

BENZENE

B.PHARM SEMESTER III

PREPARED BY

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Physical properties of Benzene

Benzene is a colourless or light yellow liquid at room temperature. It has a sweet odour and is highly flammable.

Natural sources of benzene include volcanoes and forest fires. Benzene is also a natural part of crude oil, gasoline, and cigarette smoke.

IUPAC name Benzene

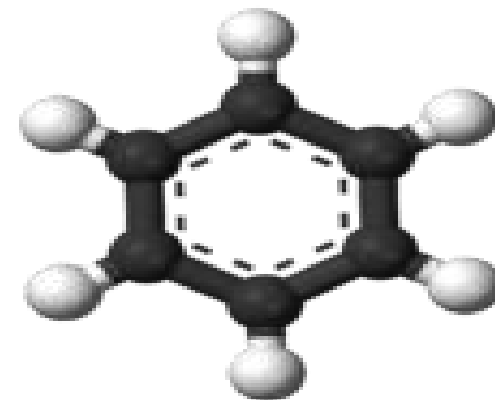
Other names

(*historic/German*)

Cyclohexa-1,3,5-triene; 1,3,5-

Cyclohexatriene

Benzol



Ball and stick model



Space-filling model

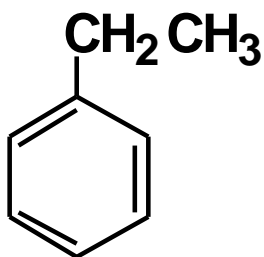
- Benzene is an organic chemical compound consisting of carbon and hydrogen atoms with alternating double bonds. As it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.
- The chemical formula of benzene is C_6H_6 , so it consists of six carbon atoms and six hydrogen atoms. joined in a ring with one hydrogen atom attached to each.



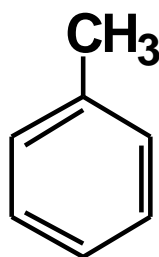
NOMENCLATURE

Monosubstituted alkylbenzenes are named as derivatives of benzene. For example, ethylbenzene.

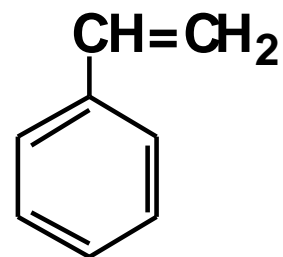
The IUPAC system retains certain common names for several of the simpler monosubstituted alkyl benzenes



Ethylbenzene



Toluene

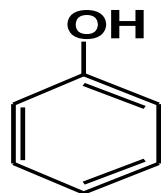


Styrene

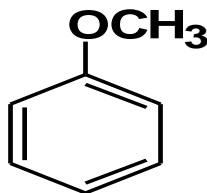


NOMENCLATURE

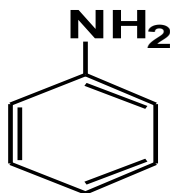
Common names for some monosubstituted benzenes are as follows



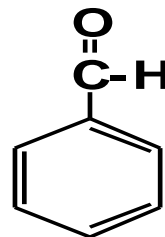
Phenol



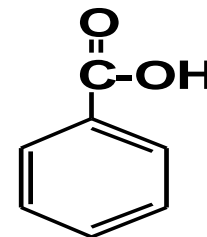
Anisole



Aniline

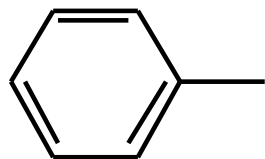


Benzaldehyde

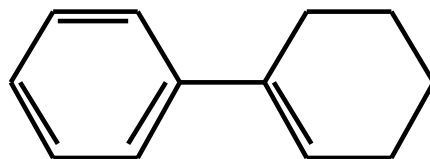


Benzoic acid

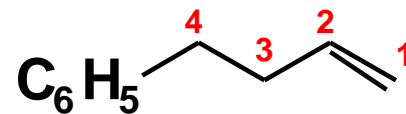
Phenyl group (C_6H_5- or $\text{Ph}-$): Derived by loss of an H from benzene,



Phenyl group



1-Phenylcyclohexene

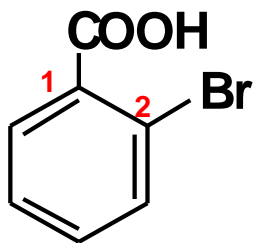


4-Phenyl-1-butene

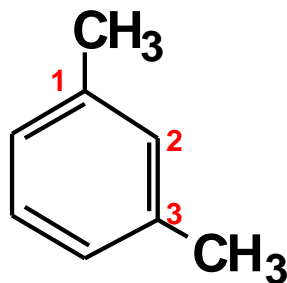
NOMENCLATURE

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

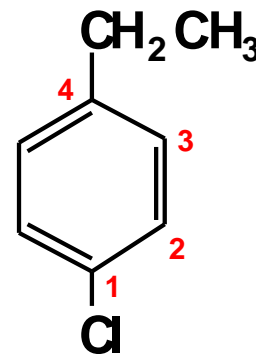
1. numbering the atoms of the ring or
2. using the locators ortho (o), meta (m), and para (p)



2-Bromobenzoic acid
(o-Bromobenzoic acid)



1,3-Dimethylbenzene
(m-Xylene)

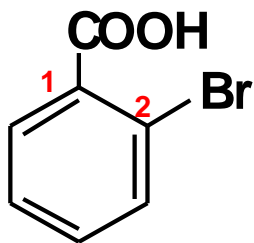


1-Chloro-4-ethylbenzene
(p-Chloroethylbenzene)

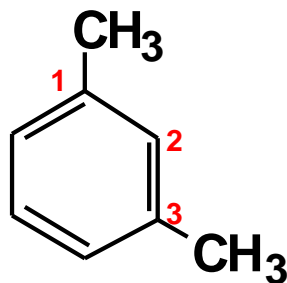
NOMENCLATURE

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

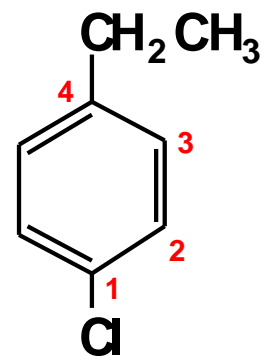
1. numbering the atoms of the ring or
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1,3-Dimethylbenzene
(m-Xylene)



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

STRUCTURE OF BENZENE

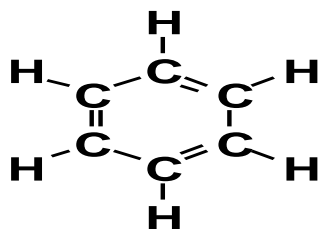
Facts that supported Kekulé Formula

- 1) Molecular formula
- 2) Open Chain Structure not accepted
- 3) Evidences in favor of Ring Structure
 - a) Catalytic Hydrogenation of benzene yields cyclohexane
 - b) Benzene yields one mono substitution product:
 - c) Benzene forms 3-di and trisubstituted product which can be explained on basic of ring structure.
- 4) Resonance hybrid Structure
- 5) Molecular Orbital Structure

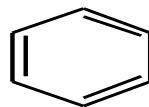
MOLECULAR FORMULA

1) Benzene has molecular formula- C_6H_6 .

