BENZENE AND ITS COMPOUNDS

Molecular formula of benzene is C_6H_6.
Structurally, the 6 carbon atoms are connected by alternate double and single bonds forming a hexagon. ie.

 or .

Qn. Explain the following observation:
The: Carbon-Carbon single bond in cyclohexane is 0.154nm,
Carbon-Carbon double bond in cyclohexene is 0.133nm,
Carbon-Carbon single and double bonds in benzene are of equal bond length of 0.139nm.

In benzene, the carbon-carbon single bond length is intermediate between the double and single bonds, so they are not true single bonds because they are shorter than normal single bonds in cyclohexane.
Also the carbon-carbon double bonds in benzene are longer than normal double bonds in cyclohexene and so they show single bond character.
This implies that all carbon-carbon single and double bonds show some partial double bond character and are of same bond length.
The electrons in the double bonds therefore do not belong to any single carbon but to all and are said to be delocalised pie electrons in the ring structure.

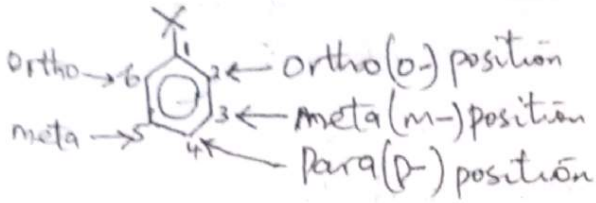
ie  or simply 

NOMENCLATURE OF BENZENE COMPOUNDS

(a) Monosubstituted benzene compounds.

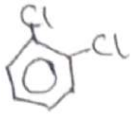
If X is	IUPAC name	If X is	IUPAC name
$-Cl$	Chlorobenzene	$-SO_3H$	Benzenesulphonic acid
$-NO_2$	Nitrobenzene	$-COOH$	Benzoic acid
$-NH_2$	Phenylamine	$-OH$	Phenol
		$-CH_3$	Methyl benzene, etc

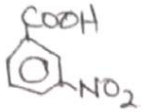
(b) Disubstituted benzene compounds.



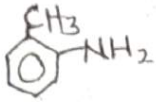
X = Substituent group.

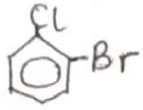
NB: If many groups are attached on the ring, selection of the major group follows the order; $-COOH$, $-SO_3H$, $-COCl$, $-CONH_2$, $-CHO$, $-NH_2$, $-R$, $-Cl$ or Br or I, etc

eg  orthoDichlorobenzene or 1,2-Dichlorobenzene.

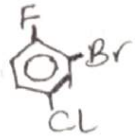
 metaNitrobenzoic acid or 3-Nitrobenzoic acid

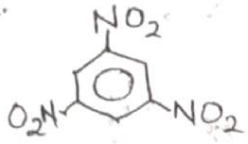
 paraBromophenol or 4-Bromophenol.

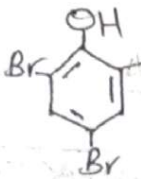
 2-Methylphenylamine, etc

 Bromochlorobenzene, etc

(c) Polysubstituted benzene compounds.

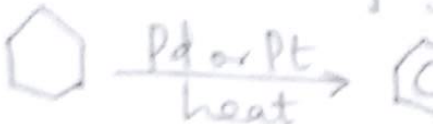
eg1  NB: (i) Follow alphabetical order.
(ii) Lowest sum rule applies.
2-Bromo-4-chloro-1-fluorobenzene.

e.g2.  1,3,5-Trinitrobenzene.

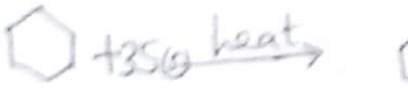
e.g3  2,4,6-Tribromophenol.

METHODS OF PREPARATION OF BENZENE

By dehydrogenation of cyclohexane.



OR



(2) By polymerisation of alkynes.

eg1 $3CH{\equiv}CH \xrightarrow[400^{\circ}C]{Fe}$ 

NB Instead of Fe, Copper tubes can be used at about 450°C.

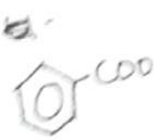
eg2.

$2CH_3C{\equiv}CH \xrightarrow[60-70^{\circ}C]{Organo\text{-}Nickel}$  $+ H_2(g)$

(3) By decarboxylation of benzoic acid using Sodalime (Solid sodium hydroxide.

 $\xrightarrow[heat]{NaOH(s)}$  $+ H_2O(l) + Na_2CO_3(aq)$.

OR

 $\xrightarrow[heat/CaO(s)]{NaOH(s)}$  $+ Na_2CO_3(aq)$.

NB: CaO is a drying agent which absorbs the water formed.

(4) From benzene diazonium salt ().

NB: The salt can be synthesised from benzene as follows:

 $\xrightarrow[Conc.H_2SO_4,\ 60^{\circ}C]{Conc.HNO_3}$  $\xrightarrow[heat/NaOH]{Sn/Conc.HCl}$ 

$\downarrow NaNO_2(aq)/Conc.HCl, <10^{\circ}C$

Benzene diazonium chloride salt.

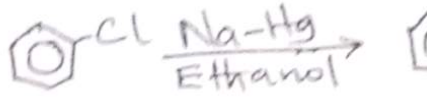
 $\xrightarrow[H_2O]{H_3PO_2}$  $+ N_2(g)$.

NB H_3PO_2 is Hypophosphorous acid.

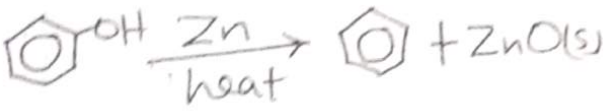
(5) By cyclisation or reforming of hexane.

$$CH_3(CH_2)_4CH_3 \xrightarrow[550^\circ C]{Cr_2O_3 + Al_2O_3} C_6H_6 + 4H_2(g)$$

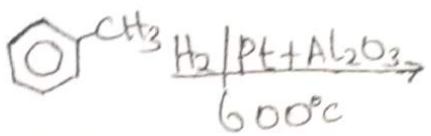
(6) From aromatic halides

e.g 

(7) From phenol



(8) From methylbenzene.



