:



Why is conjugated diene more stable than isolated diene?



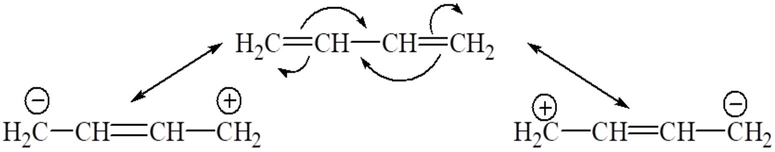
1,3-butadiene

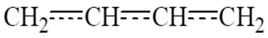


1,4-pentadiene

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

Electron Delocalization Stabilizes a Conjugated Diene:





resonance hybrid

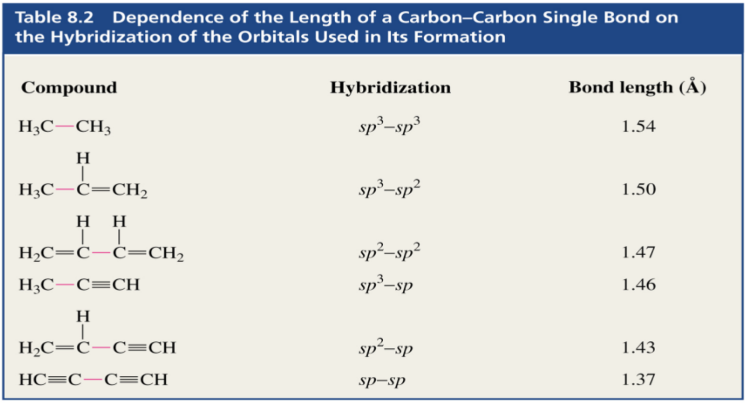
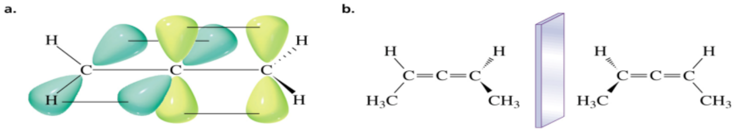


Table 8.2 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation

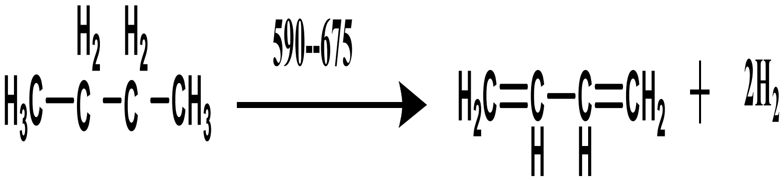
Compound	Hybridization	Bond length (Å)
H_3C-CH_3	sp^3-sp^3	1.54
$H_3C-\overset{H}{\overset{\vert}{C}}=CH_2$	sp^3-sp^2	1.50
$H_2C=\overset{H}{\overset{\vert}{C}}-\overset{H}{\overset{\vert}{C}}=CH_2$	sp^2-sp^2	1.47
$H_3C-C\equiv CH$	sp^3-sp	1.46
$H_2C=\overset{H}{\overset{\vert}{C}}-C\equiv CH$	sp^2-sp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

A cumulated diene is less stable than an isolated diene:



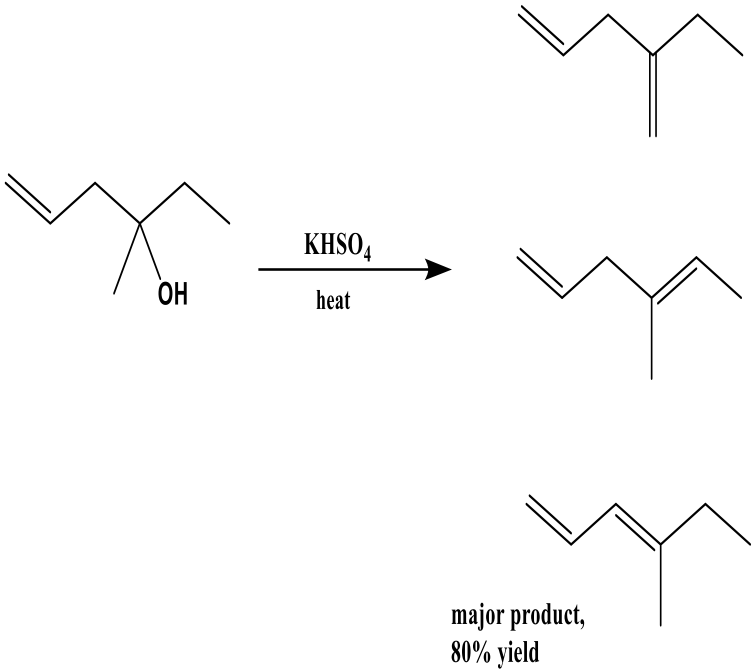
Preparation of Dienes:

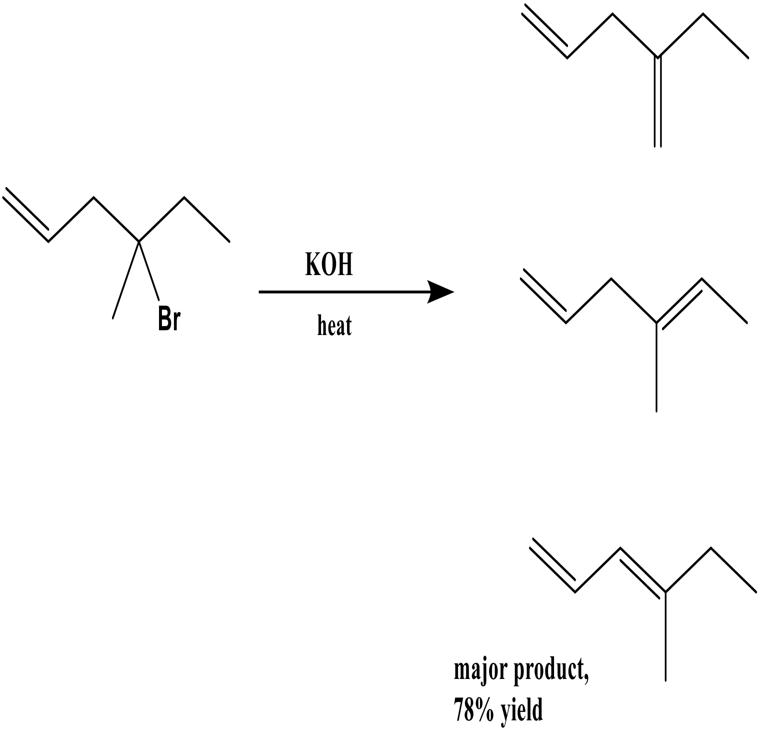
1,3-butadiene:



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

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



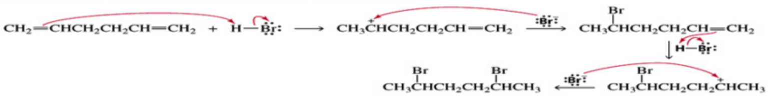

Br
KOH
heat
major product,
78% yield

Electrophilic Addition Reactions of Dienes:

Electrophilic Addition Reactions of Isolated Dienes:

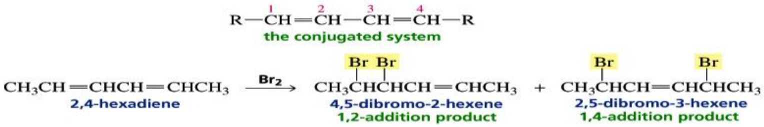
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 + \underset{\text{excess}}{HBr} \longrightarrow CH_3\underset{Br}{C}HCH_2CH_2\underset{Br}{C}HCH_3$$

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

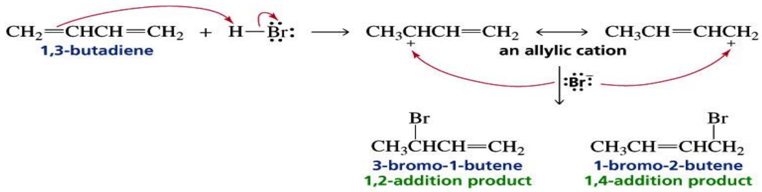


Addition can occur at only one of the double bonds when 1 mole of HBr is available

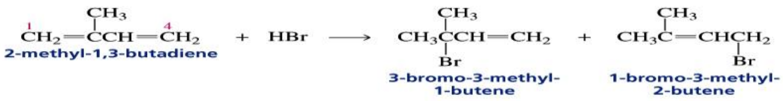
Electrophilic Addition Reactions of Conjugated Dienes:

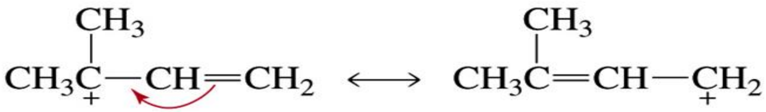


mechanism for the reaction of 1,3-butadiene with HBr



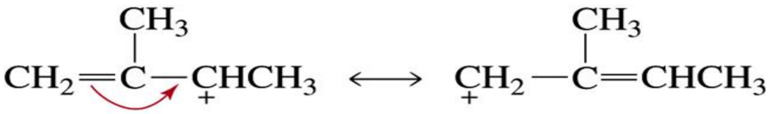
A conjugated diene undergoes both 1,2- and 1,4-addition:





$$CH_3\overset{+}{C}(CH_3)-CH=CH_2 \longleftrightarrow CH_3C(CH_3)=CH-\overset{+}{C}H_2$$

carbocation formed by adding H⁺ to C-1



$$CH_2=C(CH_3)-\overset{+}{C}HCH_3 \longleftrightarrow \overset{+}{C}H_2-C(CH_3)=CHCH_3$$

carbocation formed by adding H⁺ to C-4

Compare the two addition product distribution at different reaction temperatures:

$$CH_2{=}CHCH{=}CH_2 + HBr \xrightarrow{-80\ ^{\circ}C} \underset{\substack{\text{1,2-addition product}\\ 80\%}}{CH_3\overset{Br}{C}HCH{=}CH_2} + \underset{\substack{\text{1,4-addition product}\\ 20\%}}{CH_3CH{=}CH\overset{Br}{C}H_2}$$

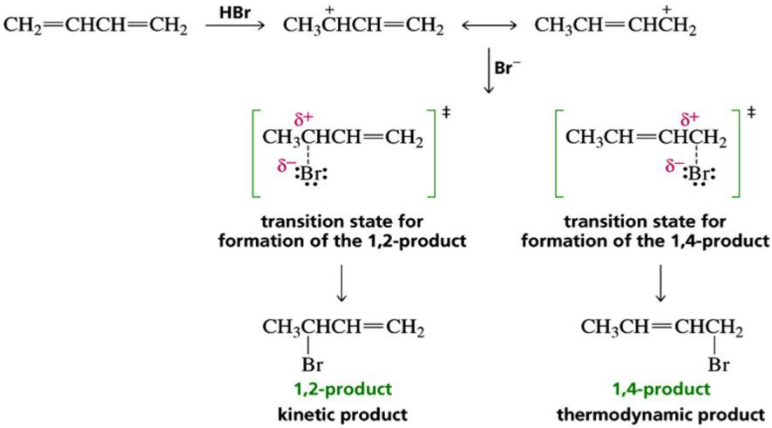
$$CH_2{=}CHCH{=}CH_2 + HBr \xrightarrow{45\ ^{\circ}C} \underset{\substack{\text{1,2-addition product}\\ 15\%}}{CH_3\overset{Br}{C}HCH{=}CH_2} + \underset{\substack{\text{1,4-addition product}\\ 85\%}}{CH_3CH{=}CH\overset{Br}{C}H_2}$$

thermodynamic or equilibrium control

Thermodynamic Versus Kinetic Control:

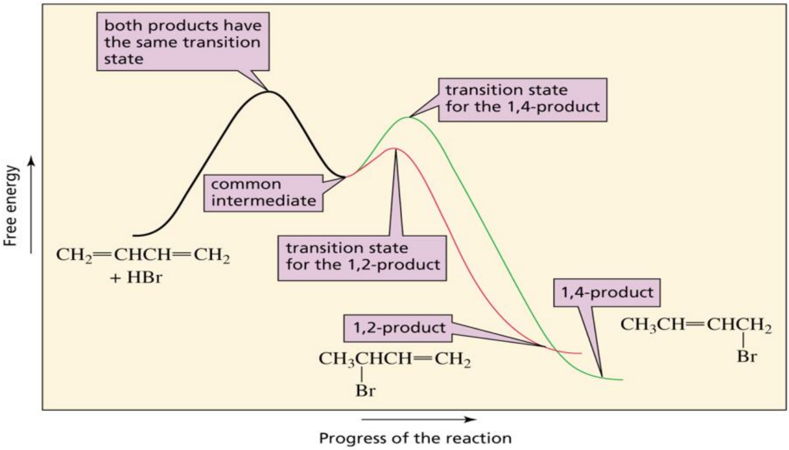
- **The thermodynamic product is the most stable product**
- **The thermodynamic product predominates when the reaction is reversible (thermodynamic control)**
- **The kinetic product is the product that is formed most rapidly**
- **The kinetic product predominates when the reaction is irreversible (kinetic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

The 1,4-addition product has the greater number of alkyl groups bonded to the *sp*^{2} carbon (more stable):



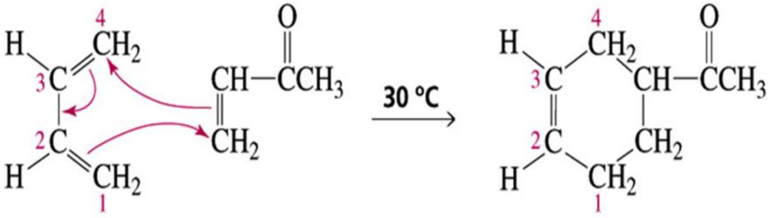
Why is the 1,2-addition product the kinetic product?