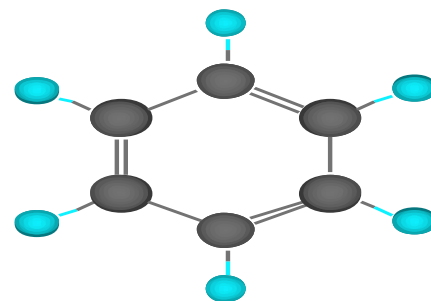
From its elemental composition and molecular weight, benzene was known to contain 6-C and 6-H atoms. Benzene has molecular formula C_6H_6 as compared to hexane C_6H_{12} which confirms that benzene is highly unsaturated than hexane. From this, it was concluded that 6-C atoms in the benzene were linked by double or triple bonds so as to form a straight chain or closed ring as proposed by Kekulé.



A Kekulé structure showing all atoms

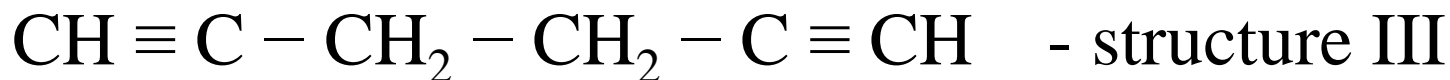
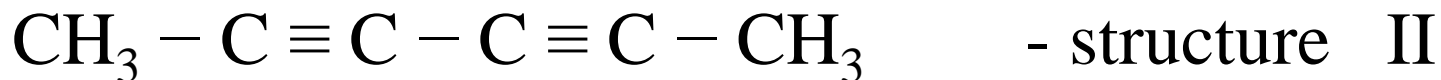


A Kekulé structure as a line-angle formula



2) OPEN CHAIN STRUCTURE NOT ACCEPTED

The possible open chain structure for benzene could have been

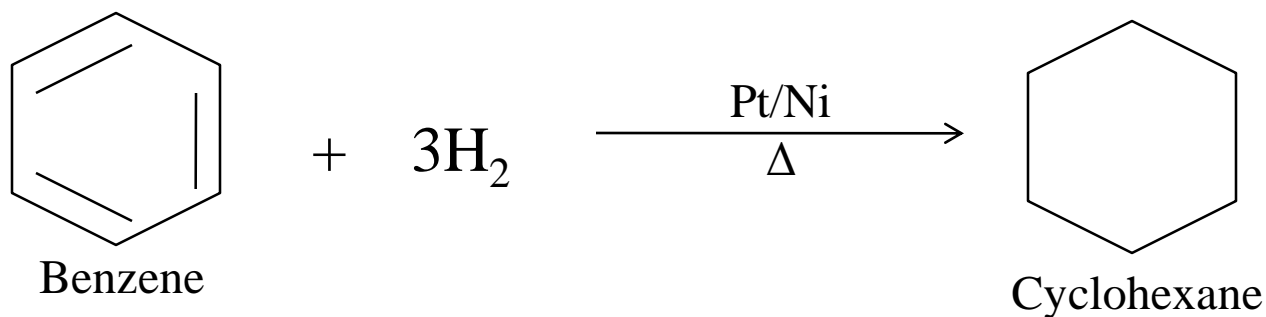


All these structures were ruled out because benzene didn't give the usual reactions of alkenes, alkynes

For example when above open chain structured compounds containing double and triple bonds are added to solution of bromine in carbon tetrachloride which is red in colour becomes colourless but benzene do not give this reactions benzene can not have open chain structure .

3) EVIDENCE IN FAVOR OF RING STRUCTURE

a) Catalytic Hydrogenation of benzene yields Cyclohexane



Since, hydrogenation is not bringing about any major structural change in carbon frame. It proves the presence of closed ring of 6-C atoms in Benzene molecule.

b) Benzene yields one mono substitution product:

If bromination is done, only one bromobenzene is obtained because 1-H atom is replaced by bromine. It is same in the case of Chlorobenzene and Nitrobenzene.

This proves that each Hydrogen must be exactly equidistant to other hydrogen since the replacement of any Hydrogen gives the same product and suppose we consider the open chain structure it would yield the isomeric monoderivatives, as all the Hydrogen atoms are not equal as shown in structures I, II & III

