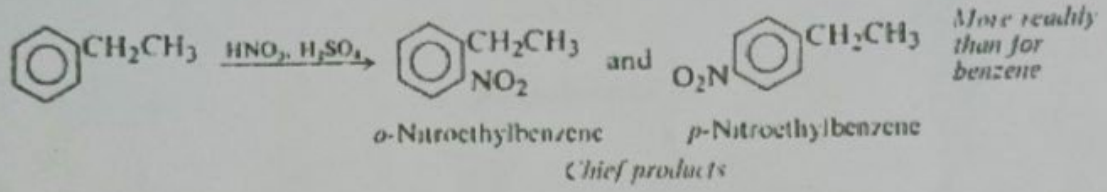
Arenes

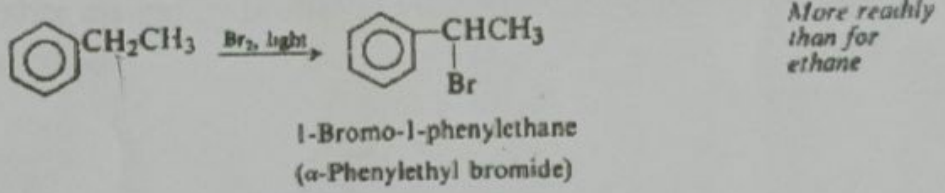
These Compounds contain both aliphatic & aromatic units

Ex...ethylbenzene

1- The ring of ethylbenzene should undergo the electrophilic substitution characteristic of benzene &
2- The side chain should undergo the free –radical substitution characteristic of ethane.

The properties of each portion of the molecule should be modified by the presence of the other portion.

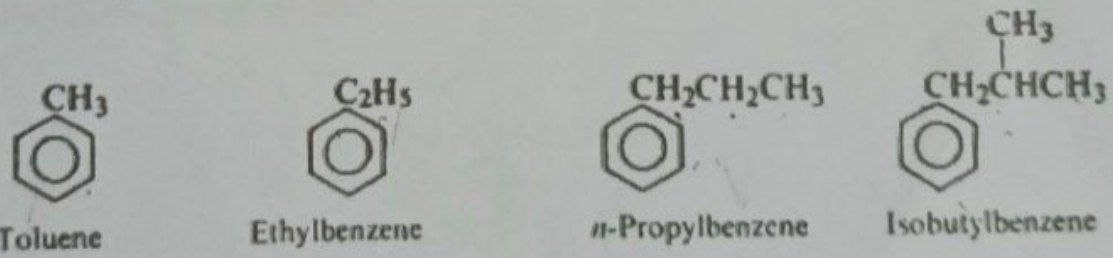




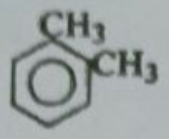
- Thus, each portion of the molecule affects the reactivity of the other potion and determine the orientation off attack

Structure and nomenclature

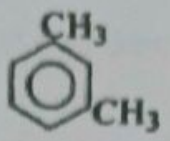
1- Prefixing the name of the alkyl group to the word-benzene



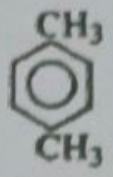
2- The simplest of the dialkylbenzene, dimethyl benzene are given the special names of xylenes.



o-Xylene

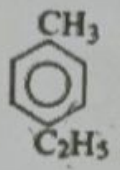


m-Xylene



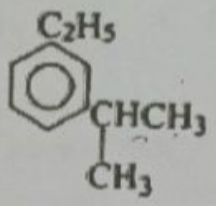
p-Xylene

3- Dialkyl benzene containing one methyl group are named as derivatives of toluene



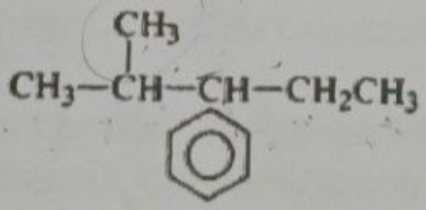
p-Ethyltoluene

4- While the other named by prefixing the names of both alkyl groups to the word-benzene

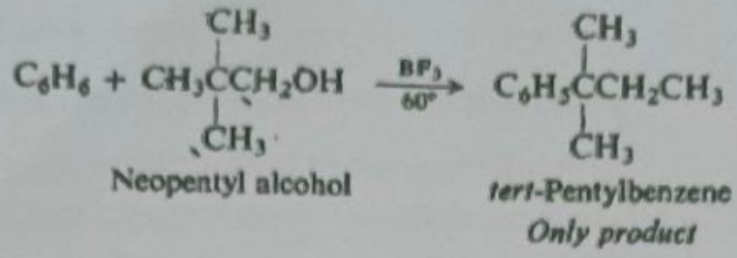


m-Ethylisopropylbenzene

5- A compound containing a very complicated side chain might be named as phenyl alkane