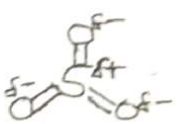
CHEMICAL RXNS OF BENZENE.

ELECTROPHILIC SUBSTITUTION RXNS.

Benzene undergoes substitution reactions with electrophiles in which one or more hydrogen atoms of the ring are replaced.

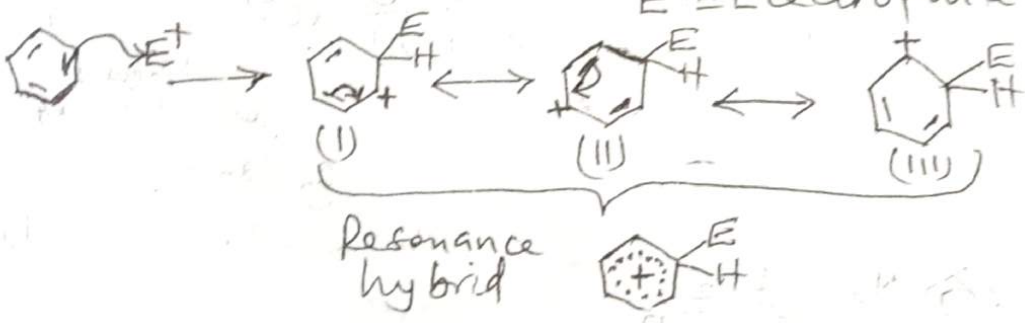
The electrophile is an electron deficient species. It can be:

(i) Charged e.g nitronium ion, $\overset{+}{N}O_2$.

(ii) neutral e.g sulphur trioxide, SO_3 or 

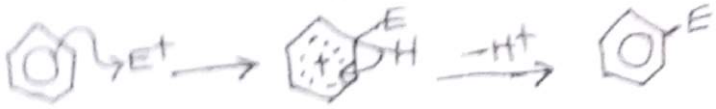
General mechanism of rxn.

E^+ = Electrophile

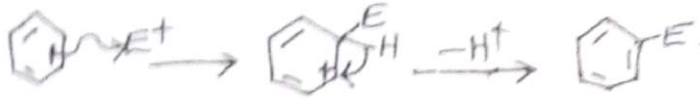


The structures I, II and III are resonance structures that show that the positive charge is delocalised over the three carbon atoms, hence the structure of the possible intermediate which is formed after attack of the ring by the electrophile is a resonance hybrid represented as:

So the summary of the mechanism is:



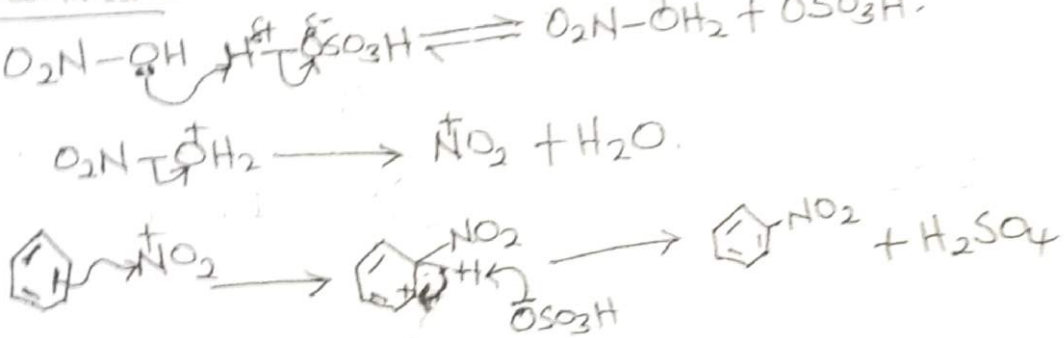
OR



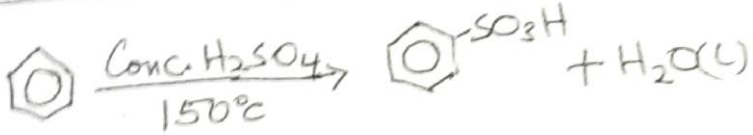
Examples of electrophilic substitution rxns of benzene are;

(1) NITRATION RXN

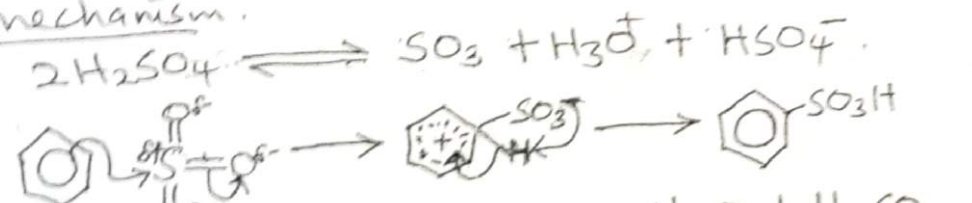
mechanism



(2) SULPHONATION RXN



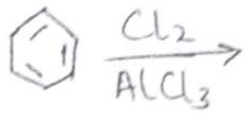
mechanism.



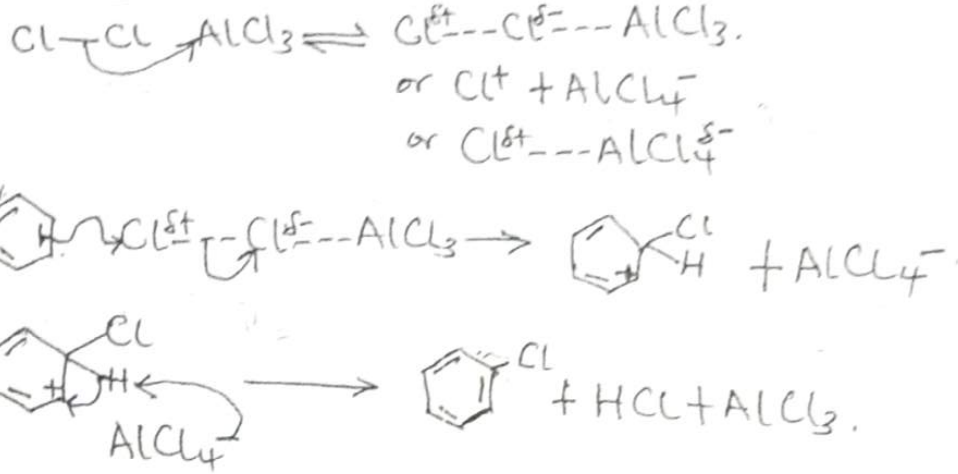
(3)

