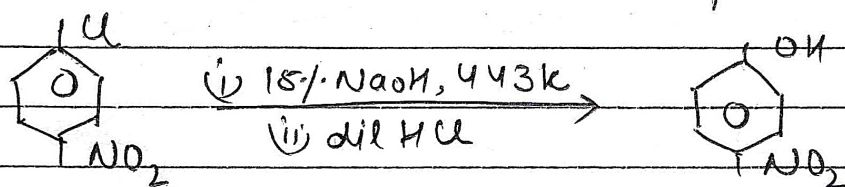
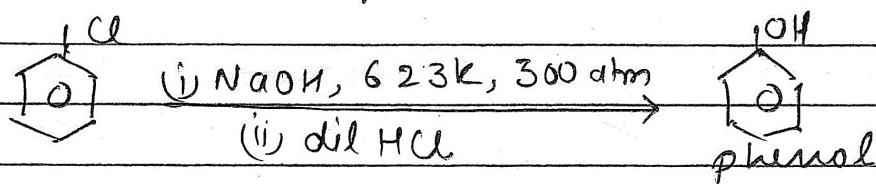
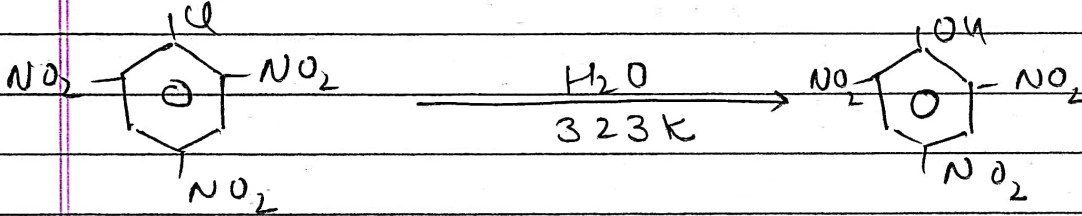
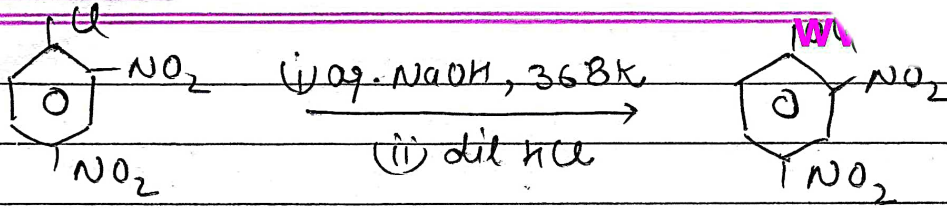


## Effect of substituents in Haloarenes on the Reactivity

→ The presence of electron withdrawing groups such as  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$  etc. at o- and p- ~~para~~ positions to the halogen atom greatly activates the halogen towards nucleophilic substitutions.

