



كلية العلوم التطبيقية
Faculty of Applied Sciences



Aryl Halides Chapter 4

COURSE NAME: Chemistry of Aromatic Compounds
COURSE CODE: 4022142-3

By the end of this chapter, you should understand:

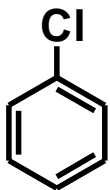
1. The definition and nomenclature of aryl halides.
2. Synthesis of aryl halides.
3. Reactions of aryl halides

Aromatic halogeno-compounds

Aryl halides

In these compounds, the halogen atom is firmly linked to the ring. It is inert, it can not be replaced by -OH, -NH₂, or -CN groups when treated with aqueous NaOH, NH₃ or KCN, respectively

Example:

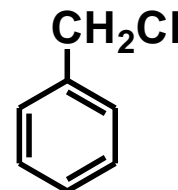


Chlorobenzene

Aralkyl halides

In these compounds, the halogen atom is active (similar to alkyl halides). It can be replaced by -OH, -NH₂, or -CN groups when treated with aqueous NaOH, NH₃ or KCN, respectively

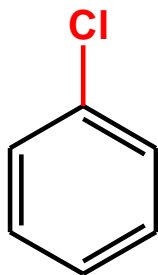
Example:



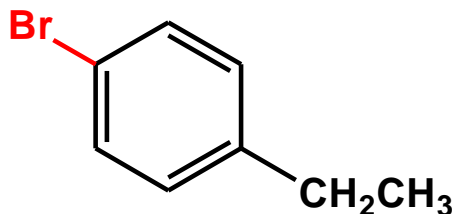
Benzyl chloride

Aromatic Halogen Compounds

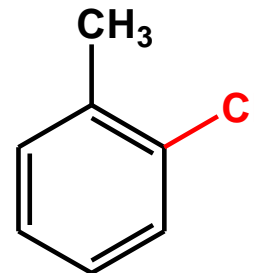
1- Aryl Halides: in which the halogen atom is directly attached to benzene ring. The substitution of halogen by nucleophiles is difficult due to strong bond between the halogen atom and benzene ring



Chlorobenzene

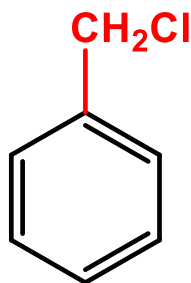


1-Bromo-4-ethylbenzene

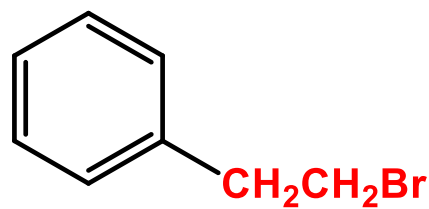


2-Chlorotoluene

2- Aralkyl Halides: in which the halogen atom is separated from benzene ring by one or more carbon atoms. The substitution of halogen by nucleophiles is easy as aliphatic halides.