Consider the reaction coordinate diagram:



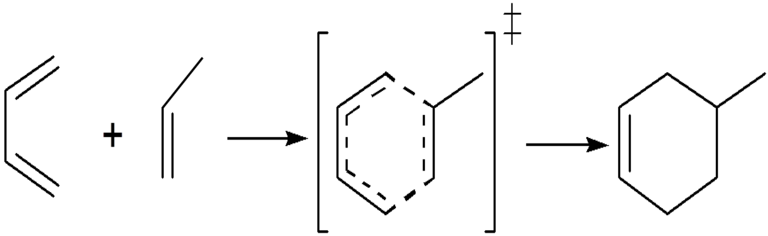
The Diels–Alder Reaction

A 1,4-Addition Reaction

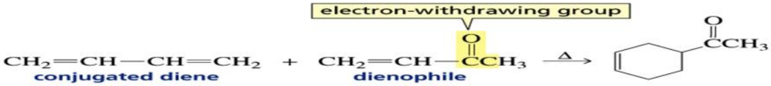


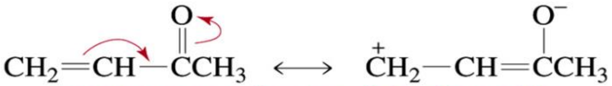
a 1,4-addition reaction to 1,3-butadiene

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



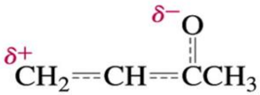
The reactivity of the dienophile is increased if one or more electron-withdrawing groups are attached to its *sp*^{2} carbons:





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

resonance contributors of the dienophile

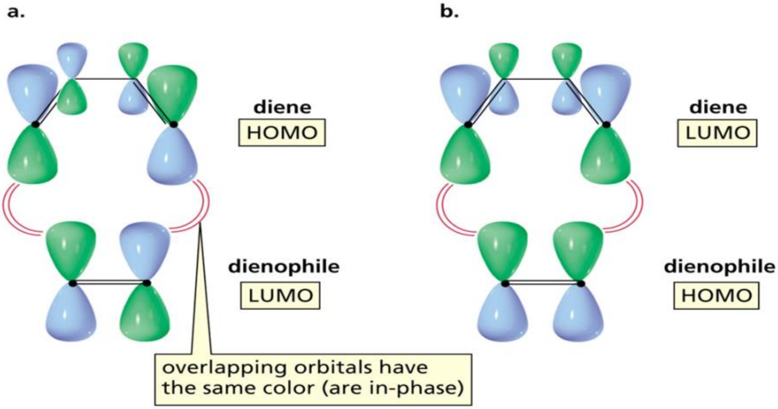


$$\mathrm{\overset{\delta+}{C}H_2{\overset{...}{-}}CH{\overset{...}{-}}\overset{\overset{\displaystyle \overset{\delta-}{O}}{\|}}{C}CH_3}$$

resonance hybrid

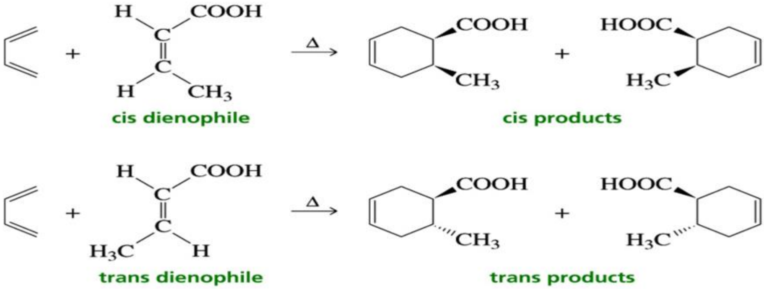
A Molecular Orbital Description of the Diels–Alder Reaction:

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



Stereochemistry of the Diels–Alder Reaction:

The reaction is a syn addition:

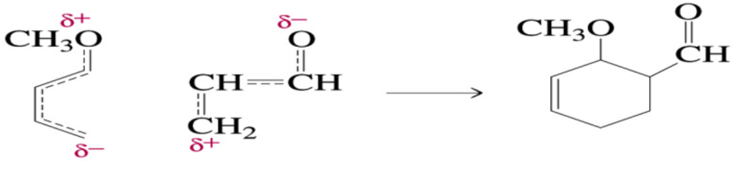


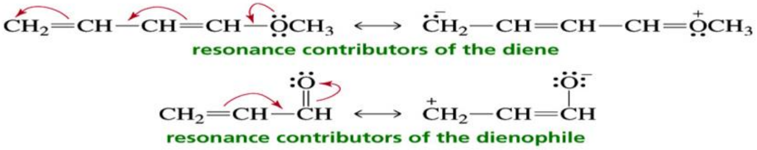
- The Diels–Alder reaction is stereospecific
- The configuration of the reactants is maintained
- The reaction is concerted

Predicting the reaction products:

1. **Consider the alignment of the reactants:**

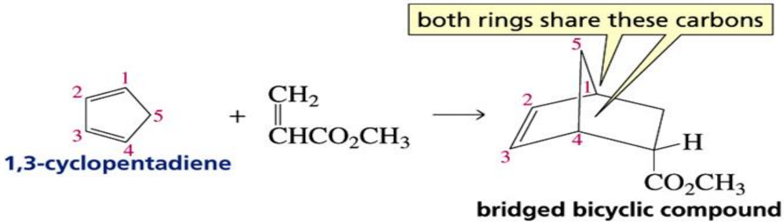
2. **Consider the charge distribution in each of the reactants:**

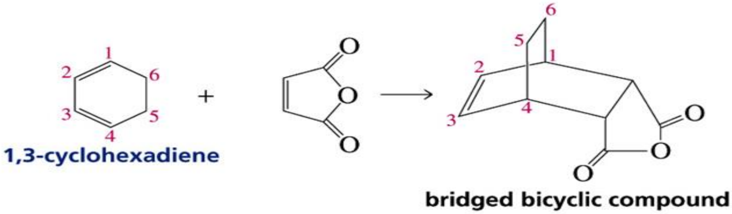



resonance contributors of the diene

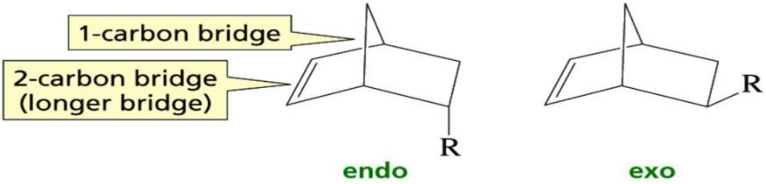
resonance contributors of the dienophile

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

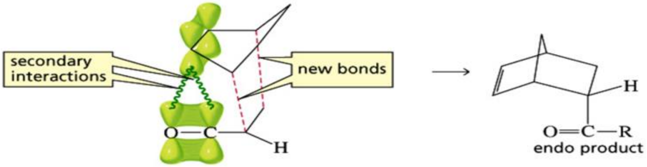




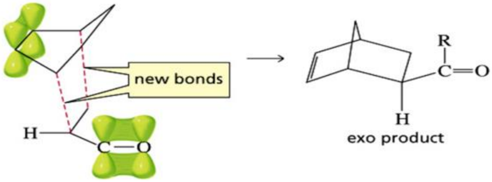
Two Possible Configurations of Bridged Bicyclic Compounds:



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

References:

1- The Chemistry of Dienes and Polyenes, Volume 1, (1997) John Willey & Sons, Ltd.

2- Synthesis of Conjugated Dienes and Polyenes, Goverdhan Mehta and H. Surya Prakash Rao (2009).

3- Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function 5th edition, New York: W.H. Freeman & Company 2007.

4- John Son, William. Invitation to Organic Chemistry. Jones & Bartlett Publishers, 1998.

5- Sorrel, Thomas, N. Organic Chemistry University & Science Books, 2006.

Polymer Chemistry

3rd year students Faculty of education (Chemistry group)

Dr/ ibrahim Abdul-Motaleb Mousa

2021/2022

Contents

Definitions

- Polymer – A very long molecule composed of repeating units connected by covalent bonds

- Monomer – A repeated unit in a polymer. The reactant for the polymerization reaction.

Classifications

- Thermoplastic
- Elastomer
- Thermoset

Thermoplastics

- Linear or branched polymers which can be melted when heat is applied.
- Can be molded into any shape with processing techniques such as injection molding or extrusion.
- Most common “plastics”

Thermoplastics

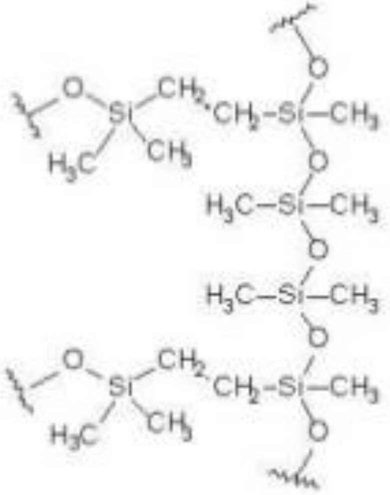
- Plastics – bottles, grocery bags, water piping, rope, fishing line, car parts
- Most are recyclable
- Natural thermoplastics – silk, cellulose (proteins), polylactic acid

Codes for Plastics

- 1 – PETE – soft drink bottles
- 2 – LDPE – plastic bags, toys
- 3 – PVC – water pipes
- 4 – HDPE – milk jugs
- 5 – PP – bottle caps
- 6 – PS – styrofoam

Elastomers

- Crosslinked (networked) rubbery polymers that can be stretched easily (3-10x original size)
- Rapidly recover original dimensions when applied stress is released.
- Low degree of crosslinking

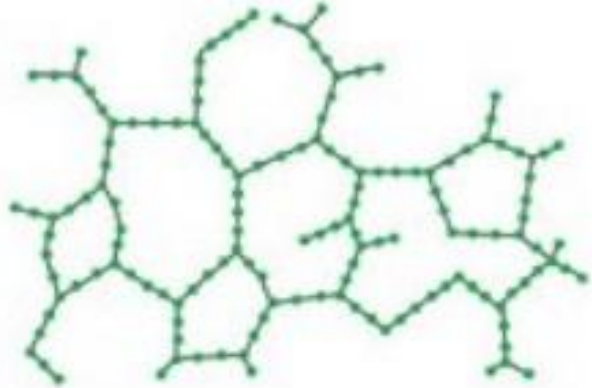


Elastomers

- Uses – examination gloves, rubber bands, bouncing balls
- Not recyclable
  - Degrades (burns/scorches) when heat is added
- Natural elastomers – natural rubber, latex

Thermosets

- Normally are rigid materials.
- Network polymers in which chain motion is greatly restricted by a high degree of crosslinking.
- Cannot be reshaped once formed.



epoxy

Thermosets

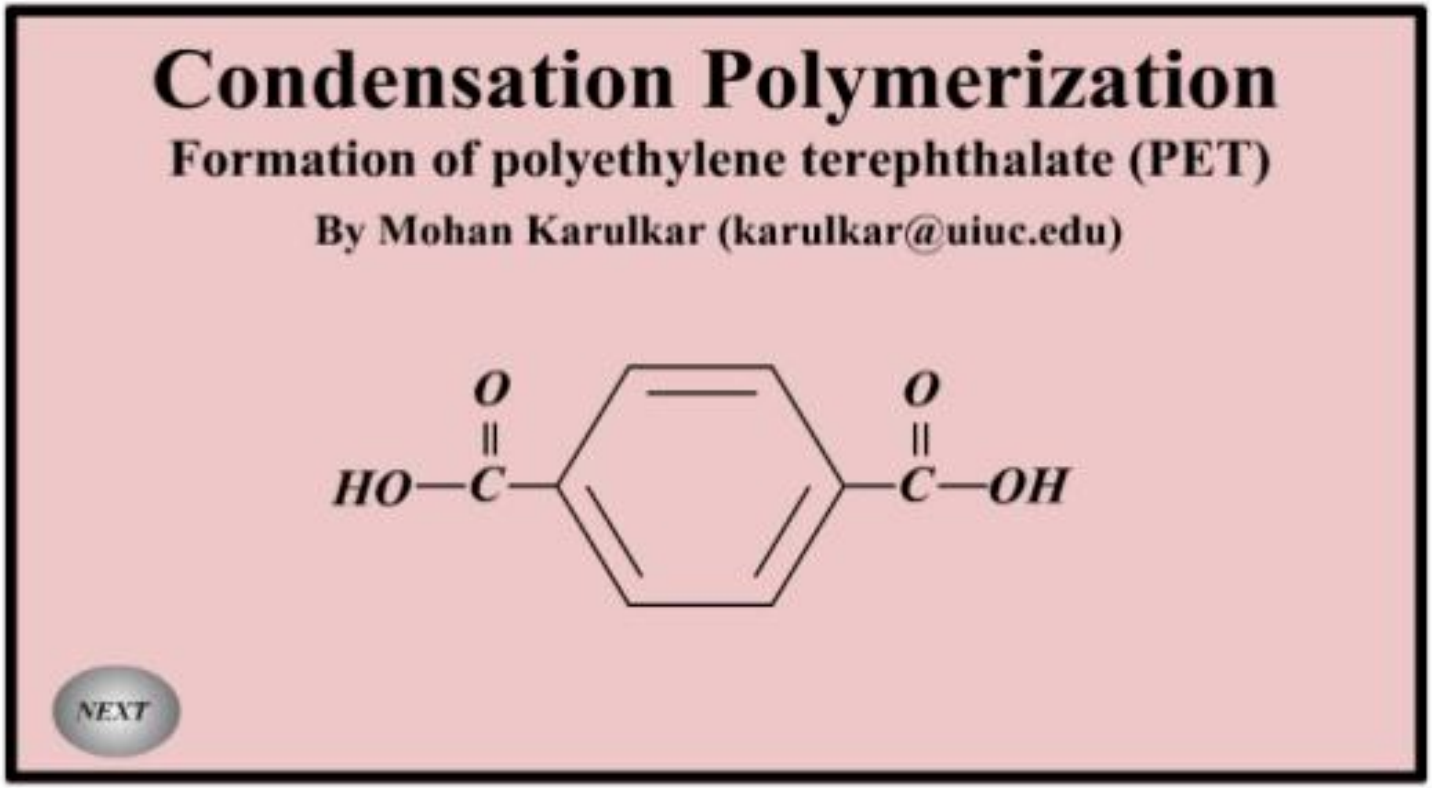
- Uses – high temperature electrical applications, super glue, counter top laminates, epoxy resins, tires (vulcanized rubber)
- Cannot be recycled (burn/scorch with heat)
- Natural* thermosets – vulcanized rubber

Polymer Chemistry

Part 2
Polymer Synthesis

Polycondensation

- Reactions in which small molecules (H_2O, HCl) are eliminated when the monomers combine.