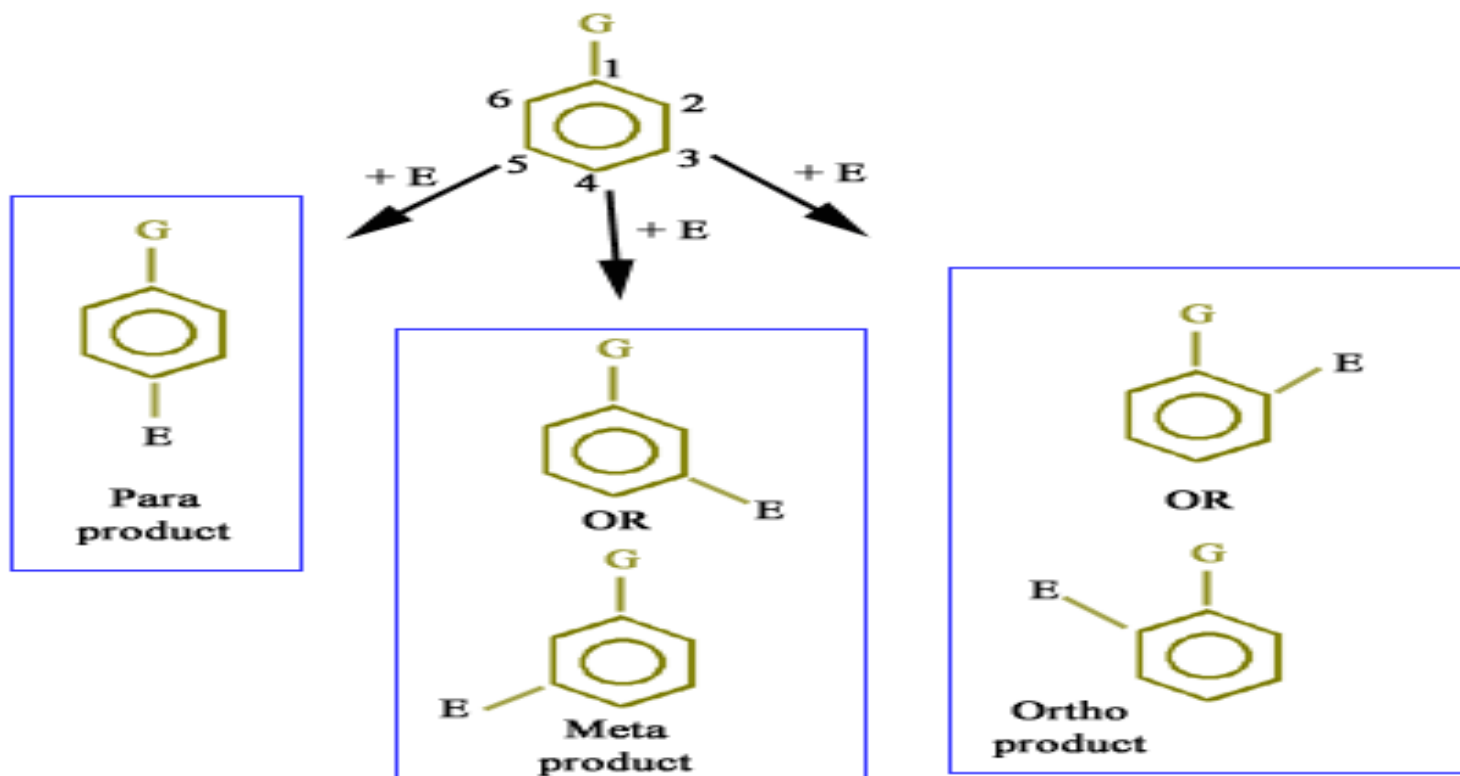
This could be possible only if 6 carbons in benzene are joined to each other to form a closed ring and one hydrogen atom is attached to each carbon.

C) BENZENE FORMS 3-DI AND 3-TRISUBSTITUTED PRODUCTS WHICH CAN BE EXPLAINED ON BASIC OF RING STRUCTURE.

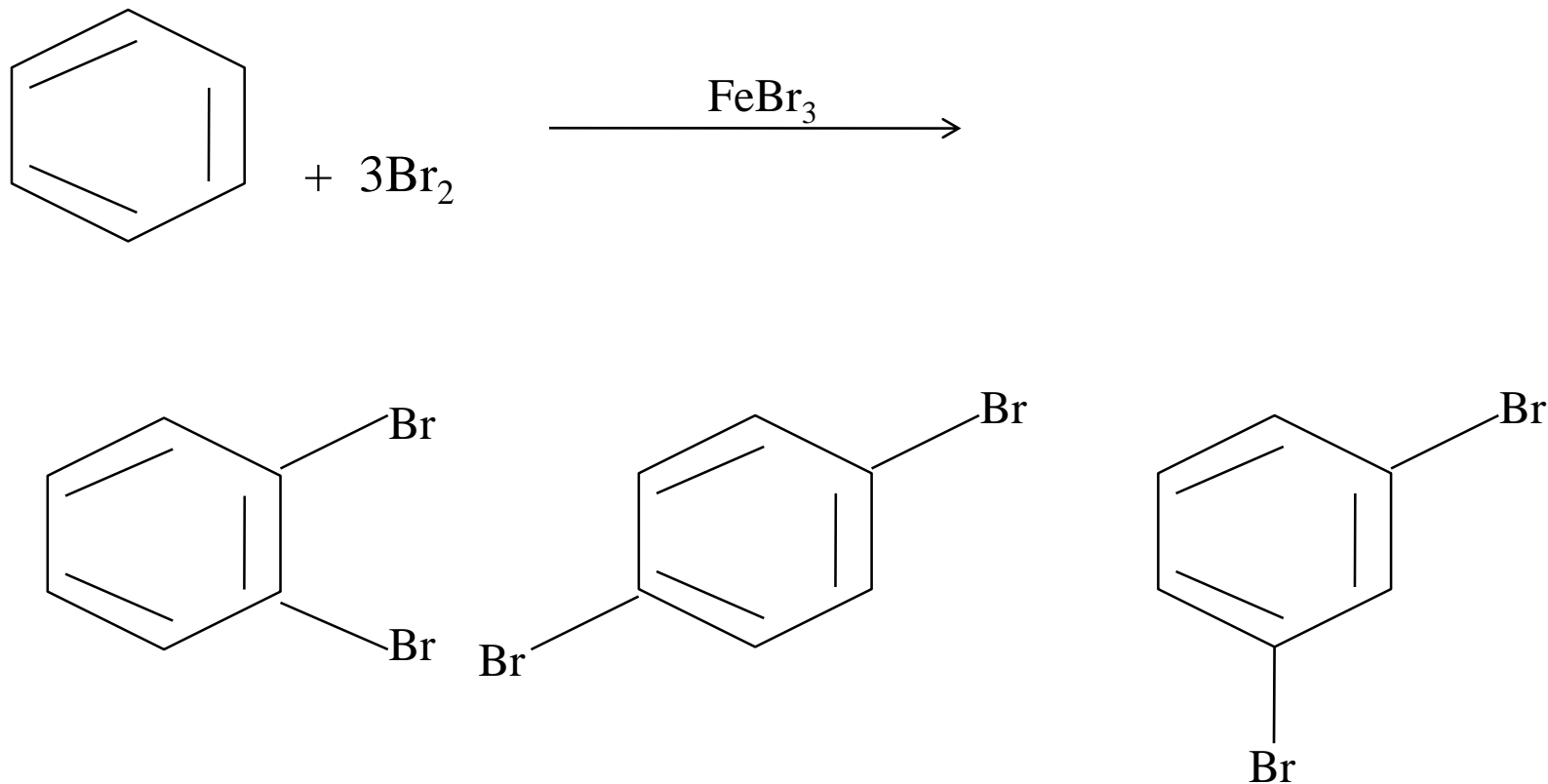
POSITIONS 2 AND 6 ARE SAME (ORTHO PRODUCT)