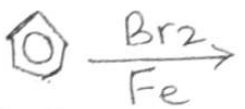
HALOGENATION

NB. Benzene does not react with Cl_2 or Br_2 on its own in the dark. This is due to the fact that there is lack of a positive centre on the non-polar halogen molecule to initiate the electrophilic attack. Therefore, in the ~~electrophilic~~ rxns of benzene and halogens, a halogen carrier is necessary. The halogen carrier is used to polarise the halogen molecule by withdrawing a pair of electrons from the halogen–halogen bond. The possible halogen carriers used are $AlCl_3$, $AlBr_3$, Fe, $FeCl_3$, $FeBr_3$, ethanoic acid, BF_3, etc

eg 1  + $HCl_{(g)}$

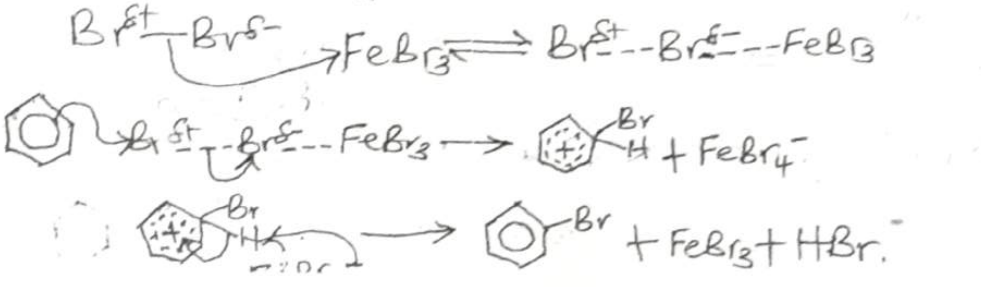
mechanism



eg 2  + $HBr_{(g)}$

Mechanism

$2Fe_{(s)} + 3Br_2 \longrightarrow 2FeBr_{3(s)}$

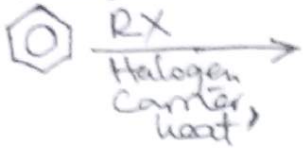


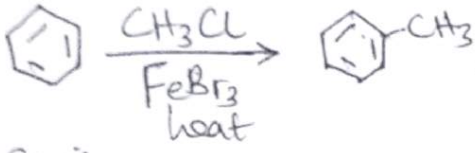
NB: Rxn with iodine does not occur because iodine is less reactive and rxn with fluorine is too fast to follow.

④ ALKYLATION RXNS

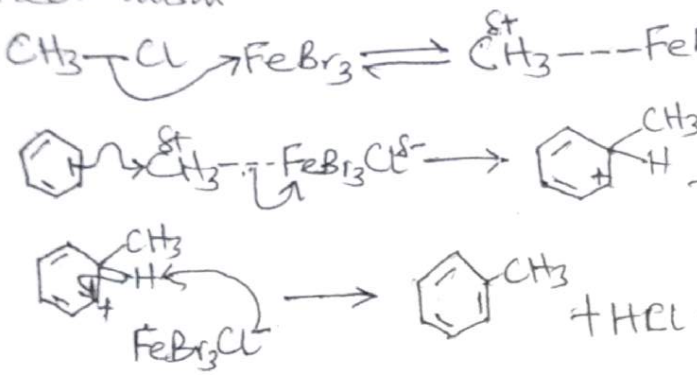
(a) REACTION WITH ALKYL HALIDES.

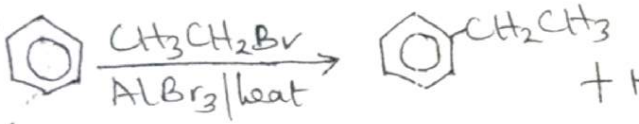
Rxn occurs in presence of halogen carrier and heat forming alkyl benzene.