2-Methyl-3-phenylpentane



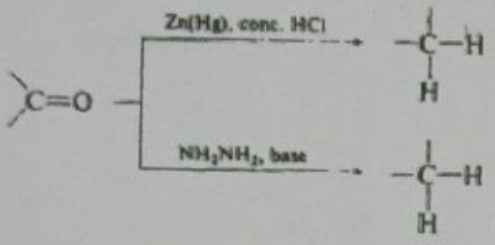
Neopentyl alcohol

tert-Pentylbenzene

Only product

2- Conversion of side chain

a- Reduction of ketone



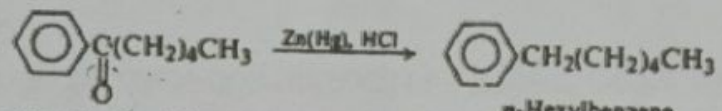
Clemmensen reduction

for compounds sensitive to base

Wolff-Kishner reduction

for compounds sensitive to acid

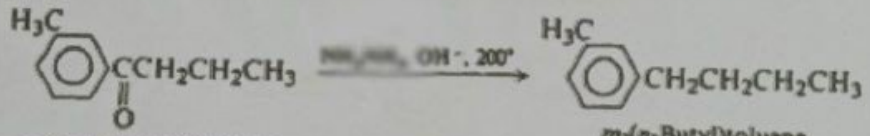
1- Clemmensen reduction



n-Pentyl phenyl ketone

n-Hexylbenzene

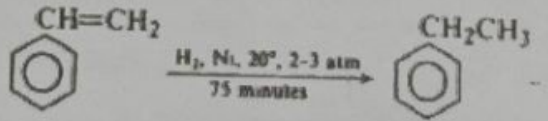
2- Wolff-Kinsher reduction



n-Propyl *m*-tolyl ketone

m-(*n*-Butyl)toluene

b- Hydrogenation of double bond of side chain



Styrene

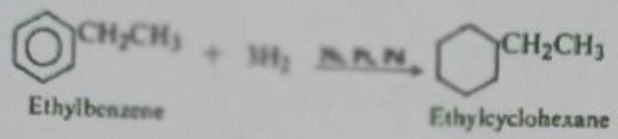
Ethylbenzene

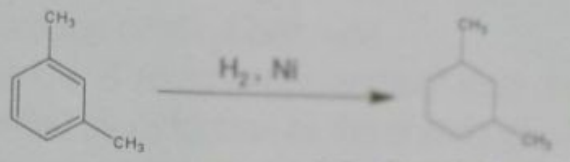
Reaction of alkyl benzene

The reaction of alkyl benzene involve either

1- Electrophilic substitution in the aromatic ring
2- Free-radical substitution in the aliphatic side chain

1- Hydrogenation .... By used hydrogen in presence of Ni , Pt & Pd

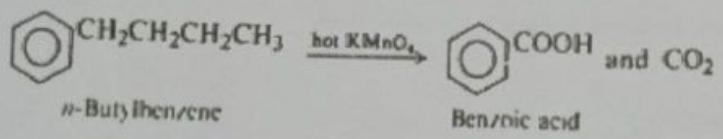




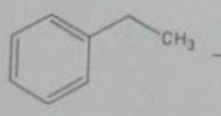
1,3- dimethyl cyclohexane

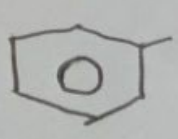
2- Oxidation

Although benzene and alkanes are quite unreactive toward the the usual oxidizing agent ($KMnO_4$, $K_2Cr_2O_7$, etc.) the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain is oxidized down to the ring, only a carboxyl group (-cooH) remaining to indicate the position of the original side chain.