Condensation Polymerization

Formation of polyethylene terephthalate (PET)

By Mohan Karulkar (karulkar@uiuc.edu)

Polyaddition

- Reactions in which monomers combine without the elimination of a small molecule.
  - Usually involves the breaking of a double bond.

Polyaddition with Radicals

- Initiation – Creation of an active site (free radical).
- Propagation – Growth of polymer chain by addition of a monomer to an active site and the creation of a new active site.

Polyaddition with Radicals

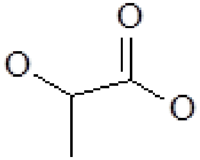
- Termination – Growth of chain stops.
  - Combination – Two growing chains collide.
  - Disproportionation – A hydrogen atom is added to the end of a growing chain.

Polymeric material

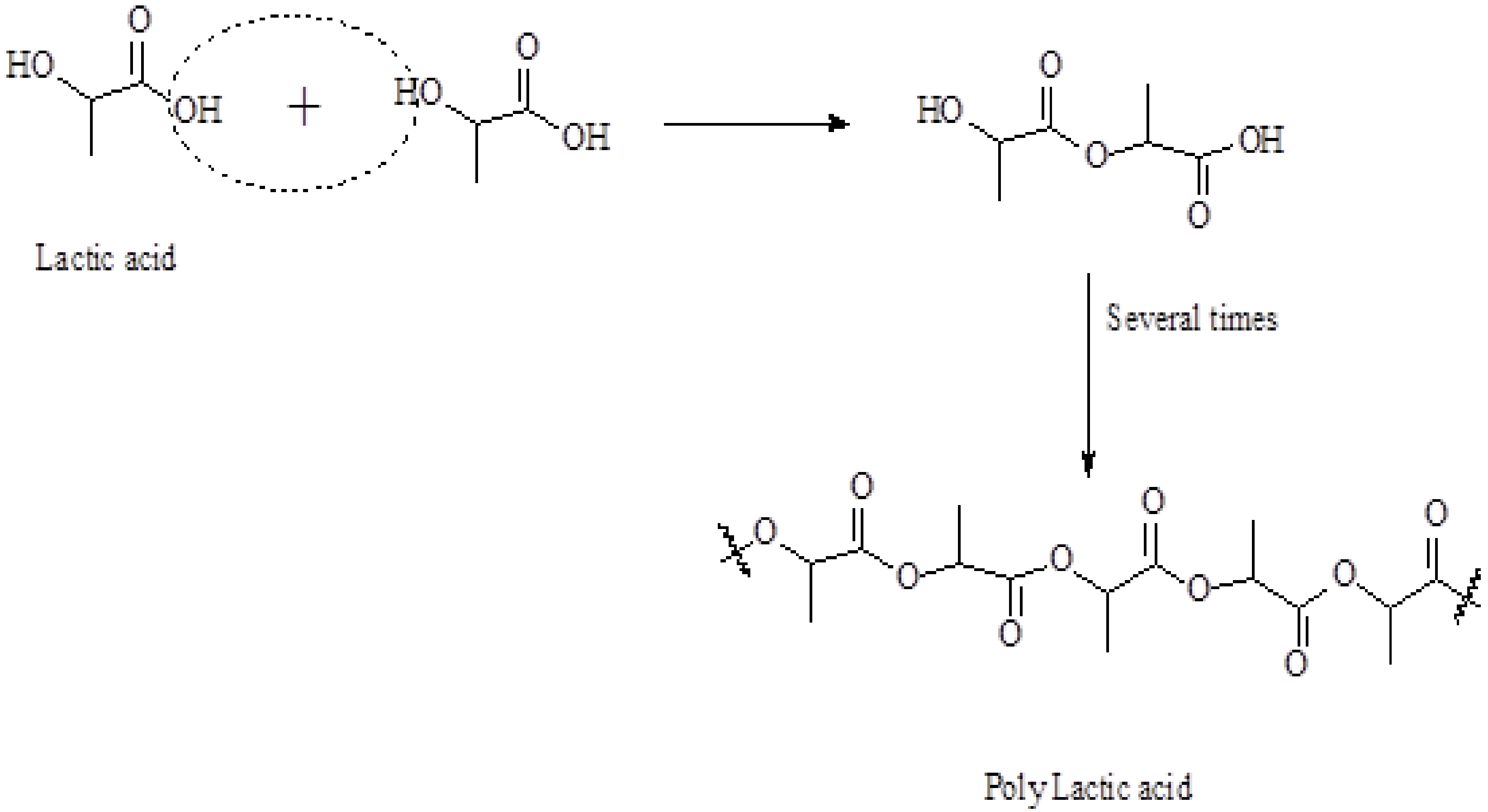
- Up to this point we have studied the properties of small molecules. However, life is fall with extremely large molecules. The basic molecules of life starch, cellulose, proteins and nucleic acids are formed of large number of repeated similar or unsimilar small molecules weight unites. Such molecules 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



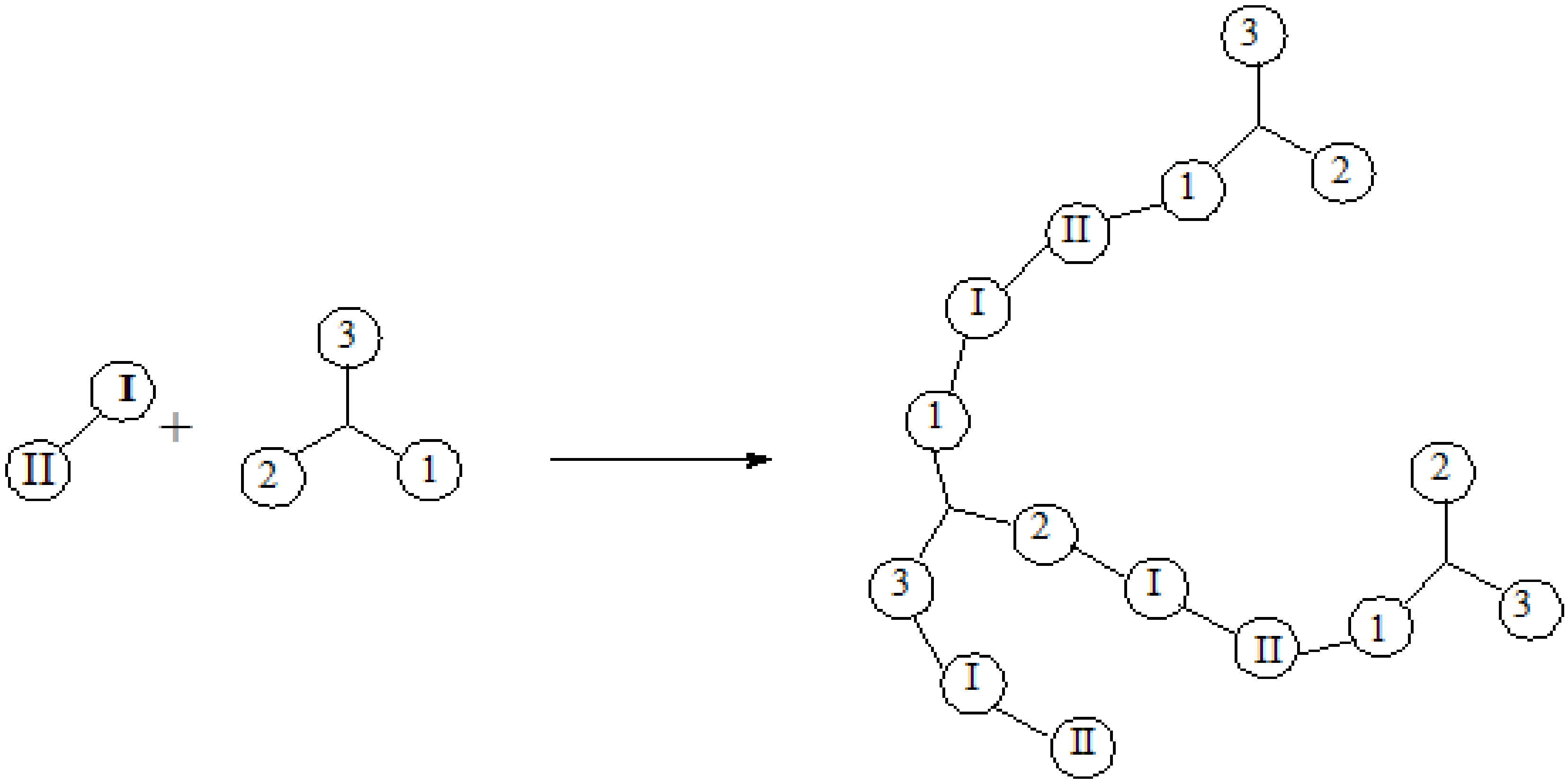
- Should have resulted from consecutive esterification of carboxylic group of that acid with its hydroxyl group.
- The process by with polylactic acid is formed from lactic acid is called polymerization. Lactic acid is thus a monomer and when self condensed it produces a dimmer and the letter when condensed with further one molecule it produces a trimmer.


HO
O
OH
+
HO
O
OH
Lactic acid
HO
O
O
OH
O
Several times
O
O
O
O
O
O
O
O
O
O
O
Poly Lactic acid

Linear and branched polymers

1. **Linear polymers**: Derived from monomer that have only two possible attachment points.
2. **Branched polymers**: These are polymers that has three or 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
+
3
2
1
3
1
2
II
I
1
2
3
2
I
II
1
3
I
II

Types of polymerization:

- The chemical transformations that result in polymers can be divided into two major classes:
- (A)- Condensation polymerization: As an example OH fraction in hydroxy acid can condense with its carboxulic group producing polyester via elimination of water.
- (B)- Addition polymerization: This results ferom addition of one molecule to another link can of polyethaylene.

Plastics

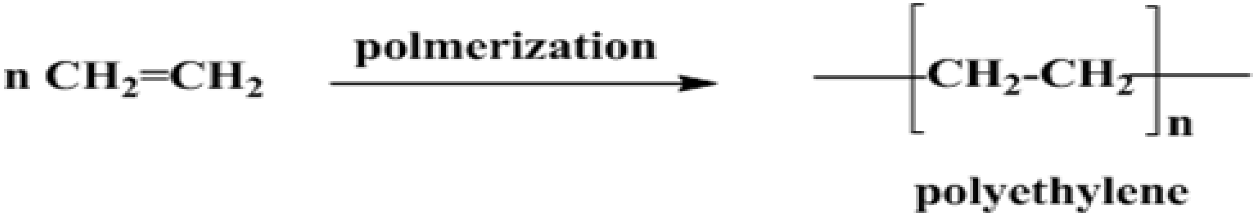
- Since the dawn of history, humankind has endeavoured to develop materials offering benefits not found in natural materials. The development of plastics started with the use of natural materials that had intrinsic plastic properties, such as shellac and chewing gum. The next step in the evolution of plastics involved the chemical modification of natural materials such as rubber, nitrocellulose, collagen and galalite. Finally, the wide range of completely synthetic materials that we would recognise as modern plastics started to be developed around 100 years ago:

Types of plastics

- There are many different types of plastics, and they can be grouped into two main polymer families:
- • Thermoplastics (which soften on heating and then harden again on cooling).
- • Thermosets (which never soften once they have been moulded).

