

AROMATIC HYDROCARBONS

CHAPTER NO. "4"

B.Sc. "ORGANIC"

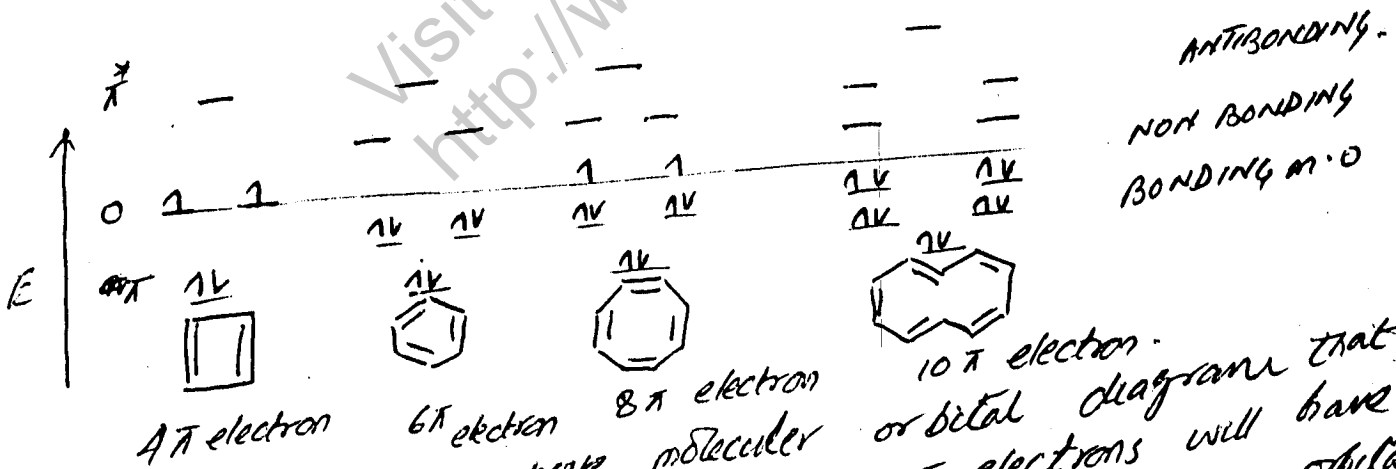
WHAT ARE AROMATIC COMPOUNDS?

The word AROMATIC means "fragrant". In the past sweet smelling compounds of benzene were called aromatic and all other compounds like alkanes, alkenes, alkynes were called ALIPHATIC. But these days word aromatic is used for all those compounds which are highly unsaturated according to their molecular formula, but show low reactivity and high stability towards addition reactions. Some examples of aromatic compounds are Benzene (C_6H_6), Naphthalene " $C_{10}H_8$ " Pyridine, Furan, Thiophene etc.

AROMATICITY - "THE HUCKEL RULE":

Huckel in 1931 noted that when Schrodinger equation is solved for a π -system of a regular planar, monocyclic polyene, there is a very simple characteristic pattern of molecular orbitals. There is always an orbital of lowest energy followed by pairs of degenerate orbitals of increasing energies. Finally there is an orbital of highest energy.

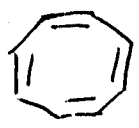
(The orbital energies of cyclobutadiene, benzene, cyclooctatetraene, and cyclodecapentaene is shown below (It is assumed that each one of these is planar))



It is clear from above molecular orbital diagrams that a system with 2, 6, 10 or more π electrons will have benzene like stability. In these system lowest energy orbital and bonding molecular orbitals are filled. Cyclobutadiene and cyclooctatetraene (4, 8, 12, ...) π electrons will be unstable because of two unpaired electrons. It is called diradical system.

Huckel rule states that, A cyclic conjugated, planar polyene will be aromatic if it contains $(4n+2)\pi$ electrons ($n=0,1,2,3,\dots$) Thus a system with 2, 6, 10 will be aromatic. On the other hand a system with 4, 8, 12 electrons will be quite unstable due to diradical. Such a system will be highly unstable.

UNSTABILITY OF CYCLOOCTATETRAENE According to Huckel rule cyclooctatetraene is expected to be highly unstable due to diradical nature. But it behaves like an alkene. It is due to nonplanar tub shaped structure.

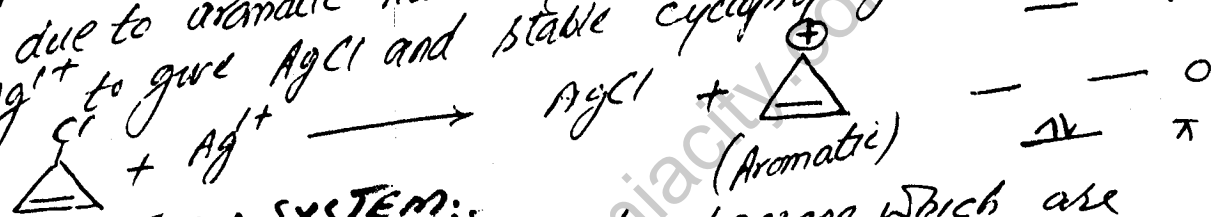


Planar cyclooctatetraene (Unstable)



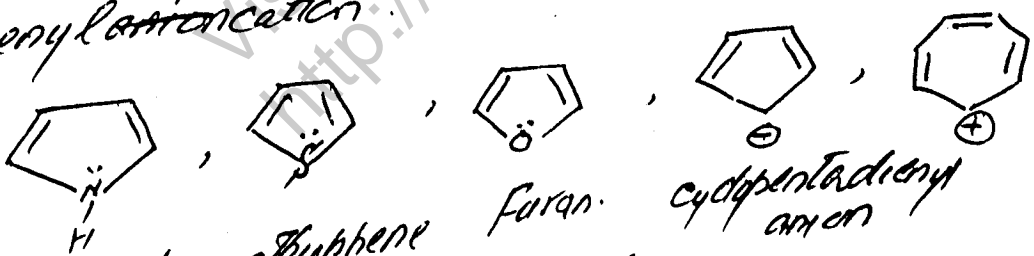
(Stable) cyclooctatetraene

"2- π -ELECTRON SYSTEM:- cyclopropenyl cation is quite stable due to aromatic nature. Thus 3-chloropropene reacts with Ag^+ to give $AgCl$ and stable cyclopropenyl cation.



6- π -ELECTRON SYSTEM:-

There are several compounds besides benzene which are cyclic conjugated planar and have 6- π electrons, and these are all aromatic. Examples of such compounds are pyrrole, furan, thiophene, cyclopentadienyl anion and cycloheptatrienyl anion.

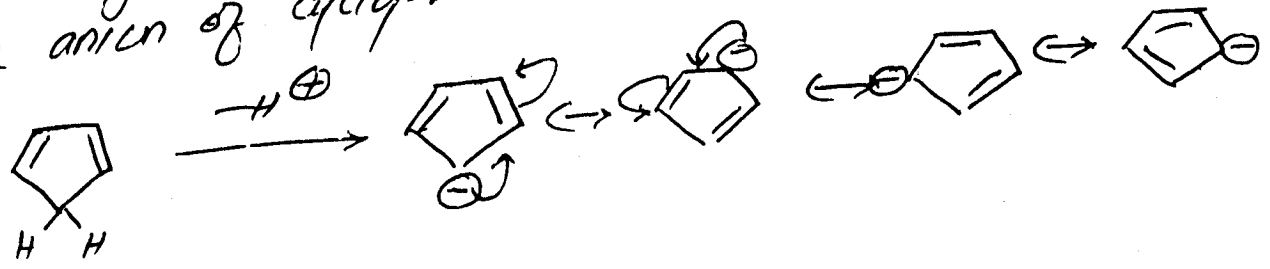


Pyrrole, Thiophene, Furan, Cyclopentadienyl anion, Tropylium ion.

The orbital of all such systems is shown below

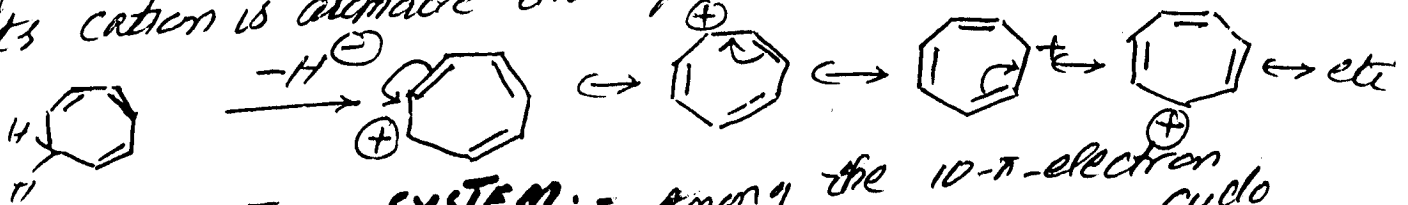
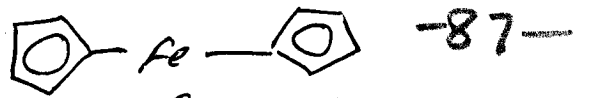
CYCLOPENTADIENE IS ACIDIC WHY?

The strength of acid depends upon stability of anion formed. The anion of cyclopentadiene is aromatic and stable.



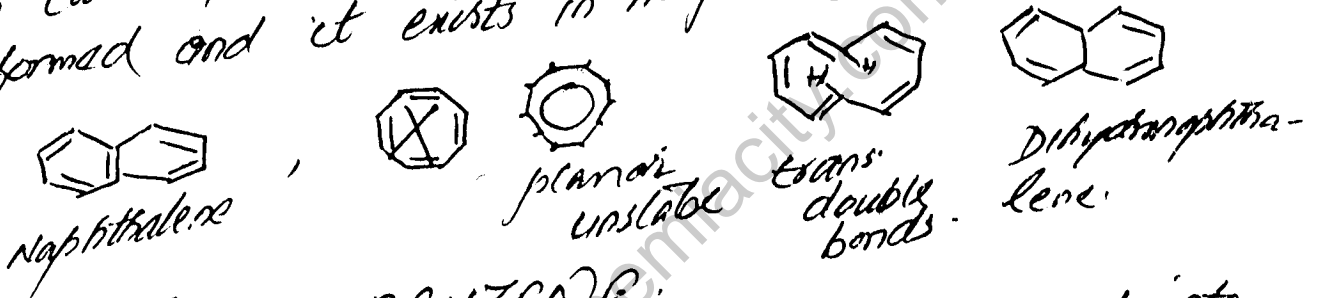
This ferrocene $[C_5H_5]_2Fe^{2+}$ is a stable complex of iron with cyclopentadienyl anion
CYCLOHEPTATRIENE IS BASIC

If cycloheptatriene loses H^+ (Hydrogen ion) ferrocene its cation is aromatic thus quite stable



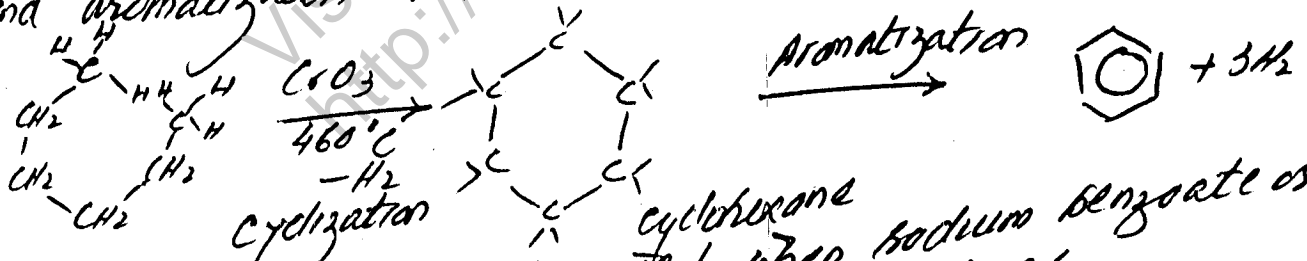
10- π ELECTRON SYSTEM:-

Among the 10- π -electron system naphthalene is a stable aromatic compound. Cyclo penta decapentaene should be stable aromatic comp. according to Huckel rule. But all cis d.b. in planar structure has serious angular strain. The two trans d.b. have two hydrogen atoms inside the ring. These two cause steric hindrance thus planar structure is deformed and it exists in nonplanar ~~planar~~ structure

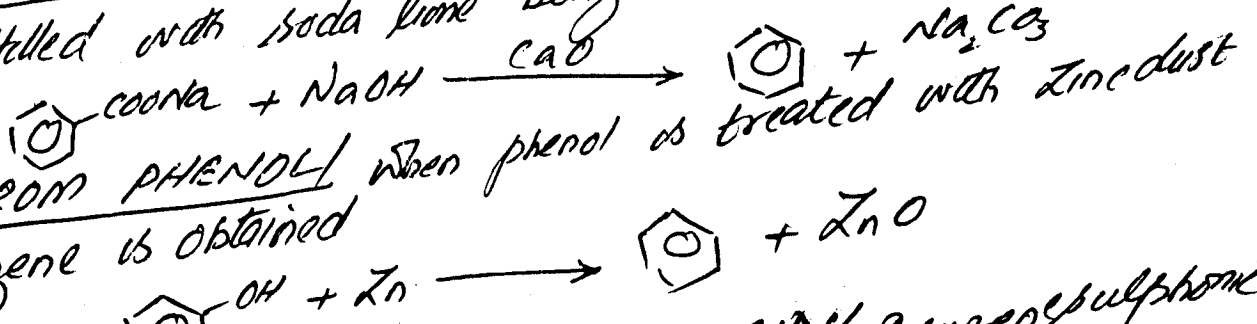


PREPARATION OF BENZENE.

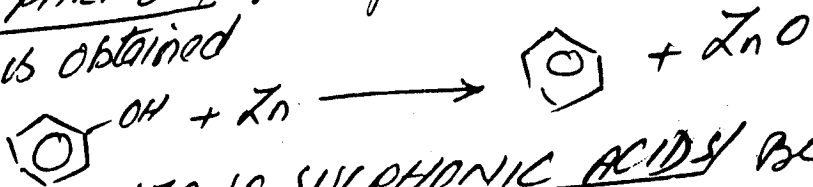
1) FROM PETROLEUM n-Hexane can be converted into benzene by catalytic reforming which includes cyclization and aromatization - n-Hexane is obtained from petroleum.



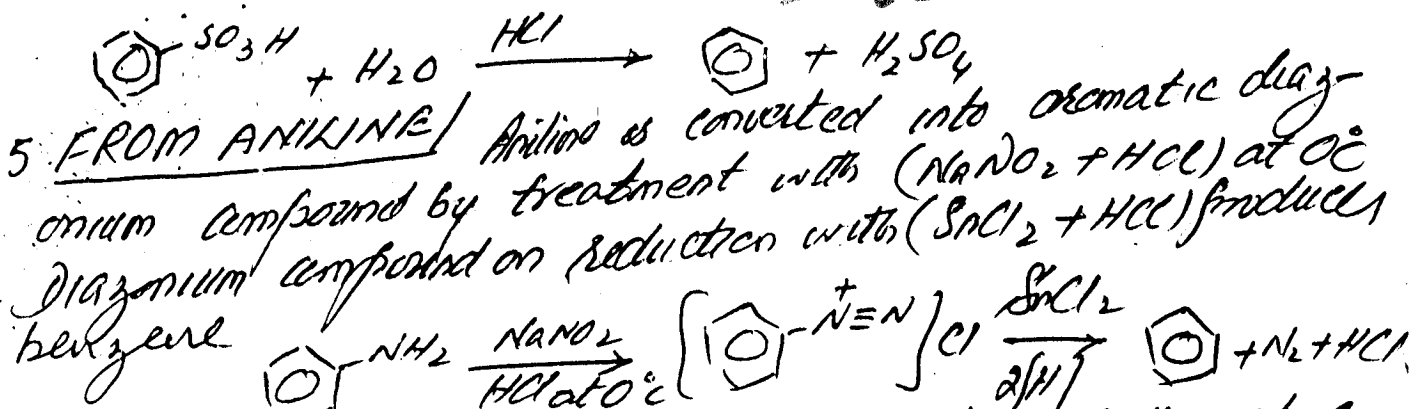
2 FROM SODIUM BENZOATE when sodium benzoate is distilled with soda lime benzene is obtained.



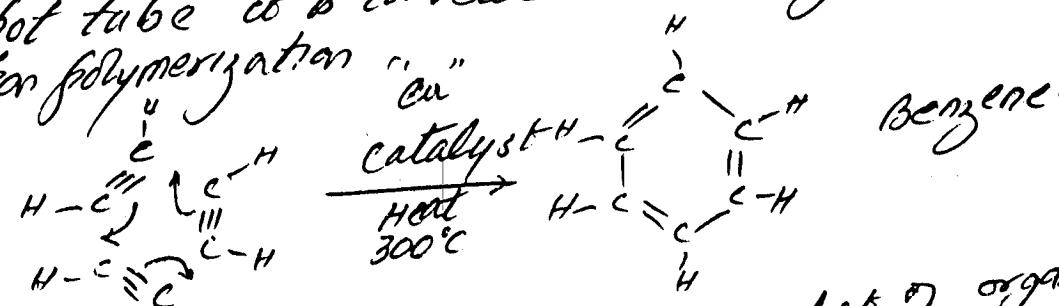
3 FROM PHENOL when phenol is treated with zinc dust benzene is obtained



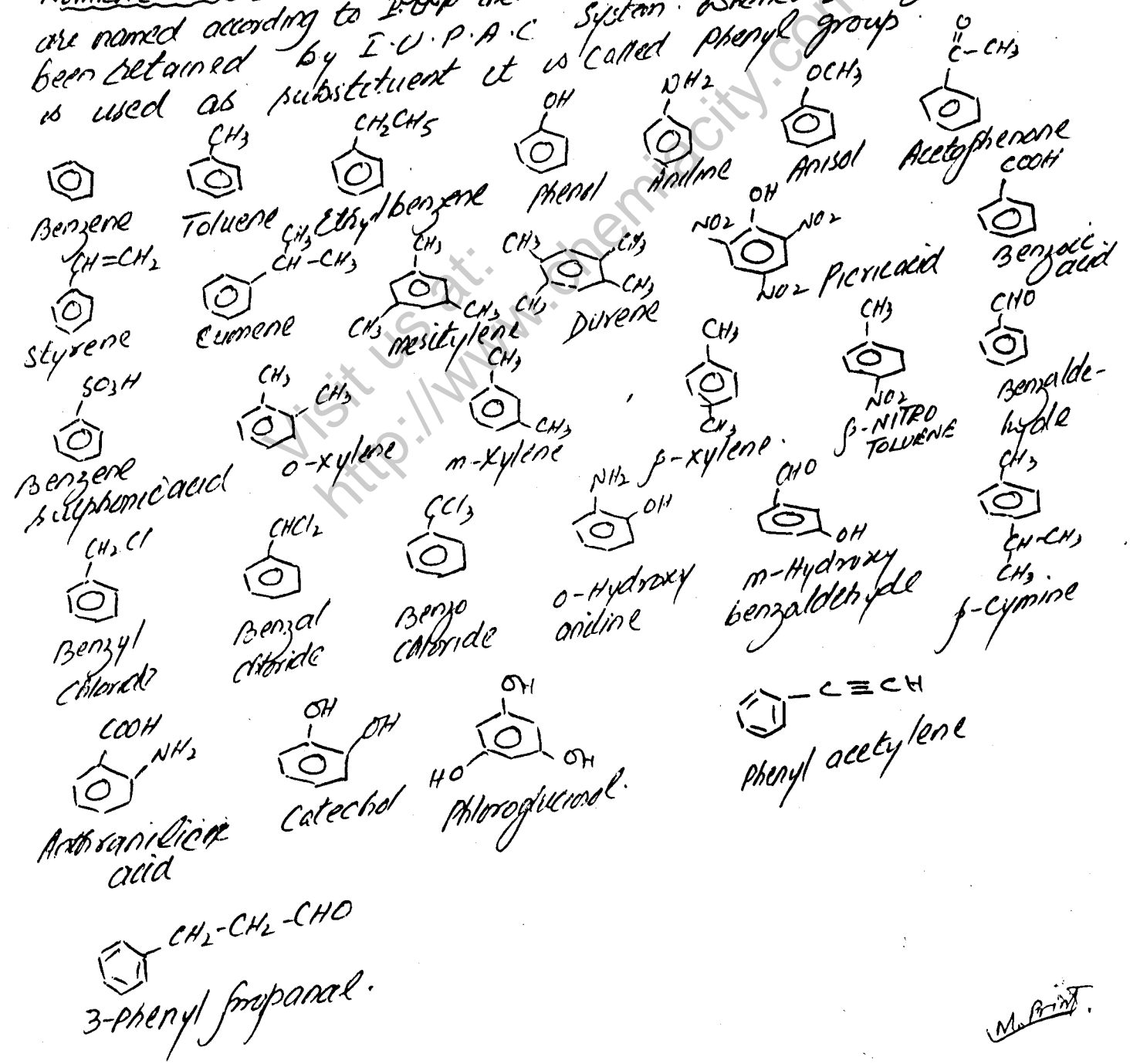
4) FROM BENZENE SULPHONIC ACIDS Benzenesulphonic acid on hydrolysis with "HCl" produces benzene



6. FROM ACETYLENE When acetylene is passed through a red hot tube it is converted into benzene. This is called addition polymerization.



NOMENCLATURE OF AROMATIC COMPOUNDS. Most of organic comp. are named according to I.U.P.A.C system. Whenever benzene ring is used as substituent it is called phenyl group.

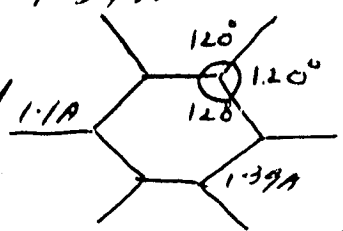


M. Prasad

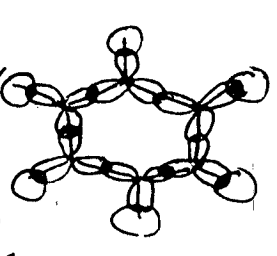
MOLECULAR ORBITAL TREATMENT OF BENZENE

Spectroscopic analysis show that benzene has a regular hexagonal planar structure with C-C bond angle 120° . Each carbon to carbon bond length is 1.39 \AA .

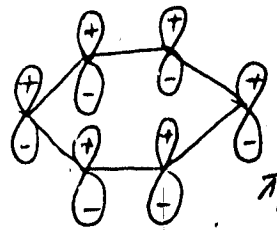
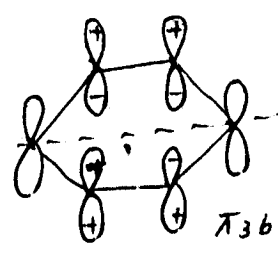
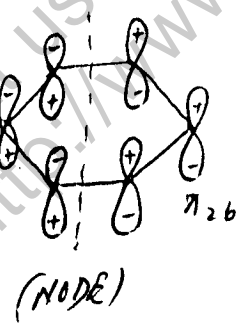
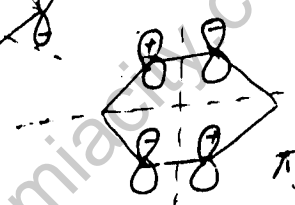
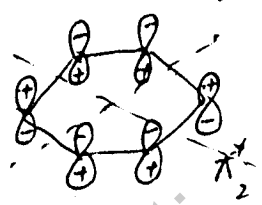
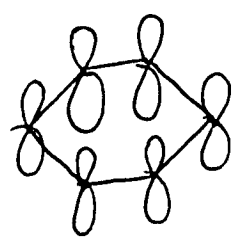
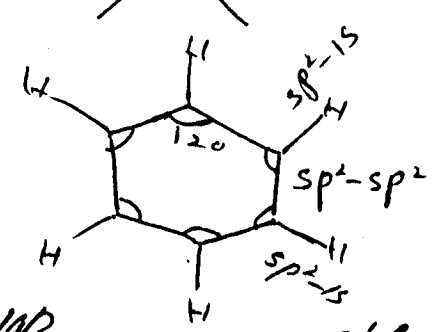
Each carbon atom is sp^2 hybridized. Carbon to carbon sigma bond is formed due to sp^2-sp^2 linear overlap. C-H sigma bond is formed due to " sp^2 and $1s$ " overlap.



There are six unhybridized p-orbitals on six carbon atoms each having 1 electron.



Six p-orbitals having their axes parallel to each other overlap and give rise to six molecular orbitals. Three are bonding m.o. and three are antibonding m.o. The six electrons fill bonding m.o. and antibonding m.o. remain empty.



The combined effect of six electrons in π_1 , π_2 , and π_3 orbitals in benzene ring may be represented as a cloud of electrons above and below benzene ring. The benzene ring is sandwiched between two electron clouds. These π -electrons are not easily available to an electrophile, thus benzene behaves like a saturated compound under normal conditions.