eg. 1

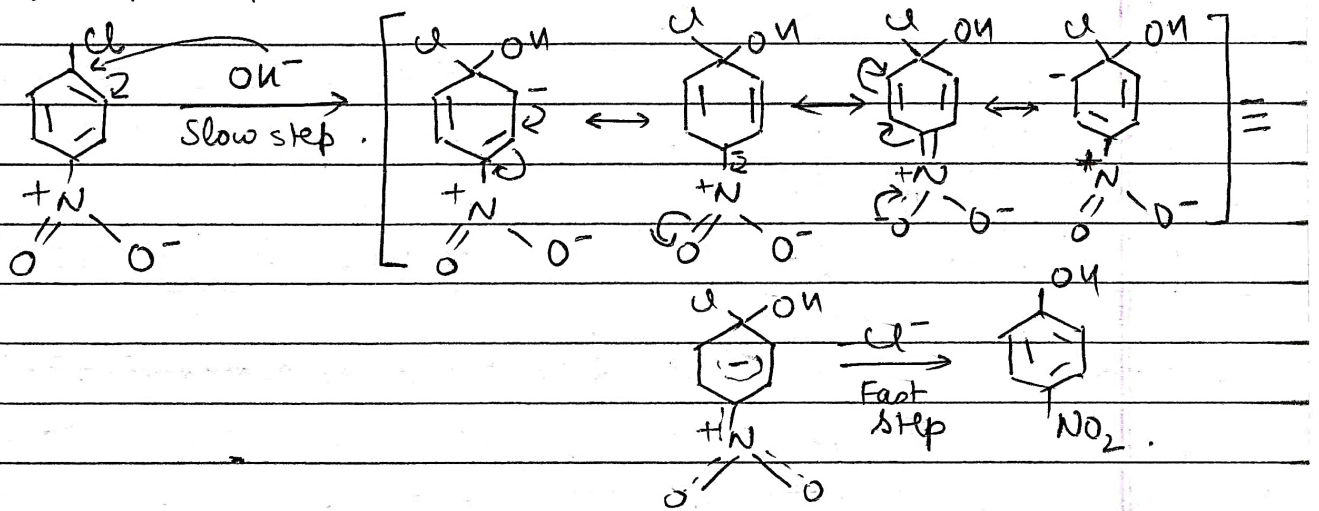




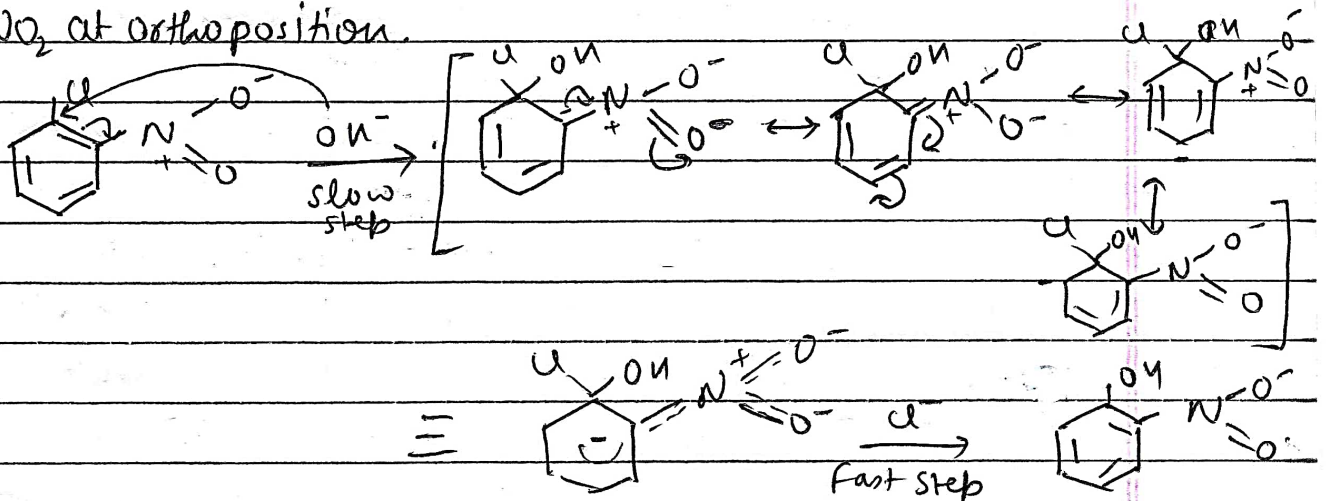
Note: Nitro group (-NO<sub>2</sub>) meta to the Chlorine has no effect on Reactivity.

Explanation: -

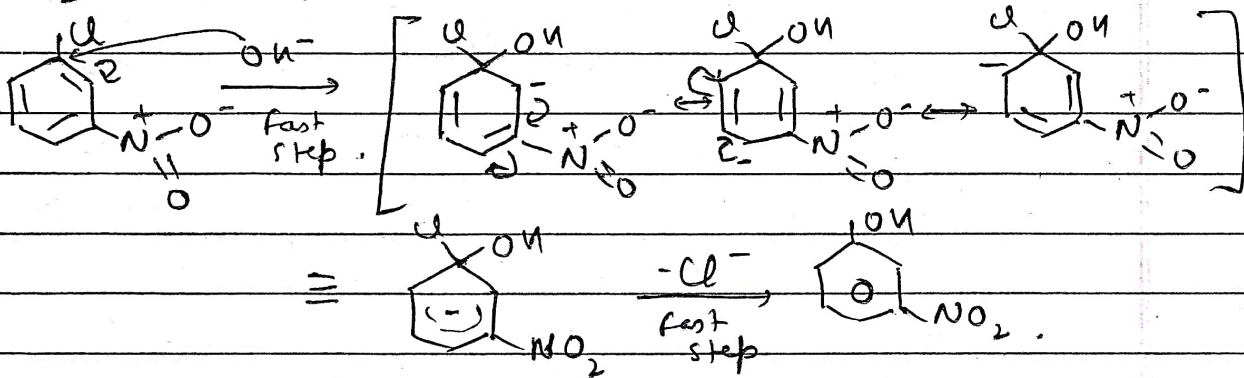
NO<sub>2</sub> at para position.



NO<sub>2</sub> at ortho position.