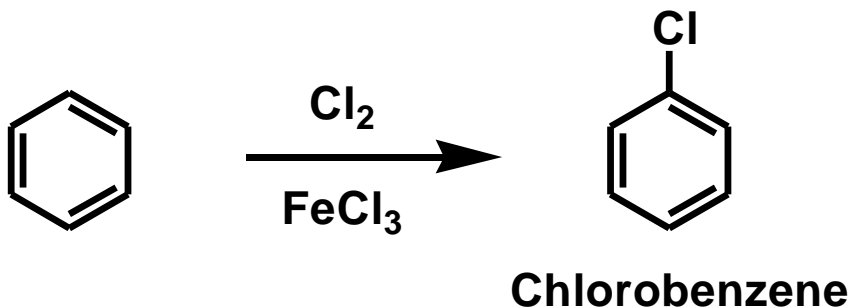
Benzyl chloride



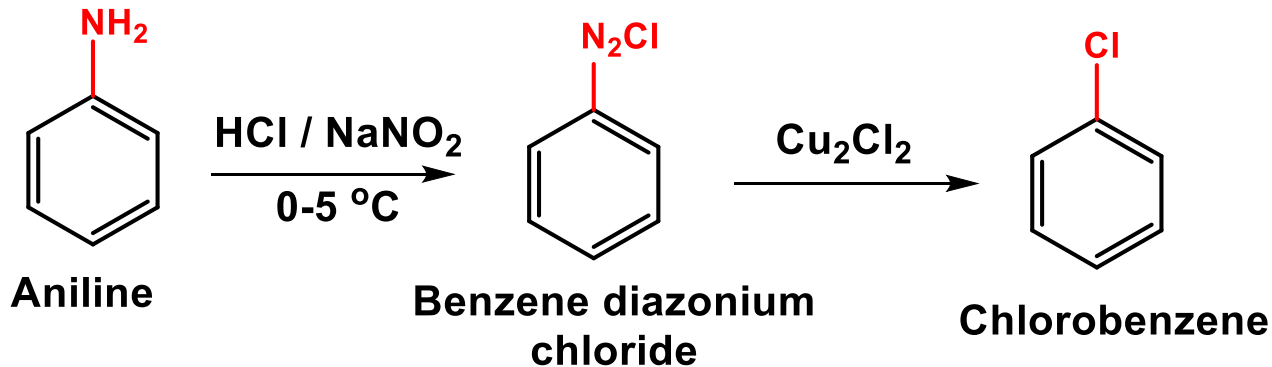
1-Bromo-2-phenylethane

Methods of preparation of Aryl halides

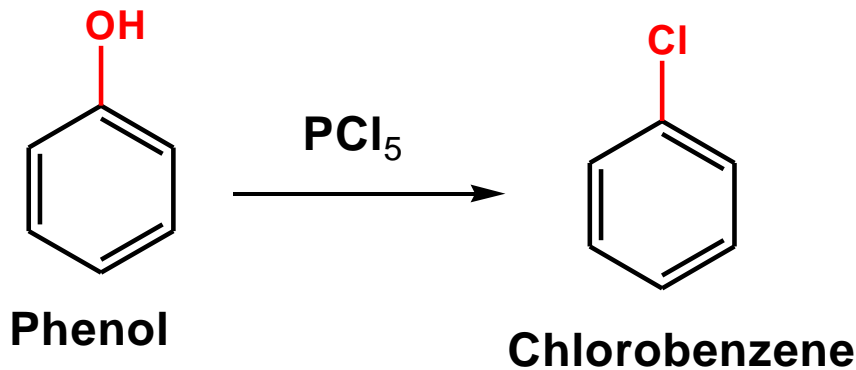
1) From benzene



2) From aniline

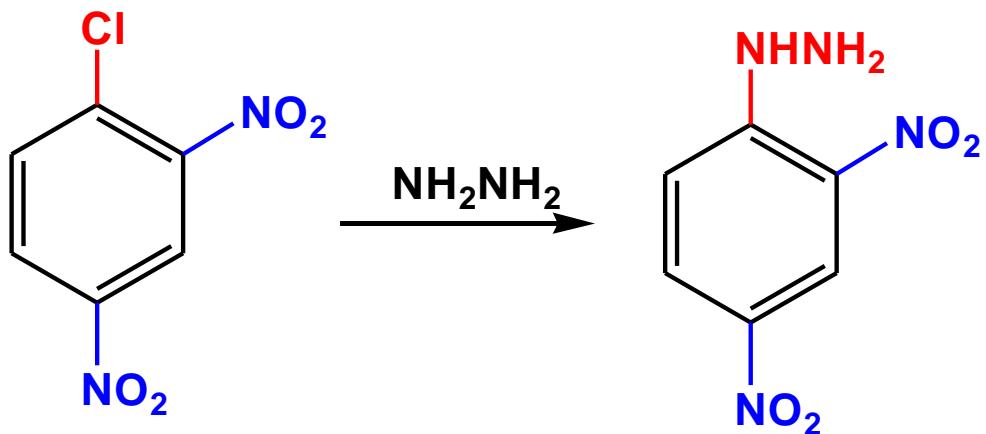
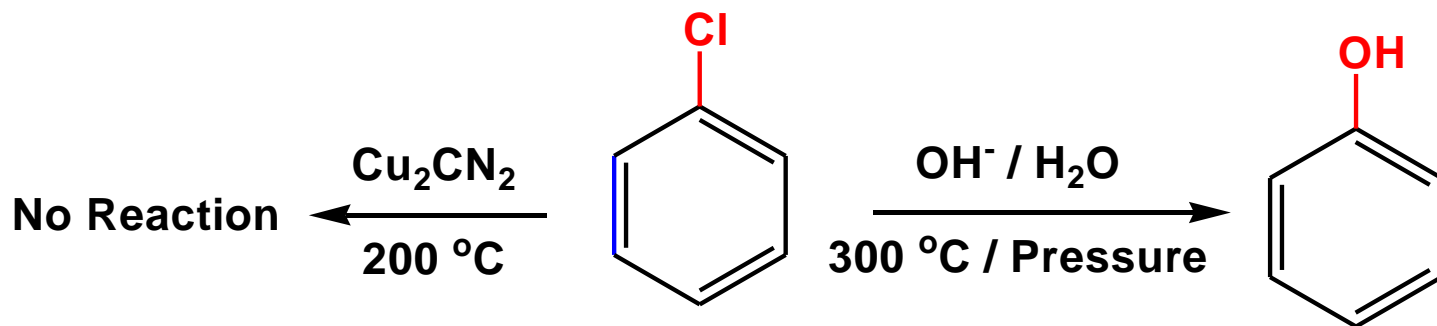