POSITIONS 3 AND 5 ARE SAME (META PRODUCT)

POSITION 4 IS PARA POSITION

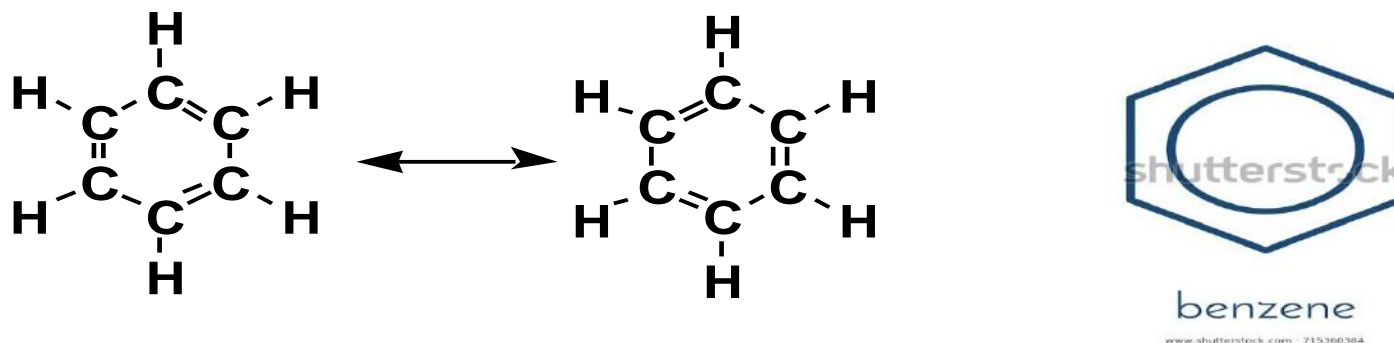


Benzene forms 3-di and trisubstituted product which can be explained on basis of ring structure.



Positions 2 and 6 are same (ortho product) Positions 3 and 5 are same (meta product) therefore only three dibromobenzene are possible. Straight Chain structure will give more than 3 di or trisubstituted products.

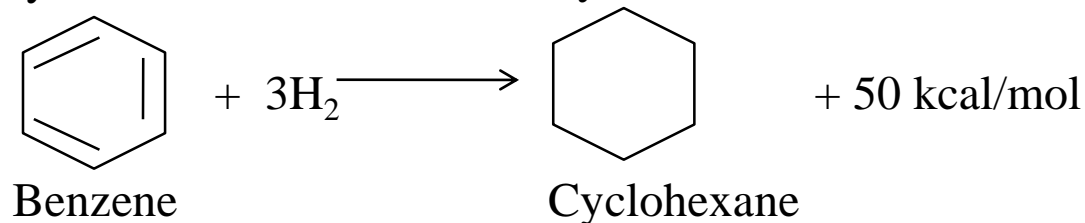
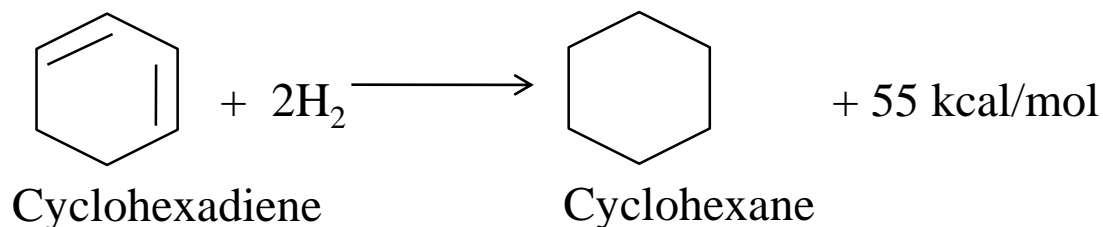
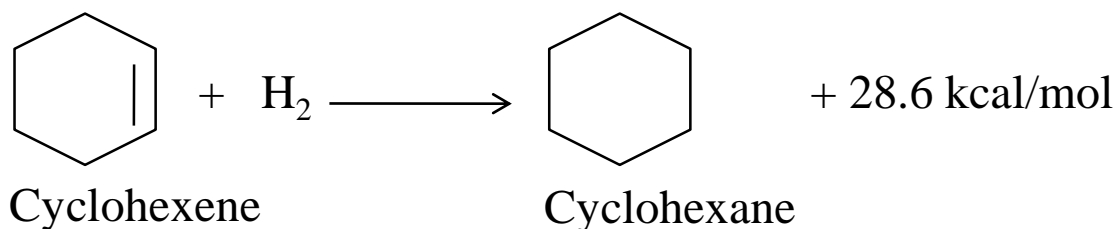
RESONANCE HYBRID STRUCTURE OF BENZENE



The above Kekulé structures of benzene differ in position of electrons. Benzene is a hybrid of structures I & II are exactly equivalent and have same stability and they make equal contribution to the hybrid structure. The resonance stabilization energy which is responsible for the unusual stability of benzene can be calculated from the measurement of heat of combustion or heat of hydrogenation

STABILITY OF BENZENE

Stability of benzene can be explained in the following way Heat of Hydrogenation is the quantity of heat evolved when mole of an unsaturated compound is hydrogenated. Addition of Hydrogen to a double bond is an exothermic reaction. As heat is given out in hydrogenation means the product in each case is more stable than the original one.