$\text{NO}_2$  at meta position:-

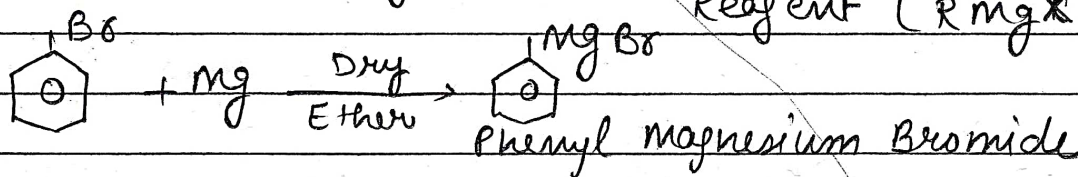


→ In case of o- & p- structures, one of the Resonating structures bears a negative charge on the Carbon atom bearing the  $-\text{NO}_2$  group. ∴ These carbanions are stabilised by the  $-\text{NO}_2$  group as well as  $\pi$  electrons of benzene ring.

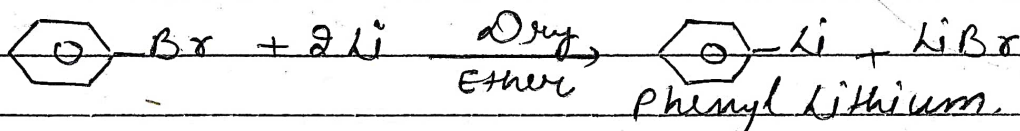
However, in case of -m structure, none of the Resonating structures bears the negative charge on the carbon atom bearing the  $-\text{NO}_2$  group. ∴ The  $-\text{NO}_2$  group does not stabilise the Carbanion and thus has no effect towards the Reactivity.

### B. Reaction with Metals.

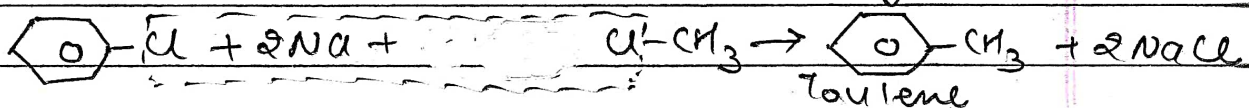
1. Reaction with Magnesium: formation of Grignard Reagent ( $\text{RMgX}$ )



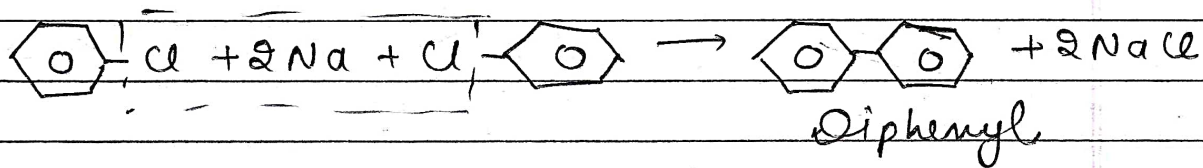
2. Reaction with Lithium:



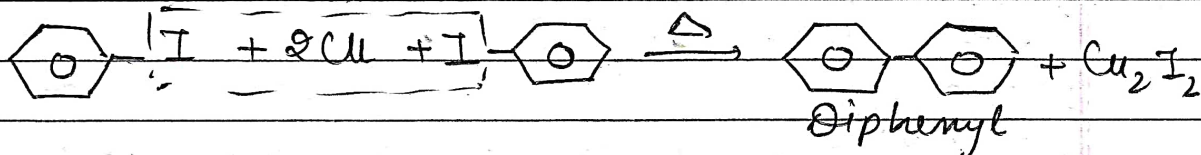
3. Reaction with sodium: (Wurtz-Fitting Reaction)



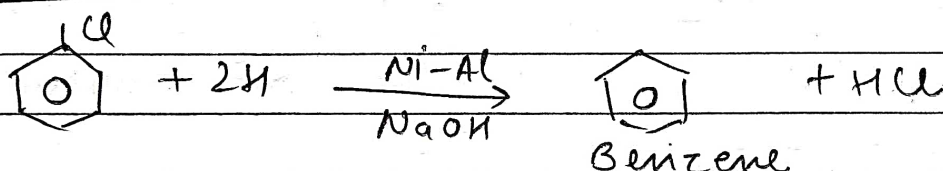
However, when haloarenes react with Na, it is called Fitting Reaction.