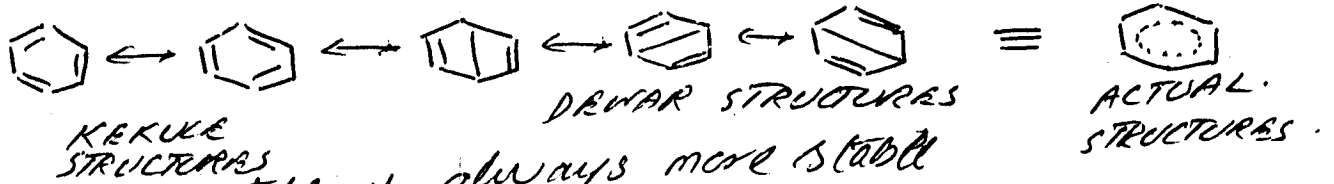


But under drastic conditions these π -electrons can be donated

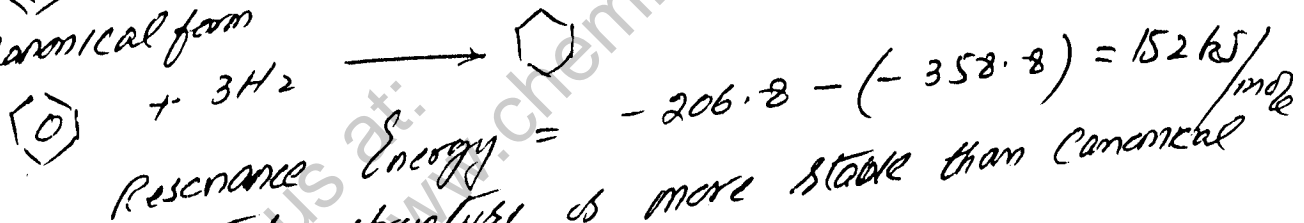
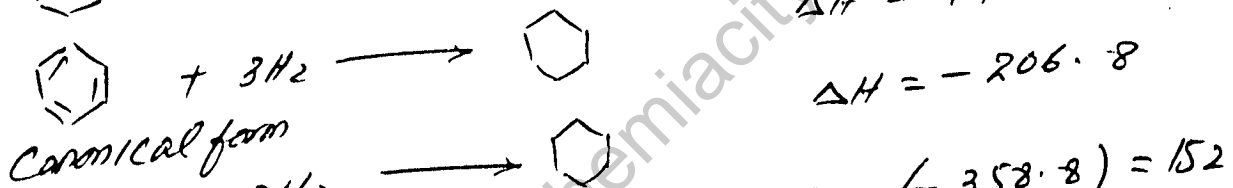
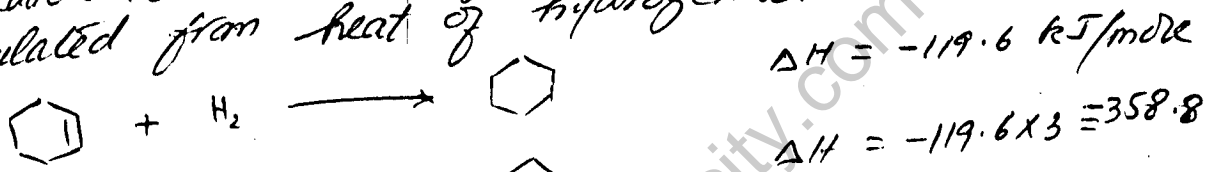
to an electrophile. Thus benzene can behave like an unsaturated hydrocarbon.

RESONANCE METHOD / when a compound can be represented by more than one Lewis structures and actual structure is hybrid of all these structures the compound is said to possess resonance. These structures are called Canonical structures. For example benzene can be represented by following canonical structures

-90-



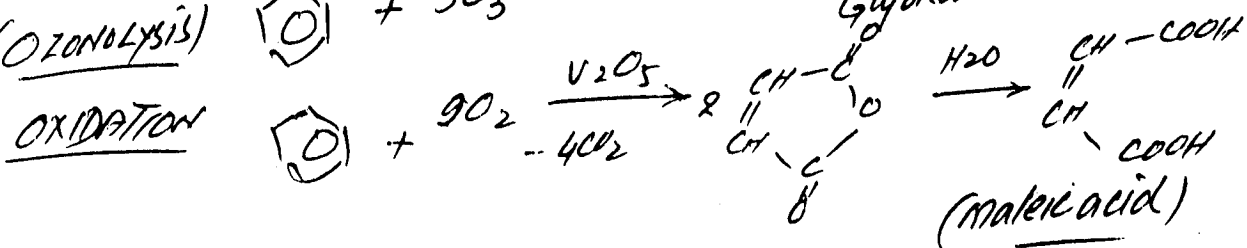
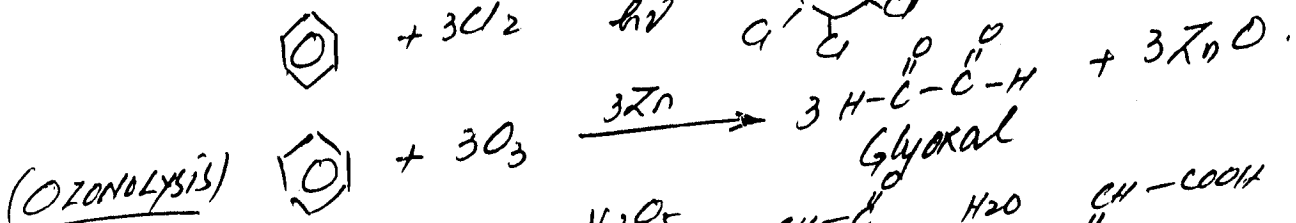
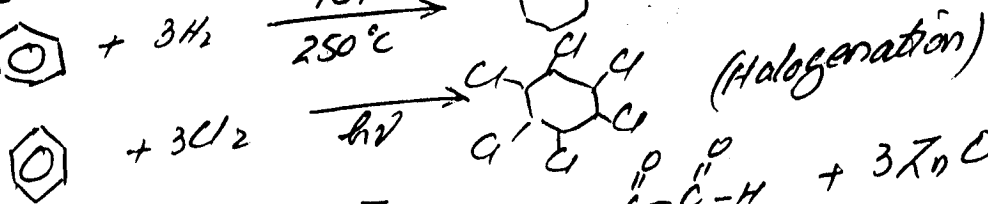
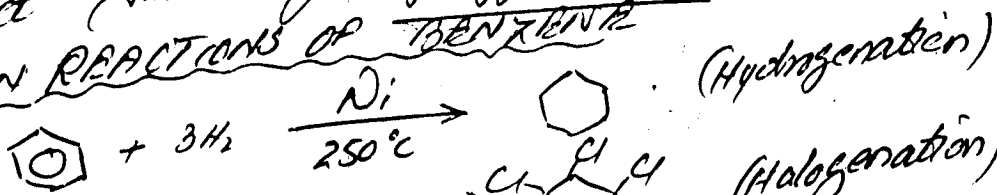
Actual structure is always more stable than any one of canonical structures. RESONANCE ENERGY The difference of energy between actual structure and most stable canonical structure is called resonance energy. Resonance energy can be calculated from heat of hydrogenation data.



Resonance Energy = $-206.8 - (-358.8) = 152 \text{ kJ/mole}$
 It means actual structure is more stable than canonical structure by 152 kJ.

Benzene normally does not undergo addition reaction due to loss of extra stability in addition product. This extra stability is retained in substitution reactions. Thus benzene prefers substitution reactions.

ADDITION REACTIONS OF BENZENE

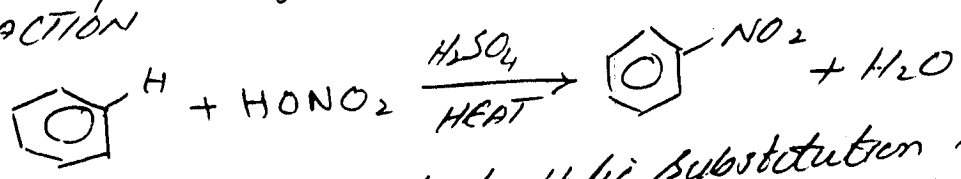


(6)

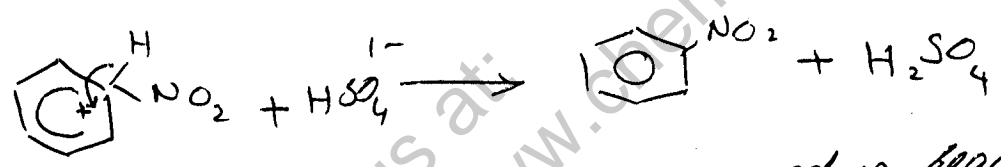
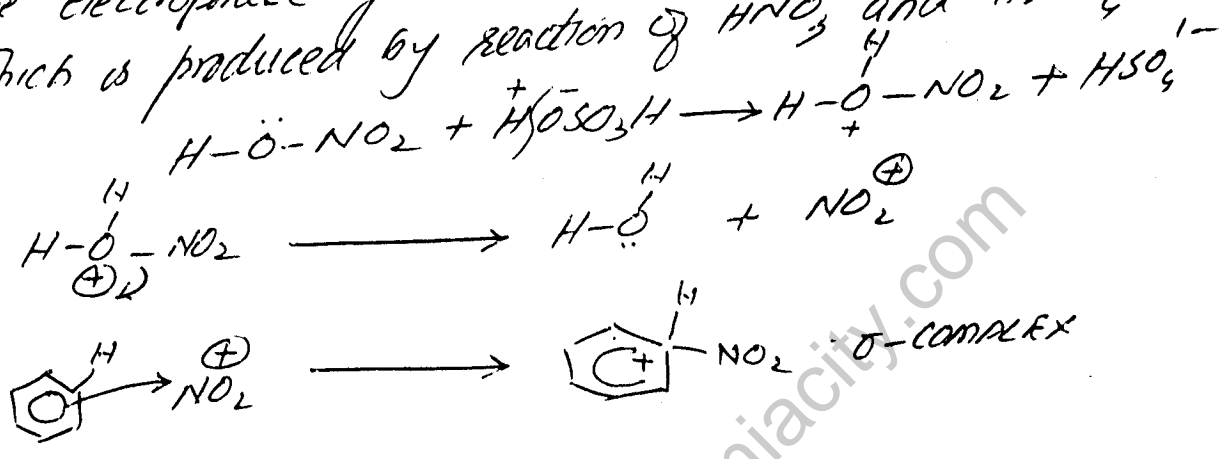
WRITE NOTE ON EACH OF FOLLOWING

NITRATION OF BENZENE: - The replacement of hydrogen of benzene by nitro group is called NITRATION. It can be carried out by reaction of benzene with concentrated nitric acid in presence of conc. H_2SO_4 , at high temperature

NET REACTION

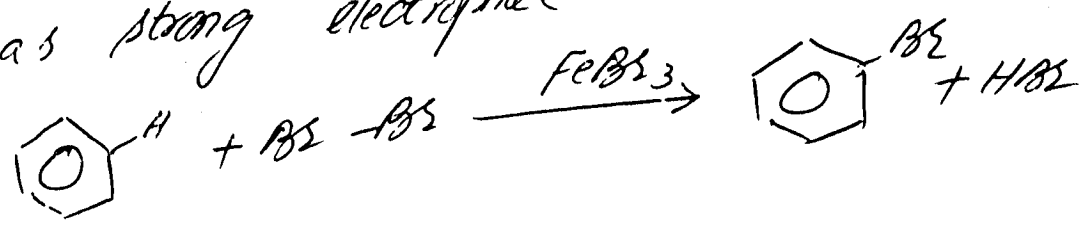


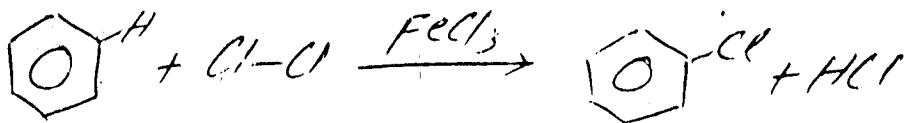
MECHANISM: - This is an electrophilic substitution reaction. The electrophilic agent is NO_2^+ ion (Nitronium ion) which is produced by reaction of HNO_3 and H_2SO_4



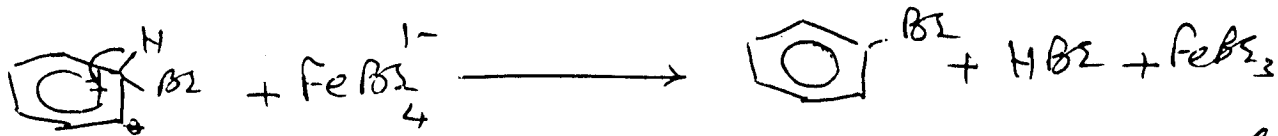
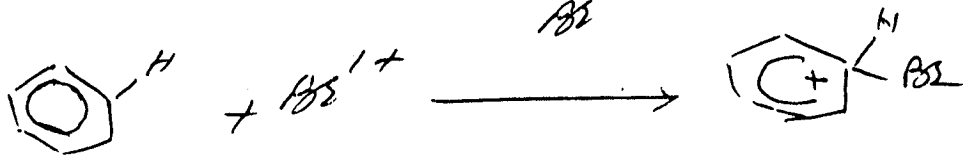
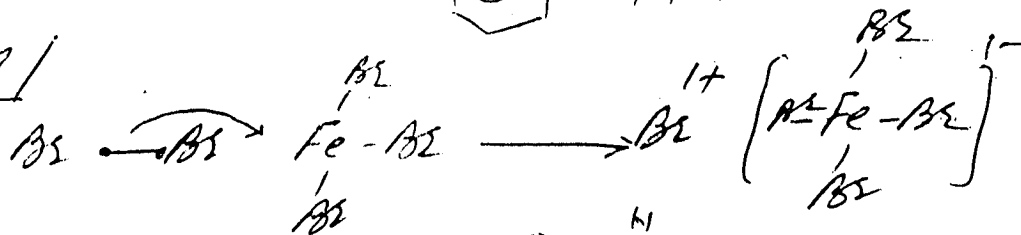
The NO_2^+ presence had been confirmed in reaction mixture of H_2SO_4 and HNO_3 . Recently crystalline salt like $NO_2^+ClO_4^-$ have been isolated and used for nitration of Benzene

HALOGENATION OF BENZENE: - The replacement of hydrogen of benzene by halogen atom is called halogenation. The chlorination and bromination occurs in presence of Lewis acid catalyst. Catalyst changes Br_2 or Cl_2 into Br^+ or Cl^+ ion which acts as strong electrophile

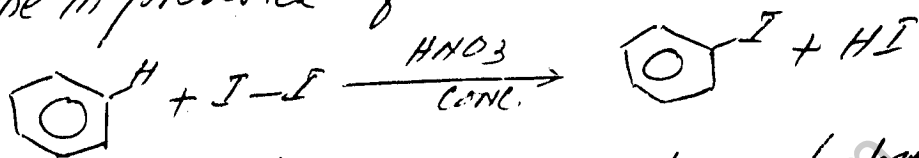




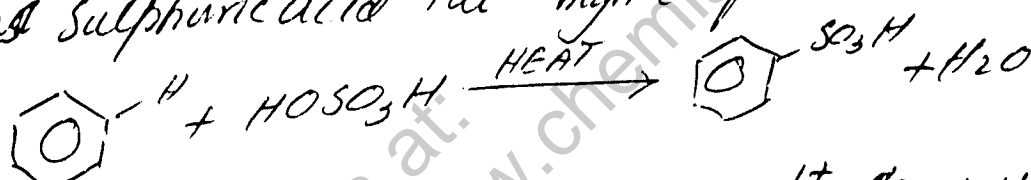
MECHANISM



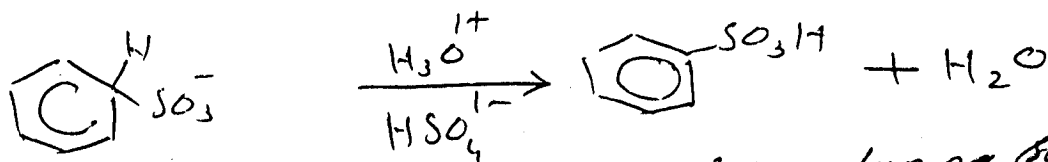
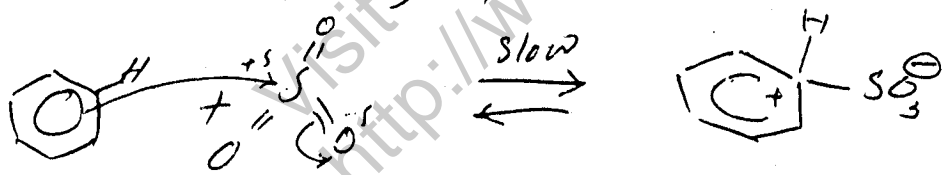
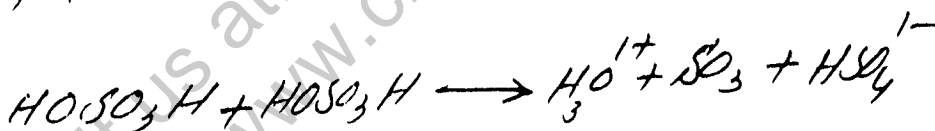
Iodobenzene can be obtained by reaction of benzene with iodine in presence of NITRIC ACID



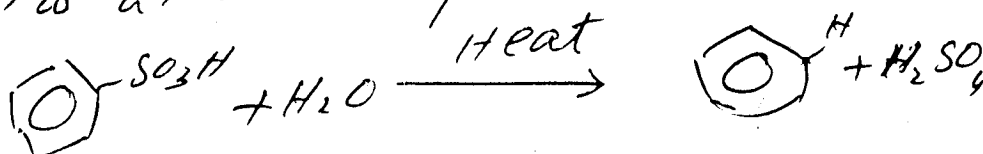
SULPHONATION The replacement of hydrogen of benzene by sulphonic acid group is called sulphonation. It can be carried out by reaction of benzene with conc. sulphuric acid at high temperature.



MECHANISM



The reaction proceeds more easily if fuming sulphuric acid is used. It contains dissolved SO_3 . If H_2SO_4 is diluted reaction does not occur. Sulphonation is a reversible process.



Q:- WRITE A NOTE ON EACH OF FOLLOWING REACTIONS.

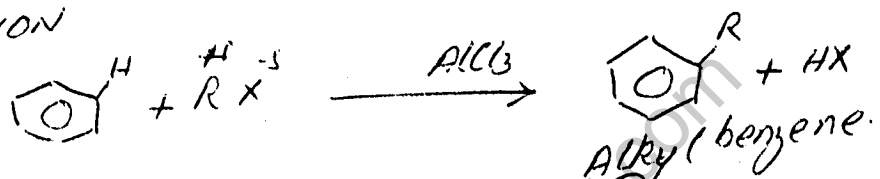
ANS:- FRIEDEL-CRAFT REACTION The reaction of an

ALKYL HALIDE OR ACYL HALIDE with benzene in presence of Lewis acid catalyst ($AlCl_3$ or $FeBr_3$) is called FRIEDEL CRAFT REACTION. These are further divided into two categories.

- (1) FRIEDEL-CRAFT ALKYLATION.
- (2) " " ACYLATION.

www.chemicity.com

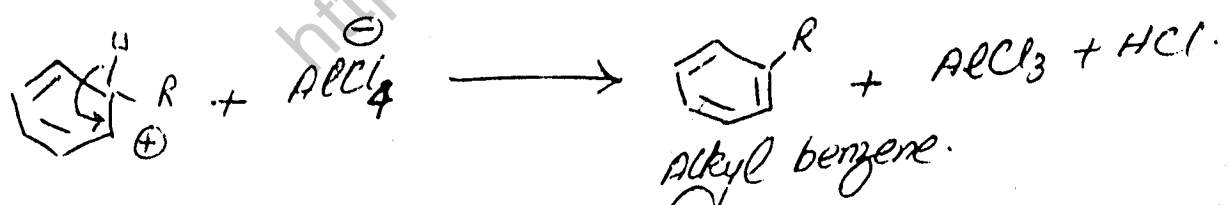
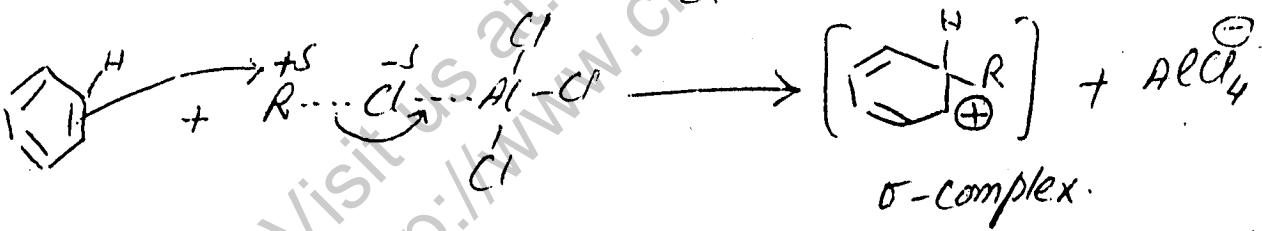
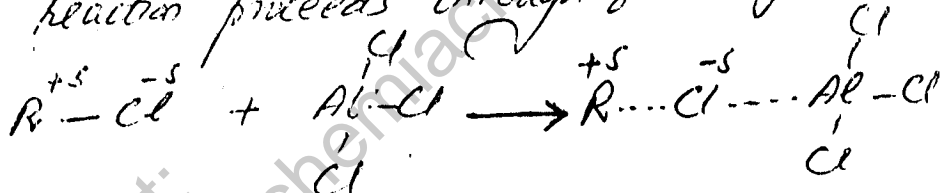
FRIEDEL CRAFT ALKYLATION The reaction of an alkyl halide with benzene in presence of Lewis acid catalyst is called Friedal Craft Alkylation. The NET REACTION



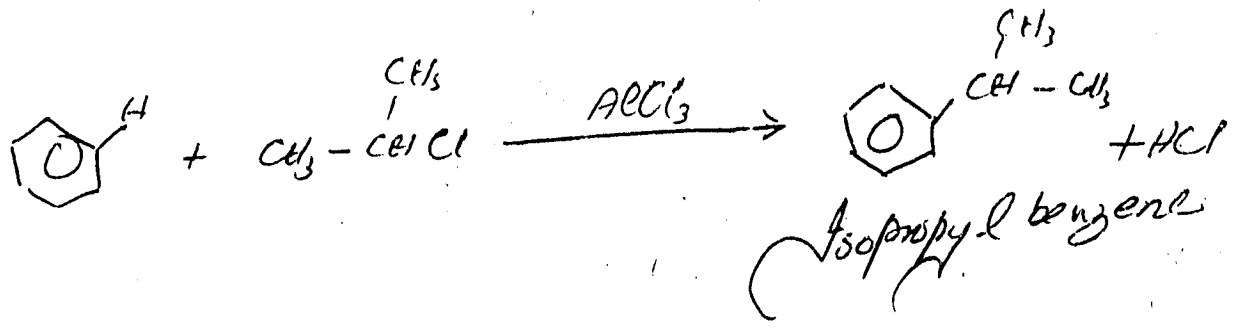
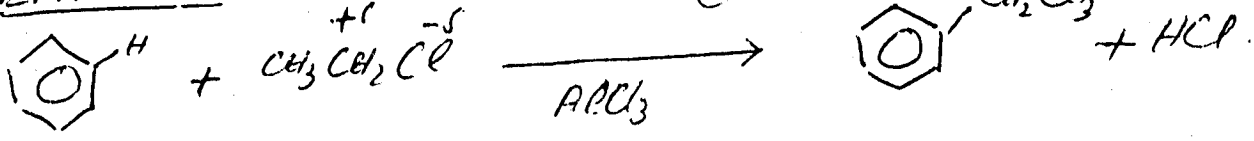
MECHANISM!