Examples of Thermoplastics	**Examples of Thermosets**
Acrylonitrile butadiene styrene (ABS)	**Epoxide (EP)**
Polycarbonate (PC)	**Phenol-formaldehyde (PF)**
Polyethylene (PE)	**Polyurethane (PUR)**
Polyethylene terephthalate (PET)	**Polytetrafluoroethylene (PTFE)**
Polyvinyl chloride (PVC)	**Unsaturated polyester resins (UP)**
Polymethyl methacrylate (PMMA)	
Polypropylene (PP)	
Polystyrene (PS)	
Expanded Polystyrene (EPS)	

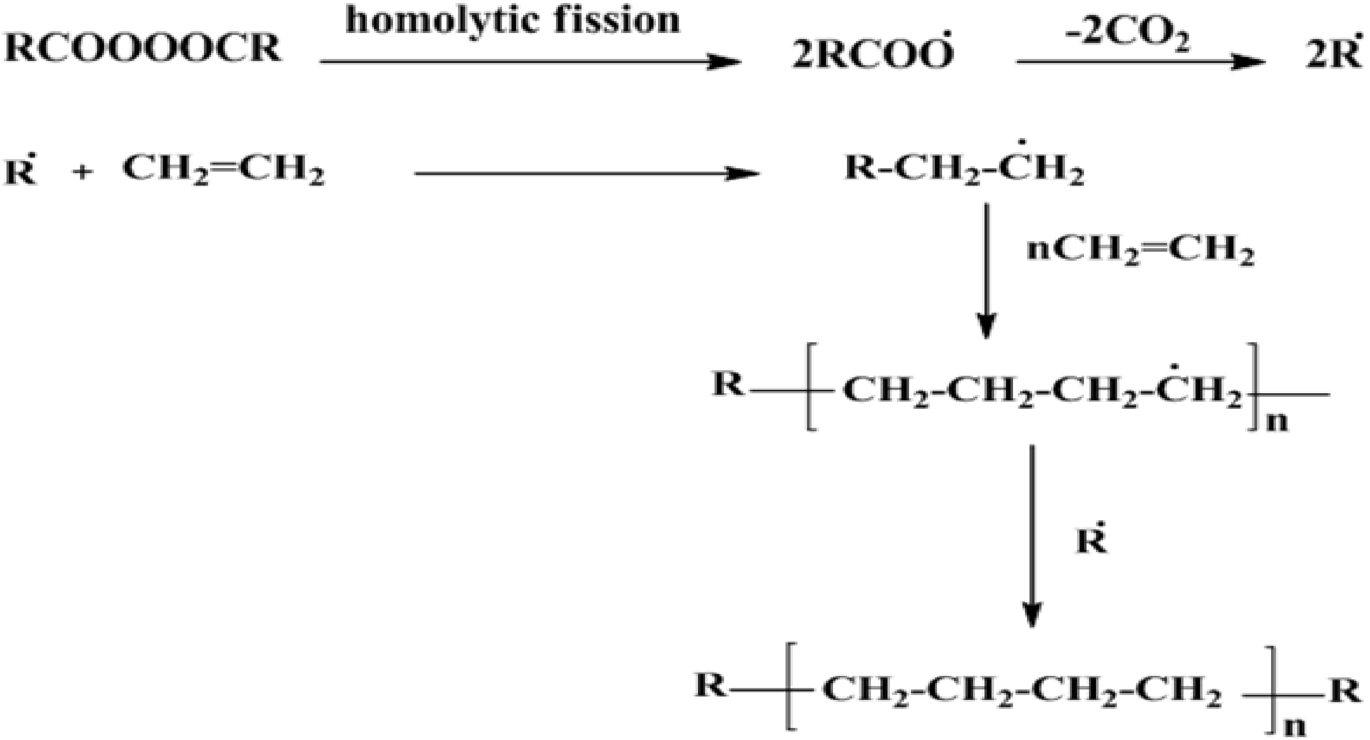
Poly ethylene:



$$n\,CH_2{=}CH_2 \xrightarrow{\text{polmerization}} -\!\!\left[CH_2\text{-}CH_2\right]_n\!\!-$$

polyethylene

Mechanism:



$$RCOOOOCR \xrightarrow{\text{homolytic fission}} 2RCO\dot{O} \xrightarrow{-2CO_2} 2\dot{R}$$

$$\dot{R} + CH_2{=}CH_2 \longrightarrow R\text{-}CH_2\text{-}\dot{C}H_2$$

$$\big\downarrow \; nCH_2{=}CH_2$$

$$R-\!\!\left[CH_2\text{-}CH_2\text{-}CH_2\text{-}\dot{C}H_2\right]_n\!\!-$$

$$\big\downarrow \; \dot{R}$$

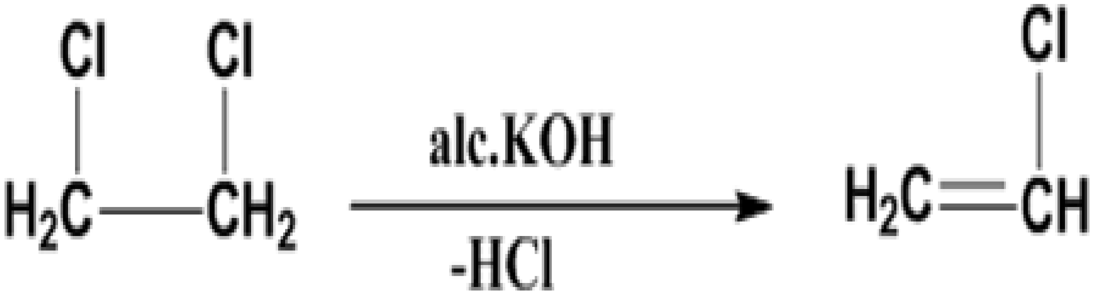
$$R-\!\!\left[CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\right]_n\!\!-R$$

Polyvinyl chloride (PVC)

- **Polyvinylchloride can be prepared from:**
- **From acetylene:**

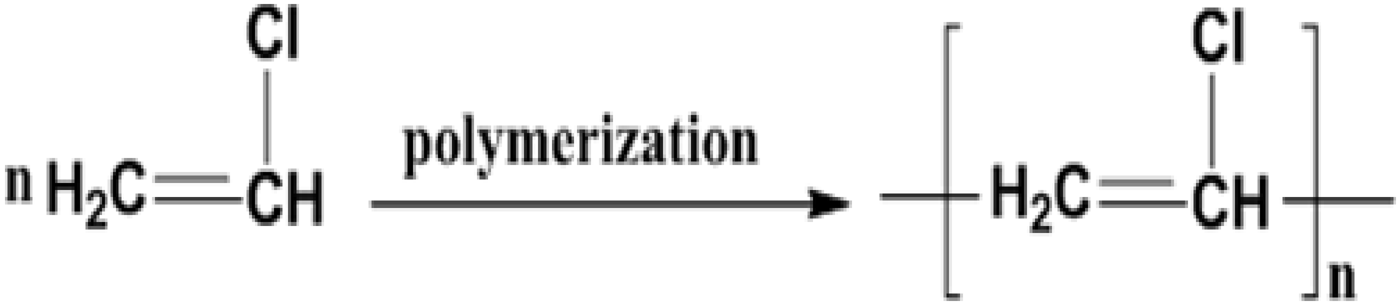
$$HC\equiv CH + HCl \longrightarrow H_2C=\underset{H}{C}-Cl$$

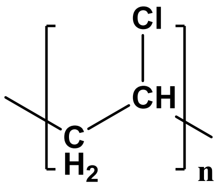
- **From dichloroethylene:**



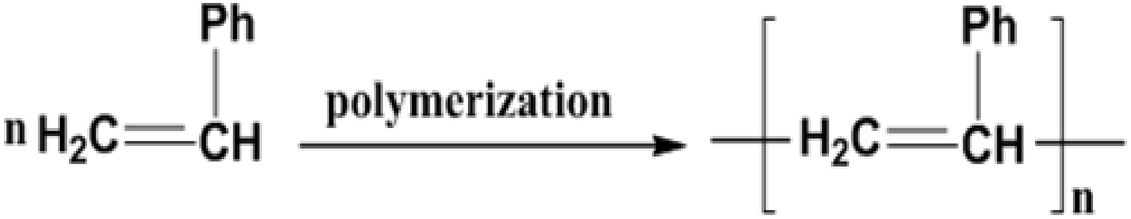
$$H_2\overset{Cl}{C}-\overset{Cl}{C}H_2 \xrightarrow[-HCl]{alc.KOH} H_2C=\overset{Cl}{C}H$$

Preparation of polyvinylchloride:



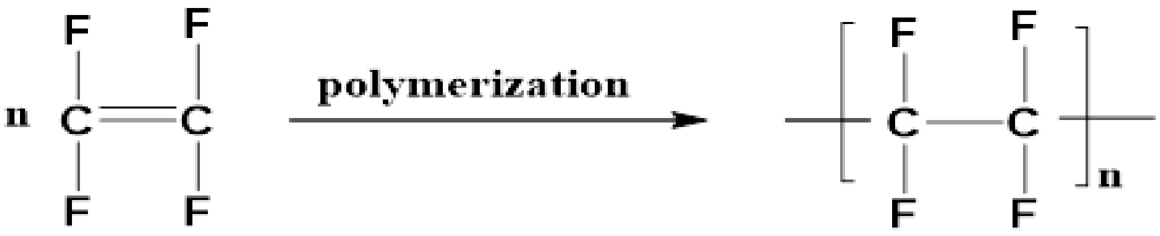


Polystyrene:

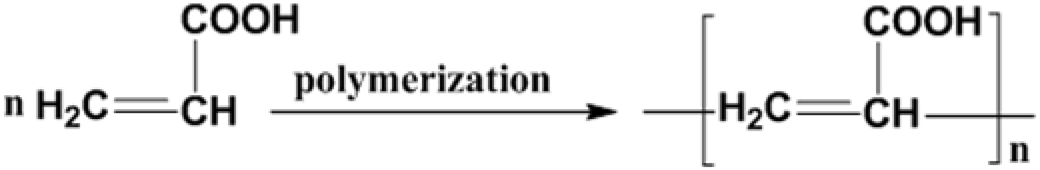


Polytetrafluroethylene:

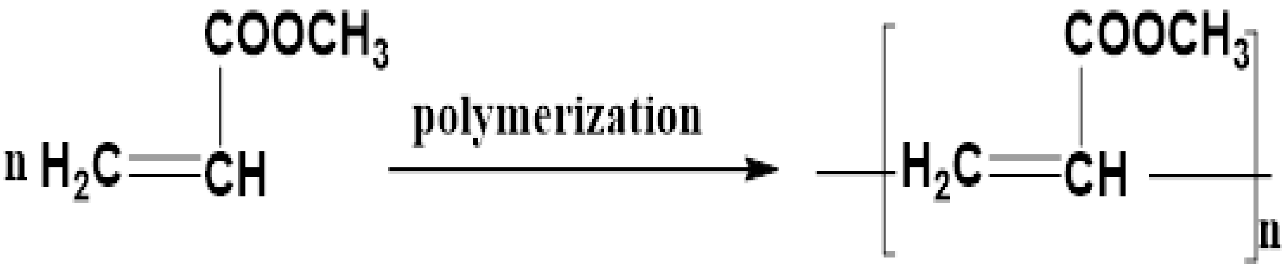
-



Polyacrylic acid:



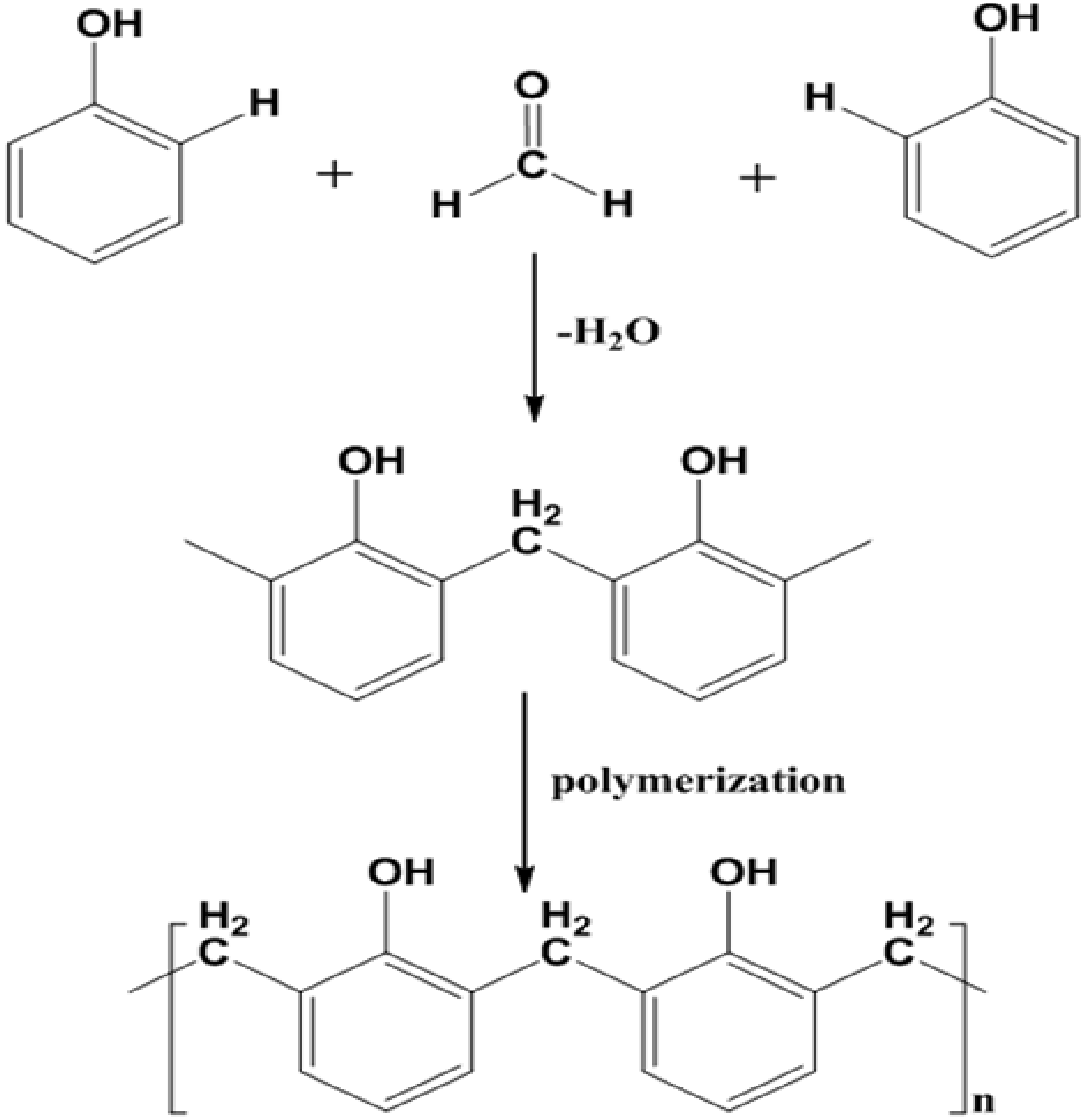
Polymethylacrylate: •



$$n\,H_2C{=}\overset{COOCH_3}{\overset{|}{CH}} \xrightarrow{\text{polymerization}} -\!\!\left[H_2C{=}\overset{COOCH_3}{\overset{|}{CH}}-\right]_n$$