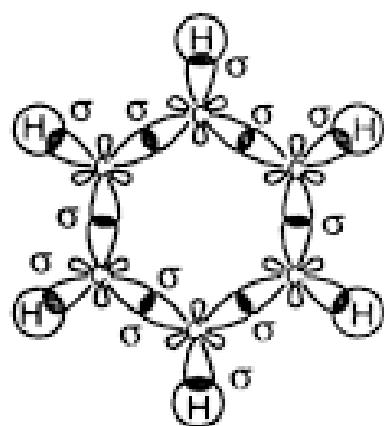
Cyclohexene has heat of hydrogenation 28.6 kcal/mol and cyclohexadiene has its twice i.e. 55 kcal/mol so we expect cyclohexatriene to have heat of hydrogenation about three times as large as cyclohexene which should be about 85.8 kcal/mol and value of benzene is 50 kcal/mol i.e. when benzene is actually hydrogenated only 50 kcal/mol of heat is evolved .So difference

$85.8 - 50 \text{ kcal/mol} = 35.8 \text{ kcal/mol}$. It is resonance stabilization energy of benzene

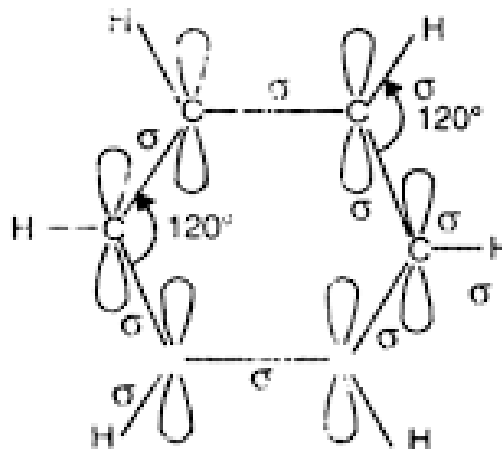
MOLECULAR ORBITAL STRUCTURE

By the X ray diffraction mechanism ,it is proved that benzene consists of planar hexagon of 6-c atoms havinh all c-c bonds equal in length i.e. 1.4 Angstron c-c-c bond angle is 120 degrees .Therefore ,it can be proved that each of this 6-c in benzene ring is in the state of trigonal hybridization.The ring system is costructed from six sp^2 -hybridized carbons by the overlapping of two hybrid orbitals each to form sigma bonds

The structure of benzene molecule is best described in terms of molecular orbital treatment theory. According to this theory, all the C-atoms in benzene are sp^2 -hybridized. Remaining six sp^2 -orbital of six C-atoms overlap with 1s orbital of six H-atoms individually to form six sigma bonds.



Formation of C-C
and C-H
sigma bonds



Sigma skeleton of
benzene molecule

HUCKEL'S RULE AND AROMATICITY

The complete delocalization of π electrons caused by side-side overlapping gives benzene aromatic character. An aromatic compound must contain $4n+2$ electrons ($n=0, 1, 2$, and so forth). Cyclic, planar and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be antiaromatic. Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is antiaromatic and especially unstable because it contains 4π electrons.

Benzene
An aromatic compound



$$4n + 2 = 4(1) + 2 = 6 \pi \text{ electrons}$$

aromatic

Cyclobutadiene
An antiaromatic compound



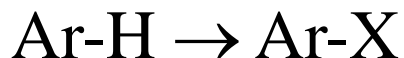
$$4n = 4(1) = 4 \pi \text{ electrons}$$

antiaromatic

Reactions of Benzene

Characteristic reaction of benzene involves substitution in which resonance stabilized ring is preserved. This reaction is called Aromatic Substitution.

Compared to sigma bonds pi electrons are loosely held and are available to the reagent i.e. seeking electrons. So typical reaction of benzene is electrophilic substitution reaction, where hydrogen of aromatic ring is substituted by an atom or group



GENERAL MECHANISM OF ELECTROPHILIC SUBSTITUTION REACTIONS.

Aromatic substitution reactions are initiated by the attack of electrophile on the ring followed by the elimination of proton. Such reactions are called electrophilic substitution reactions.

Benzene with its pi electrons behaves as an electron rich system. Electrons in the pi clouds are readily available to form a new bond with electron deficient species, i.e. the electrophile. Electrophilic substitution reactions follow the following mechanism

Step-1:Generation of electrophile either by spontaneous dissociation of reagent or by acid catalyzed dissociation

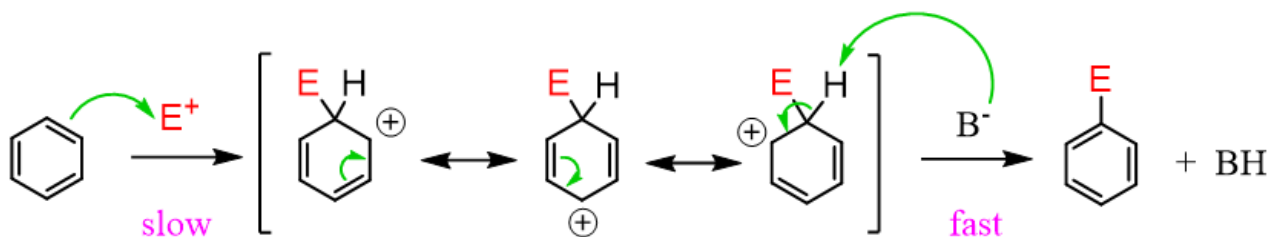


Step-2:Formation of the π -complex first then σ -complex

π -complex forms by association of electrophile with the aromatic ring .In this π -complex,an electrophile is not attached to any specific position of ring but later it rearranges to give σ -complex. σ -complex is a resonance hybrid of stabilized carbonium (arenium) ion produced by the attack of electrophile on benzene ring

Step-3:A proton H^+ is then eliminated from σ -complex by the base to yield the final substitution product.

The Mechanism of Electrophilic Aromatic Substitution



Step 1. Addition of
the electrophile-
Making the C-E bond

Sigma Complex
Resonance stabilized Arenium ion

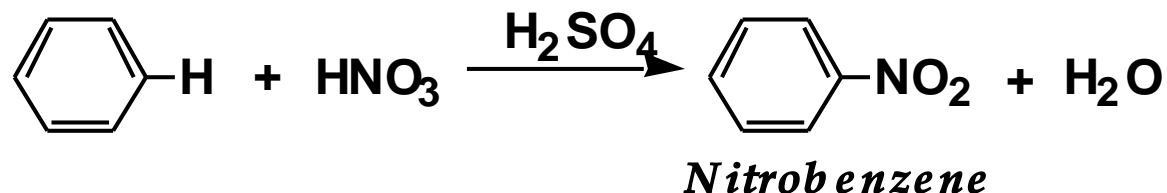
Step 2. Proton transfer-
Restoring Aromaticity