The reaction proceeds through following

mechanism

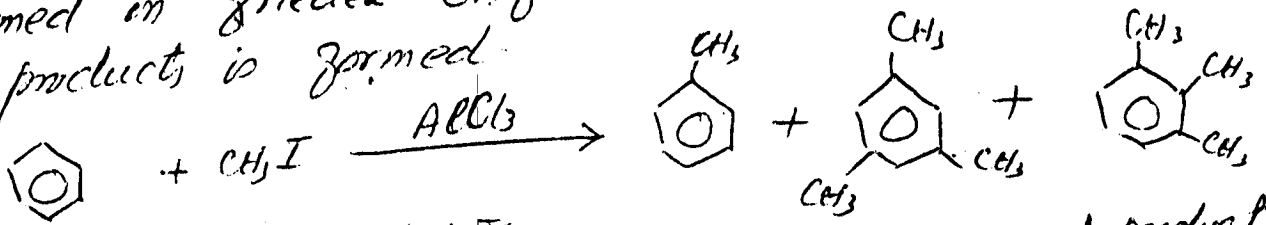


EXAMPLE



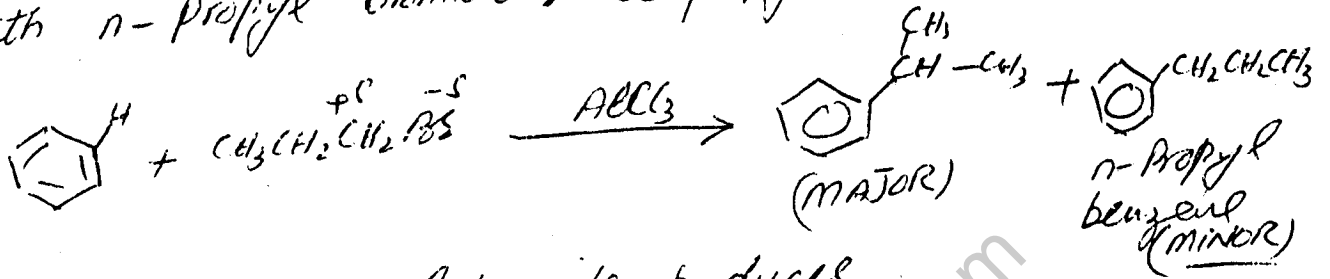
LIMITATIONS OF FRIEDEL-CRAFT

(1) POLYALKYLATION! Polyalkylated products are usually formed in Friedel-Craft Reaction. So a mixture of products is formed.

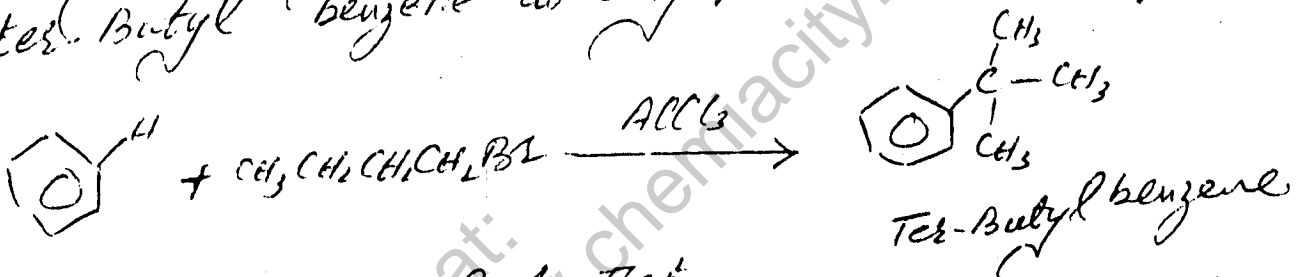


(2) REARRANGED PRODUCTS

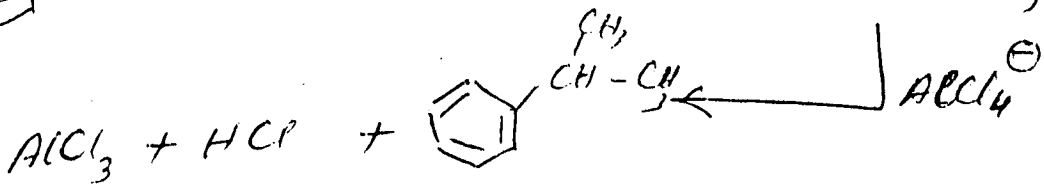
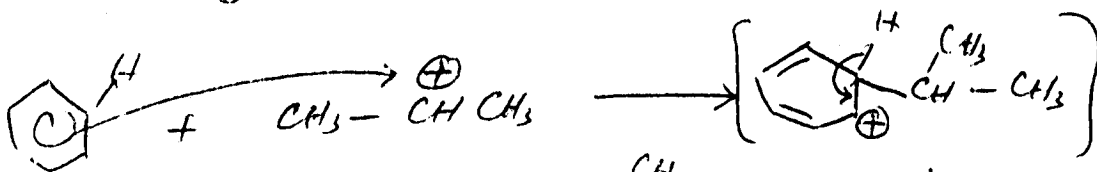
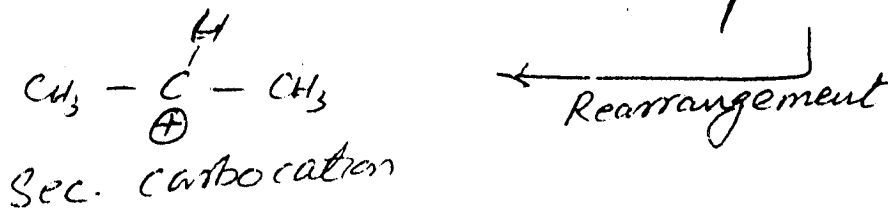
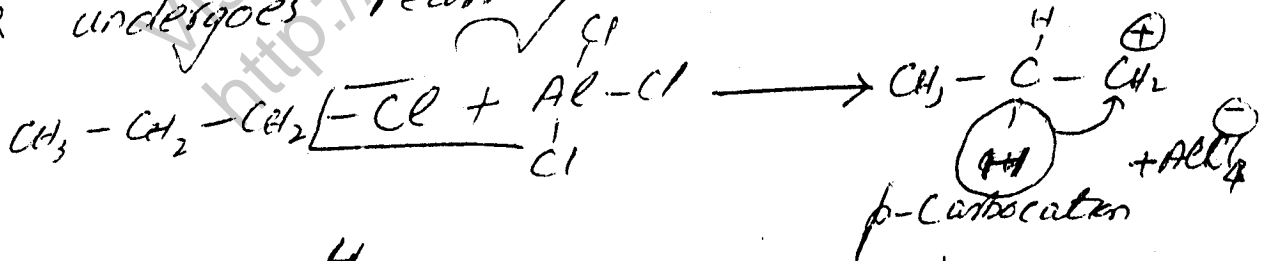
In alkylation rearranged products are obtained. For example when benzene is treated with n-propyl bromide, Isopropyl benzene is obtained.



Similarly n-butyl bromide produces tert-butyl benzene as only product.



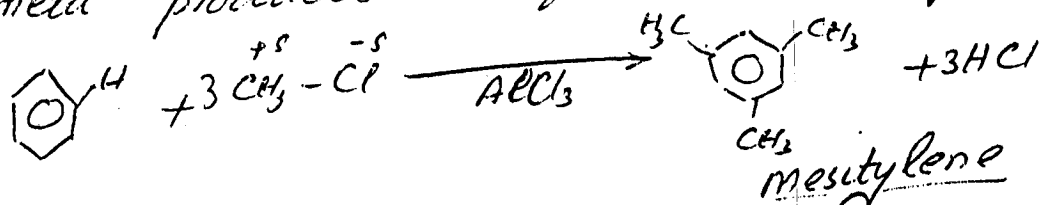
This is due to the fact that reaction proceeds through formation of carbanium ion which undergoes rearrangement.



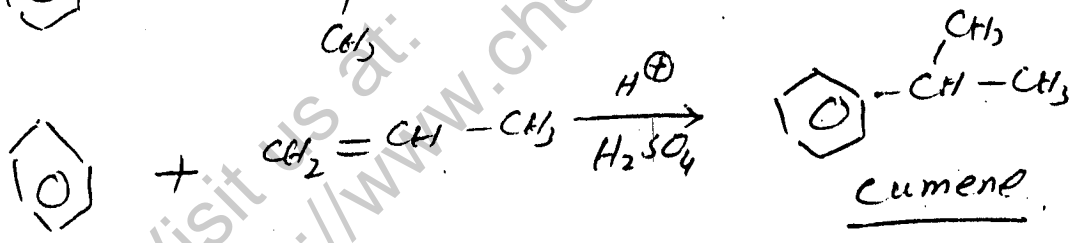
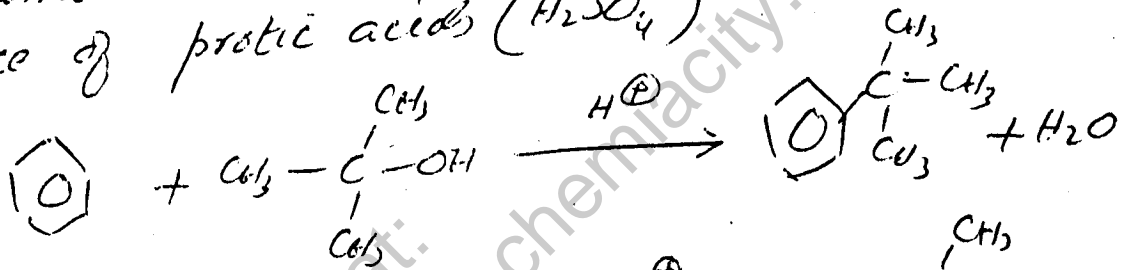
DEACTIVATED GROUPS It is difficult to carry out Friedel and Craft Alkylation if some deactivating group is present over benzene ring. Consider Friedel craft Alkylation of NITRO-Benzene which occurs with difficulty.

META-PRODUCTS FAVOURED

Inspite of the fact that alkyl groups are ortho-para directing yet meta products are favoured in polyalkylation.



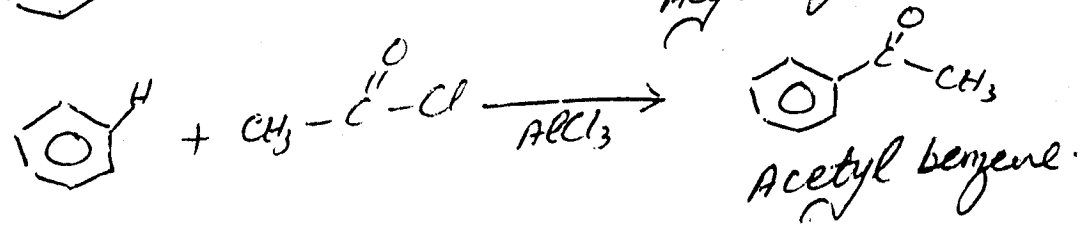
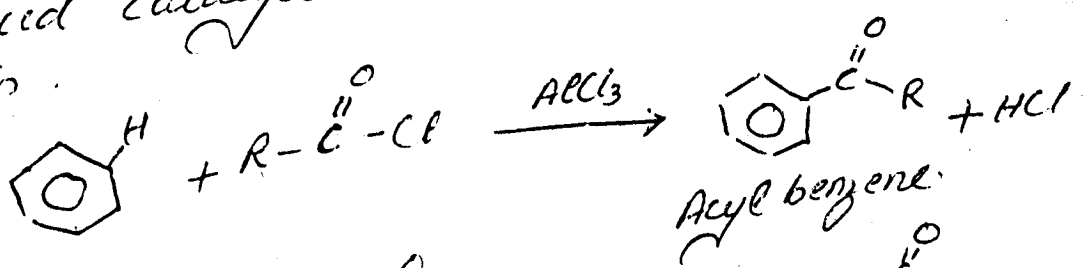
Friedal craft Alkylation can also be carried out with alcohol or alkene in presence of protic acids (H₂SO₄)

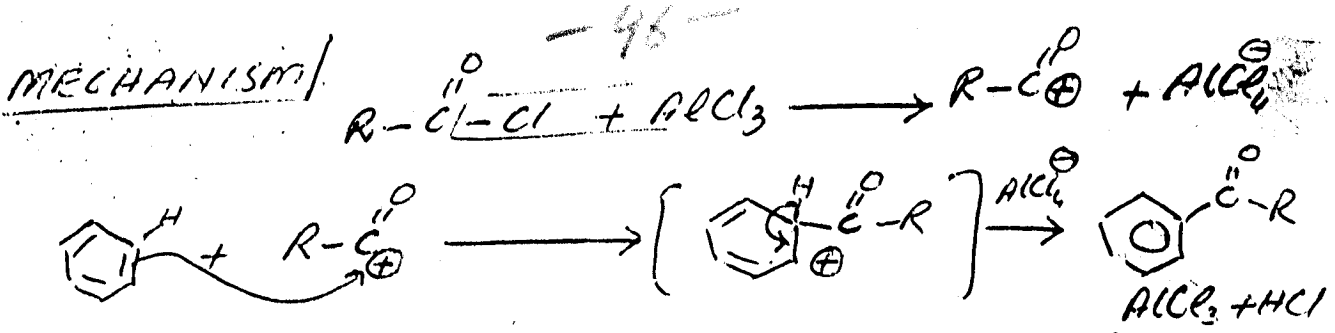


This is called MODIFIED FRIEDAL CRAFT ALKYLATION.

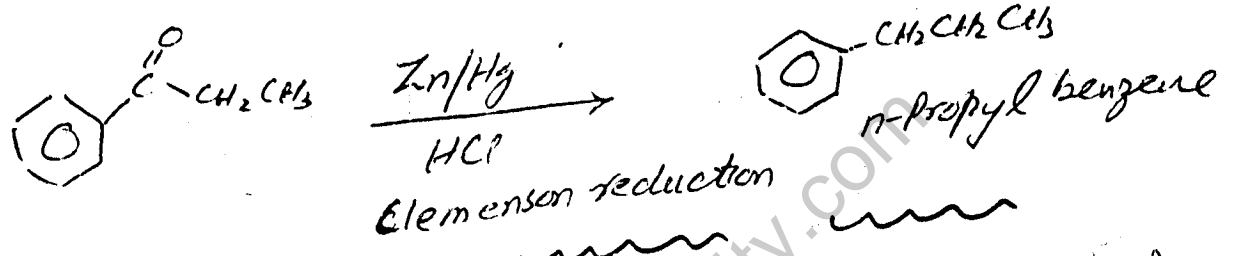
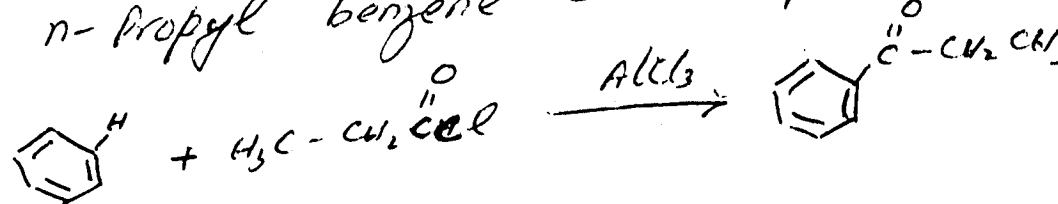
FRIEDAL CRAFT ACYLATION.

The reaction of an acyl halide with benzene in presence of Lewis acid catalyst is called Friedal craft Acylation.

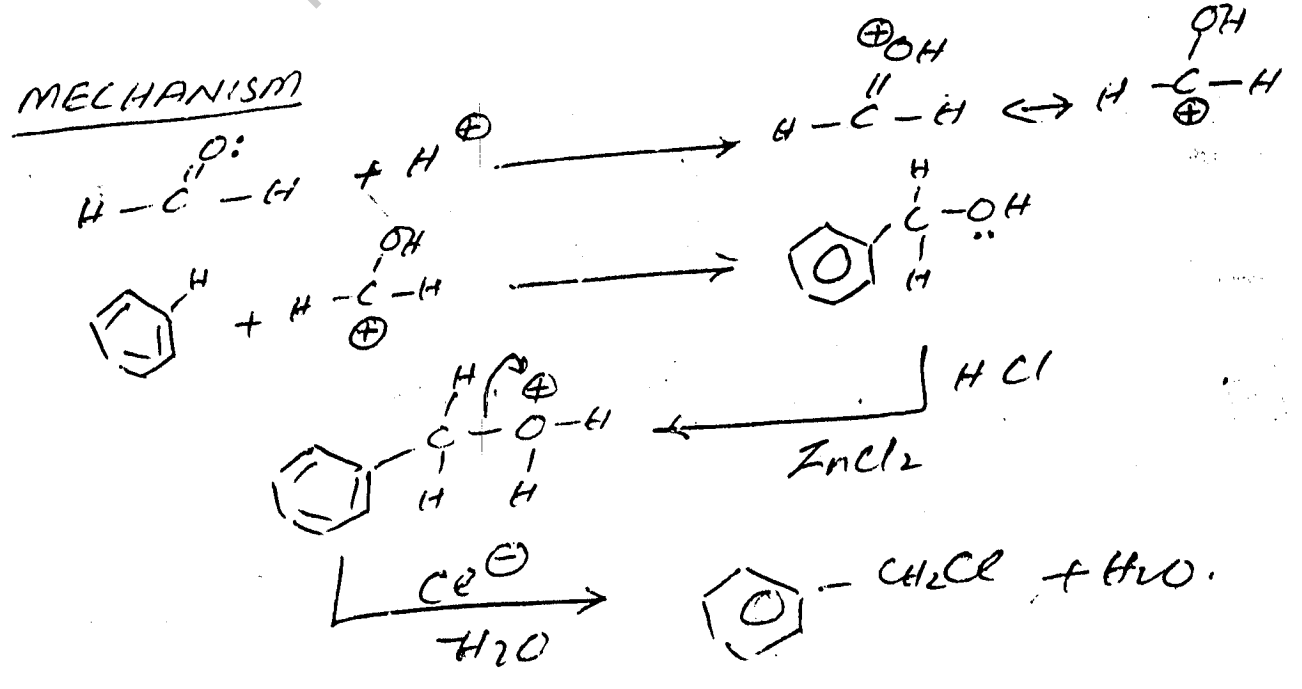
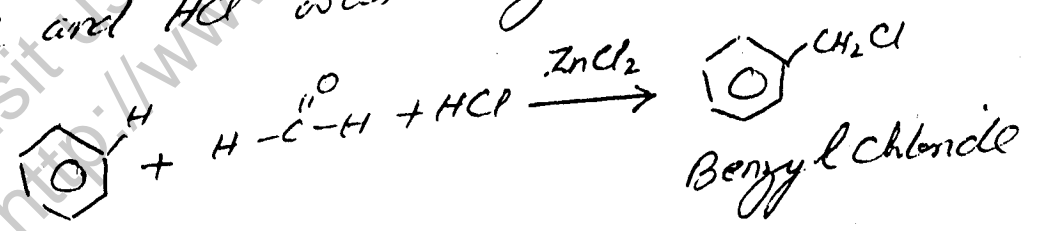




- ADVANTAGES
- (i) NO polyacylated products.
 - (ii) NO rearrangement takes place.
 - (iii) n-Propyl benzene can be prepared as follows

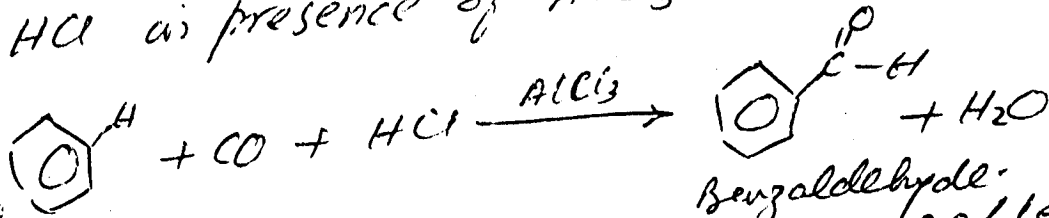


CHLOROMETHYLATION The replacement of hydrogen of chloromethyl group (-CH₂Cl) is called CHLOROMET-
HYLATION. This is carried out by reaction of formaldehyde and HCl with benzene in presence of ZnCl₂.

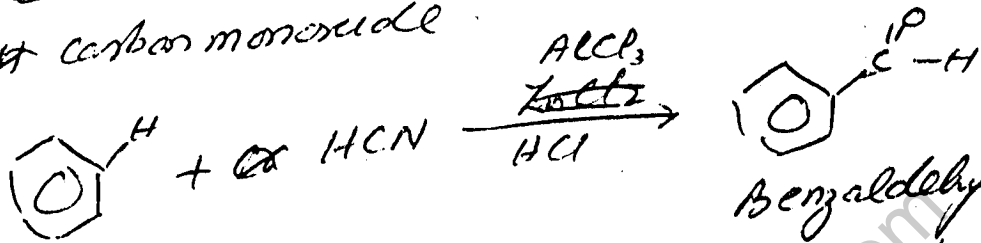


GATTERMAN REACTION

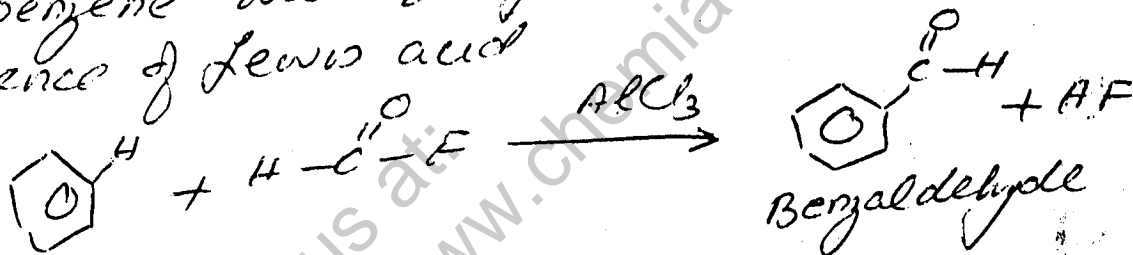
This reaction is used for preparation of formyl benzene (BENZALDEHYDE). Benzene is treated with a mixture of CO and HCl in presence of $AlCl_3$.



In another modification of reaction called GATTERMANN REACTION "HCN" is used instead of a carbon monoxide.



Formylation can also be carried out by reaction of benzene with formyl fluoride, $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{F}$ in presence of Lewis acid.

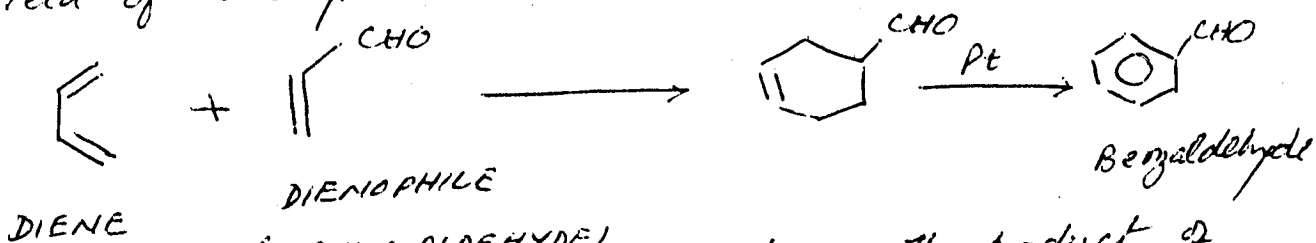


Muhammad Irfan
Lecturer (Chemistry)
G.I.C. 90-S.B. (Sargodha)

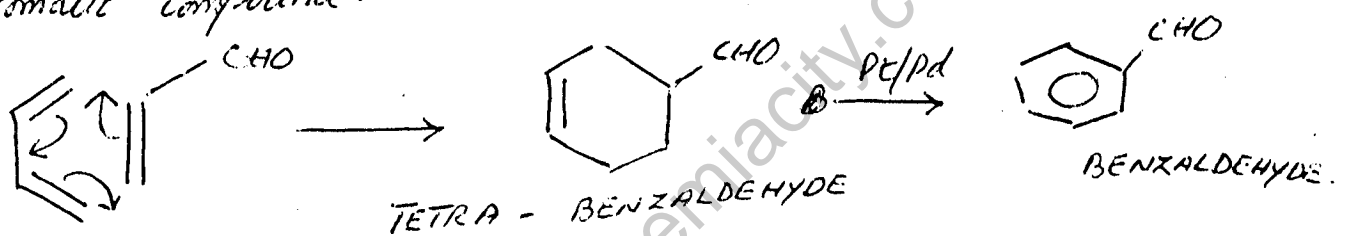
Q: WRITE NOTE ON FOLLOWING REACTIONS FOR PREPARATION OF HOMOLOGUES OF BENZENE.

Ans: DIELS ALDER REACTION is very important reaction.

discovered by Diels and Alder in 1928. The reaction involves 1,4-addition of diene to an olefin. The diene is called DIENE and the olefin is called DIENOPHILE. The reaction gives better yield if dienophile has unsaturated group (-CHO, etc).

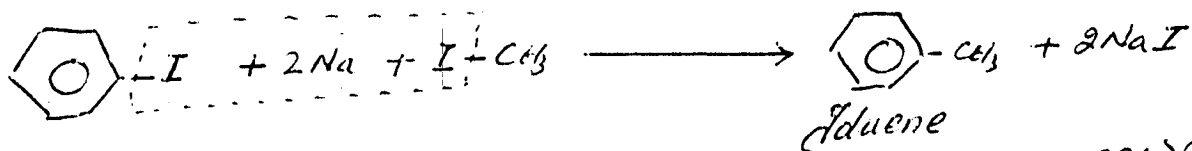


The reaction is cyclic concerted reaction. The product of Diels Alder reaction are heated with "Pt" or "Pd" to form aromatic compound.