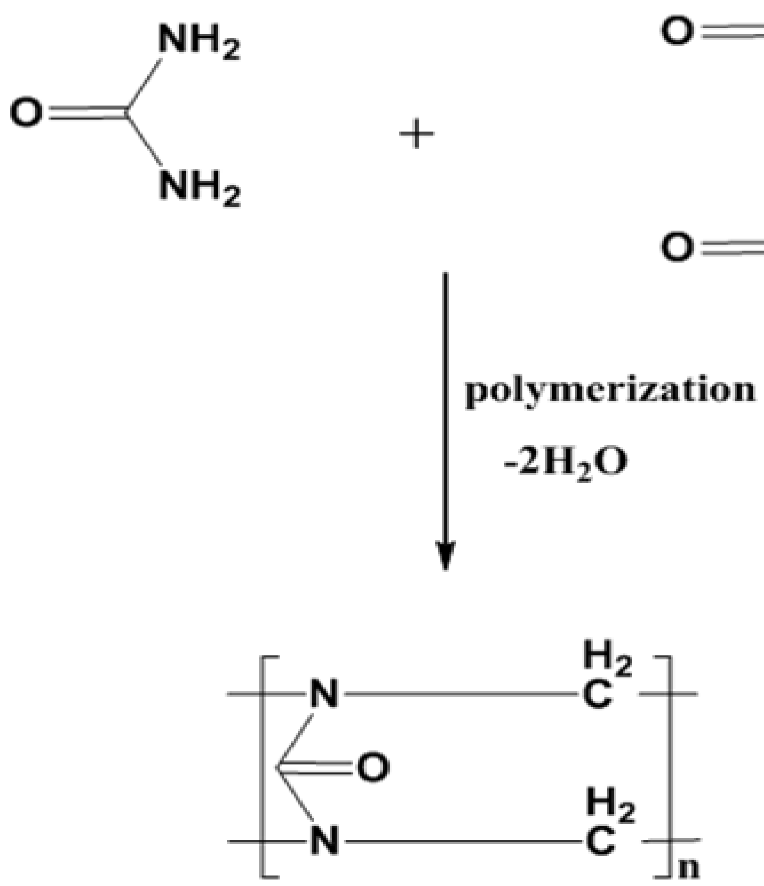
Thermosetting Plastics

- (Backalite) (Backland 1908)
- 1-Phenol-aldehyde plastics:
- Prepared from formaldhyde with phenol:



Backalite

2-Urea or Amino Plastics:
Prepared form condensation of urea with formaldehyde

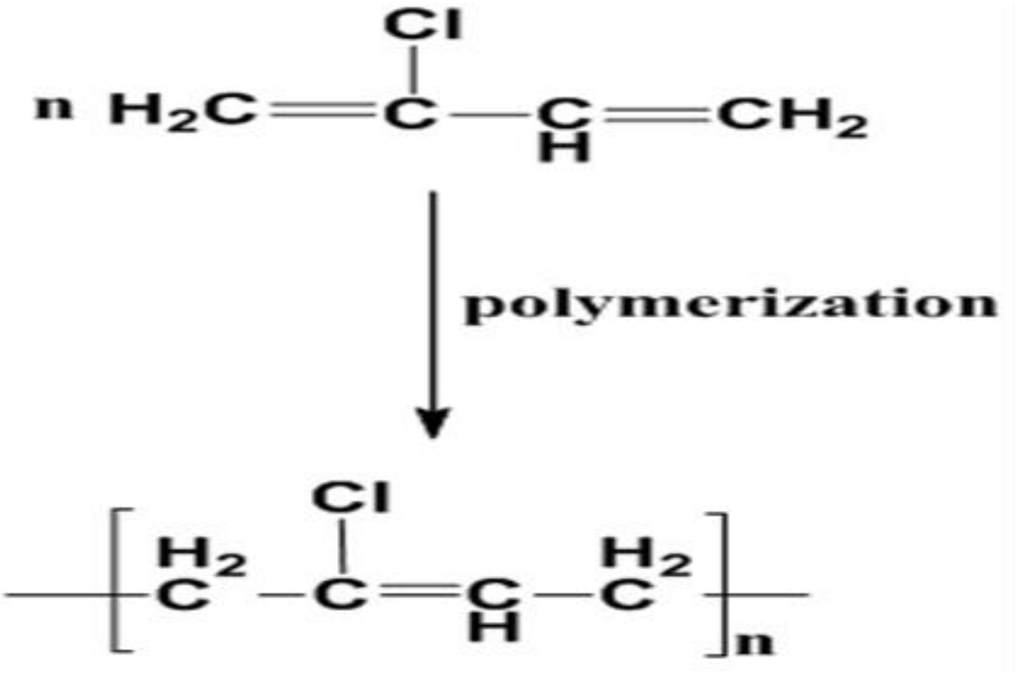


Rubber

- **1-Natural Rubber:**
- The natural rubber is formed from isoprene units $(C_5H_8)_n$, so it called polyisoprene:

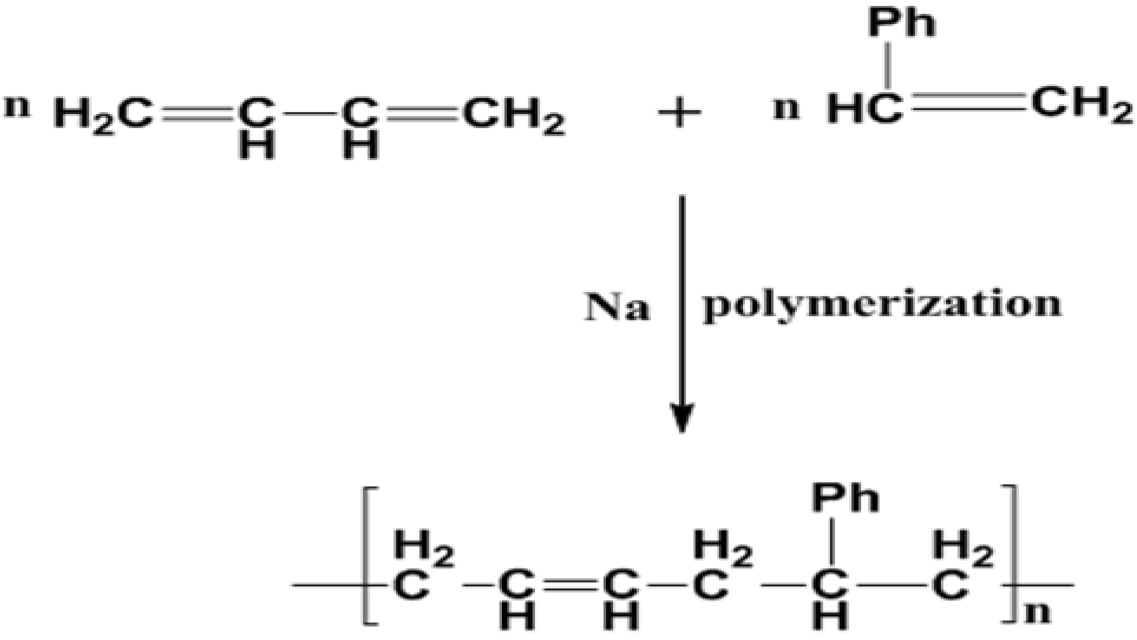
2-Synthetic Rubber:

- **a-Neoprene Rubber:**



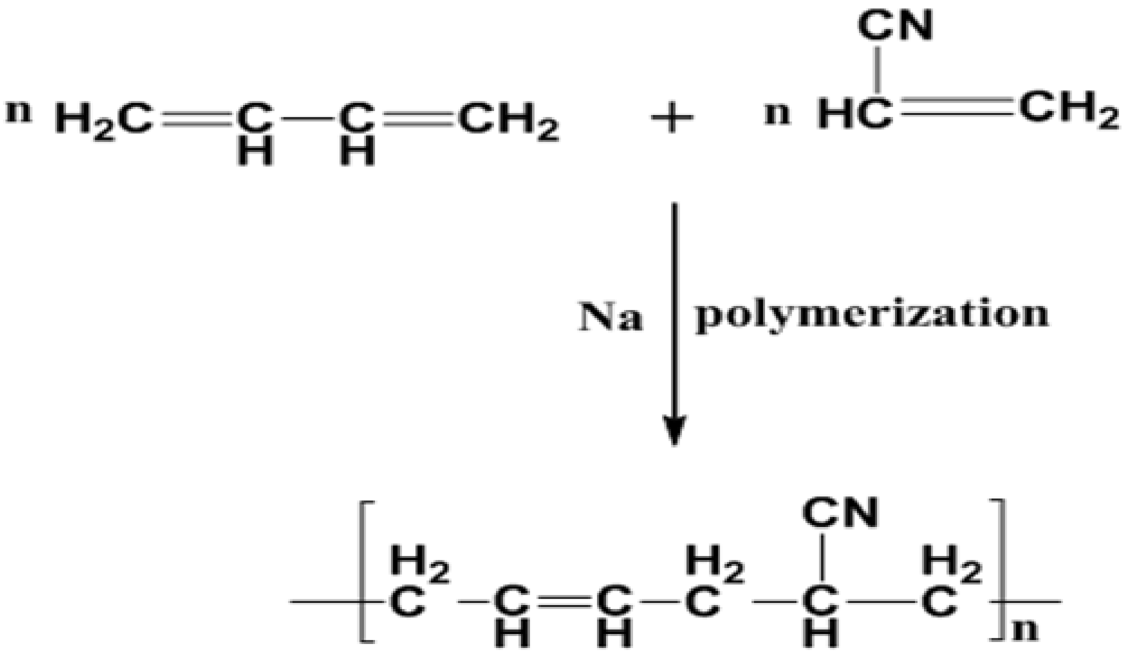
b-BuNa-s Rubber:

- **The BuNa-S rubber was formed by Bayer company since 1935 from the polymerization reaction between 1,3-butadiene and styrene in the presence of sodium metal as catalyst.**



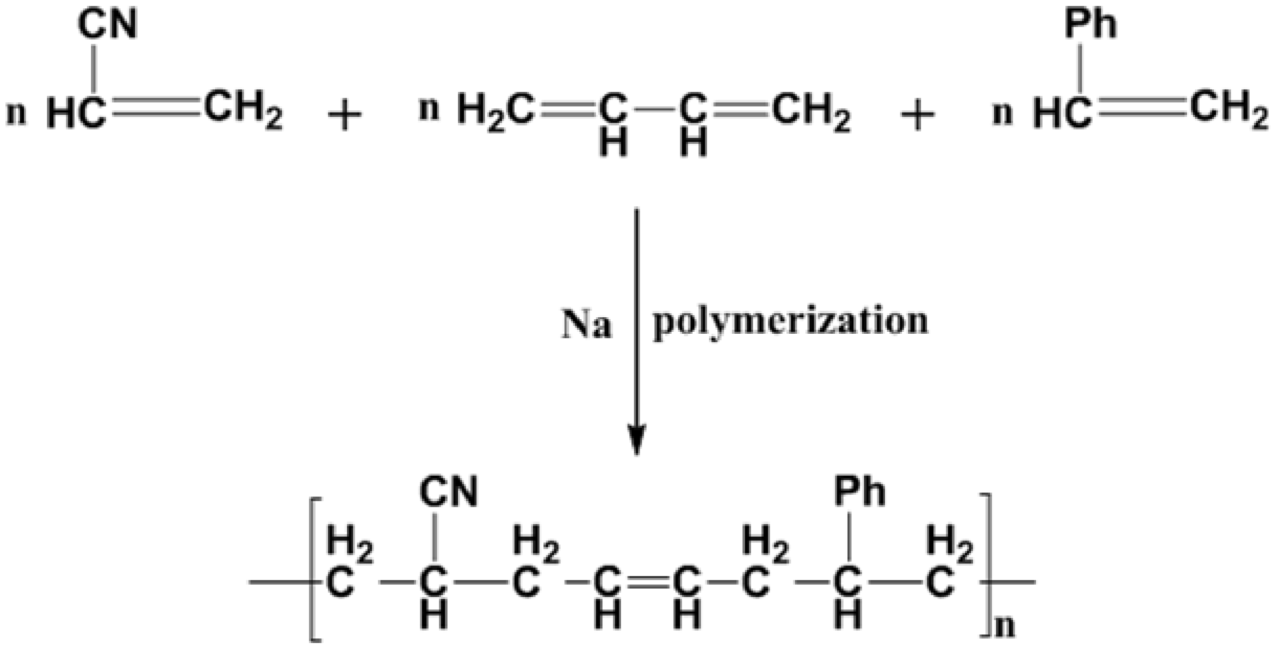
c-BuNa-N rubber:

- **The BuNa-N rubber was formed by the polymerization reaction between 1,3-butadiene and acrylonitrile in the presence of sodium metal as catalyst.**



d- A.B.S. Rubber:

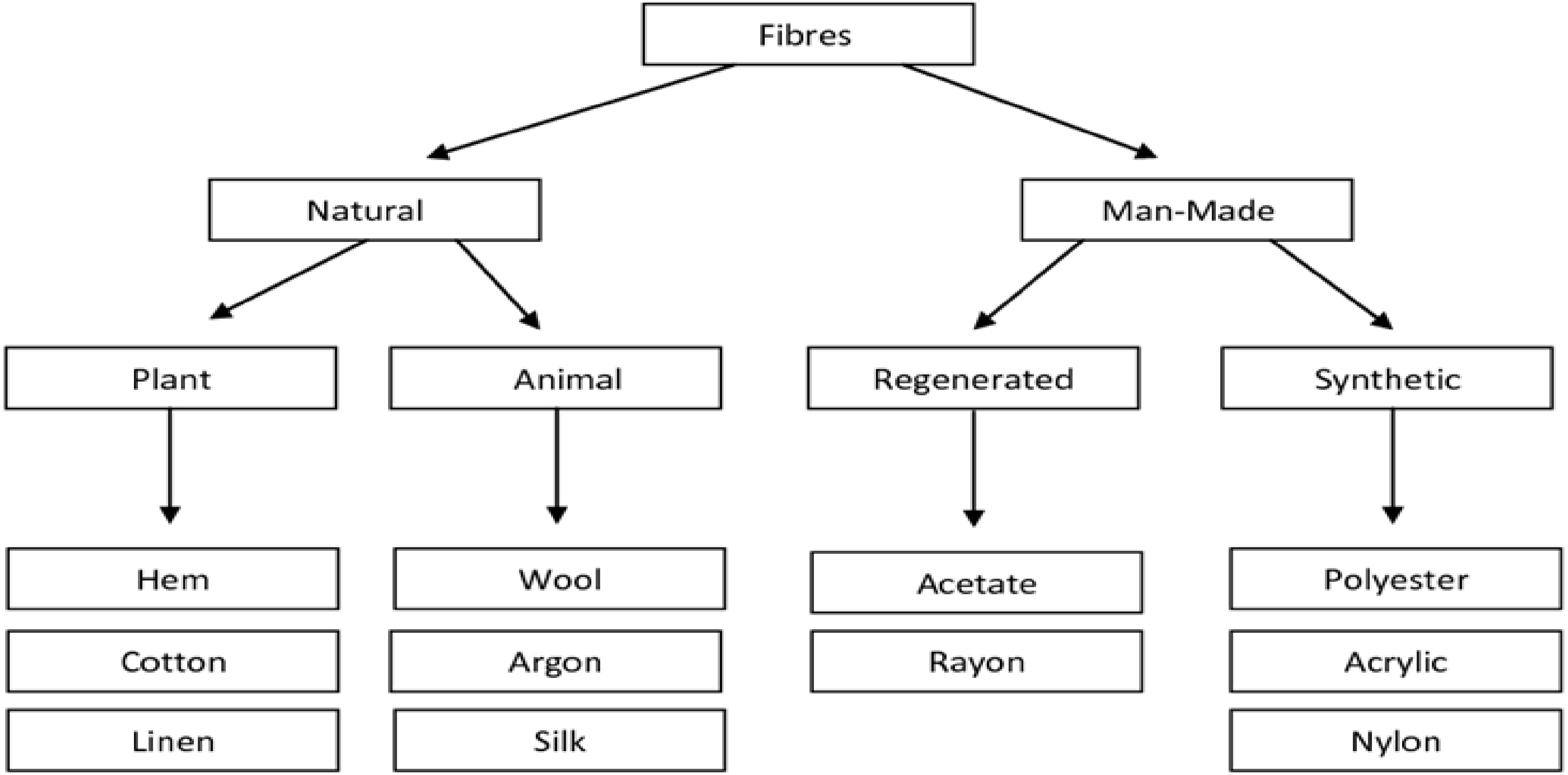
- **The A.B.S. rubber was formed by the polymerization reaction between acrylonitrile, 1,3-butadiene and styrene in the presence of sodium metal as catalyst.**



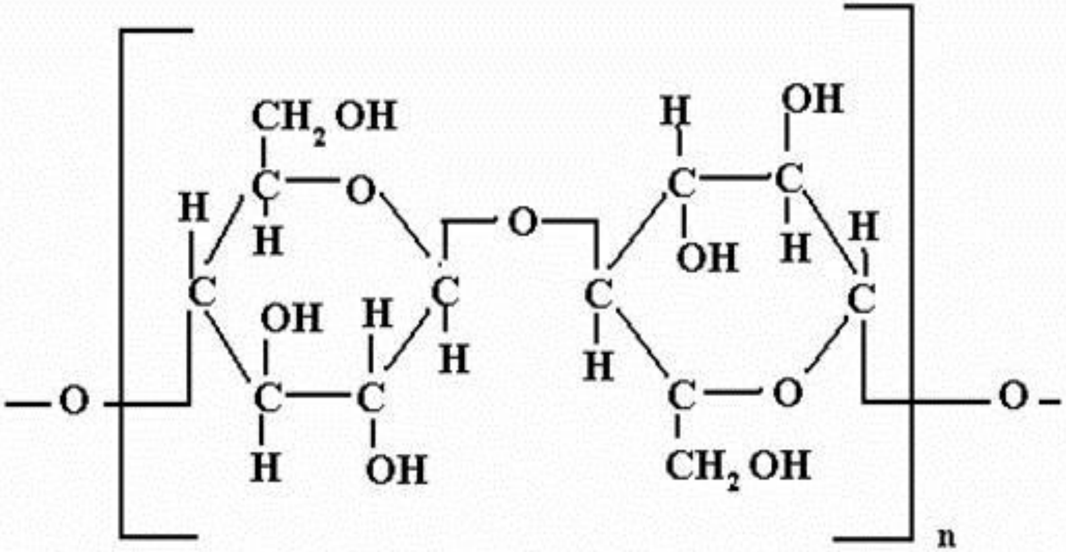
Synthetic fibers

Fibre Classification

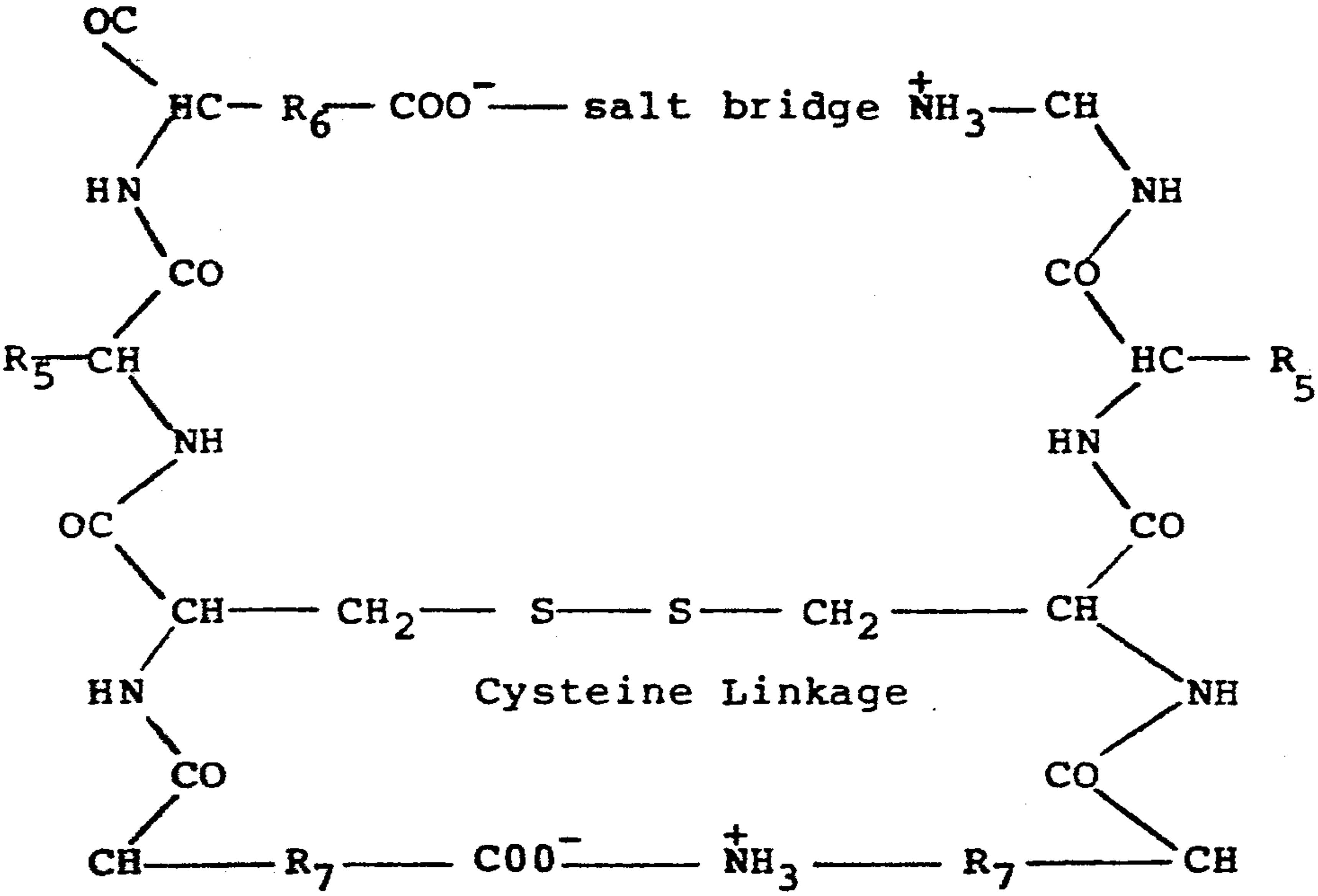
Activity 1: Complete the chart on Fibre Classification.