3) From Phenol

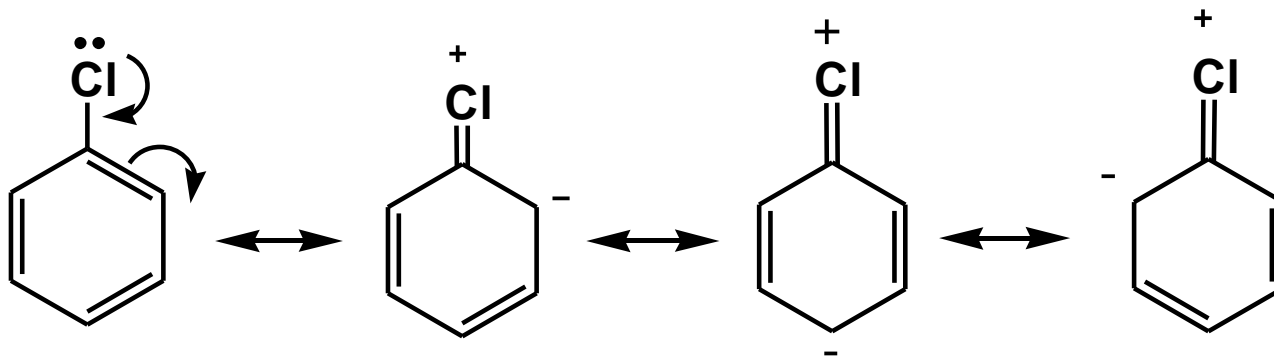


I) Nucleophilic substitution reactions of aryl halides

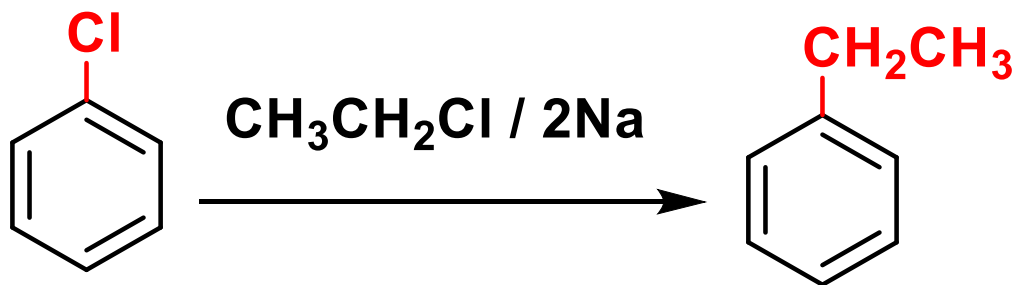
Chlorobenzene is less reactive towards nucleophilic substitution reactions. The reactions proceed under drastic condition or presence of Electron-Withdrawing groups



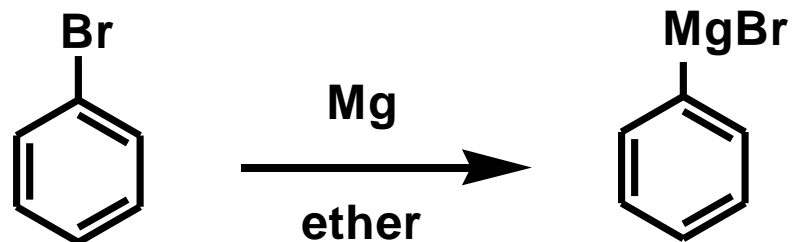
The low reactivity of chlorobenzene is due to resonance effect which increase the strength C-Cl bond (double bond character) as shown