WURTZ FITTIG REACTION

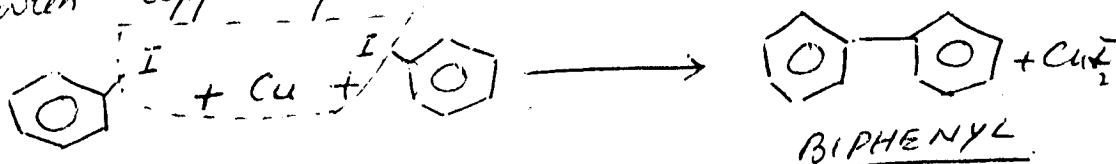
This is slight modification of WURTZ REACTION. In this reaction Aryl Halide is treated with Alkyl iodide in presence of metallic sodium. The reaction is carried in dry ether or benzene as solvent.



The order of reactivity of alkyl halide is RI > RBr > RCl

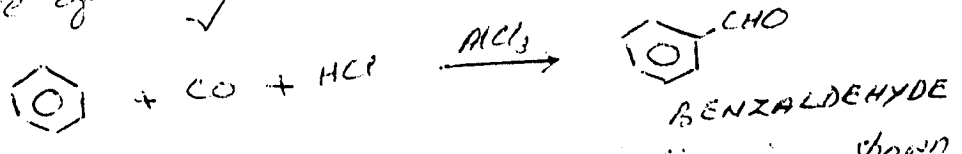
ULLMANN REACTION

This is a useful reaction for preparation "BIPHENYLS". In this reaction Phenyl iodide is treated with copper powder.

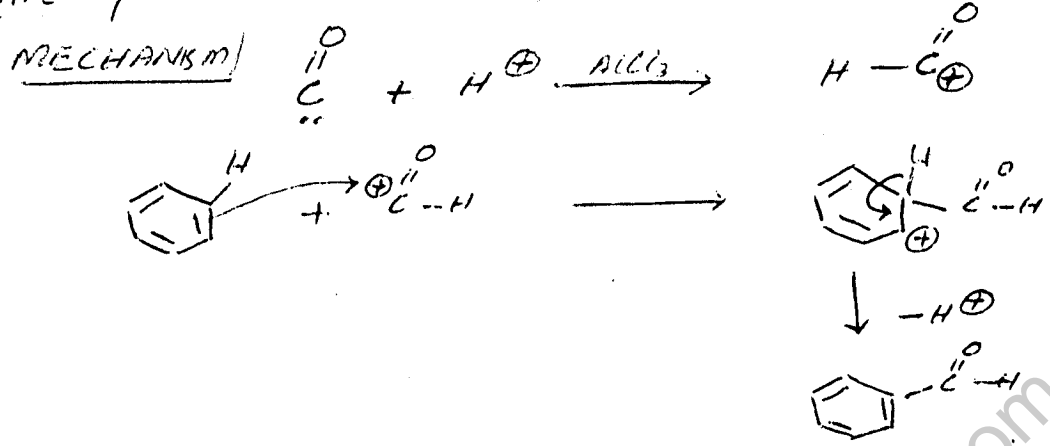


GATTERMAN KOCH REACTION

This reaction is used to prepare ~~formyl~~ benzene (BENZALDEHYDE). Carbon monoxide and HCl gas is passed through benzene solution in presence of anhydrous aluminium chloride.

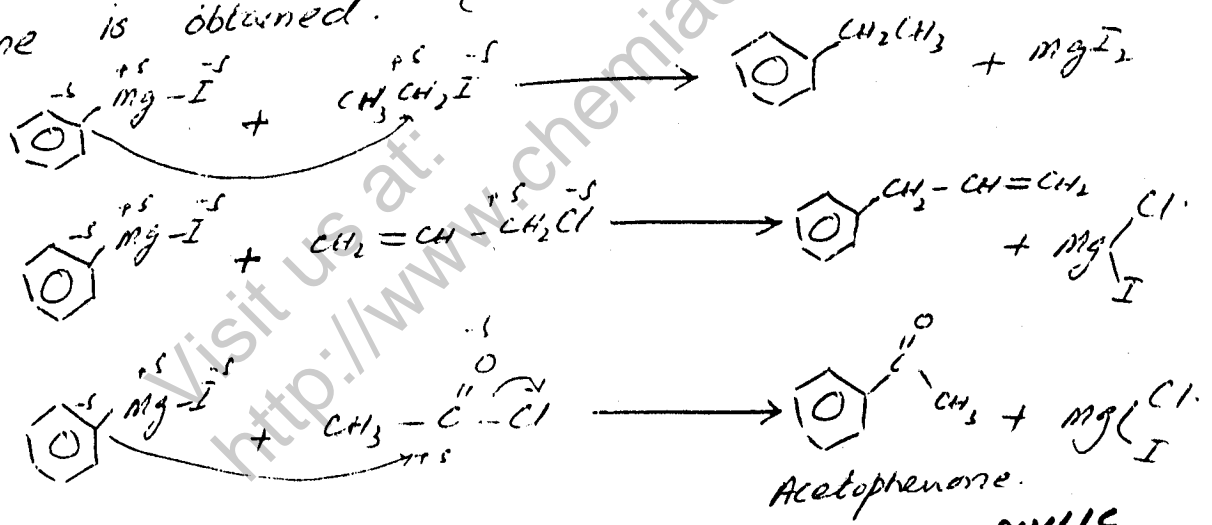


The probable mechanism of reaction is shown below.



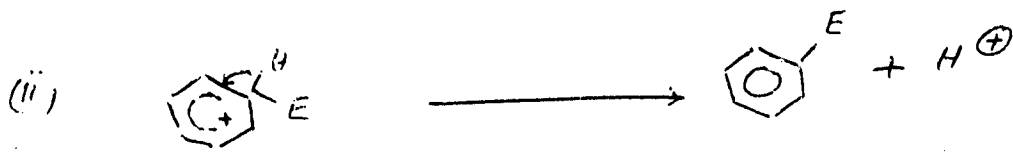
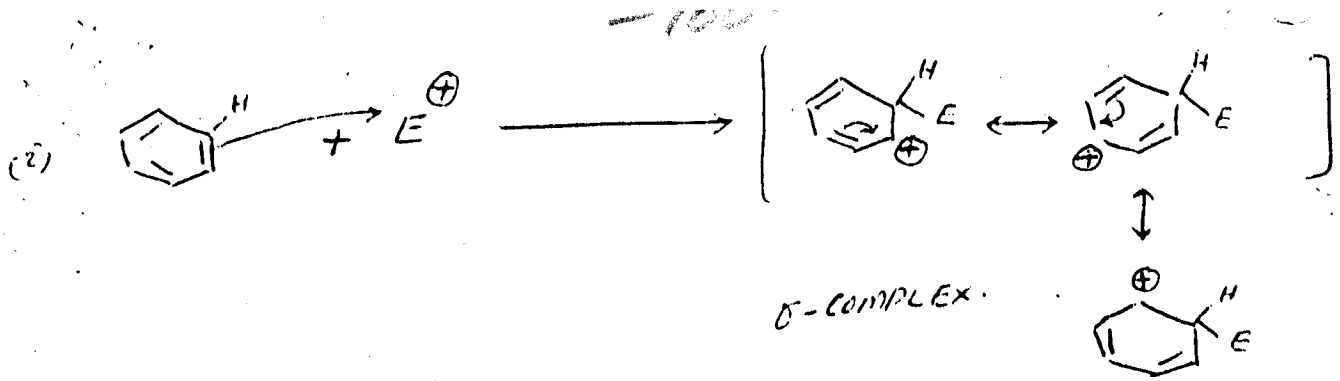
GRIGNARD SYNTHESIS

When benzene is treated with phenyl magnesium iodide (halide substituted benzene) is obtained.



Q:- WRITE GENERAL MECHANISM FOR ELECTROPHILIC SUBSTITUTION REACTION?

Ans: There is delocalized π -electron density in benzene. Benzene has resonance energy of 152 kJ/mole. Thus benzene does not undergo addition reactions rather it undergoes substitution reaction. The reaction in which hydrogen of benzene is replaced by an electrophile is called ELECTROPHILIC SUBSTITUTION REACTION.



The electrophilic substitution reactions involve two steps.

(i) In FIRST step electrophile attacks benzene ring and an intermediate is formed called "SIGMA COMPLEX" sigma complex is stabilized by resonance.

In SECOND step sigma complex loses proton and regains aromaticity. The net result is replacement of hydrogen by a proton.

SIDE CHAIN OXIDATION OF BENZENE

Visit us at:

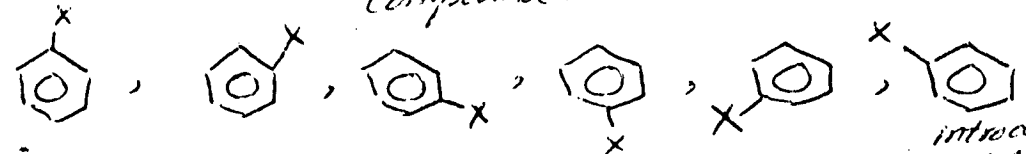
<http://www.chemistry.com>

Q. WRITE A NOTE ON ORIENTATION OF BENZENE.

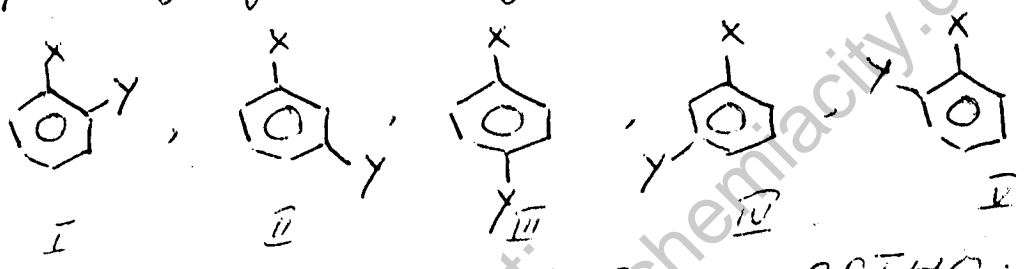
Ans:-

DEFINITION The substituent already present on benzene ring determines position of incoming electrophile. It is called Orientation in BENZENE.

EXPLANATION Since benzene has regular hexagonal structure so all six positions are equivalent. Thus there is only one monosubstituted product of benzene as shown. All these structures are for the same compound.



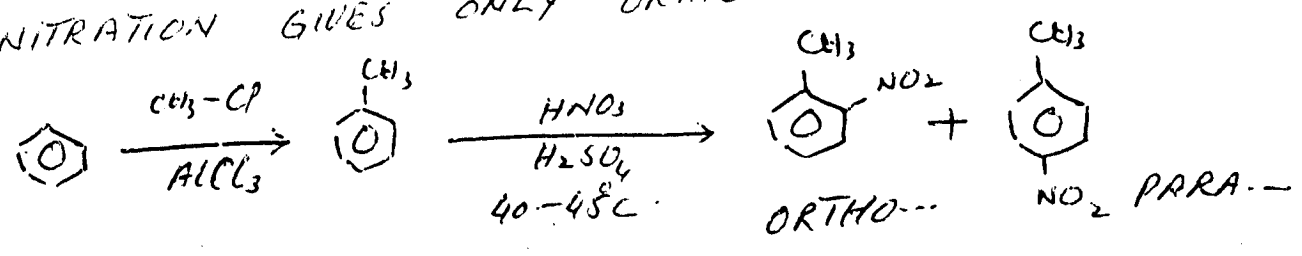
But if a second substituent is introduced to benzene it may take any one of five vacant spaces giving following possible structures.



structures I AND V - ORTHO.
 II AND IV - META.
 III IS ONLY PARA.

It means there should be 40% ortho, 40% meta and 20% para disubstituted product, but its not the same in actual practice. Consider following example.

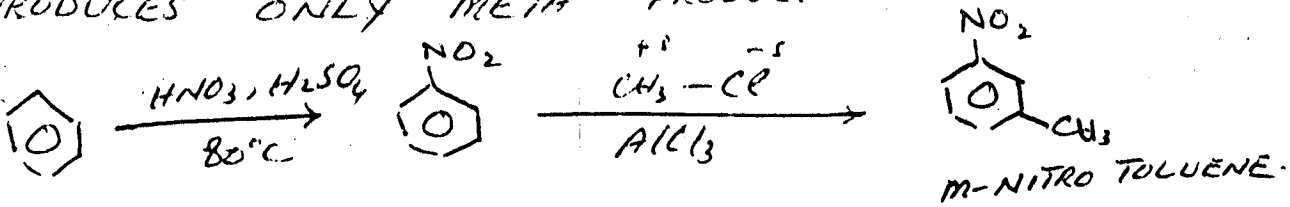
ALKYLATION OF BENZENE FOLLOWED BY NITRATION GIVES ONLY ORTHO AND PARA PRODUCT



No meta product is obtained in this reaction

NITRATION OF BENZENE FOLLOWED BY ALKYLATION

PRODUCES ONLY META PRODUCT.



No ortho and para product is obtained in this case.

It means group already present on benzene ring determines position of incoming electrophile. Methyl group directs incoming electrophile to ortho and para position but NITRO group directs incoming electrophile to meta position.

Thus METHYL is ORTHO, PARA directing.

NITRO is META directing group.

Further alkyl group has increased

reactivity of benzene (nitration of toluene takes place at low temperature as compared to BENZENE) while nitro group has decreased its reactivity.

The groups which increase reactivity of benzene are called Activating groups while groups which decrease reactivity of benzene are called deactivating groups.

The groups present on π

benzene ring are divided into five categories.

- ① Substituents with lone pair of electron. ($-\overset{\cdot\cdot}{\text{O}}\text{H}$, $-\overset{\cdot\cdot}{\text{N}}\text{H}_2$ etc.)
- ② Alkyl groups or Aryl groups. ($-\text{R} = -\text{CH}_3, -\text{CH}_2\text{CH}_3$)
- ③ Groups with multiple bonds. ($-\text{NO}_2, -\text{COOH}, -\text{CHO}$)
- ④ Substituent on a single atom ($-\overset{\cdot\cdot}{\text{C}}\text{l}, -\overset{\cdot\cdot}{\text{B}}\text{r}, -\overset{\cdot\cdot}{\text{I}}$)
- ⑤ Groups bearing positive charge. ($-\overset{\oplus}{\text{N}}(\text{C}_2\text{H}_5)_3$ etc.)

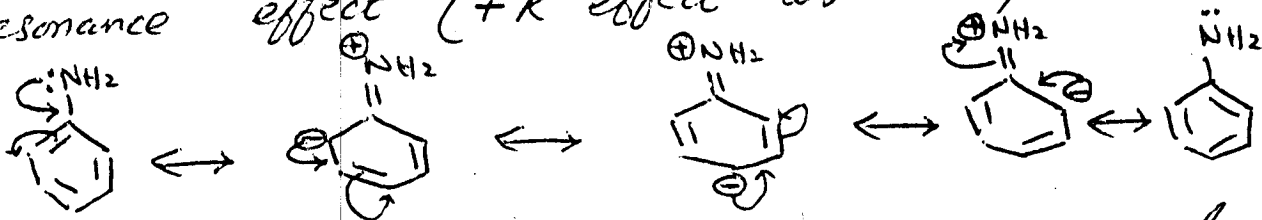
Let us consider details of these groups.

GROUP WITH LONE PAIR OF ELECTRON

The groups with lone pair of electron are ORTHO, PARA directing and increase reactivity of benzene. It means these are ACTIVATING GROUP.

This can be explained as follows.

The lone pair is delocalized over ring due to resonance effect (+R effect as shown)

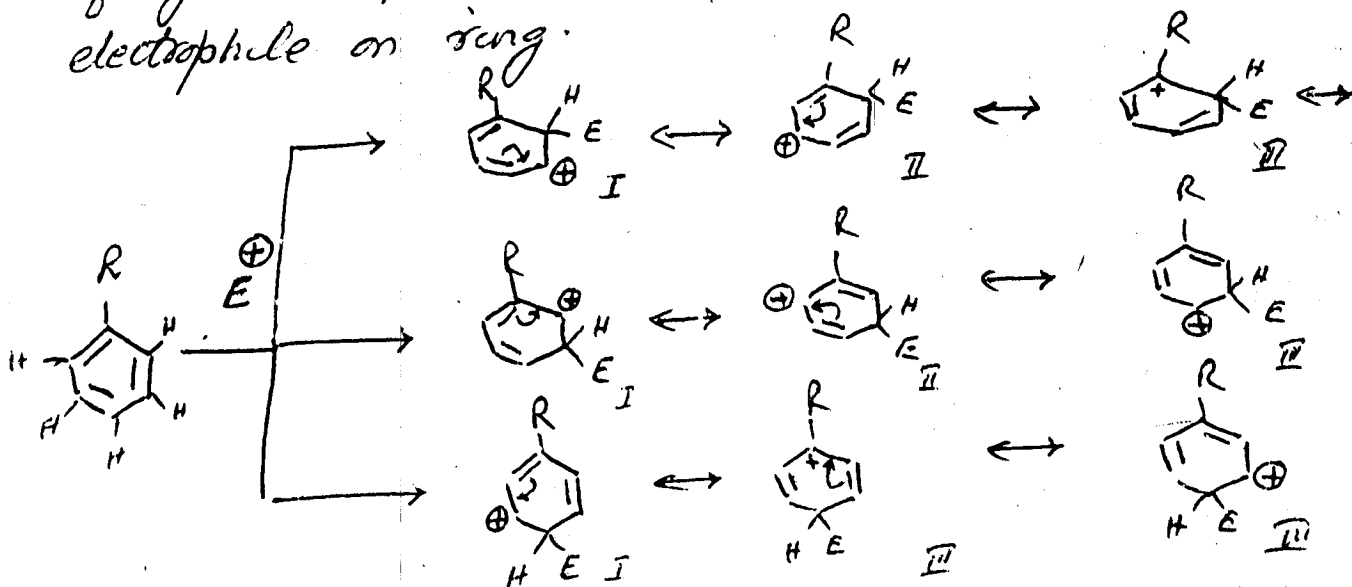


It is clear that electron density on benzene has been increased as whole. The e^- density is increased especially at ortho and para position. Thus incoming electrophile will attack these positions. The common examples of such groups are: $-\text{OCH}_3$, $-\text{OH}$, $-\text{NH}_2$.

ALKYL OR ARYL GROUPS These are ORTHO, PARA directing and activating groups.

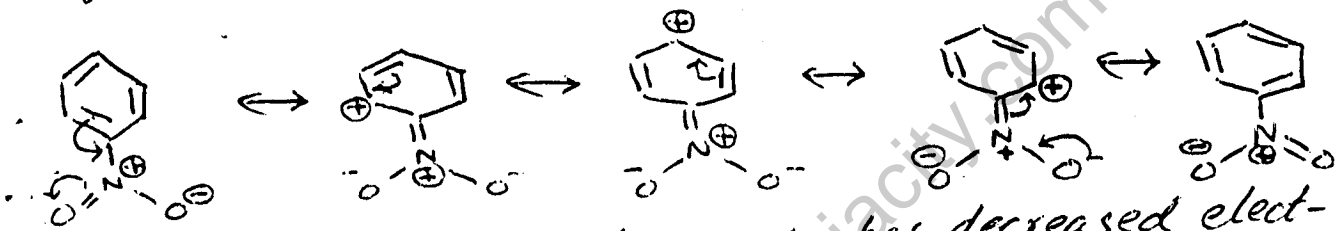
The ACTIVATING nature can be explained on the basis of electron releasing inductive effect of ALKYL groups. The ortho, para directing nature can be explained from following canonical forms.

Let us consider canonical forms of sigma complex formed by attack of alkyl second electrophile on ring.

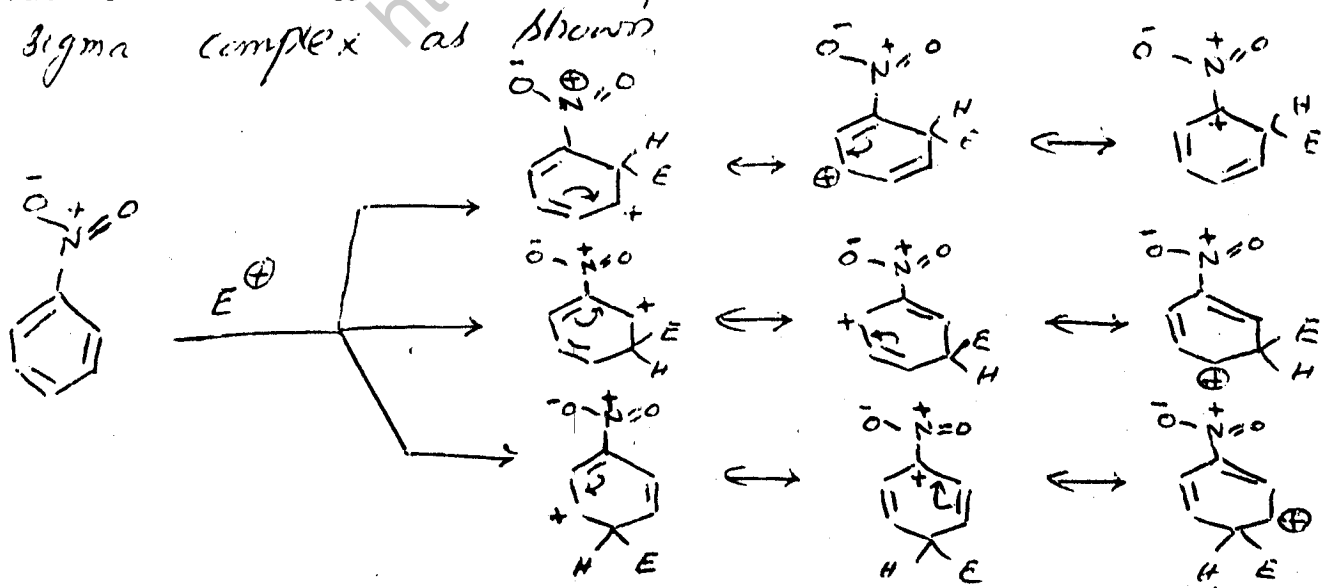


when attack takes place at ortho and para position one canonical form has positive charge on carbon bearing alkyl group (III for ortho and II for para). This positive charge is more stabilized due to electron releasing inductive effect of Alkyl group. Thus sigma complex formed due to attack at ortho and para position is more stable than that for meta sigma complex. Thus attack preferably take place at ORTHO OR PARA POSITION.

GROUPS WITH MULTIPLE BONDS Groups as $-\overset{\oplus}{N}(=O)_2$ ($-\overset{\oplus}{C}-R$), $-C\equiv N$ etc are DEACTIVATING and META directing. The deactivating nature and meta directing influence can be explained as follows.



The nitro group has decreased electron density on benzene ring as whole especially at ortho and para position. Thus electrophile cannot attack ortho or para position. The only position left for attack is meta position. The META directing nature can also be explained on the basis of sigma complex as shown

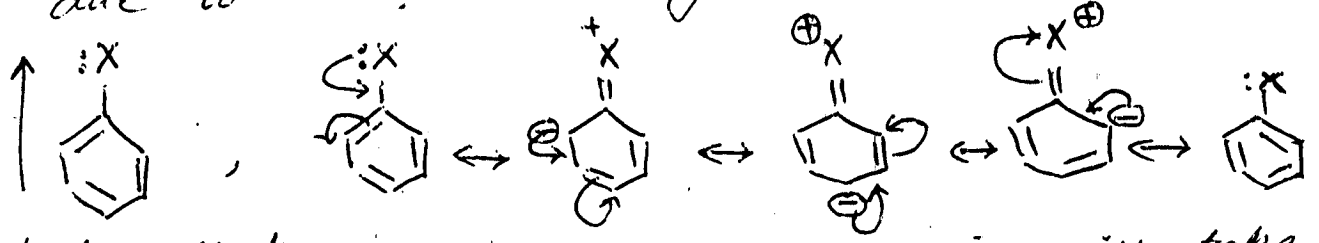


When attack takes place ortho or para position one canonical form of sigma complex has

positive charge on two adjacent atoms thus making it quite unstable. Thus attack preferably takes place at meta position.

HALOGENS AS SUBSTITUENT (SINGLE ATOM)

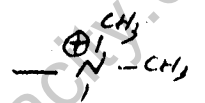
Halogens are deactivating groups and ORTHO, PARA directing. DEACTIVATION is due to electron withdrawing inductive effect of halogens thus it decreases electron density on ring. The ORTHO-PARA nature is due to electron releasing RESONANCE EFFECT.