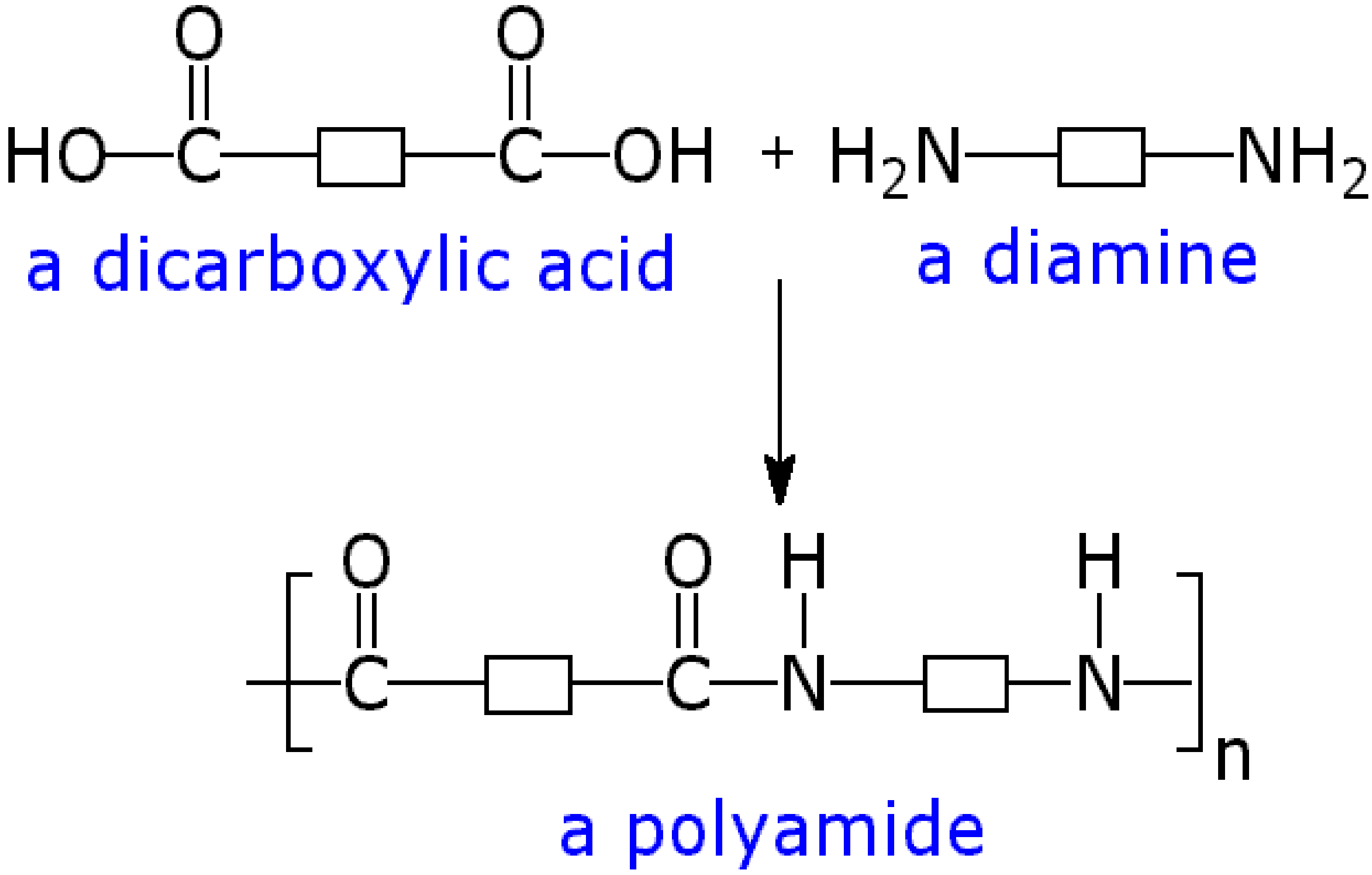


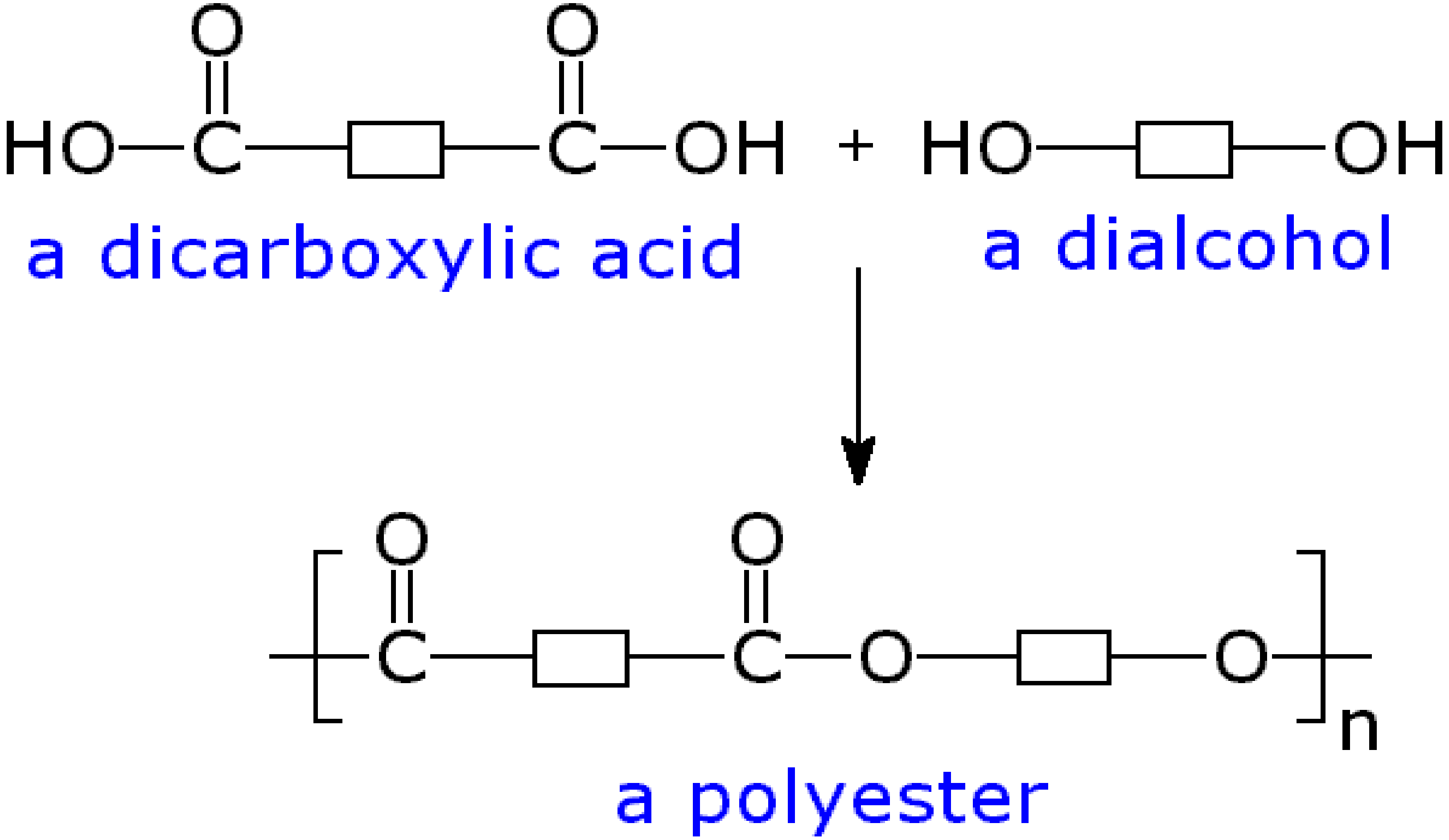
- Fibres
  - Natural
    - Plant
      - Hem
      - Cotton
      - Linen
    - Animal
      - Wool
      - Argon
      - Silk
  - Man-Made
    - Regenerated
      - Acetate
      - Rayon
    - Synthetic
      - Polyester
      - Acrylic
      - Nylon

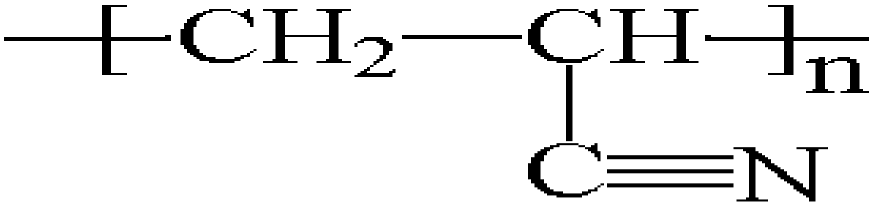


CH₂ OH
H
C
O
H
C
OH
H
C
H
C
C
H
OH
O
H
OH
C
C
OH
H
H
C
C
O
H
C
CH₂ OH
O
n
O

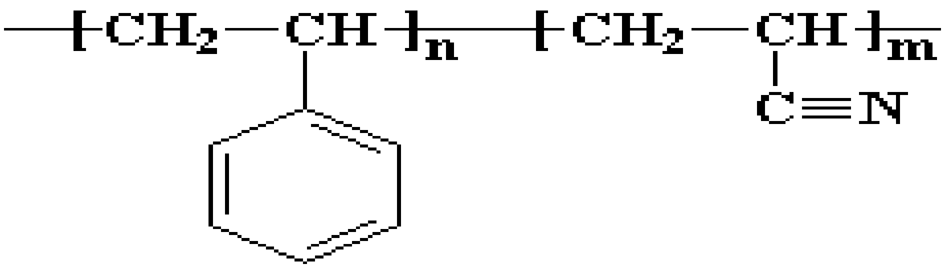

salt bridge
Cysteine Linkage


a dicarboxylic acid
a diamine
a polyamide

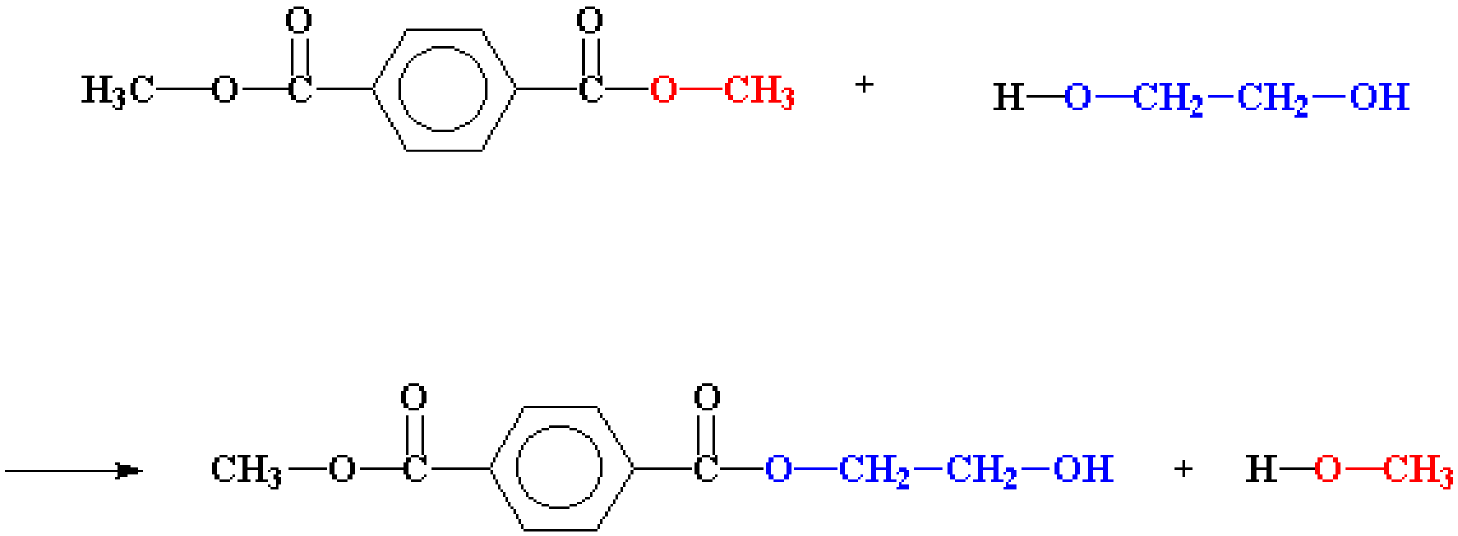

HO—C(=O)—▭—C(=O)—OH
+
HO—▭—OH
a dicarboxylic acid
a dialcohol
[—C(=O)—▭—C(=O)—O—▭—O—]n
a polyester

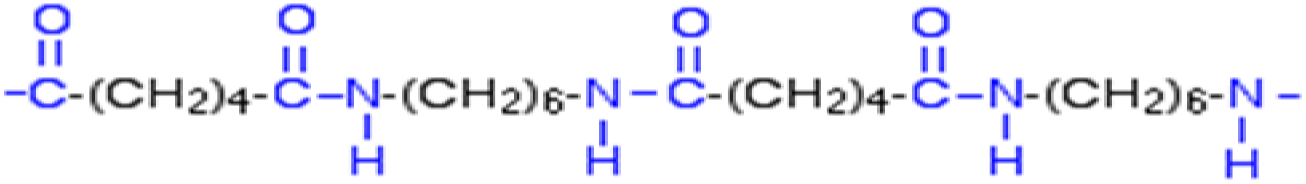


$$-\!\!\left[\mathrm{CH_2-\underset{\underset{\displaystyle C\equiv N}{|}}{CH}}\right]_n\!\!-$$

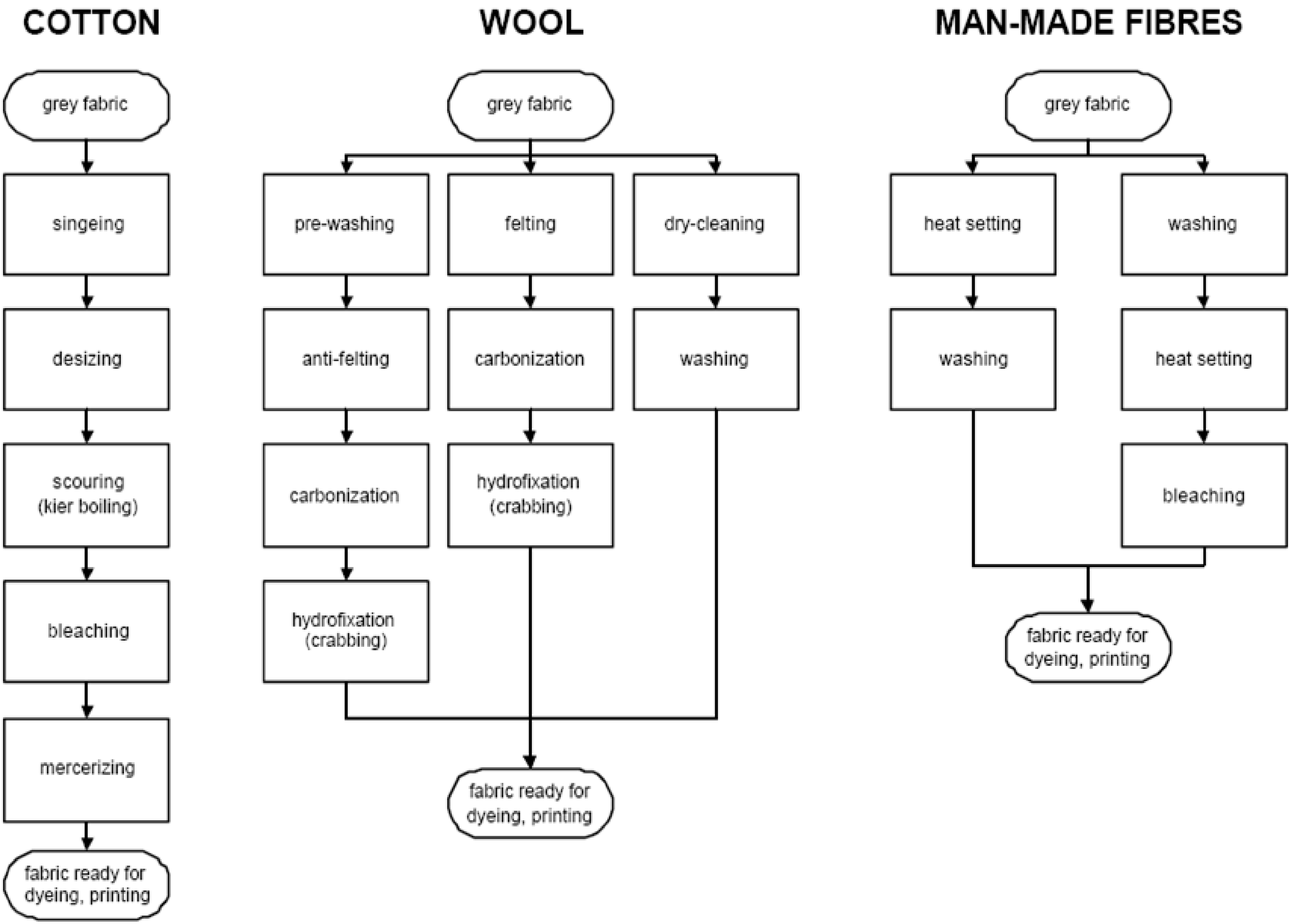


SAN





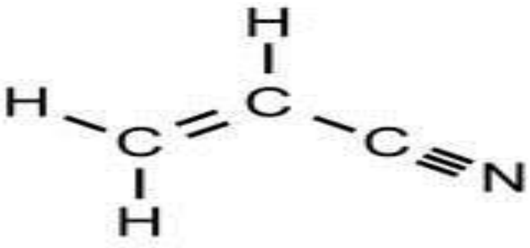
$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-$$