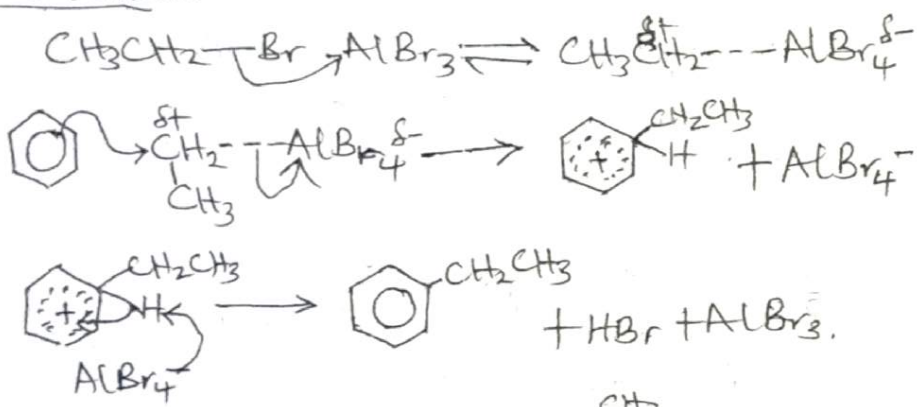
eg 1 

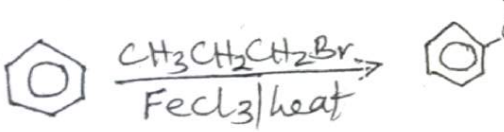
mechanism



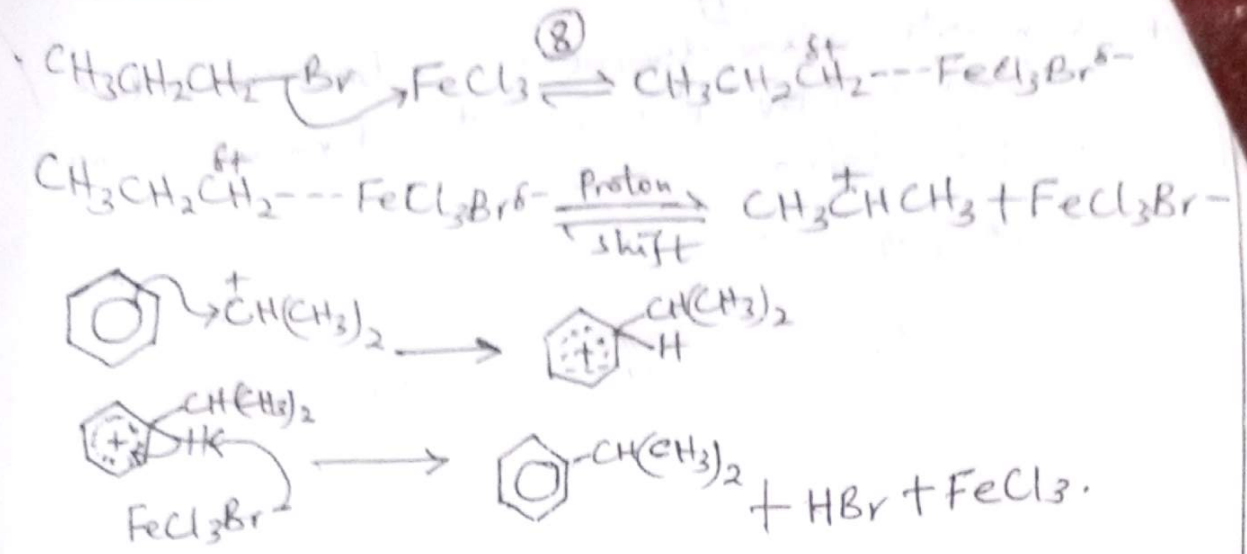
eg 2. 

mechanism



eg 3 

mechanism

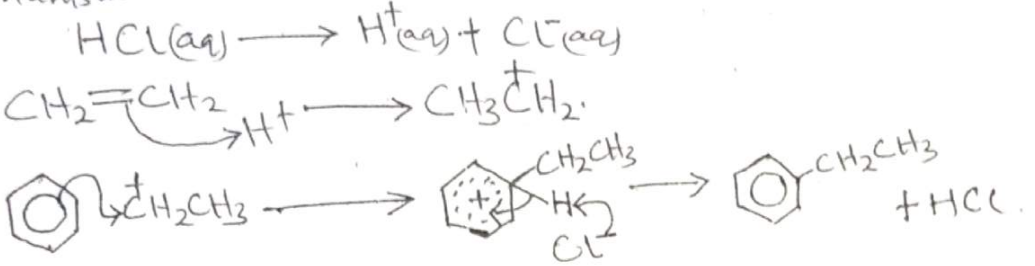


(b) REACTION WITH ALKENES.

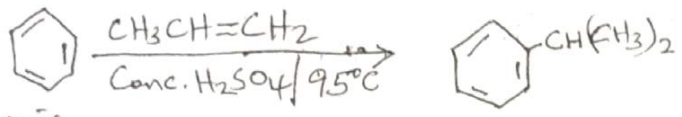
Reaction occurs in presence of acid and heat forming alkylbenzene

e.g 1

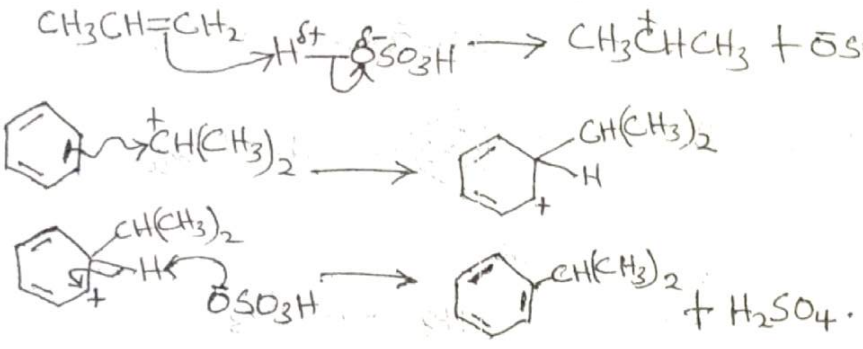
mechanism



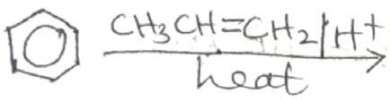
e.g 2



mechanism.

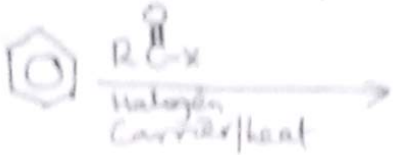


Qn. Complete and write mechanism.

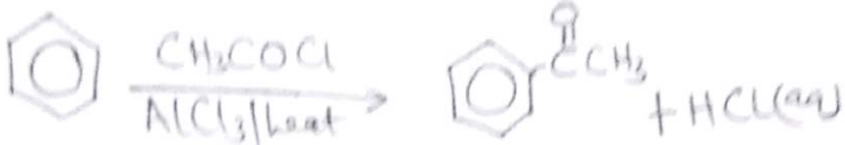


(c) ACYLATION OF BENZENE RING

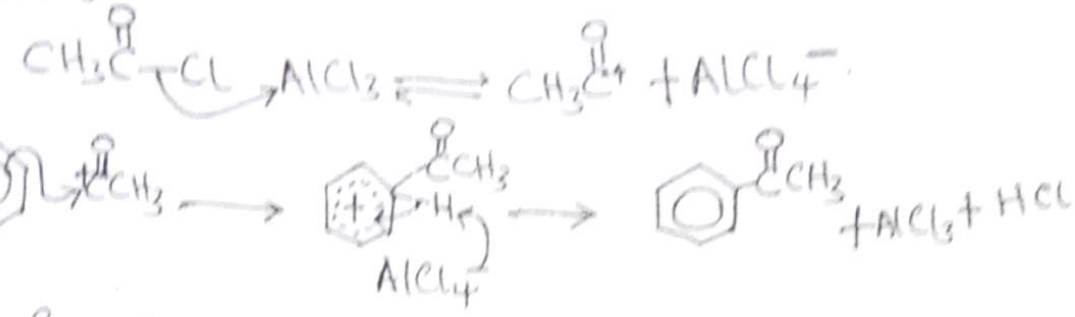
Rxn occurs in presence of a halogen carrier forming aromatic ketones.