Inductive effect

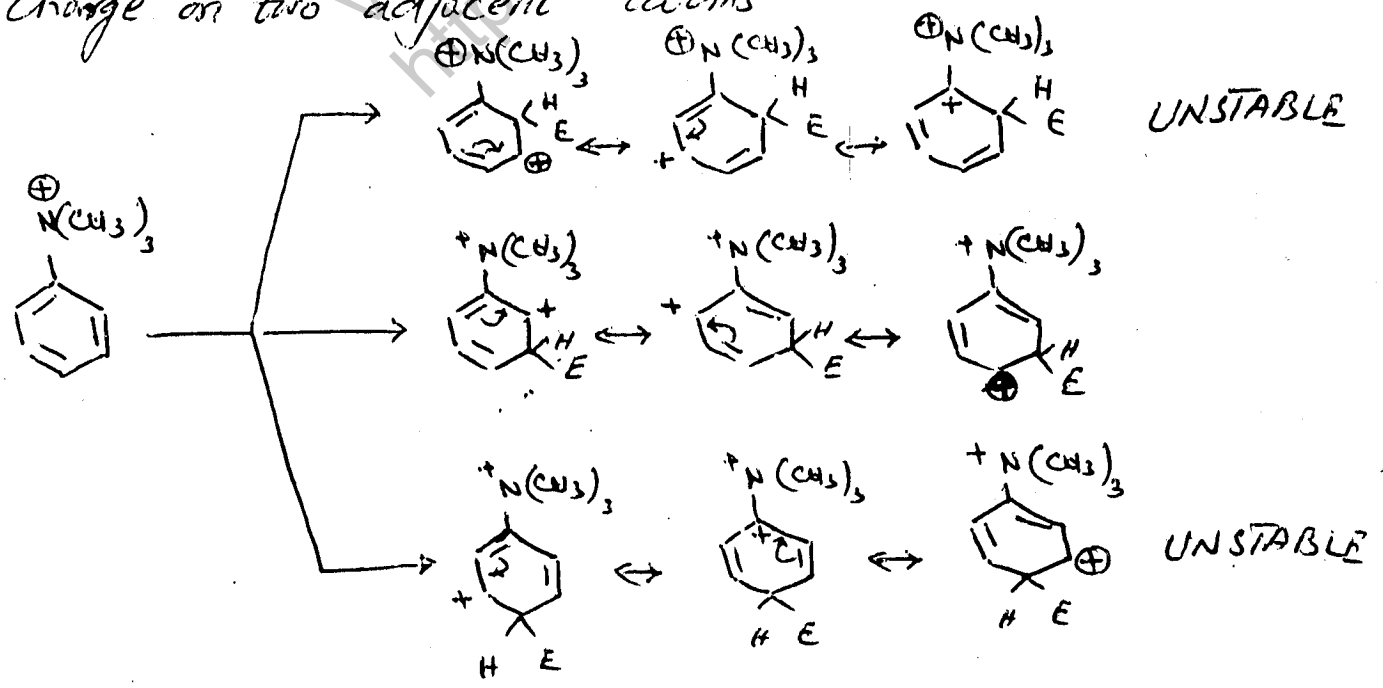
Whenever attack of electrophile will take place at it will be on ortho para position because electron density has been increased at these positions

GROUPS WITH POSITIVE CHARGE



These are DEACTIVATING and META directing groups.

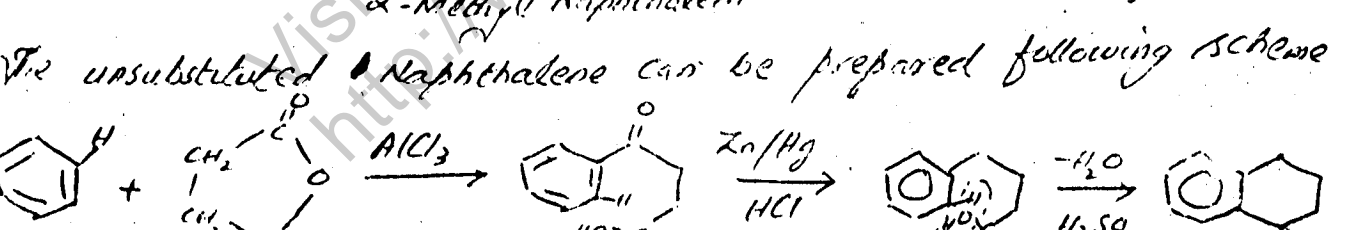
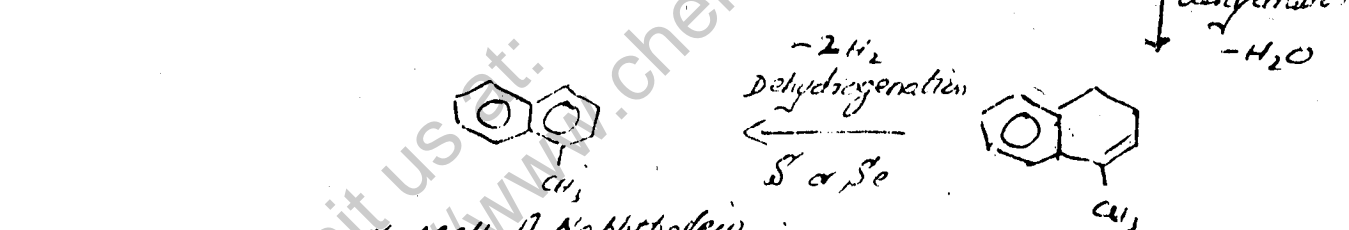
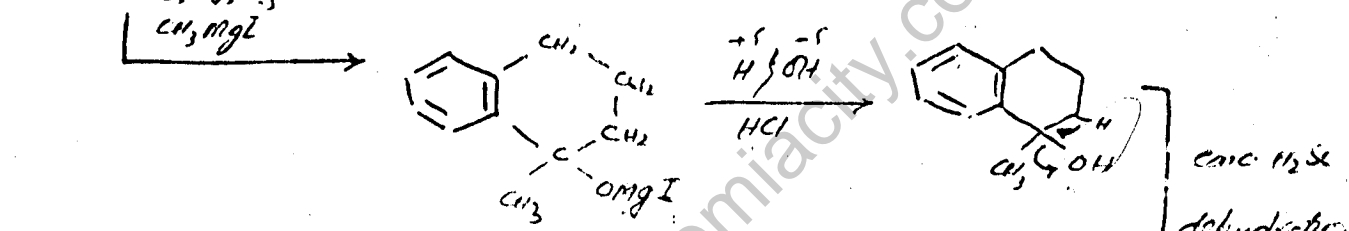
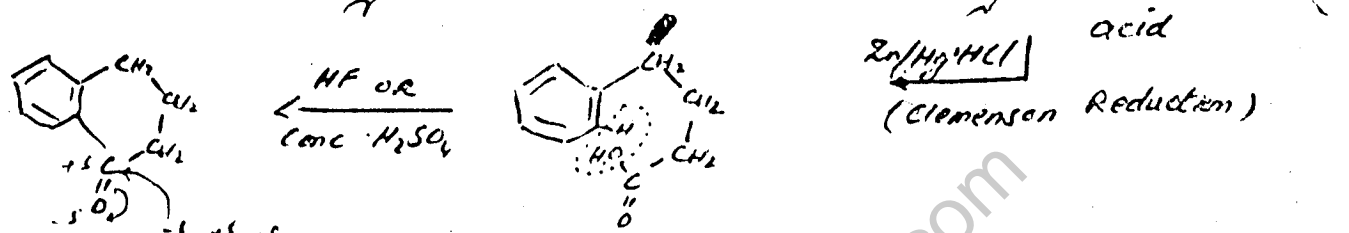
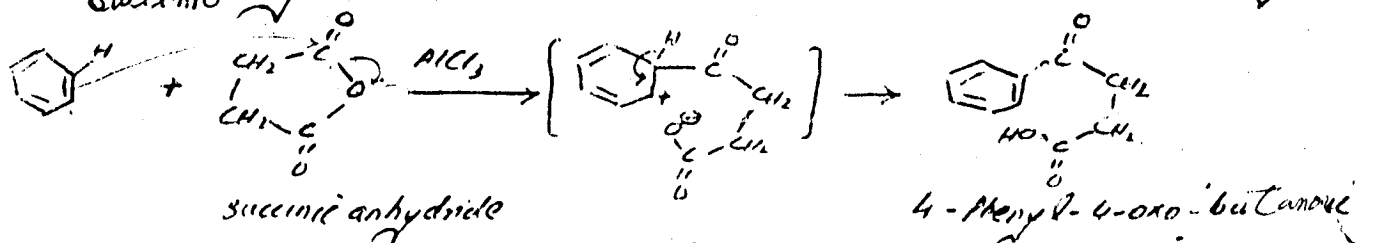
The deactivation is due to electron withdrawing INDUCTION EFFECT while meta directing nature is due to the fact that sigma complex for ortho para position is quite unstable due to positive charge on two adjacent atoms.



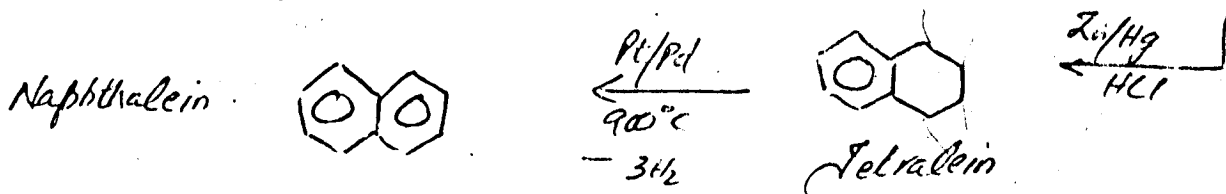
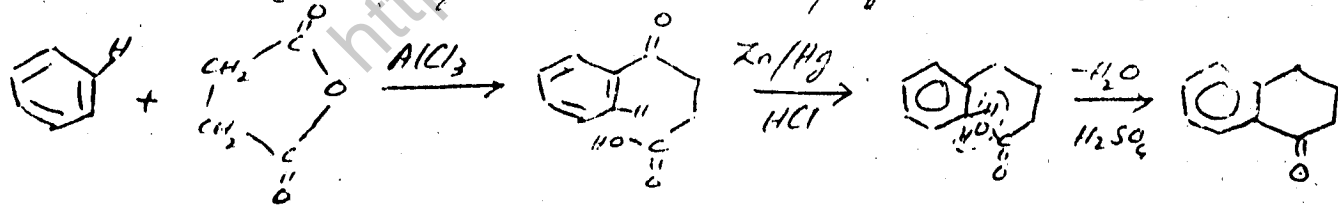
DISCUSS METHODS OF PREPARATION OF NAPHTHALENE

Naphthalene is a condensed aromatic system with 10 π -electrons. It is mostly obtained from coal tar along with other aromatic hydrocarbons. However, it can be obtained in laboratory by following general reactions.

FROM BENZENE AND SUCCINIC ANHYDRIDE (HAWORTH'S SYNTHESIS)
 Naphthalene can be prepared by Friedel-Craft Acylation benzene with succinic anhydride. The reaction scheme is called Haworth's synthesis.

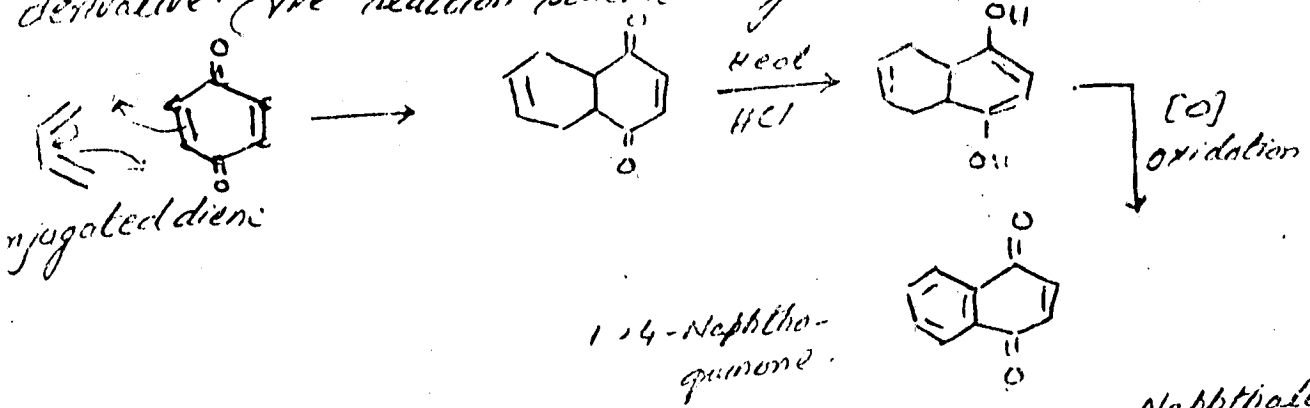


The unsubstituted Naphthalene can be prepared following scheme

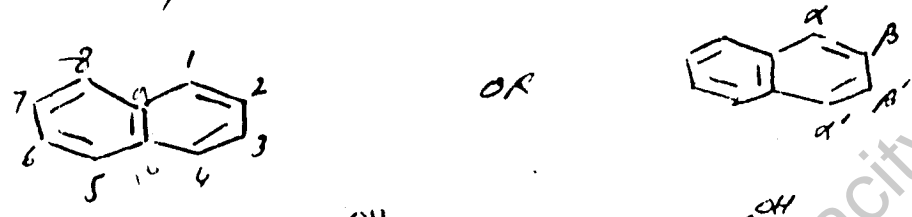


This sequence can be used to prepare any desired substituted naphthalene by using substituted benzene, or G.R. or both.

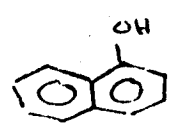
DIELS-ALDER REACTION:- The reaction of conjugated diene with 1,4-benzoquinone also produces naphthalene derivative. The reaction scheme is given below.



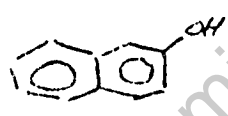
NOMENCLATURE OF NAPHTHALENE:- All positions of Naphthalene are not equivalent so numbering cannot start from any carbon. There is a special sequence of numbering as shown below



FOR EXAMPLE

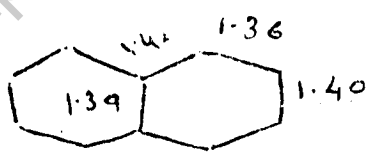


1-Naphthol
OR α -Naphthol

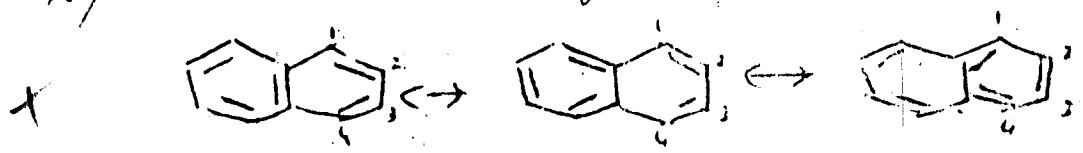


β -Naphthol } OR β -Hydroxy
2-Naphthol } Naphthalene.

STRUCTURE OF NAPHTHALENE X-ray analysis show following structures of benzene. Naphthalene



It shows that naphthalene has two benzene rings fused at ortho positions. The bond lengths are not equal and are slightly different from bond lengths in benzene. It indicates that all carbons are not equivalent w.r to reactivity in Naphthalene. That is why there is specific numbering in Naphthalene. Naphthalene is resonance hybrid of following structures.

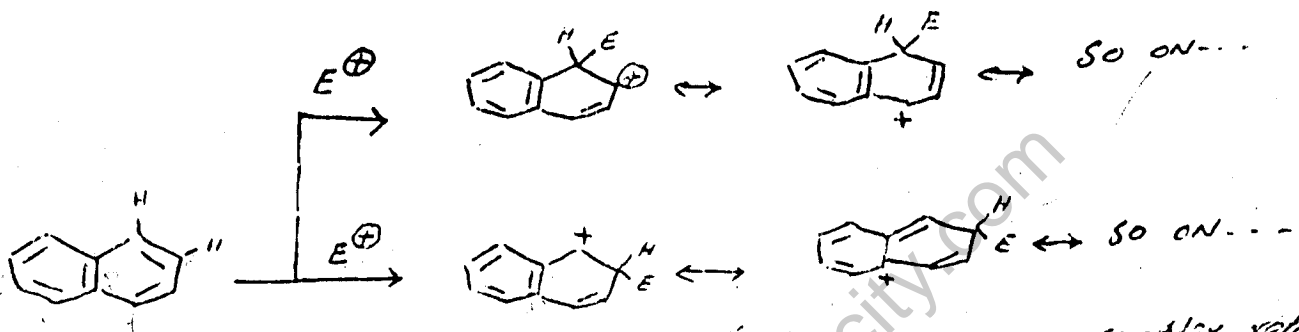


108

It is expected from canonical forms that there should be $\frac{2}{3}$ double bond character in 1-2 BOND and $\frac{1}{3}$ d.b. character 2-3 BOND. It explains why 1-2 bond length is shorter than 2-3 bond length as indicated by canonical forms, and proved by X-ray analysis.

Position "1" is MORE REACTIVE THAN POSITION "2"

Position 1 of Naphthalene is more reactive than position "2". So substitution preferably takes place position "1". The increased reactivity of position "1" than position "2" can be understood from following canonical forms of sigma complex.



When attack takes place at position "1" the sigma complex retains benzene ring in both canonical forms, while sigma complex formed by attack at position "2" is less stable because it retains benzene in one form only.

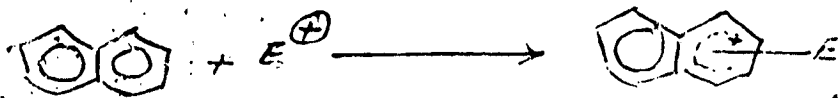
The resonance energy of Naphthalene is 252 kJ which is more than that of Benzene. It is due to the fact that for benzene only two equivalent canonical forms can be written (c1ccccc1 <-> c1ccccc1) while for Naphthalene there are three of them.

NAPHTHALENE IS MORE REACTIVE THAN BENZENE.

It is due to the fact that when electrophile attacks on the Benzene ring, the sigma complex loses aromaticity



However when attacks Naphthalene the sigma complex still retains one benzene ring (still has resonance energy 152 kJ) hence sigma complex of Naphthalene is more reactive & stable than that of benzene.



More stable σ -complex.

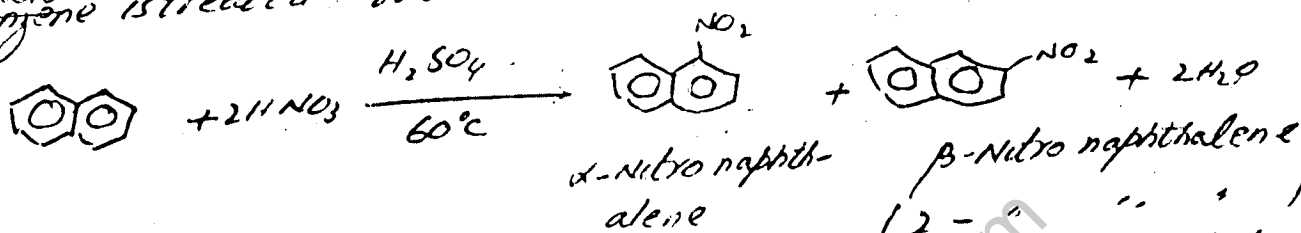
Hence Naphthalene undergoes electrophilic substitution reactions more easily as compared to benzene. The reactions of Naphthalene occur at mild conditions.

REACTIONS OF NAPHTHALENE

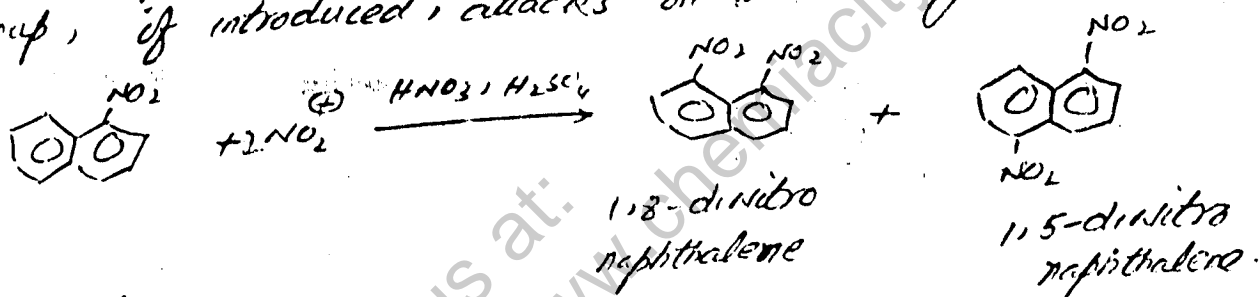
Naphthalene undergoes following

electrophilic substitution reactions

NITRATION: The replacement of hydrogen of naphthalene by $-NO_2$ group is called nitration. Nitration takes place when naphthalene is treated with conc. nitric acid and sulphuric acid.

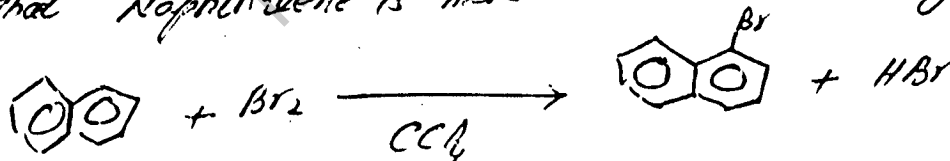


The nitro group decreases reactivity of ring, hence second nitro group, if introduced, attacks on second ring.



BROMINATION:

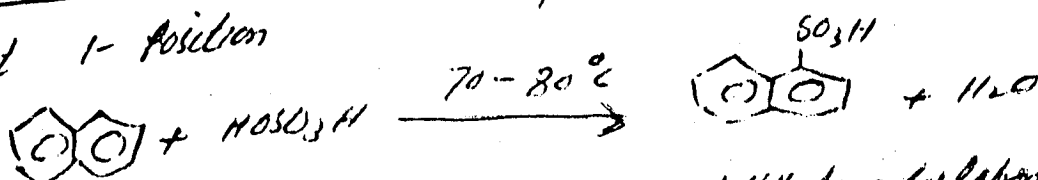
Bromination of Naphthalene gives pure 1-bromo derivative. It does not require $FeBr_3$ catalyst indicating that Naphthalene is more reactive than benzene.



SULFONATION: The replacement of hydrogen of Naphthalene by $-SO_3H$ group (sulphonic acid group) is called sulfonation. The sulfonation can be carried out at 1 or 2-position selectively.

AT LOW TEMPERATURE At low temperature sulfonation takes

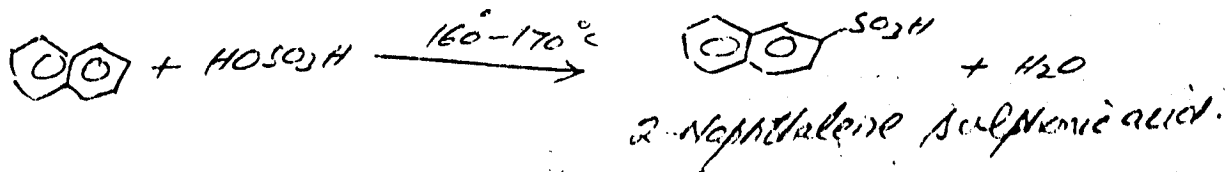
place at 1-position



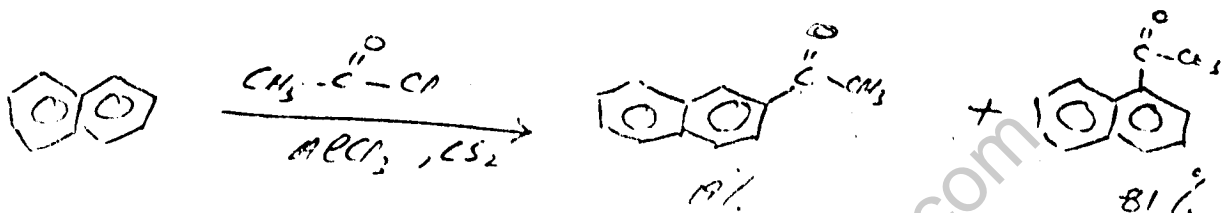
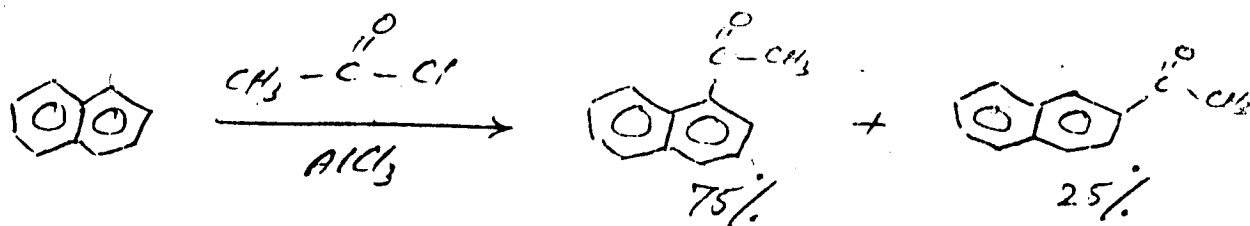
1-naphthylsulfonic acid

AT HIGH TEMPERATURE

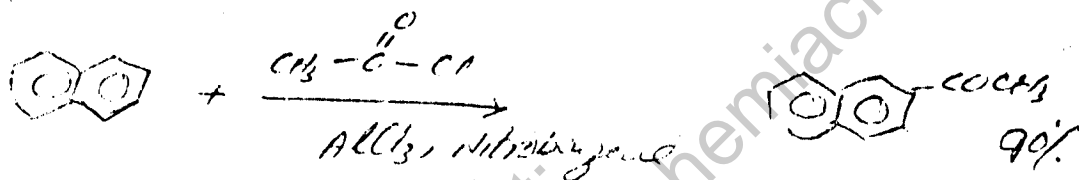
At high temperature attack takes place at 2-position.