HALOGENATION

NITRATION AND SULFONATION

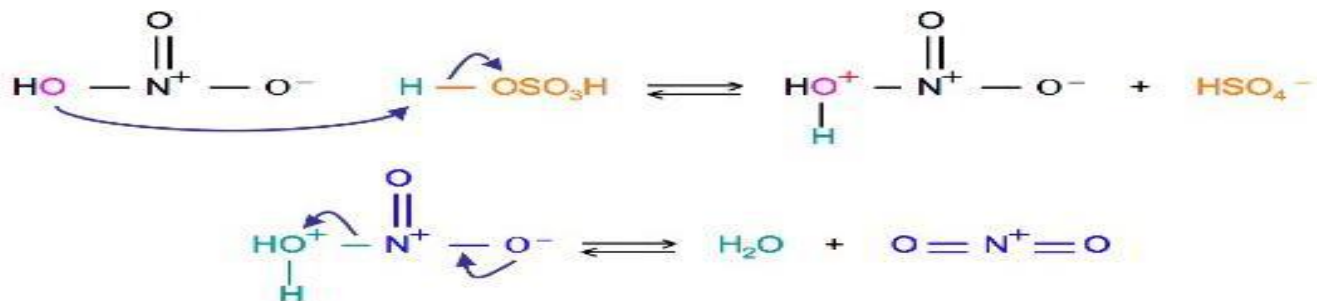
Nitration and sulfonation of benzene are two examples of electrophilic aromatic substitution. The nitronium ion (NO_2^+) and sulfur trioxide (SO_3) are the electrophiles and individually react with benzene to give nitrobenzene and benzenesulfonic acid respectively.

NITRATION OF BENZENE



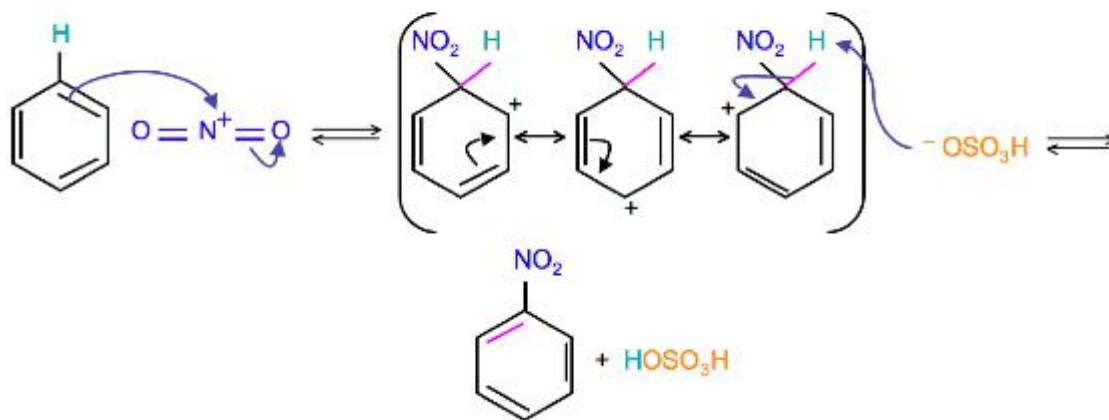
Mechanism

Step-1- Generation of electrophile HNO_3 is activated with sulfuric acid through protonation which then causes the loss of a water molecule and forms a nitronium ion, which is a stronger electrophile,.



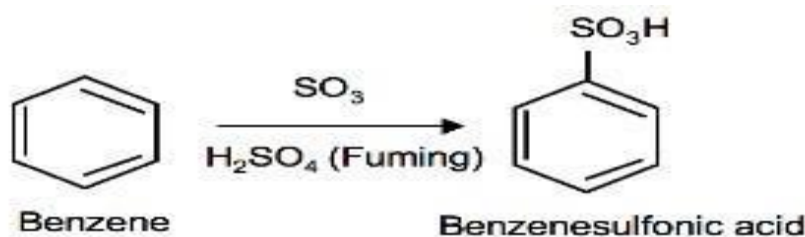
NITRATION OF BENZENE

Step-2 & Step-3- Formation of the σ -complex and then elimination of proton H^+ from σ -complex takes place to get the final product



SULFONATION

Sulfonation is a reversible reaction that produces benzenesulfonic acid by adding sulfur trioxide and fuming sulfuric acid. The reaction is reversed by adding hot aqueous acid to benzenesulfonic acid to produce benzene.