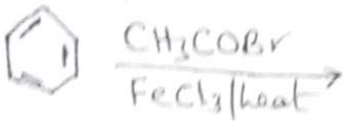
e.g.



Mechanism



Qn: Complete and write mechanism



OTHER IMPORTANT RXNS OF BENZENE

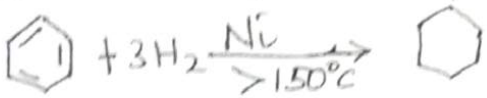
① **Combustion**

Benzene and other aromatic cpds burn with a yellow sooty flame forming carbon dioxide and water.

NB: Burning with a yellow sooty flame is used as a preliminary test for an aromatic compound in organic qualitative analysis.

② **Reaction with hydrogen.**

Cyclohexane forms.

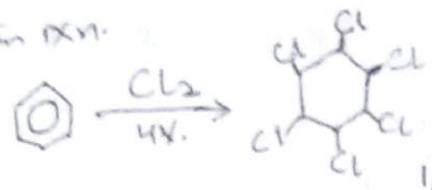


③ **Addition of Cl_2 or Br_2.**

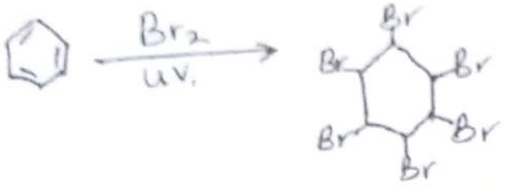
Benzene can undergo addition rxn as well as substitution rxn with Cl_2 or Br_2.

Substitution rxn occurs in presence of a halogen carrier but addition rxn occurs in presence of ultra violet light.

(a) Addition rxn.

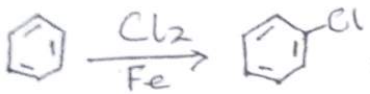
eg1 

1,2,3,4,5,6-Hexachlorocyclohexane.

eg2. 

1,2,3,4,5,6-Hexabromocyclohexane.

(b) Substitution rxn.

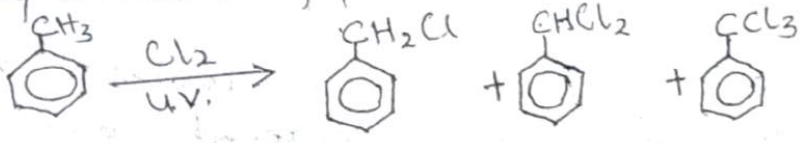
eg 

DERIVATIVES OF BENZENE:

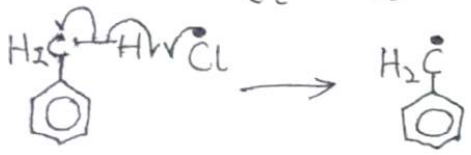
METHYLBENZENE : 

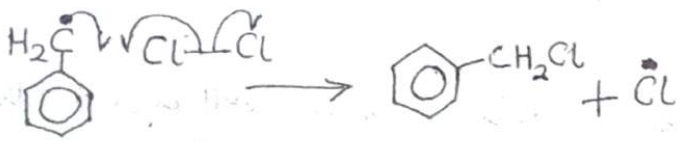
It has both an aromatic part (benzene ring) and an aliphatic part ($-CH_3$ group), which is called the side chain. These two parts make different contributions to the properties of methylbenzene and each has a modifying effect on each other as follows:

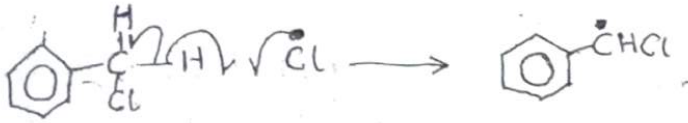
(a) The methyl group (CH_3) undergoes reactions similar to those of the straight chain alkanes. Therefore chlorination of methylbenzene in presence of UV. occurs at the side chain giving a mixture of products as follows:

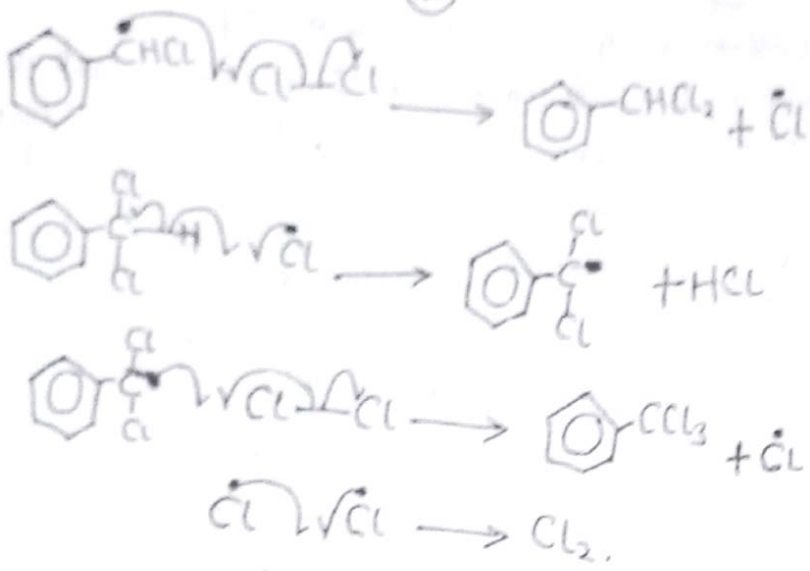


Mechanism





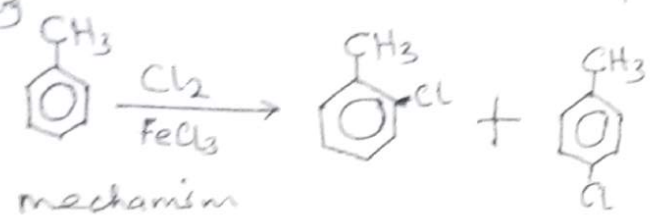




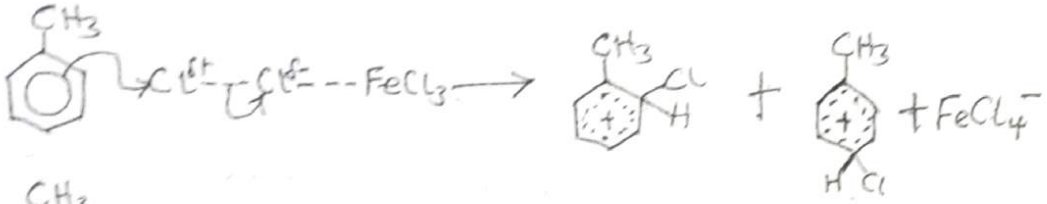
NB: Bromination in U.V. occurs in a similar way.

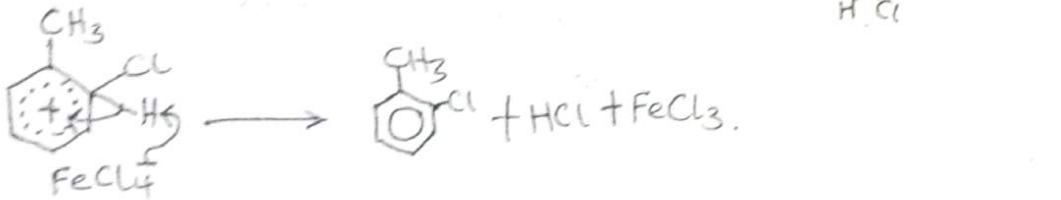
(b) When chlorine or bromine is added to methylbenzene in presence of a halogen carrier, the ring undergoes substitution rxn forming 2 pdts ie ortho-para pdts are formed.

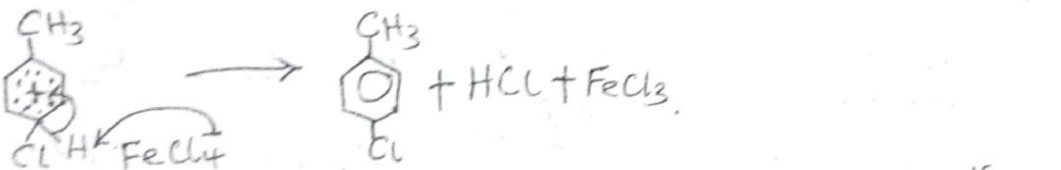
eg



mechanism

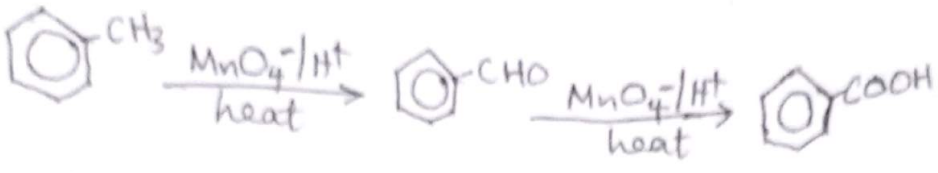




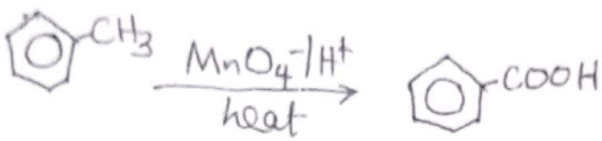


NB: This reaction proceeds faster than the corresponding rxn of benzene with chlorine. The methyl group has a positive inductive effect, so tends to push electrons to the ring. This activates the ring towards electrophilic substitution reaction and directs the incoming substituents to positions 2 and 4 forming 2 possible products.

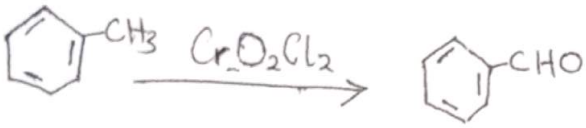
Similarly, the benzene ring with its region of very high electron density has a modifying effect on the methyl ($-CH_3$) group such that potassium permanganate can oxidise the $-CH_3$ group to the carboxyl ($-COOH$) group. This oxidation rxn is not possible with alkanes.



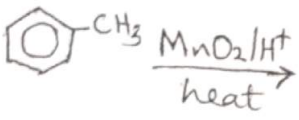
OR simply



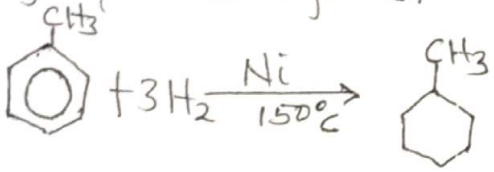
NB: If mild(weak) oxidising agent such as Chromium(VI) dichloride dioxide (CrO_2Cl_2) or manganese(IV) oxide (MnO_2) in acid is used, Benzaldehyde forms as the final product.



OR



(d) Addition of hydrogen to methyl benzene.
Methylcyclohexane forms.



Qn: Write eqns including conditions to show the following synthesis.

(a) Chloroethane to Benzaldehye

(b) Ethene to benzoic acid.

THE EFFECTS OF SUBSTITUENTS ON REACTIVITY AND POSITION OF ATTACHMENT ON THE RING OF THE INCOMING SUBSTITUENT ON FURTHER SUBSTITUTION.

Groups of atoms attached to the benzene ring tend to affect the rate of rxn of the ring and also position of attachment on the ring of the incoming substituent during further substitution.

Some of the substituents activate the ring while others deactivate it. These substituents are divided into 3:

GROUPS THAT ACTIVATE THE BENZENE RING AND DIRECT FURTHER SUBSTITUTION TO POSITIONS 2 AND 4 i.e ortho-para directing groups

In their order of strength, they include:

Phenoxide ion, $Ar-O^- > -NR_2 > -NHR > -NH_2 > -OH > \bar{O}R > -NHCOR > -OCOR > Ar- > -CH_3$ & other alkyl groups.