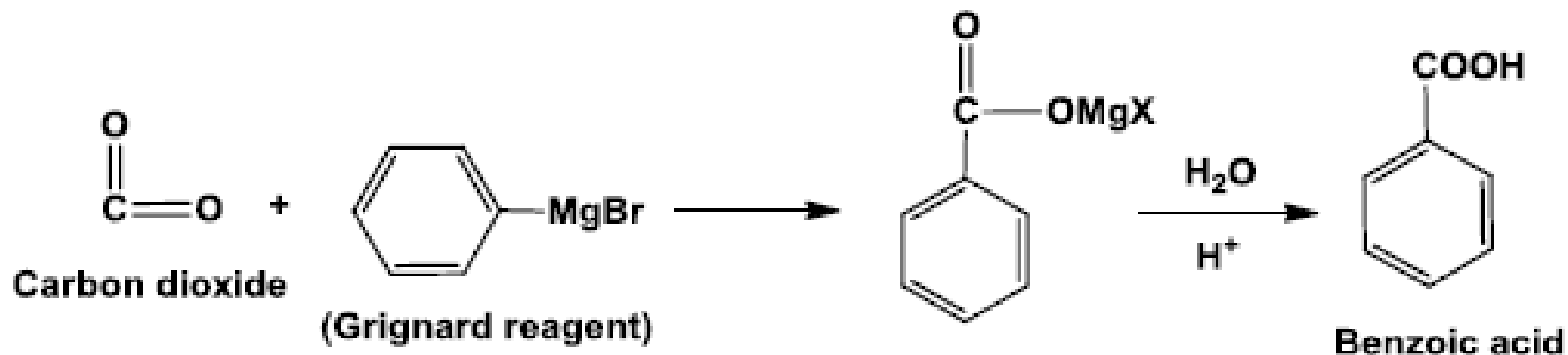
II) Wurtz-Fittig reaction

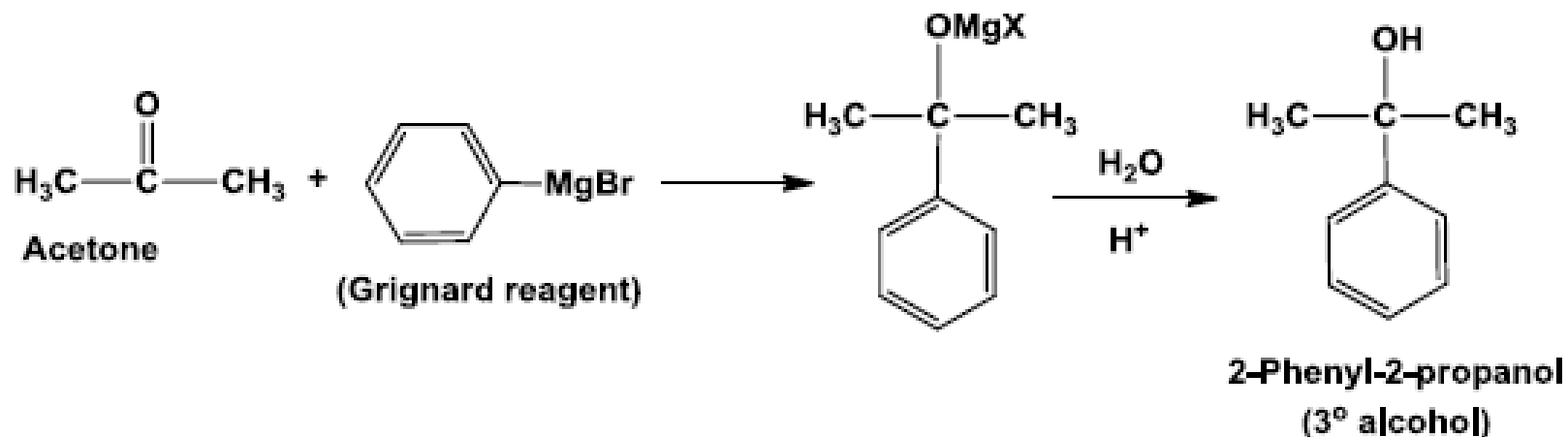