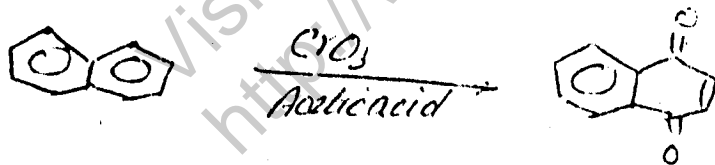
FRIEDAL CRAFT ACYLATION: - The Friedel Craft acylation also produces mixture of 1- and 2- isomers, which are difficult to separate. If CS_2 is used as solvent 1-isomer is favoured.



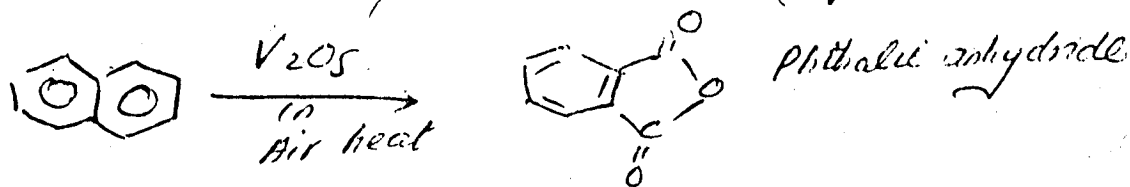
Acylation at 2-position is favoured in nitrobenzene solvent.



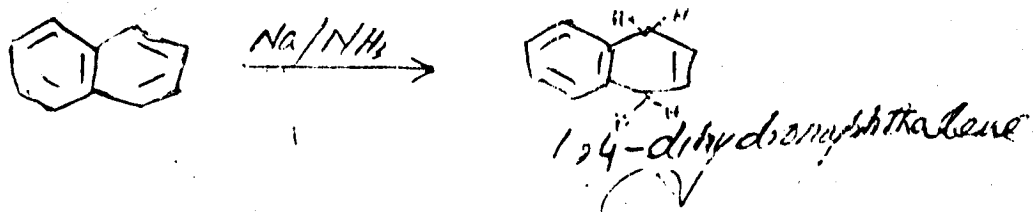
Oxidation: - When CrO_3 in acetic acid is used as solvent oxidizing agent 1,4-Naphthoquinone is formed.



More vigorous oxidation produces phthalic anhydride.



REDUCTION: - The Birch reduction of naphthalene using Na in liquid NH_3 yields 1,4-dihydronaphthalene.

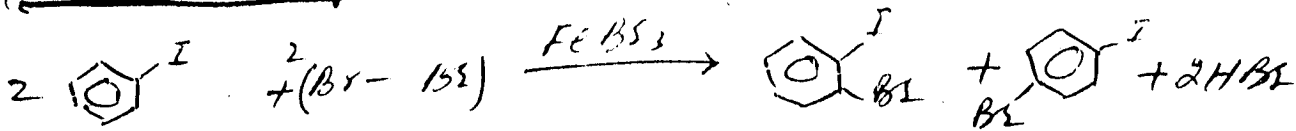


EXERCISE III

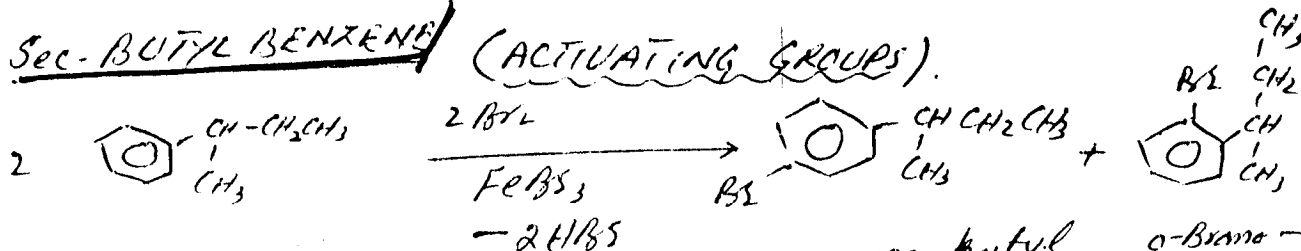
B.Sc.

WRITE STRUCTURES OF PRODUCTS OBTAINED BY MONO-BROMINATION OF FOLLOWING COMPOUNDS.

(i) Iodobenzene :- REACTION WILL OCCUR SLOWER THAN BENZENE



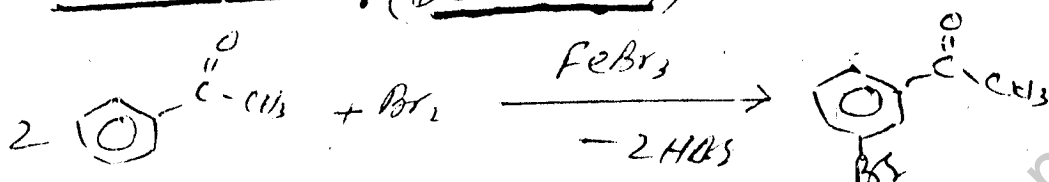
(ii) Sec-Butyl Benzene (ACTIVATING GROUPS)



p-Bromo-sec-butyl benzene

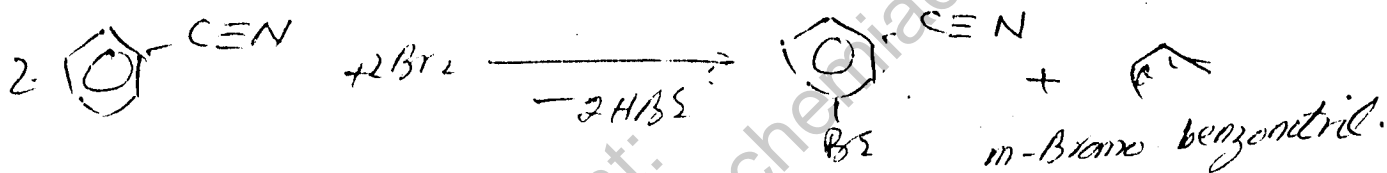
o-Bromo-

(iii) Acetophenone (DEACTIVATING)



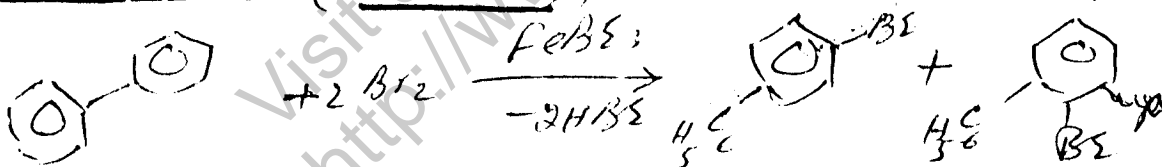
m-Bromo-acetophenone

(iv) Benzonitrile (DEACTIVATING)

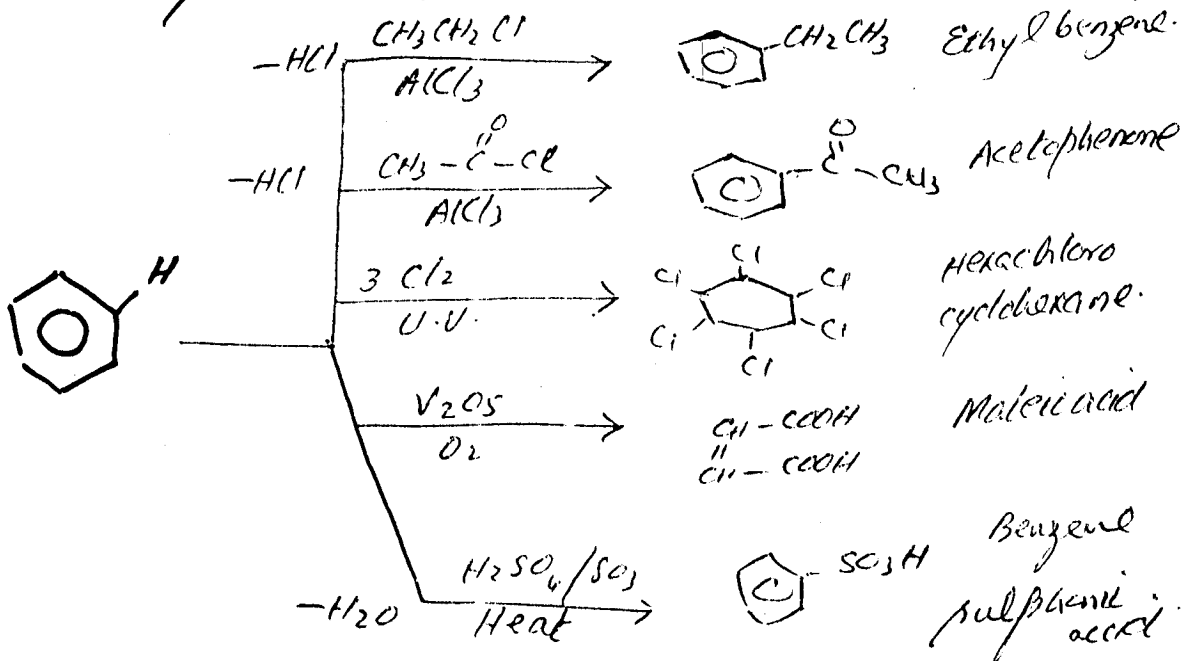


m-Bromo benzonitril.

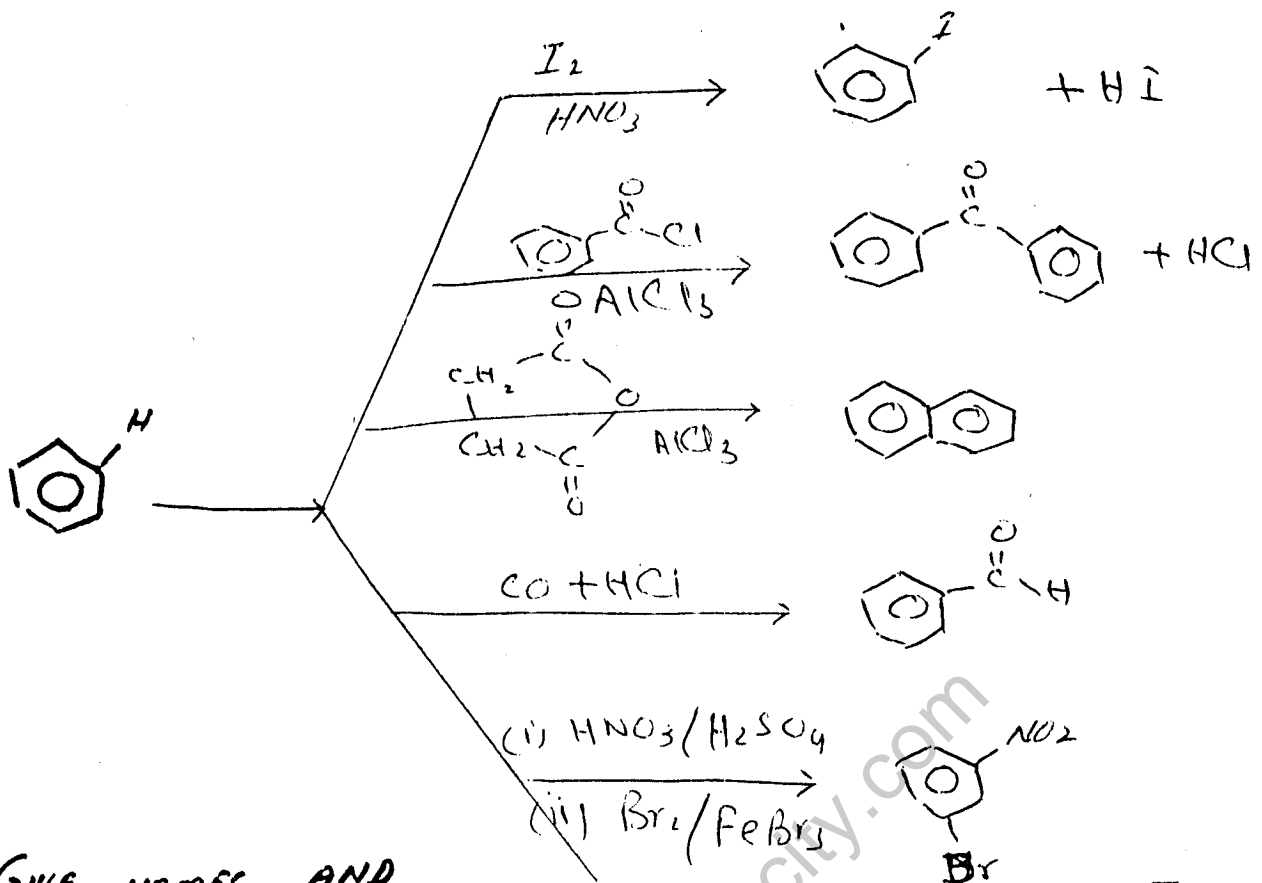
(v) Biphenyl (ACTIVATING)



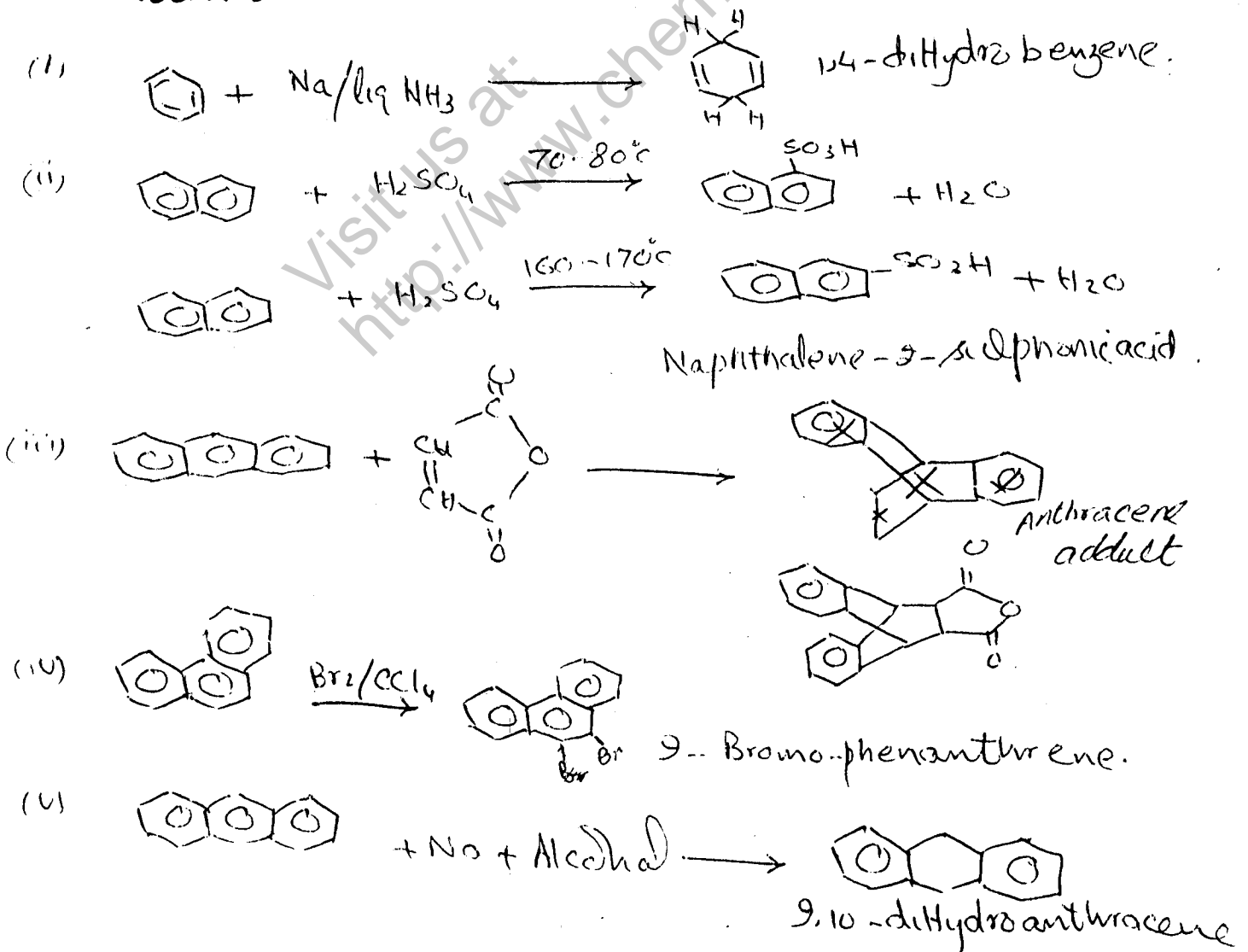
HOW WILL YOU CHANGE BENZENE INTO FOLLOWING.



HOW WILL YOU CONVERT BENZENE INTO FOLLOWING



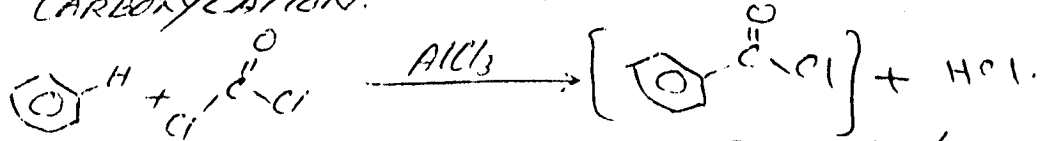
Q:- GIVE NAMES AND STRUCTURES OF PRODUCTS FORMED IN FOLLOWING REACTIONS.



WRITE NOTE ON FOLLOWING.

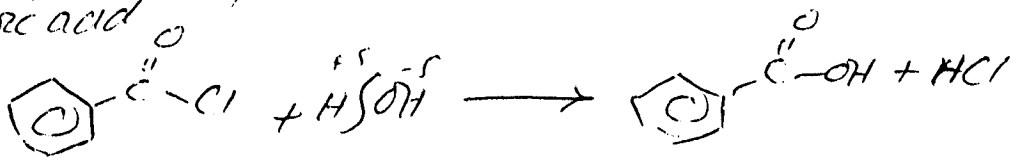
CARBOXYLATION OF BENZENE

Benzene reacts with acetyl chloride to form acetylbenzene. It is called CARBOXYLATION.



The intermediate product on hydrolysis produce

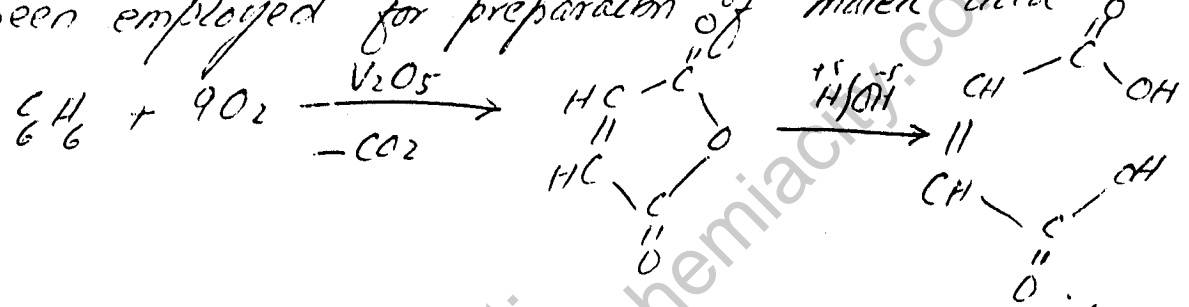
benzoic acid



OXIDATION OF BENZENE

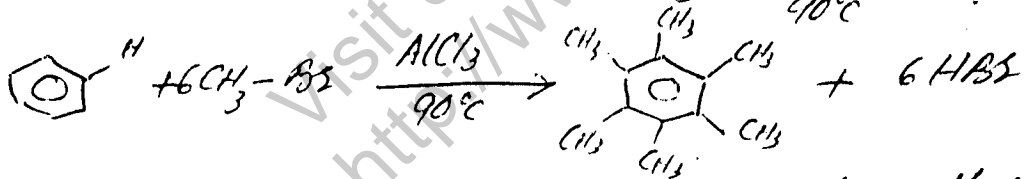
Benzene is not oxidized by alkaline KMnO_4 or chromic acid at room temperature.

Air oxidation of benzene using a V_2O_5 catalyst has been employed for preparation of maleic acid



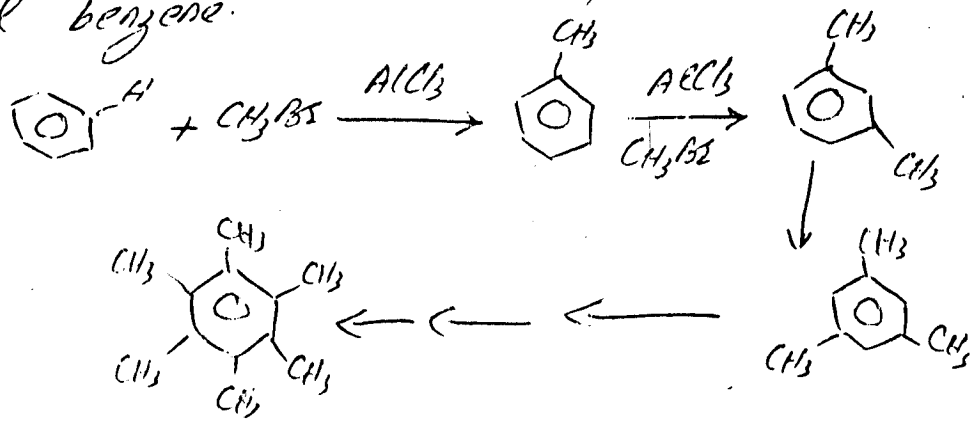
COMPLETE THE FOLLOWING REACTIONS.

BENZENE + EXCESS OF CH_3Br $\xrightarrow[90^\circ\text{C}]{\text{AlCl}_3}$?



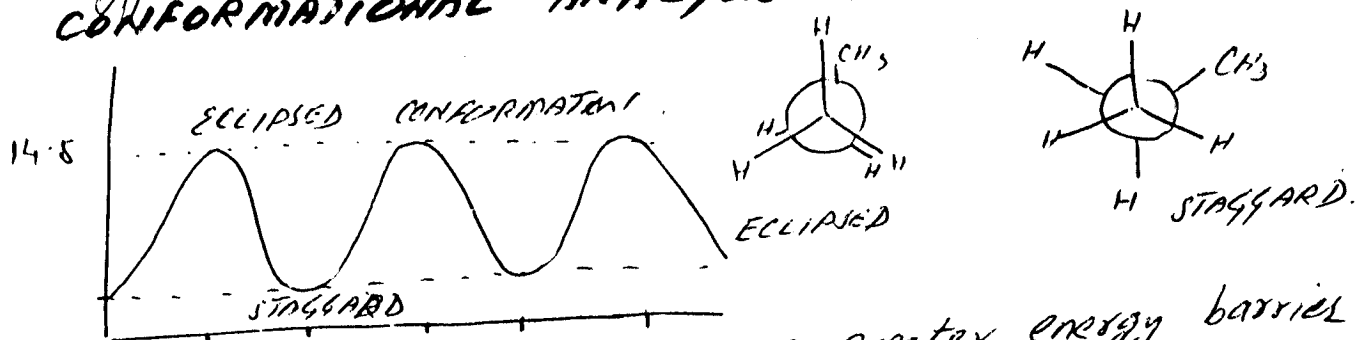
Maleic acid

The monoalkylated products once formed will undergo further polyalkylation which ultimately produce hexa methyl benzene.



conformation. The staggered conformation and eclipsed conformation has energy difference of 12.5 kJ. At room temperature thermal energy of molecule is sufficient to interchange these conformations. These conformations are not separable. These two remain in equilibrium with staggered conformation in high concentration.