H.W ;

1- 

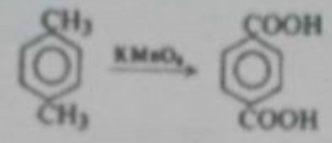
1- hot $KMnO_4$, OH^- 2- H_3O^+ or
2- $K_2Cr_2O_7 / H^+$


2- CH_4 [O] → ~~$C_6H_5OHCOOH$~~ N.R

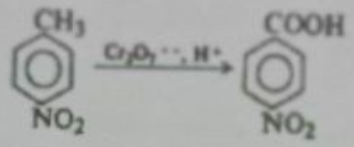
3-  [O] → N.R

The reaction is used for two purposes

1- Synthesis of carboxylic acids



p-Xylene — Terephthalic acid (1,4-Benzenedicarboxylic acid)

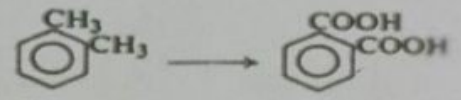


p-Nitrotoluene — *p*-Nitrobenzoic acid

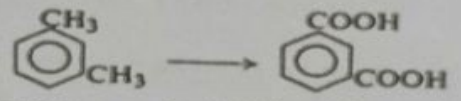
2- Identification of alkyl benzene

The number & relative positions of side chains can frequently be determined by oxidation to the corresponding acids

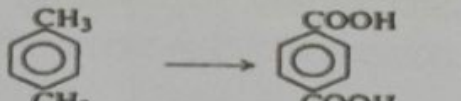
Ex. Unknown liquid of formula C_8H_{10} & B.P. 137- 139^0



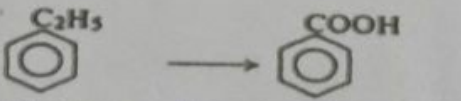
o-Xylene (b.p. 144°) — Phthalic acid, m.p. 231°