4. Reaction with Copper powder: (Ullmann Reaction)



C. Reduction

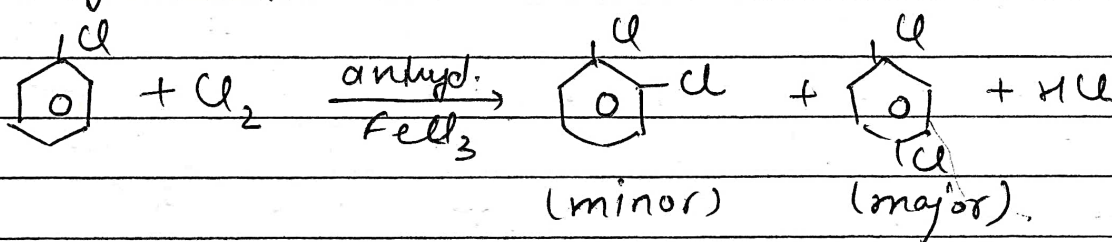


D. Ring substitution or Electrophillic substitution Reactions.

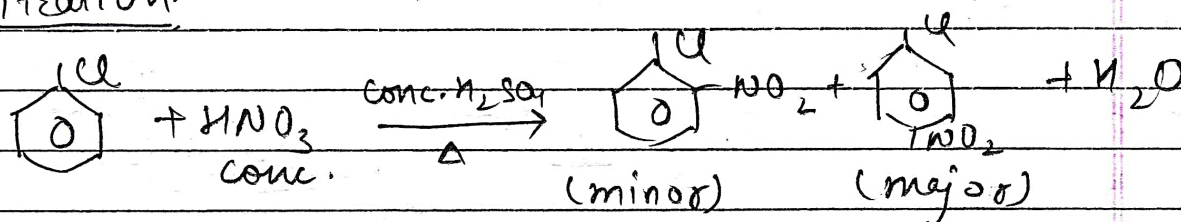
Note: (i) Haloarenes undergo electrophillic substitution Reactions slowly as compared to Benzene.

(ii) Halogen group is ortho & para director.

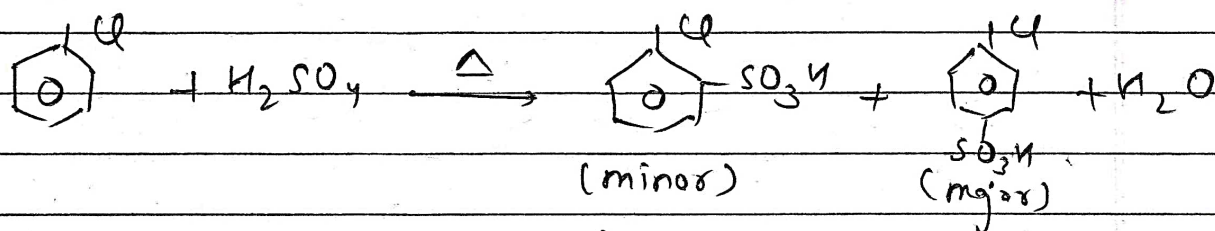
1. Halogenation



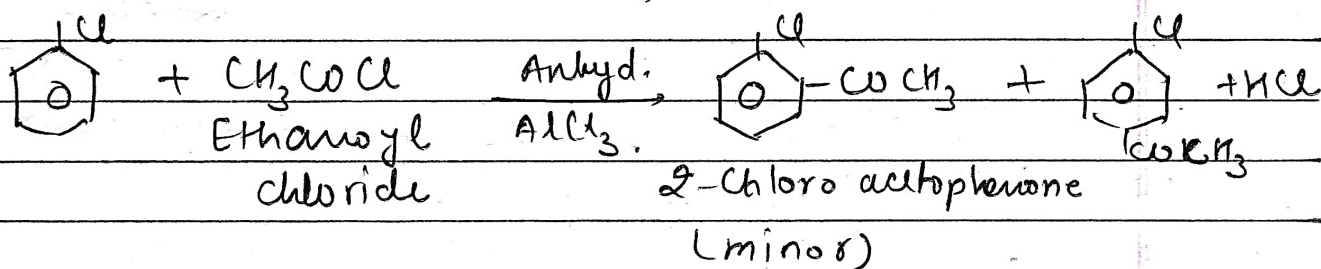
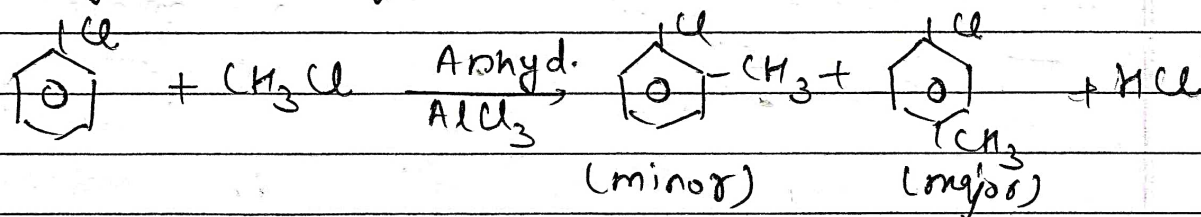
2. Nitration



### 3. Sulphonation



### 4. Alkylation & Acylation, : (Friedel-Craft Reactions)



Note:- Vinyl & Aryl Halides are less reactive than alkyl halides. This is mainly because the vinyl and aryl halides have partial double bond character between carbon and halogen atoms. As a result, carbon halogen bond of a vinyl or aryl halide is stronger than that of an alkyl halide & the bond cleavage is difficult.