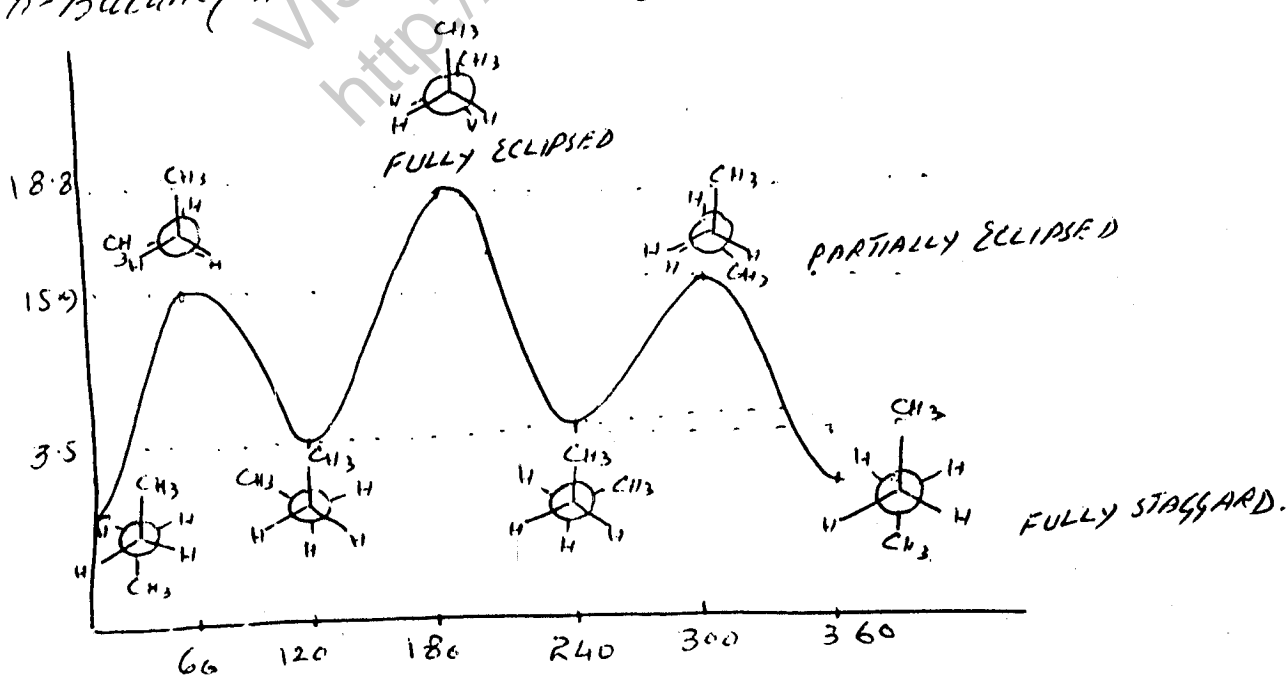
CONFORMATIONAL ANALYSIS OF PROPANE:-



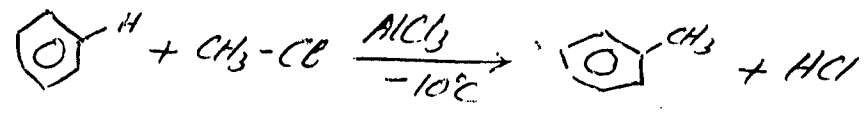
The groups larger than Hydrogen cause greater energy barrier. In eclipsed conformation methyl hydrogen interaction cause torsional strain and also Vander Waals non-bonding repulsive interactions. Thus energy difference between eclipsed and staggered conformation is greater than that in ethane. This barrier to rotation is 14.2 kJ/mole. The conformational energy diagram for propane is similar to that of ethane.

CONFORMATIONAL ANALYSIS OF n-BUTANE:-

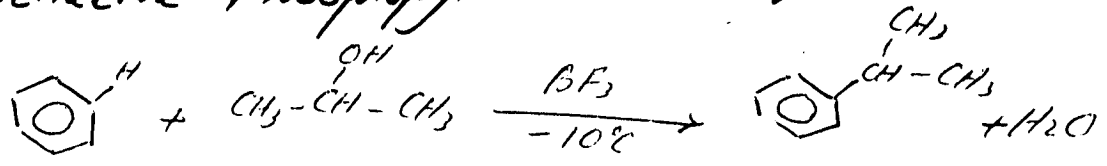
The following eclipsed and staggered conformations are possible for n-Butane. Their relative energies are shown below.



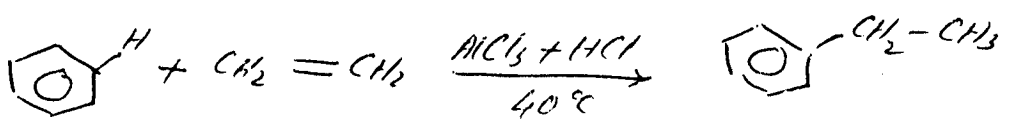
BENZENE + METHYL CHLORIDE $\xrightarrow[-10^{\circ}\text{C}]{\text{BF}_3}$?



BENZENE + Isopropyl alcohol \longrightarrow



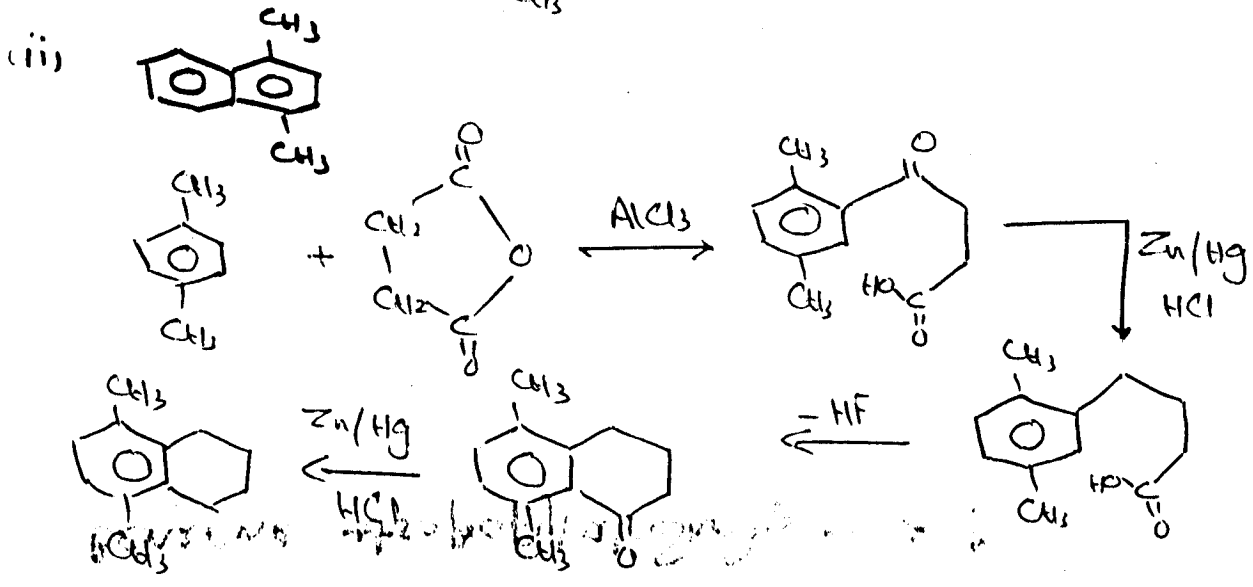
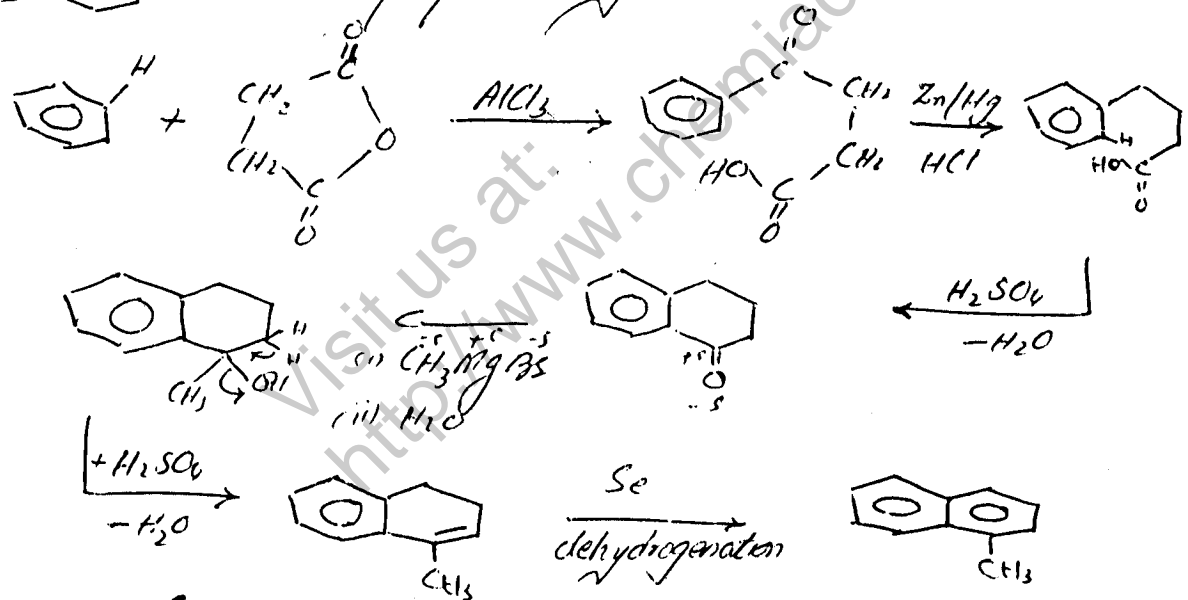
BENZENE + ETHENE \longrightarrow

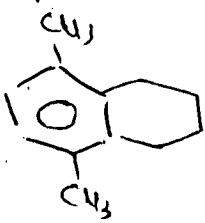


SHOW PRACTICAL SYNTHESIS OF FOLLOWING COMPOUNDS FROM SUITABLE BENZENE DERIVATIVES.

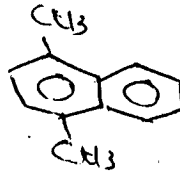
(i) Cc1ccc2ccccc2c1 α -METHYL NAPHTHALEIN.

Cc1ccc2ccccc2c1 can be prepared by Haworth synthesis.

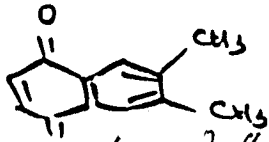




DEHYDROGENATION
Pd Heat

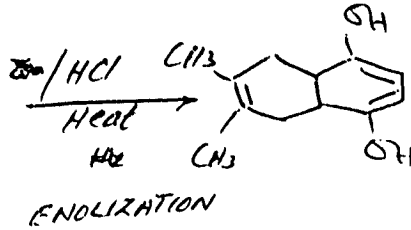
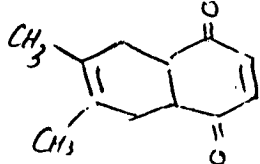
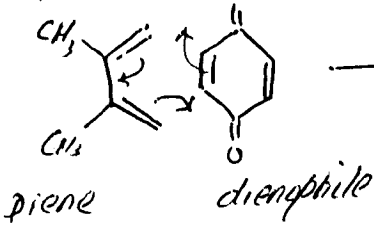


SYNTHESIS OF

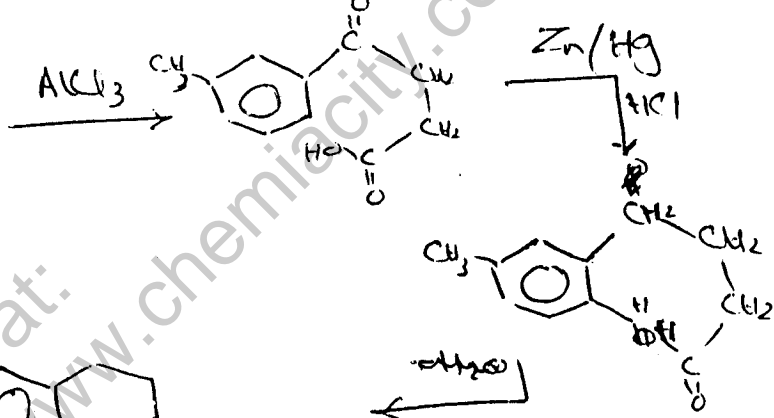
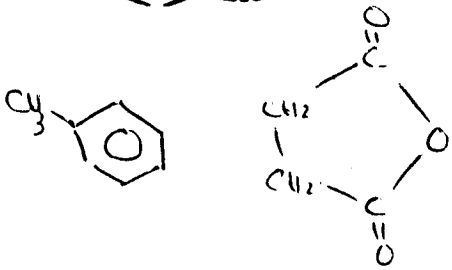
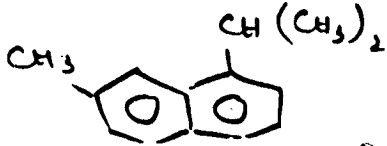
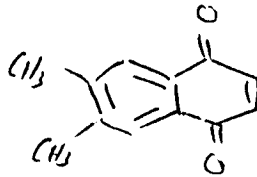


(This can be prepared by following

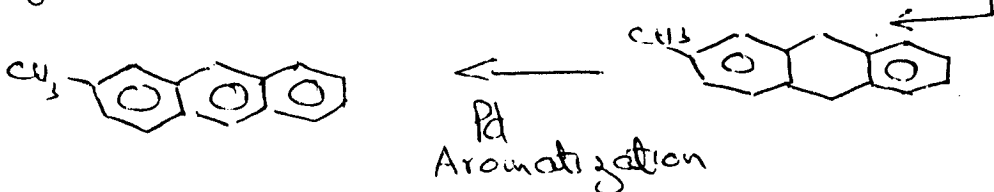
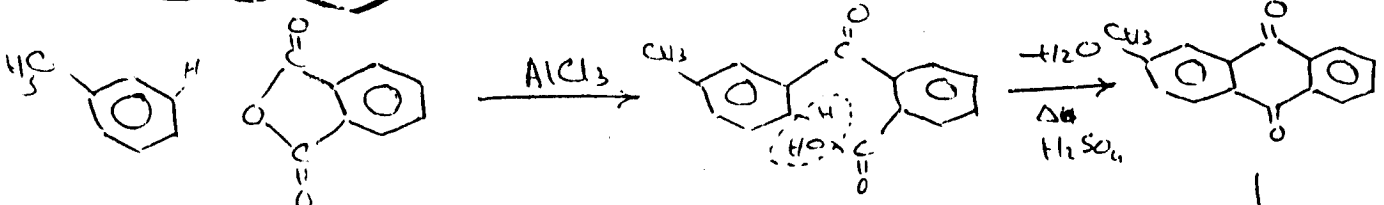
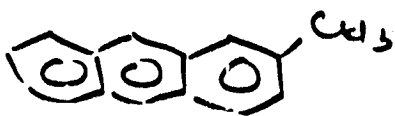
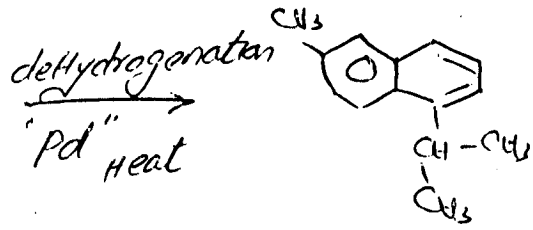
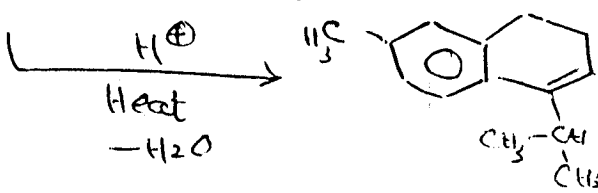
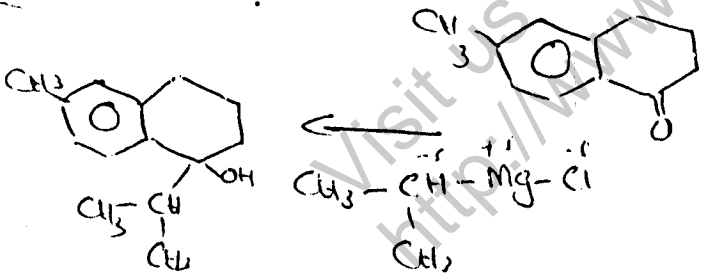
Diels Alder Reaction:



OXIDATION



-H₂O



Q. WHAT ARE DIAZONIUM COMPOUNDS? WHY AROMATIC DIAZONIUM COMPOUNDS ARE MORE STABLE THAN ALIPHATIC DIAZONIUM SALTS.

Ans: The compounds containing $-N^+ \equiv N$ group are called diazonium compounds. If these are associated with an anion they are called diazonium salts. But most of the time we write it as diazonium ion $[R-N^+ \equiv N]$.

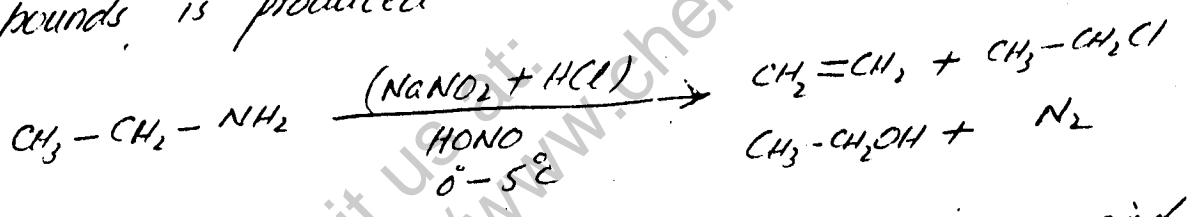
The diazonium compounds are basically

divided into two types.

- (1) ALIPHATIC DIAZONIUM COMPOUNDS.
- (2) AROMATIC DIAZONIUM COMPOUNDS.

ALIPHATIC DIAZONIUM COMPOUNDS:- The open chain diazonium salts are called aliphatic diazonium salts. These are highly unstable and cannot be isolated.

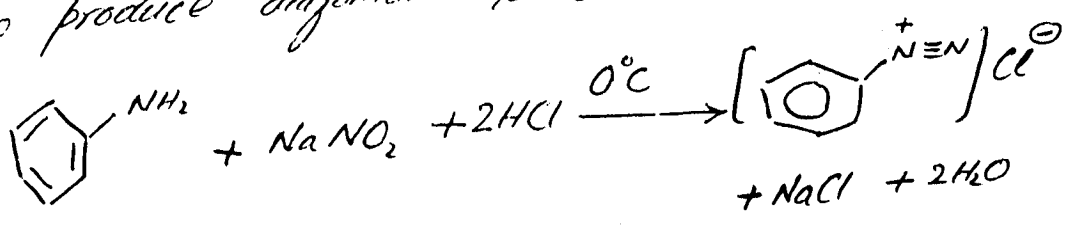
For example when p-amine is treated with nitrous acid ($NaNO_2 + HCl$) a mixture of compounds is produced



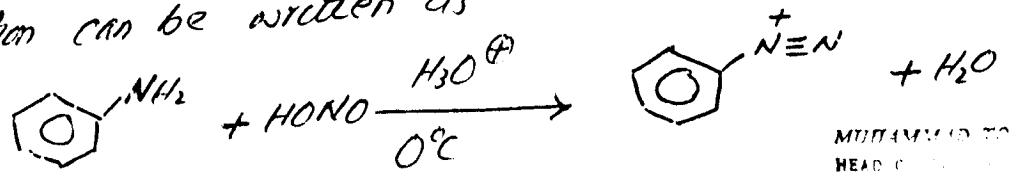
The reaction of aliphatic primary amines with nitrous acid is of little synthetic importance because it yields a mixture of products.

AROMATIC DIAZONIUM SALTS:-

Primary aromatic amine (ANILINE) reacts with nitrous acid to produce diazonium salts.



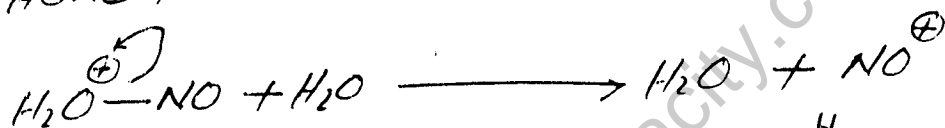
The reaction can be written as



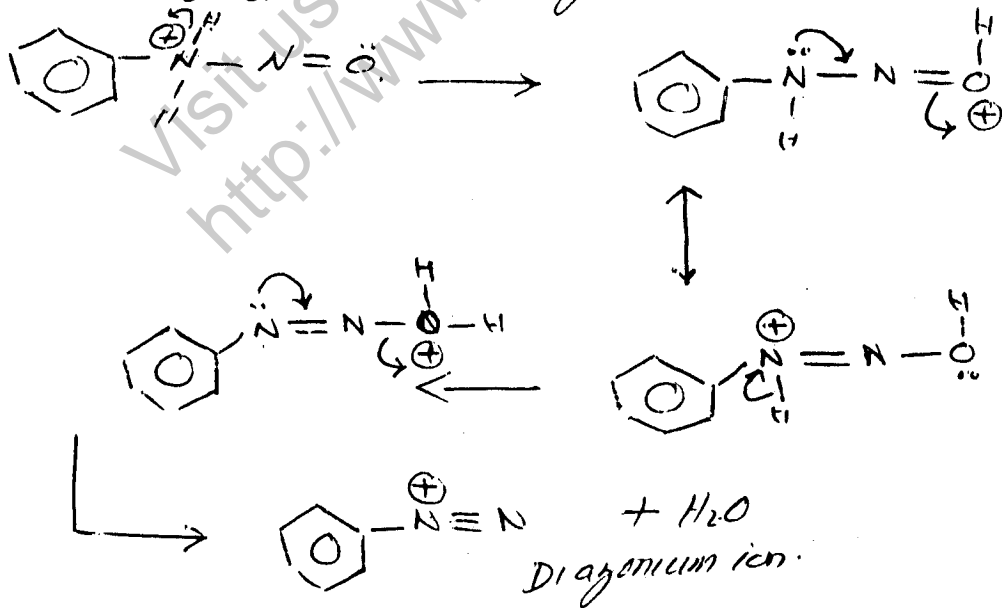
The reaction of aromatic amine with nitrous acid at 0°C yielding an Aromatic diazonium salt is called DIAZOTIZATION.

MECHANISM OF DIAZOTIZATION:- ^{For} ~~During~~ diazotization aromatic amine is treated with ice cold hydrochloric acid solution. The reaction mixture is kept in ice and aqueous solution of NaNO₂ is slowly added to it. The temperature is kept between 0°C to 5°C.

MECHANISM:- The reaction proceeds through formation of NO⁺ ions. This ion reacts with nitrogen of amine to form an unstable N-Nitroso ammonium ion. This step is called NITROSATION.

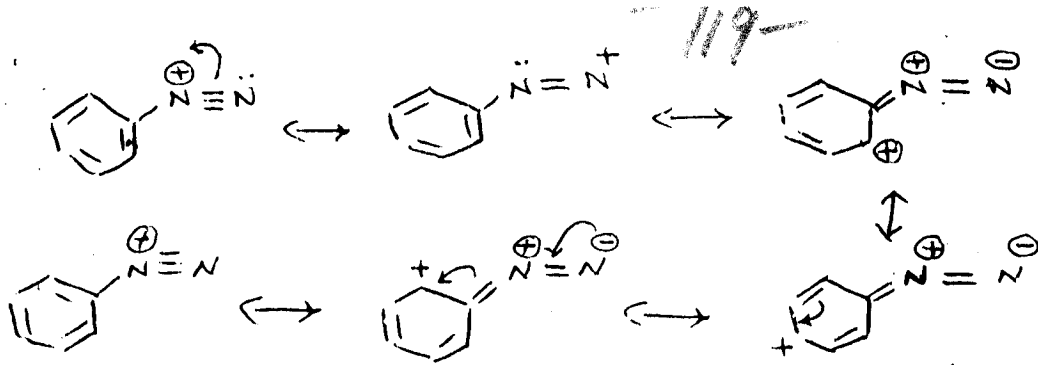


The N-NITROSO AMMONIUM ion undergoes several proton shifts.



STABILITY OF AROMATIC DIAZONIUM ION

The stability of Aromatic diazonium salt ion is due to greater number of canonical forms.



The solid diazonium salts are not isolated because they are highly explosive. Their reactions are studied in solution form.

SYNTHETIC APPLICATIONS:-

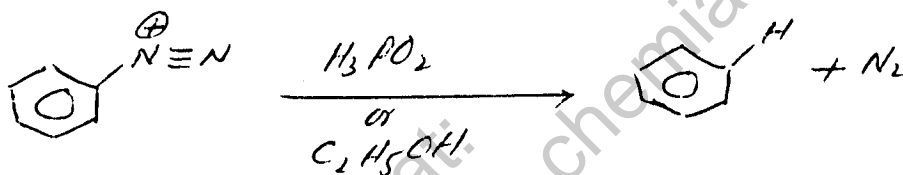
Diazonium compounds undergo two types of reactions

- (1) Those in which $-N \equiv N^+$ is lost as N_2 gas (Replacement).
- (2) Those in which $-N \equiv N^+$ is retained (coupling reactions)

REPLACEMENT REACTIONS:-

(1) REPLACEMENT BY HYDROGEN (DEAMINATION).