m-Xylene (b.p. 139°) — Isophthalic acid, m.p. 348°

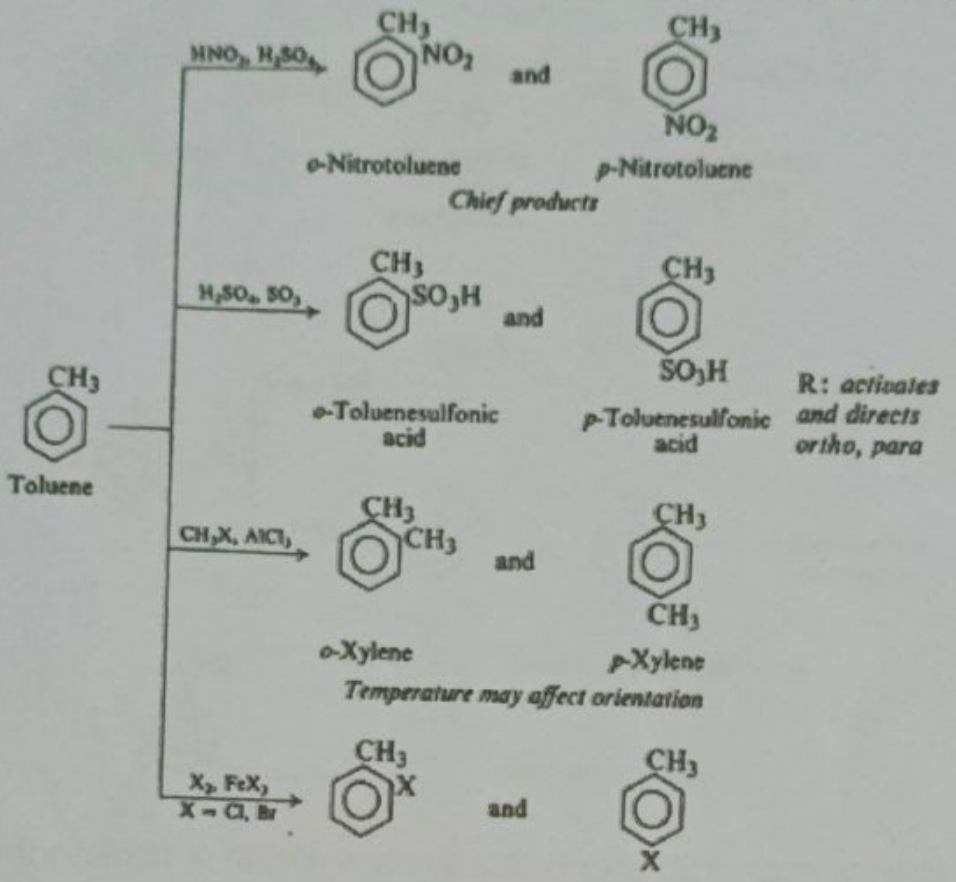


p-Xylene (b.p. 138°) — Terephthalic acid, m.p. 300°



Ethylbenzene (b.p. 136°) — Benzoic acid, m.p. 122°

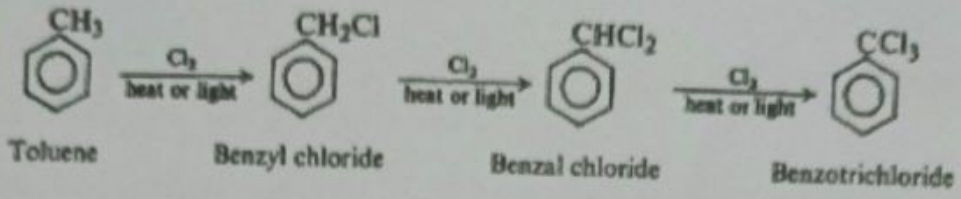
3- A- Substitution in the ring. Electrophilic aromatic substitution
Because of its electron-releasing effect, an alkyl group activate a benzene ring to which it is attached, & directs ortho & para.



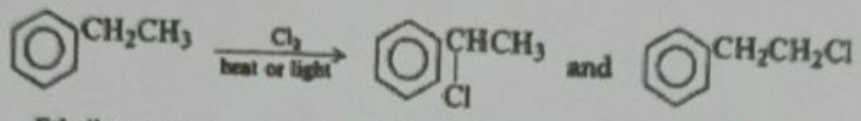
Substitution in the side chain, Free-radical halogenation

B- Halogenation of alkyl benzene; ring vs. side chain

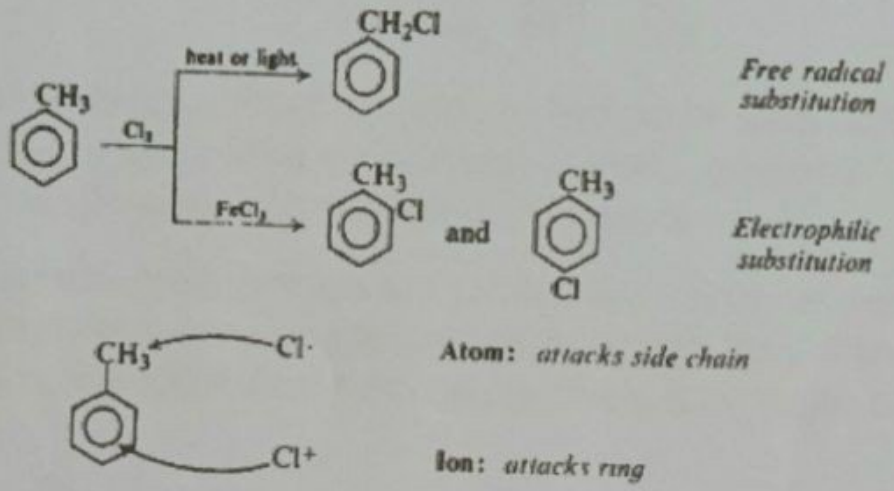
Alkyl benzenes clearly offer two main areas to attack by halogen; the ring & the side chain. We can control the position of attack by choosing the proper reaction condition.



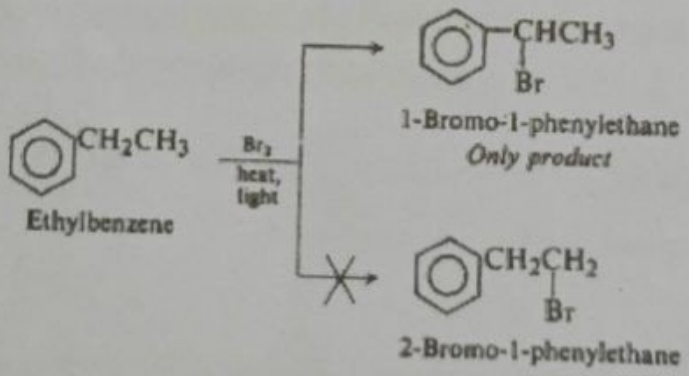
Toluene — Benzyl chloride — Benzal chloride — Benzotrichloride



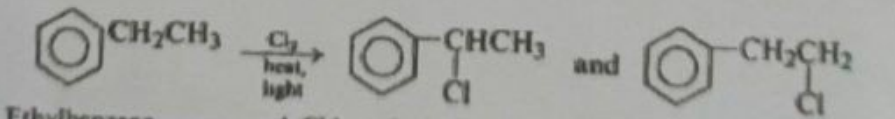
Ethylbenzene — α-Phenylethyl chloride *Chief product* — β-Phenylethyl chloride



Chlorination & bromination of side chains differ one another in orientation & reactivity



Ethylbenzene



Ethylbenzene — 1-Chloro-1-phenylethane *Major product, 91%* — 2-Chloro-1-phenylethane 9%