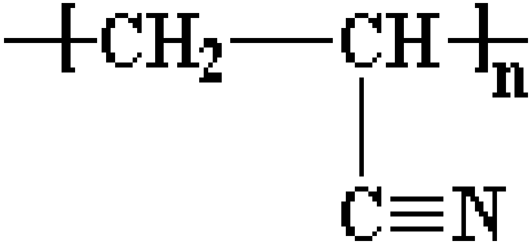


COTTON

WOOL

MAN-MADE FIBRES

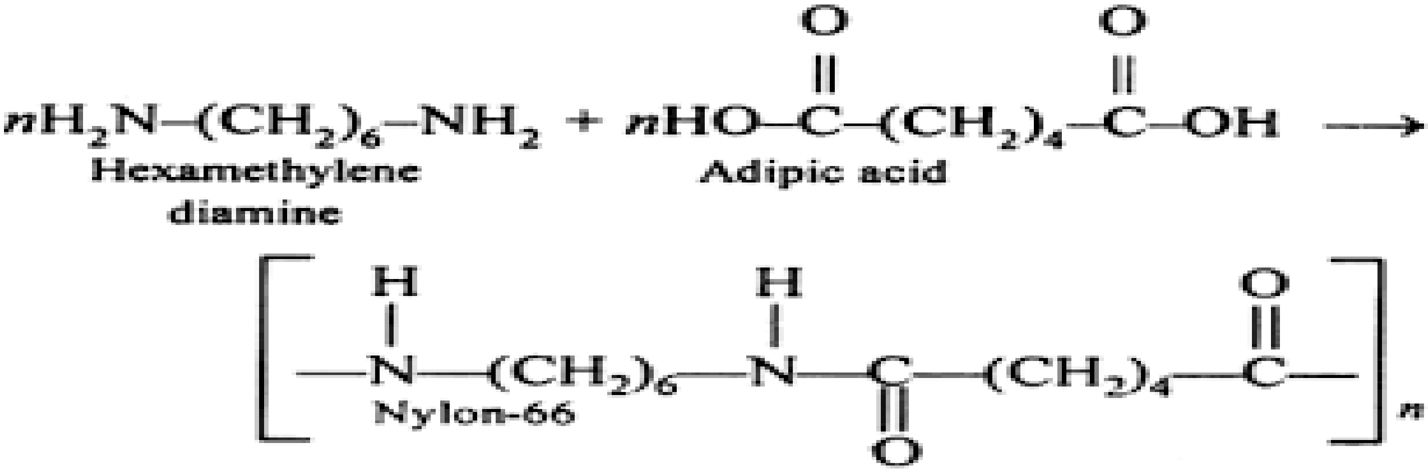




$$-\!\left[\mathrm{CH_2}-\underset{\displaystyle \mathrm{C\equiv N}}{\mathrm{CH}}\right]_{n}\!-$$

polyacrylonitrile

NYLON 6,6

- Composition:
- Nylon 6,6 is made of hexamethylenediamine and adipic acid, which give nylon 6,6 a total of 12 carbon atoms, and its name.
- 

$$nH_2N-(CH_2)_6-NH_2 + nHO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH \longrightarrow \left[-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\right]_n$$

Petrochemicals

These processes which use petroleum or natural gas or its derivatives to produce many of chemical compounds are called petrochemicals.

Steps for manufacture of petrochemicals

- First step:
- Convert petroleum derivatives as methane, ethane, butane and naphtha to basic petrochemicals as methanol, ammonia, ethylene, propylene, butadiene and benzene.
- Second step:
- Production of intermediate petrochemicals by conversion of basic petrochemicals to intermediate petrochemicals as vinyl chloride and ethylene oxide.

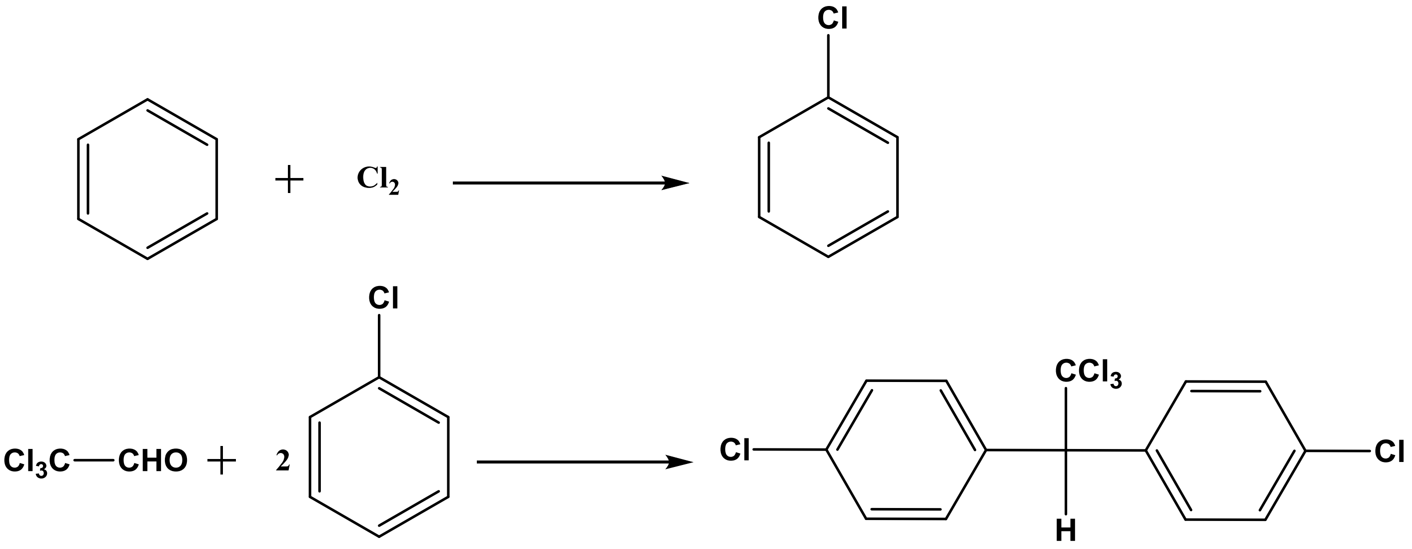
- Third step:
- Production of final petrochemicals by conversion of intermediate petrochemicals to final petrochemicals as polyethylene, polypropylene, PVC., and polystyrene.
- Fourth step:
- Production of consumed materials by conversion of final petrochemicals to consumed materials as plastics and water bottles.

Petrochemicals from Methane

- 1- Synthesis gas:
- CH_4 + H_2O -------------- $3H_2$ + CO
- CH_3-CH_2-CH_3 + $3H_2O$ ----------- $7H_2$ + 3CO
- $2CH_4$ + O_2 -------------- $4H_2$ + 2CO
- 2- Methanol:
- $2H_2$ + CO ---------------- CH_3OH

Petrochemicals from Methanol

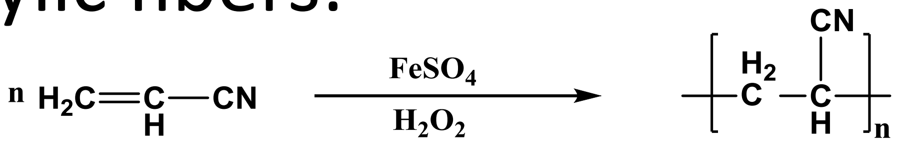
- CH_3OH ---------------- HCHO
- CH_3OH ---------------- CH_3COOH
- Insecticide:



D.D.T
dichlorodiphenyl-trichloro ethane

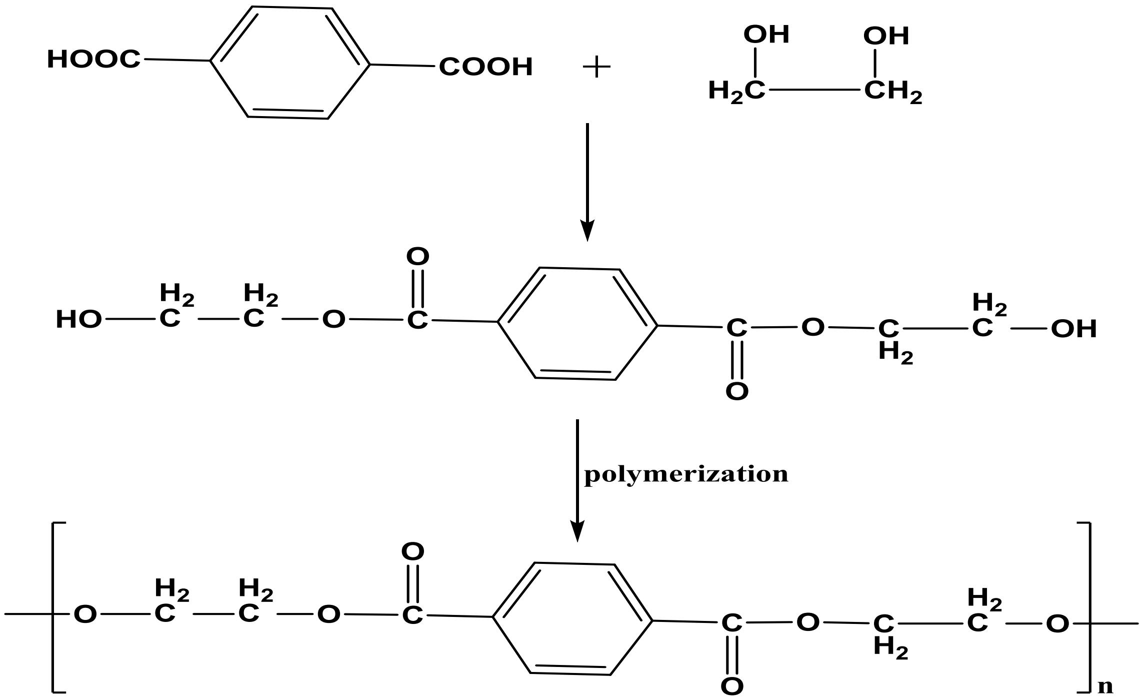
Synthetic Fibers

- 1- Acrylic fibers:

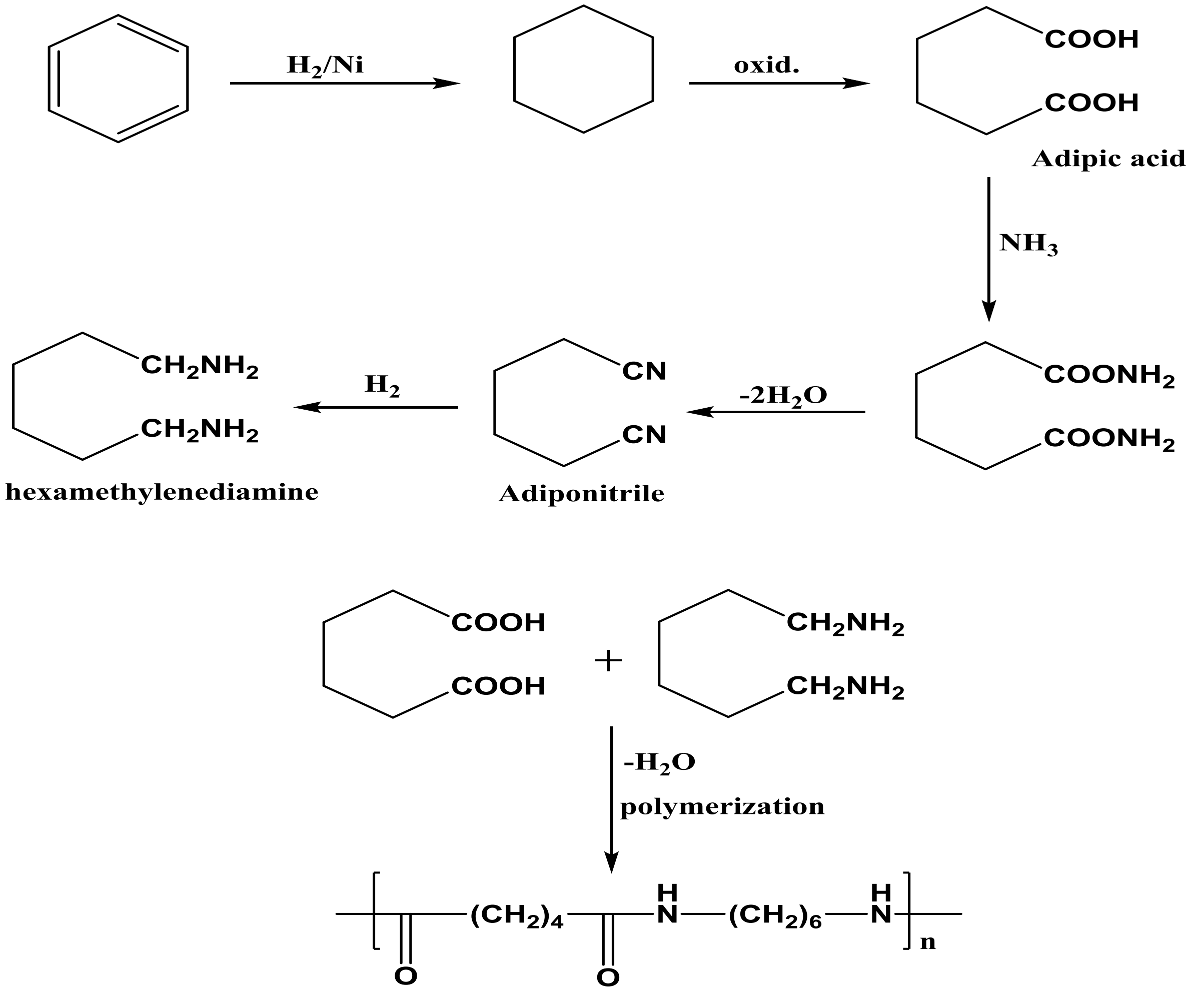


Arolon (Acrylic)

2- Polyester fibers:



3- Nylon6,6 fibers:



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