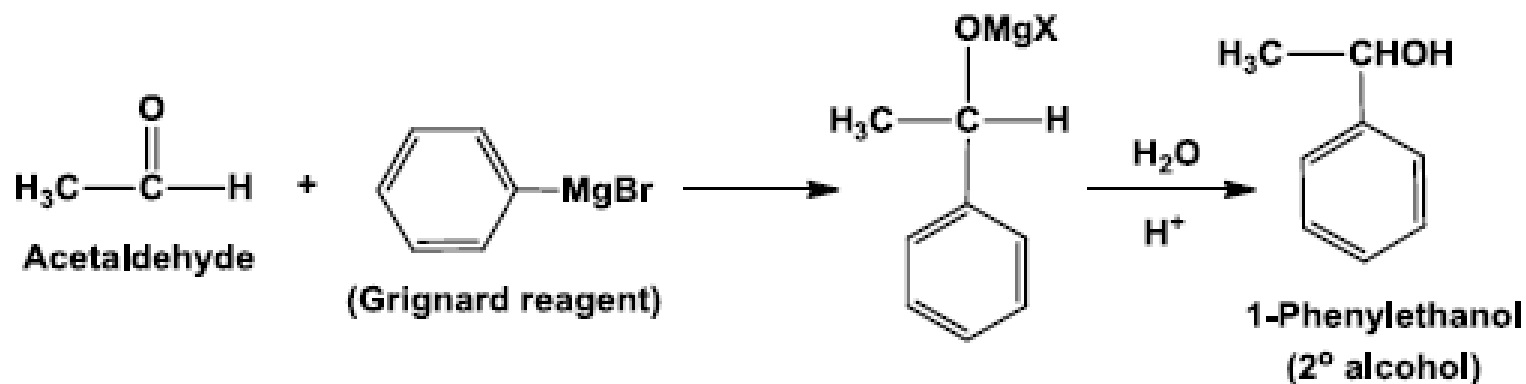
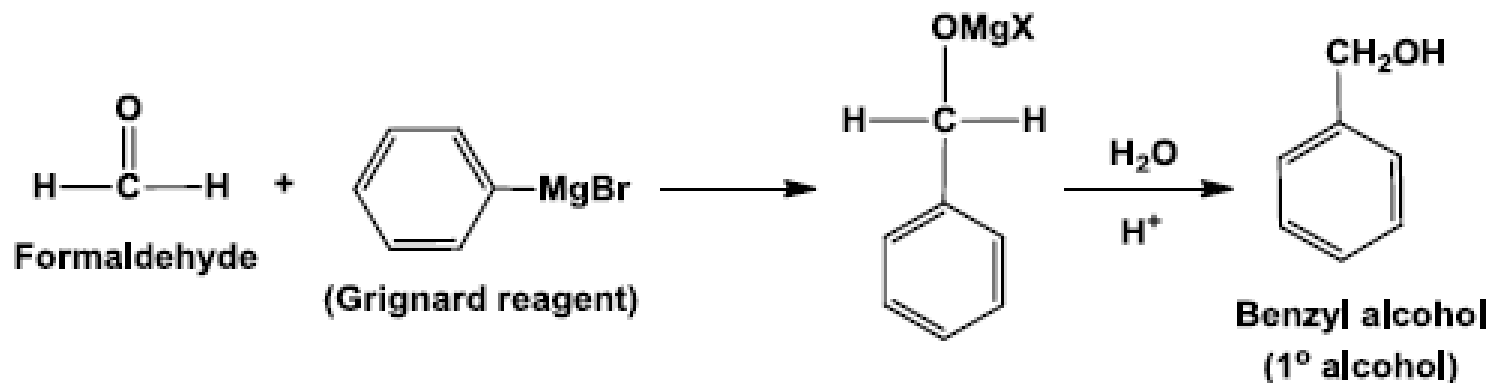


III) Reaction with magnesium metal (Grignard reagent)