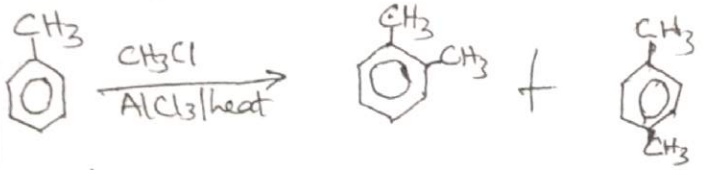
These groups activate the benzene ring towards electrophilic substitution rxn by making the pie electrons easily available to an attacking electrophile.

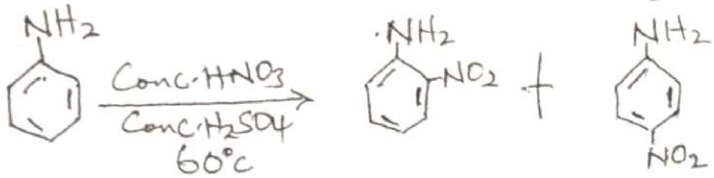
For some of them, the lone pair of electrons on the atom directly attached on the ring tends to associate with the delocalised electrons of the ring so increasing election density around the ring.

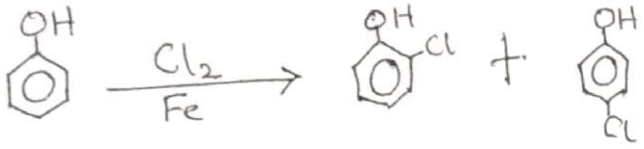
For the phenyl or alkyl group, has positive inductive effect, so tends to push electrons into the ring increasing the its election density

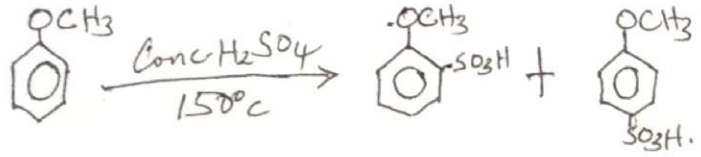
The election density around the ring increases in ortho-para position i.e 2 or 6 and 4 forming 2 possible products.

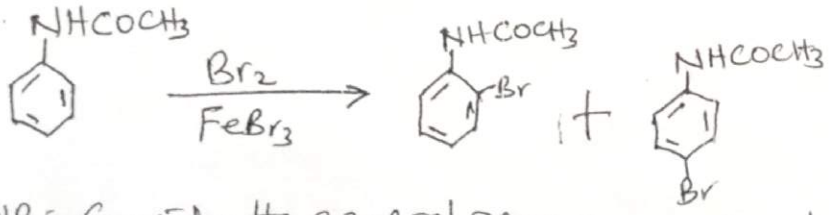
Examples include:

(a) 

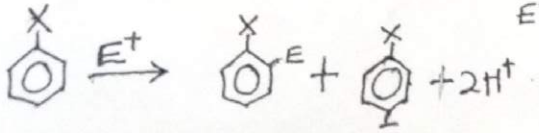
(b) 

(c) 

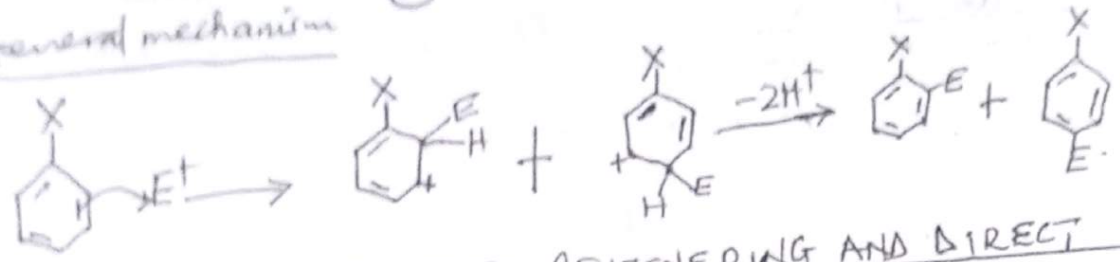
(d) 

(e) 

NB: Consider the general rxn: X = 2 or 6 and 4 directing species.
E^+ = Electrophile / incoming substituent



General mechanism



2. GROUPS THAT DEACTIVATE THE BENZENE RING AND DIRECT FURTHER SUBSTITUTION TO POSITION 3. i.e meta directing groups

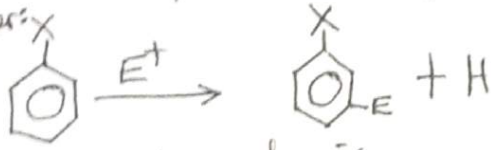
These groups make the benzene ring less reactive with the electrophile by withdrawing the pie electrons from the ring thus decrease the electron density of the ring and direct further substitution to position 3 or 5 but not both forming one product.

In order of deactivating strength, they include:

$-NR_3 > -N^{+} > -NO_2 > -COOH > -CHO > -COR > -CN > -SO_3H > -COOR$, etc

The atom directly bonded to the ring has a positive charge on it which tends to pull electrons from the ring making it less reactive.

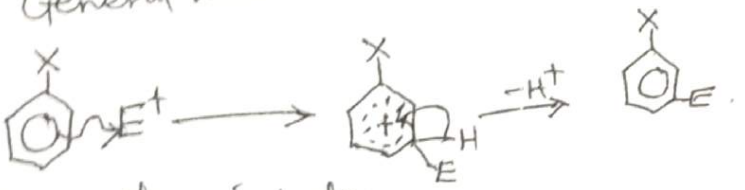
Consider:



E^{+} = incoming electrophile

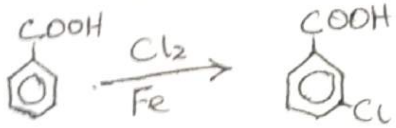
X = meta directing group.

General mechanism.