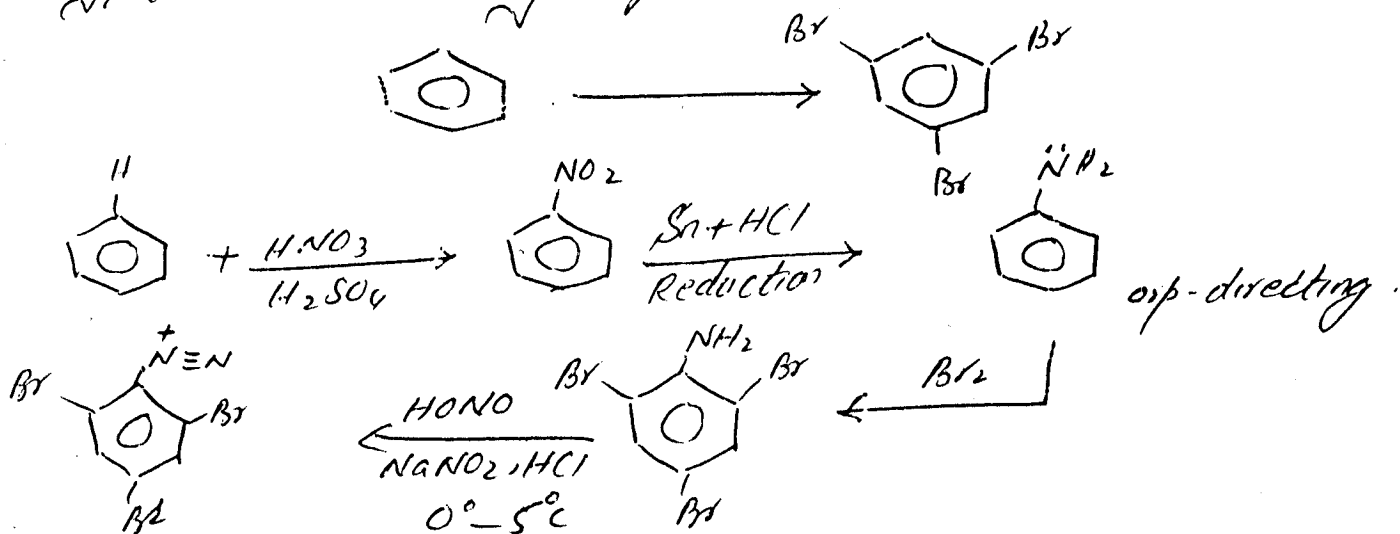
When diazonium salt is treated with hypophosphorous acid H_3PO_2 or ethanol, $-N \equiv N^+$ group is replaced by hydrogen.

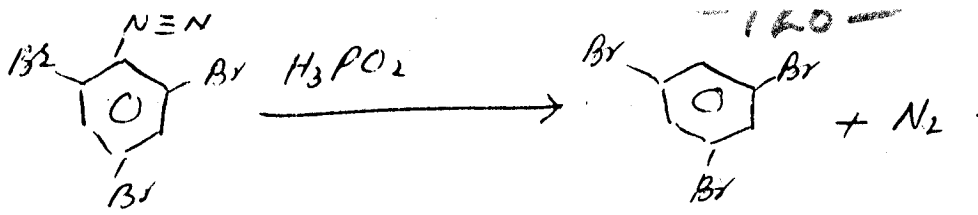


The reaction is used for removing $-NH_2$ group. It is called deamination.

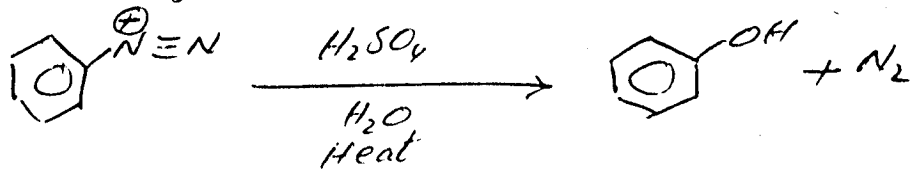
APPLICATION OF DEAMINATION

This reaction is used to prepare 1,3,5-tribromobenzene by introducing $-NH_2$ group and then removing $-NH_2$ via diazotization. It is called dummy group.

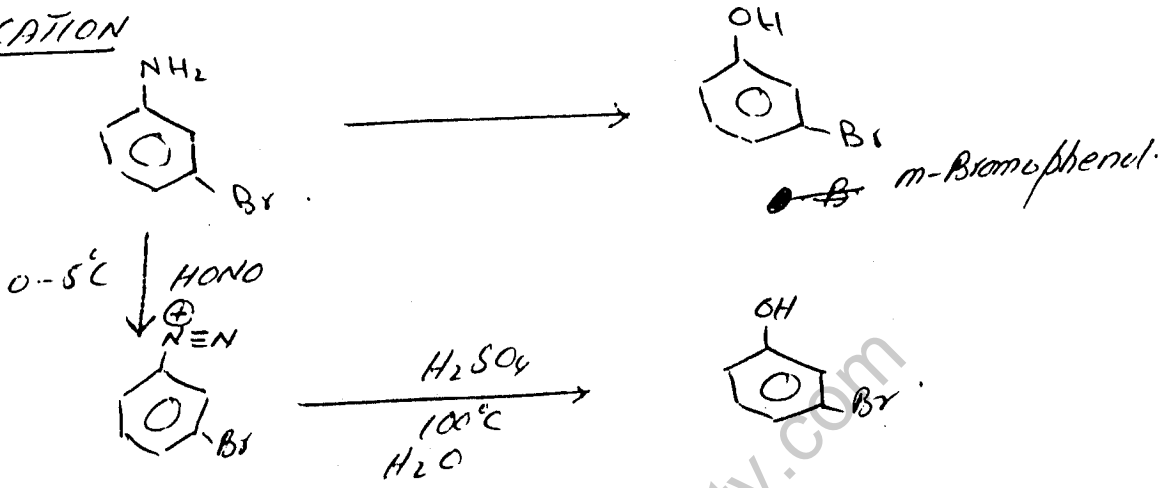




REPLACEMENT BY "-OH" when ~~phen~~ diazonium salt is treated with strong acid -N≡N⁺ is replaced by -OH

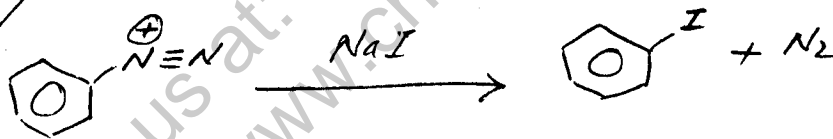


APPLICATION



REPLACEMENT BY "-I"

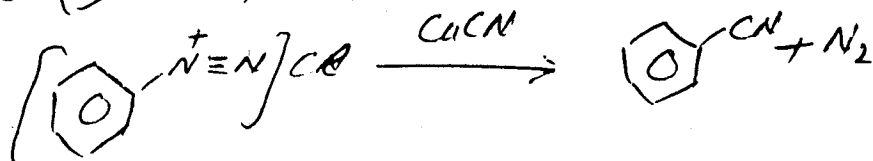
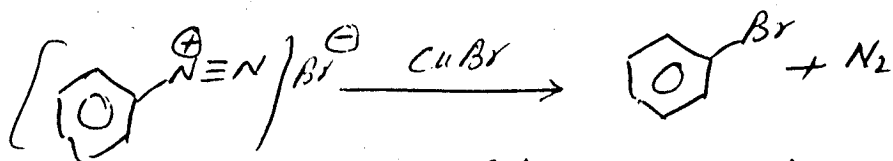
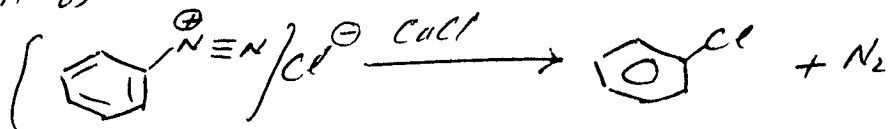
The diazonium salt solution reacts with sodium iodide to give aryl iodide.



REPLACEMENT BY -Cl, -Br, ~~-NO₂~~, -CN
(SANDMAYER REACTION).

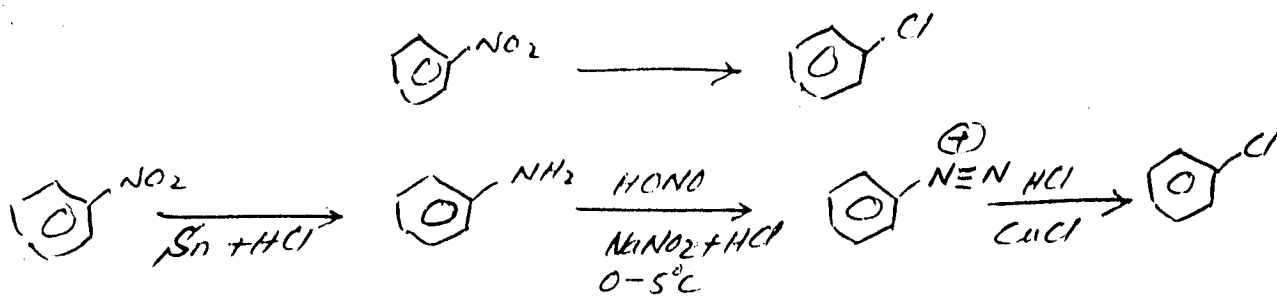
Benzene diazonium salts react with cuprous chloride, cuprous bromide and cuprous cyanide to form products in which diazonium group is replaced by -Cl, -Br, -CN.

The reaction is called SANDMAYER REACTION

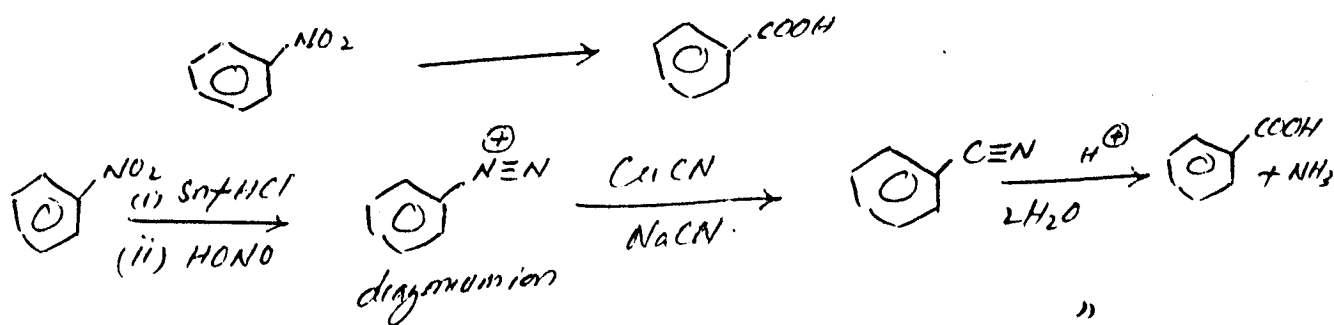


APPLICATIONS OF SANDMAYERS REACTION:-

(i) CONVERSION OF NITROBENZENE TO CHLOROBENZENE

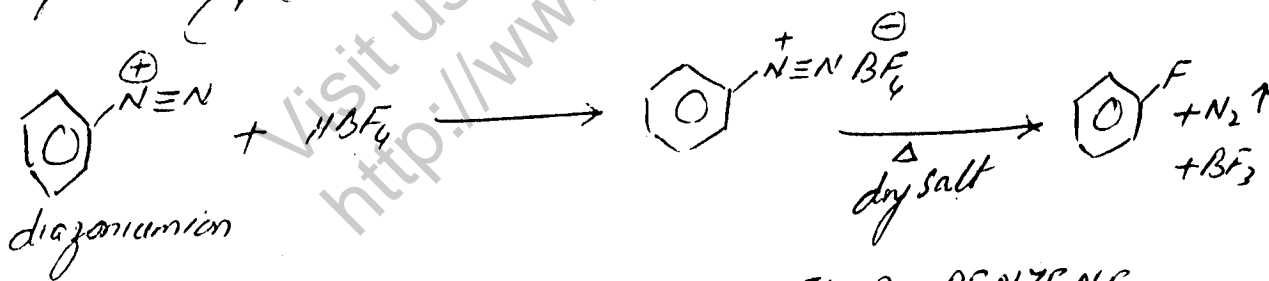


(ii) CONVERSION OF NITROBENZENE TO BENZOIC ACID.

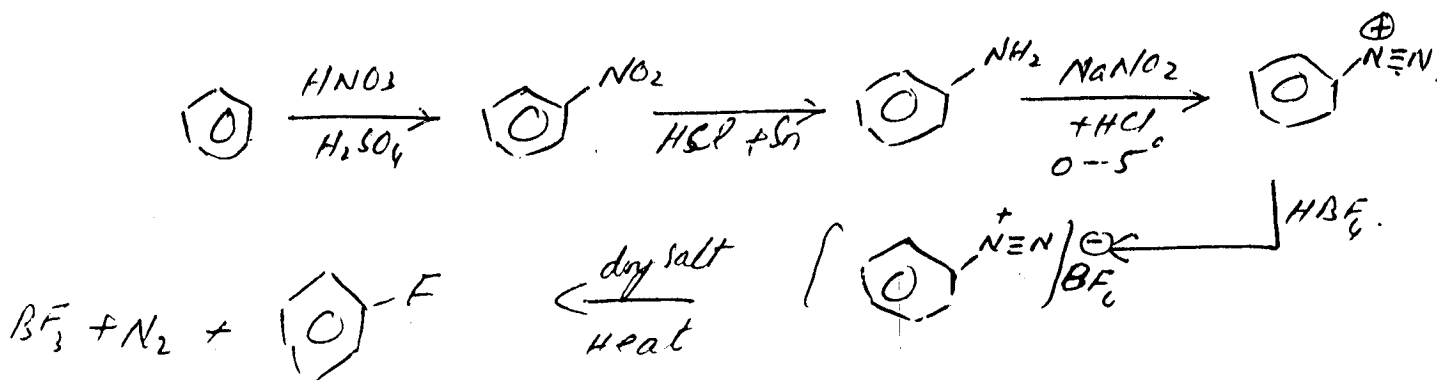


"REPLACEMENT BY-F" Schiemann Reaction:-

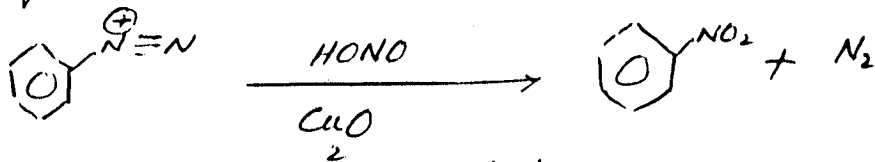
The reaction of diazonium salt with aqueous solution of HBF_4 (fluoroboric acid) produces precipitate of insoluble diazonium salt $(\text{ArN}_2^+)\text{BF}_4^-$. On gentle heating dried salt decomposes to fluoro benzene. The reaction is called SCHIEMANN REACTION. It is general method for preparation of Aromatic fluoro compounds. The reaction scheme is given below



CONVERSION OF BENZENE INTO FLURO BENZENE

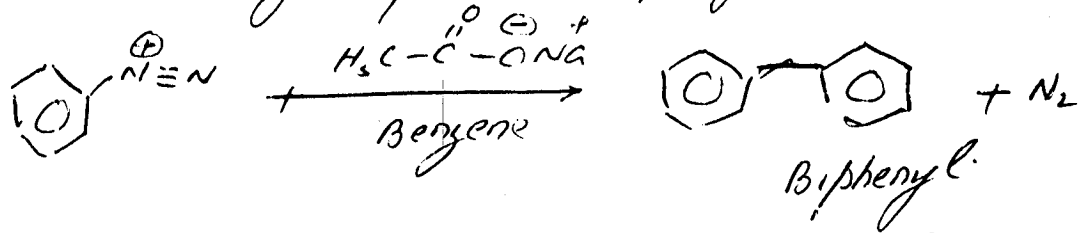


REPLACEMENT BY $-NO_2$ GROUP: Diazogroup $-N \equiv N^+$ is replaced by nitrogroup on treatment with nitrous acid.



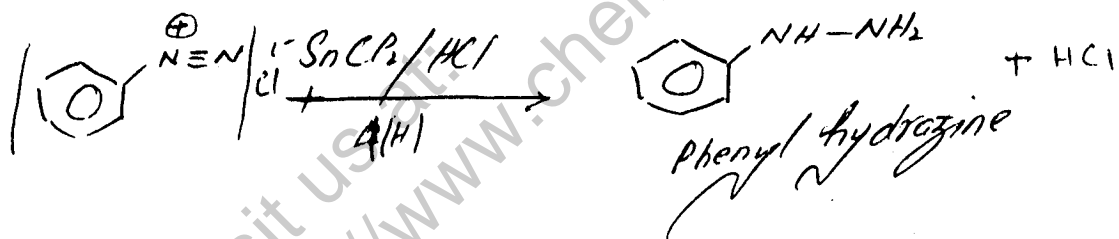
Cuprous oxide acts as catalyst.

REPLACEMENT BY ARYL GROUP: - The decomposition of diazonium salt in presence of aqueous solution of sodium acetate and benzene produces biphenyl.

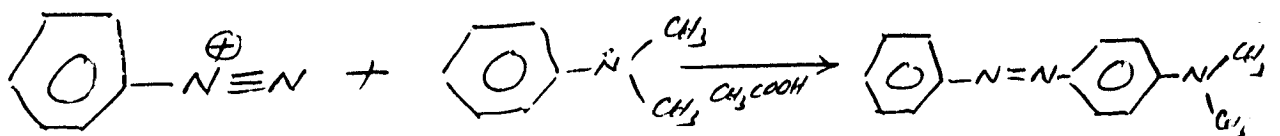
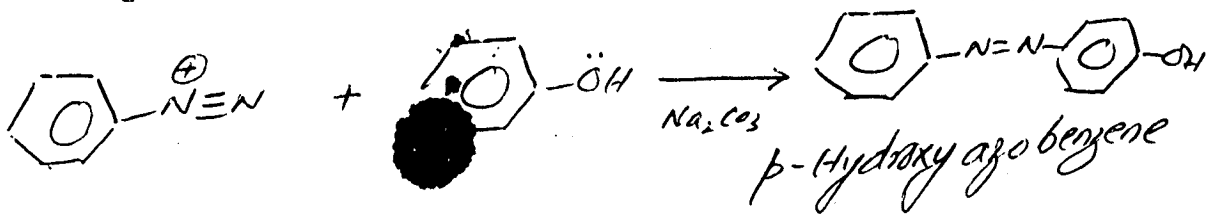


REACTIONS IN WHICH ~~BENZENE RING~~ DIAZONIUM GROUP IS RETAINED.

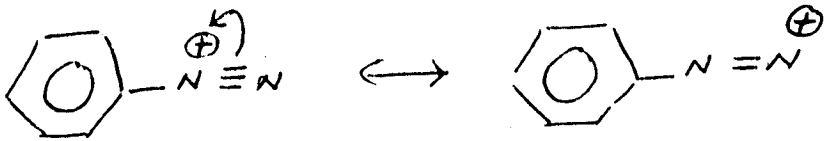
REDUCTION TO HYDRAZINE: - When diazonium salt is treated with stannous chloride SnCl_2 and HCl , $-N \equiv N^+$ group is reduced to $-NH-NH_2$.



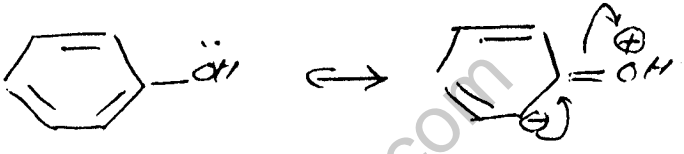
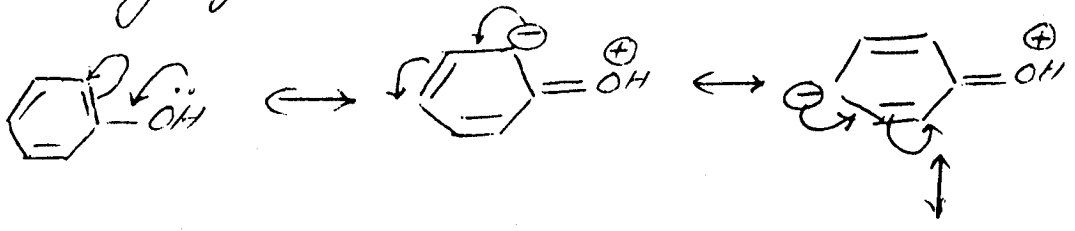
COUPLING REACTION: - The reaction of diazonium salt with sufficiently activated benzene ring produces an 'azo dye'. This is called COUPLING REACTION.



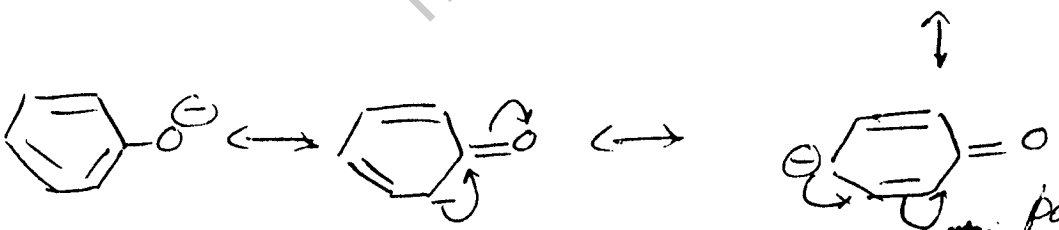
Terminal nitrogen of diazonium ion is weakly electrophilic due to following canonical form



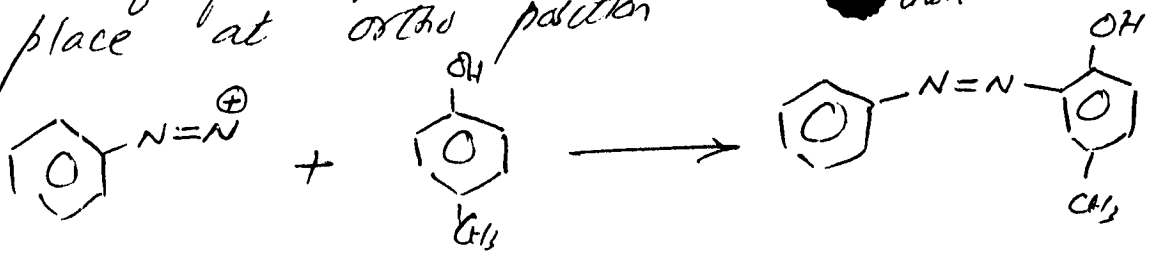
Thus it can react with sufficiently activated benzene ring. For example consider an example of phenol. The -OH group is an activating group due to resonance effect.



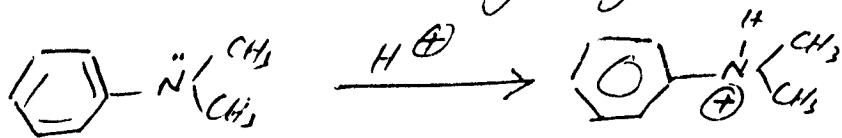
Thus ortho and para positions are sufficiently activated to undergo coupling with diazonium ion. The coupling with phenol is carried out in slightly alkaline medium to produce phenoxide ion which is still even more reactive than phenol itself.



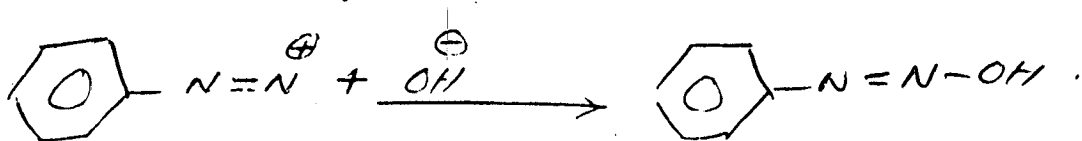
The coupling preferably takes place at para position. However if para position is blocked then coupling can take place at ortho position.



Careful pH control is necessary for coupling reaction. If solution is acidic (pH is low) the lone pair of $-OH$ or $-N(CH_3)_2$ will be protonated and it will be no more an activating group.



In strongly basic medium the terminal nitrogen of diazonium ion (electrophilic nitrogen) will no more be available for coupling.



Coupling reaction is very important tool for preparing coloured compounds (azo dyes). The important indicators like Methyl orange are azo dyes obtained by coupling reactions.

M. RAMANUJAN TOPIQUE
HEAD OF THE CHEM. DEPTT
GOVT. DEGREE COLLEGE,
PO S. S. SARGODHA.