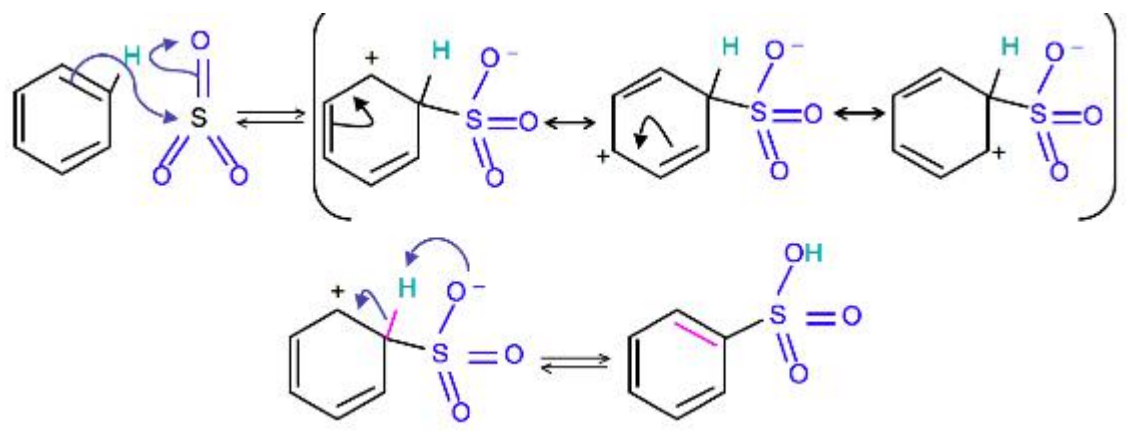


MECHANISM OF SULFONATION

Step-1-Generation of electrophile

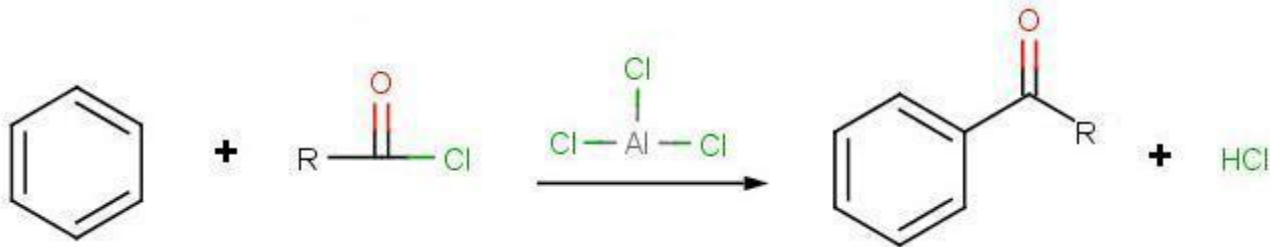
The sulfur in sulfur trioxide is electrophilic because the oxygens pull electrons away from it as oxygen is very electronegative. To produce benzenesulfonic acid from benzene, fuming sulfuric acid and sulfur trioxide are added. Fuming sulfuric acid, also referred to as *oleum*, is a concentrated solution of dissolved sulfur trioxide in sulfuric acid.

STEP-2 & STEP-3- THE BENZENE ATTACKS THE SULFUR AND SUBSEQUENT PROTON TRANSFERS OCCUR TO PRODUCE BENZENESULFONIC ACID. I.E. FORMATION OF THE σ -COMPLEX AND THEN ELIMINATION OF PROTON H^+ FROM σ -COMPLEX TAKES PLACE TO GET THE FINAL PRODUCT



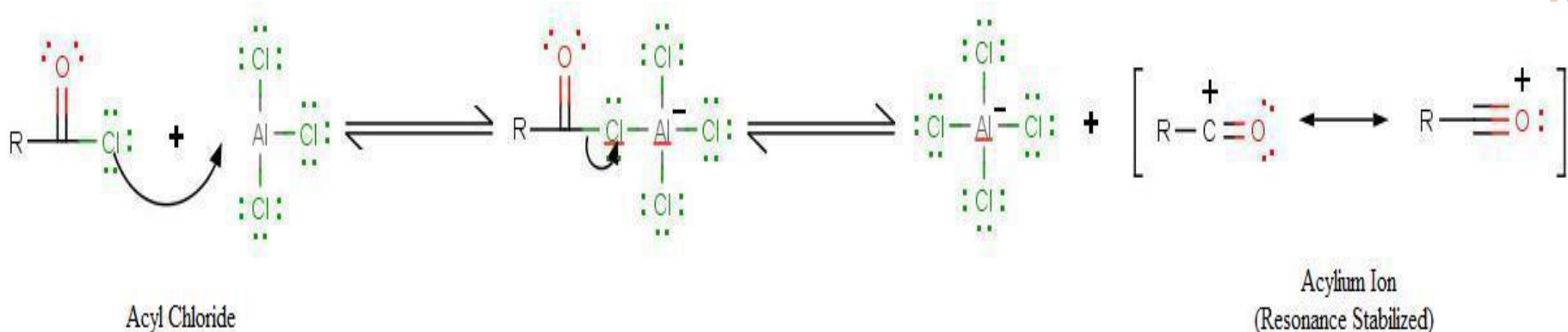
FRIEDEL CRAFTS ACYLATION

This reaction involves the introduction of RCO (acyl) group in the aromatic ring in presence of AlCl_3 , BF_3 , FeCl_3 etc

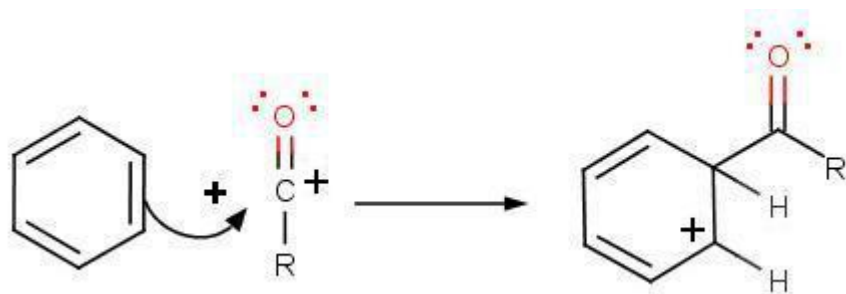


MECHANISM

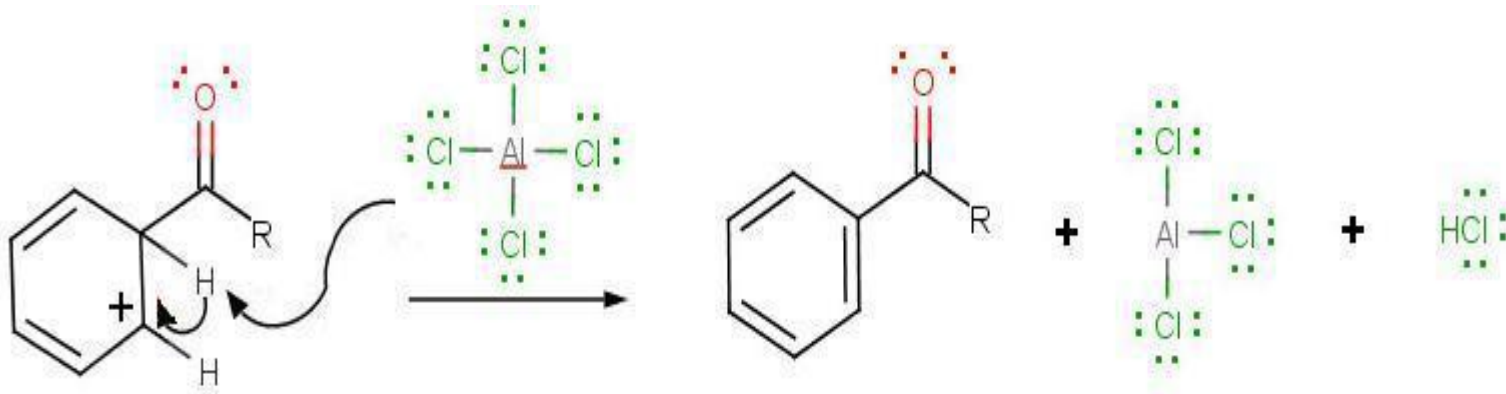
Step 1- The very first step involves the generation of the electrophile i.e. the acylium ion