Examples include:

(a)



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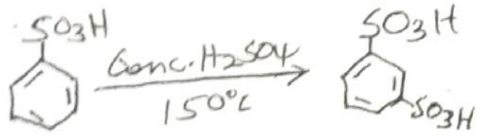
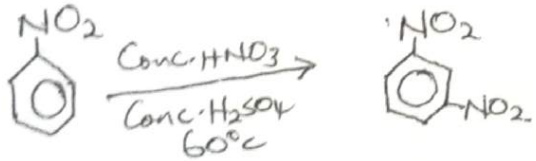
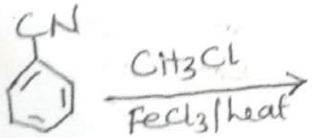


(c)

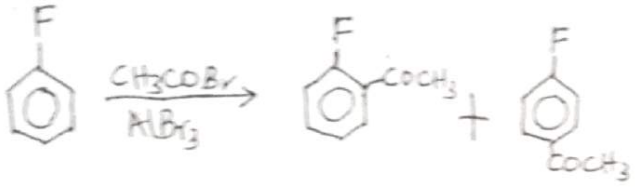


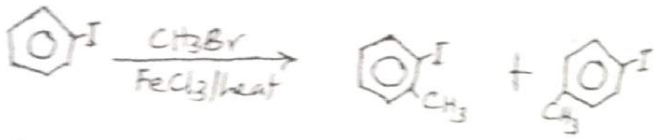
(d)

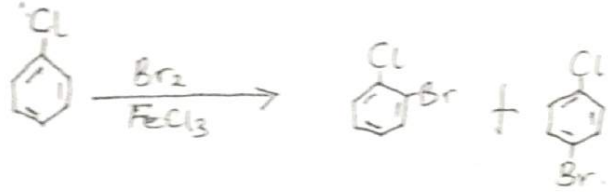


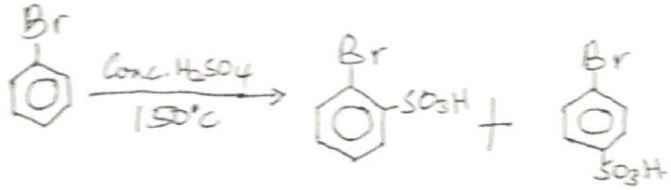
3. GROUPS THAT DEACTIVATE THE BENZENE RING AND DIRECT FURTHER SUBSTITUTION AT POSITION 2 or 6 AND 4:

They are mainly halogen atoms; F, Cl, Br or I.
The halogen atom has negative inductive effect i.e it tends to withdraw or pull pie electrons from the benzene ring and therefore, the electron density decreases making the benzene ring less reactive with the incoming electrophiles and directs further substitution at 2 or 6 and 4 forming 2 possible products. e.g.

(a) 

(b) 

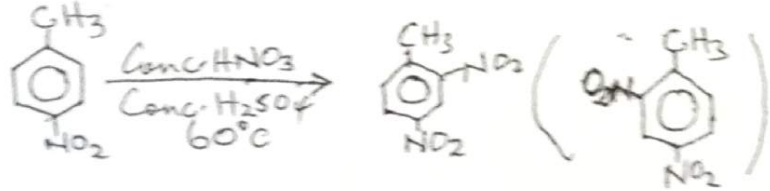
(c) 

(d) 

ORIENTATION IN BENZENE RING WITH MORE THAN ONE SUBSTITUENT:

The net orientation effect of 2 or more substituents is predicted by examining the effect of each substituent separately.

Qn: In each of the following reactions, explain the formation of the products given.

(i) 

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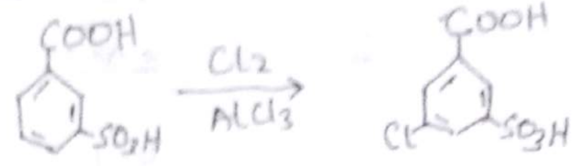

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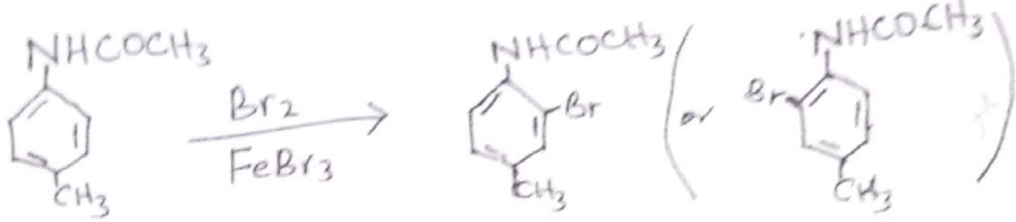

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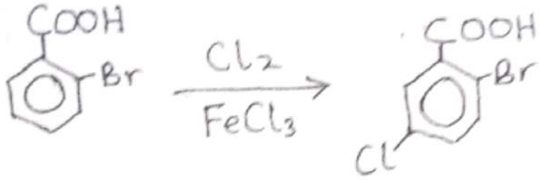

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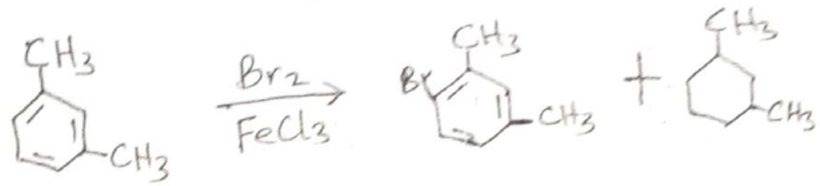

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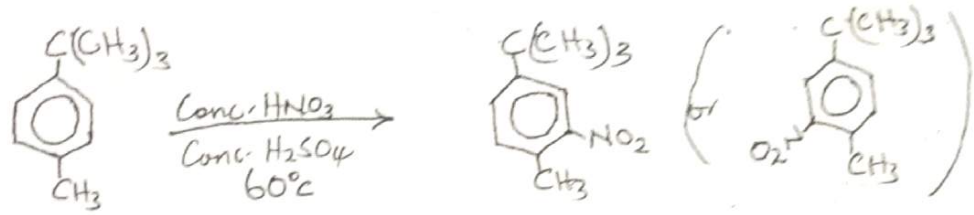

-END-

Muiruga zu (E)