Step 2- The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:

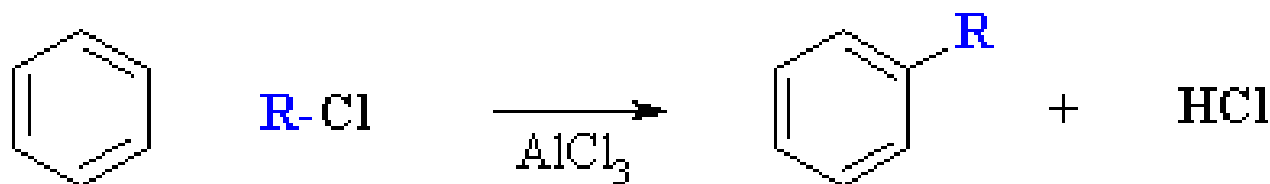


Step 3- The third step involves the departure of the proton in order for aromaticity to return to benzene



FRIEDEL CRAFTS ALKYLATION

This reaction involves the attack of an alkyl group in benzene in presence of anhydrous aluminum chloride. This reaction is called the **Friedel-Crafts alkylation reaction**. Overall transformation: **Ar-H** to **Ar-R**



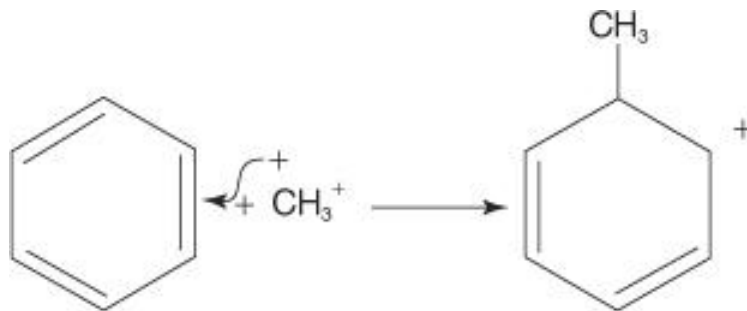
The mechanism for this reaction begins with the generation of a methyl carbocation from methylbromide. The carbocation then reacts with the π electron system of the benzene to form a nonaromatic carbocation that loses a proton to reestablish the aromaticity of the system.

FRIEDEL CRAFTS ALKYLATION

1. **Step 1-** The first step involves the generation of the electrophile methyl carbocation by the reaction of methylchloride with aluminum chloride.

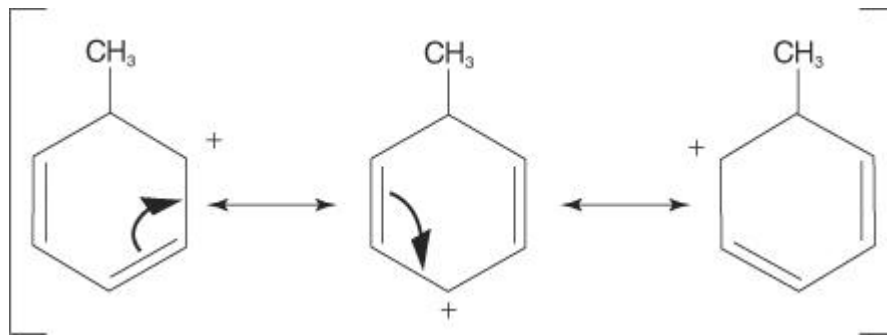


2. **Step 2-** The electrophile attacks the π electron system of the benzene ring to form a nonaromatic carbocation.

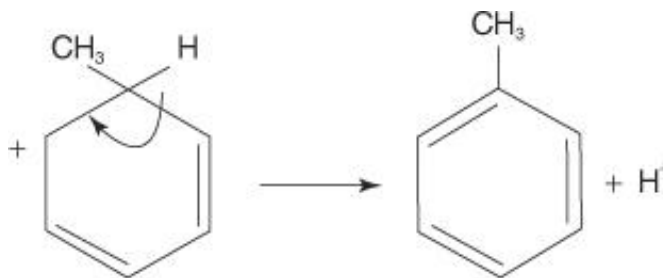


FRIEDEL CRAFTS ALKYLATION

The positive charge on the carbocation that is formed is delocalized throughout the molecule.



Step 3- The aromaticity is restored by the loss of a proton from the atom to which the methyl group has bonded.

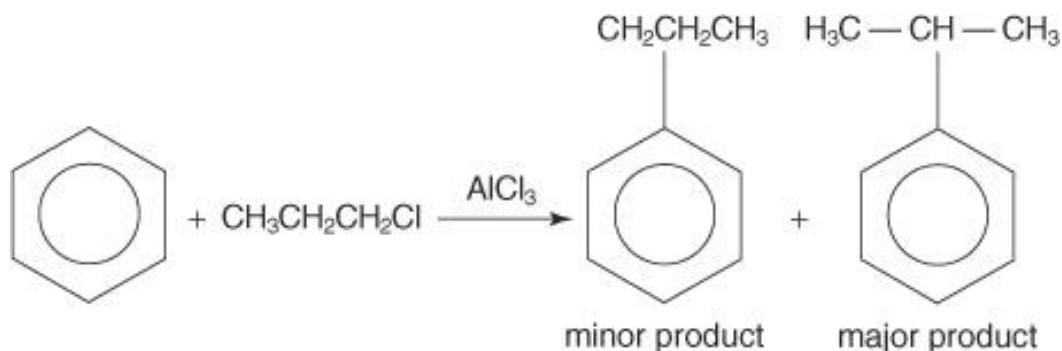


FRIEDEL CRAFTS ALKYLATION

Step 4- Finally, the proton reacts with the AlCl_4^- to regenerate the AlCl_3 catalyst and form the product HCl .



Carbocations can rearrange during the Friedel-Crafts alkylation reaction, leading to the formation of unpredicted products. One example is the formation of isopropyl benzene by the reaction of propyl chloride with benzene.



REFERENCES

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- Textbook of Organic Chemistry: Arun Bahl, B.S.Bahl.
- Essentialsof Physical Chemistry Arun Bahl, B.S.Bahl.G.D.Tuli
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THANK YOU