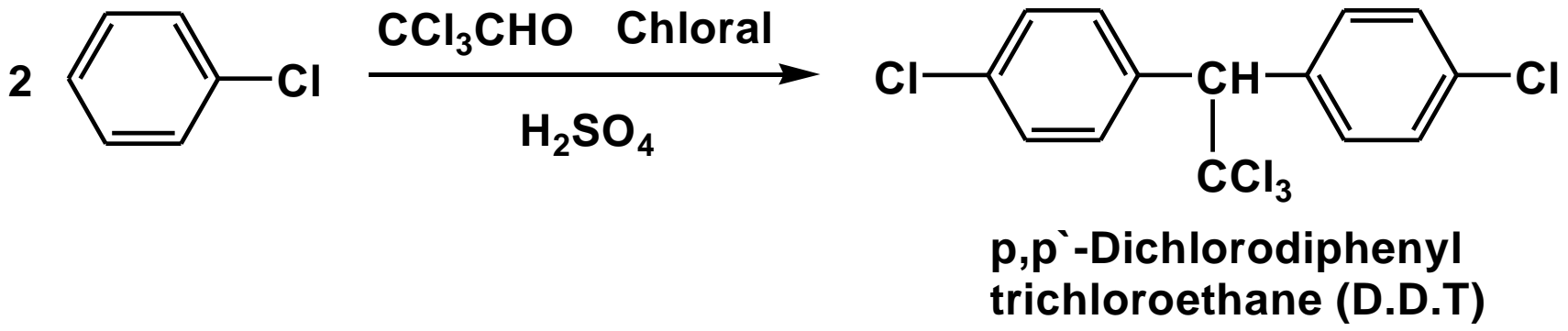


Phenylmagnesium bromide
(Grignard reagent)



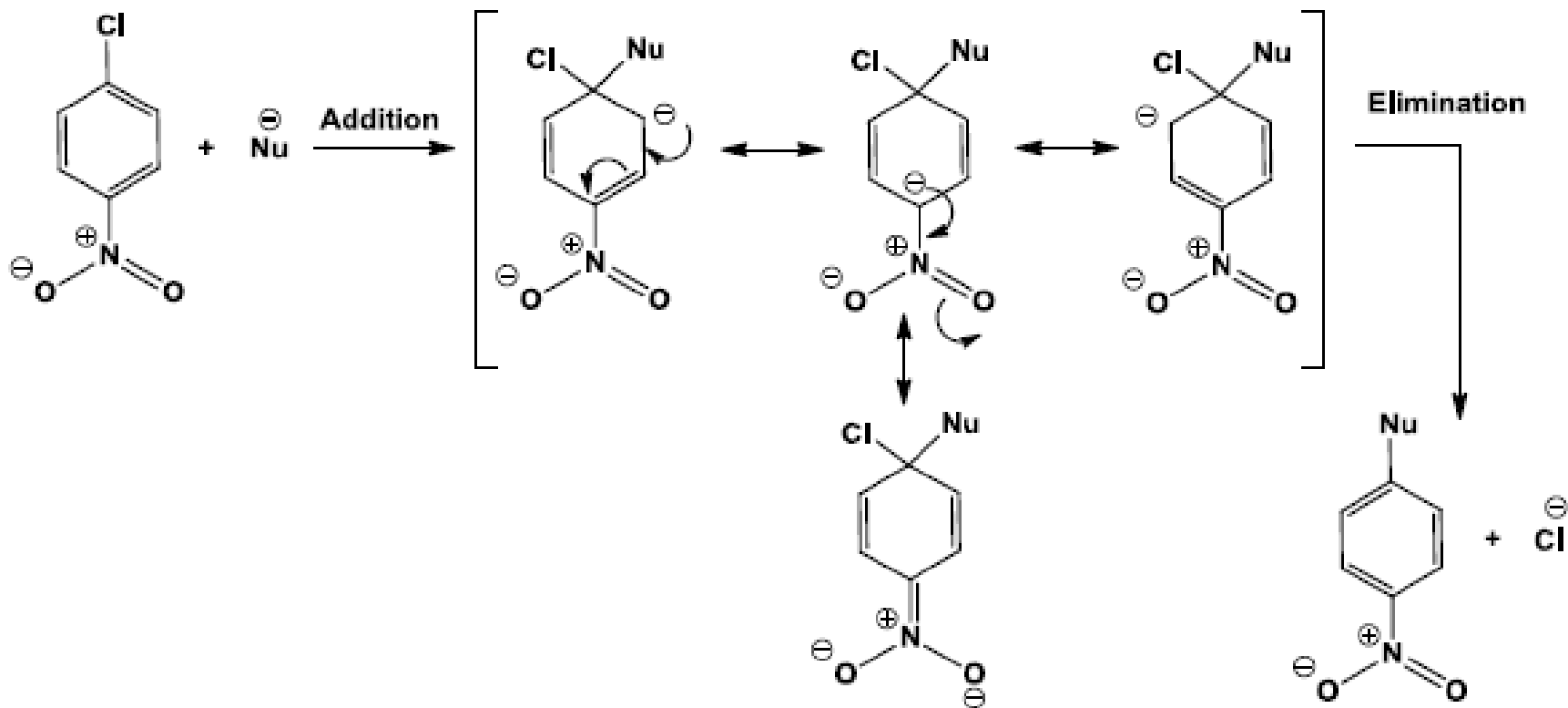


IV) D.D.T. formation

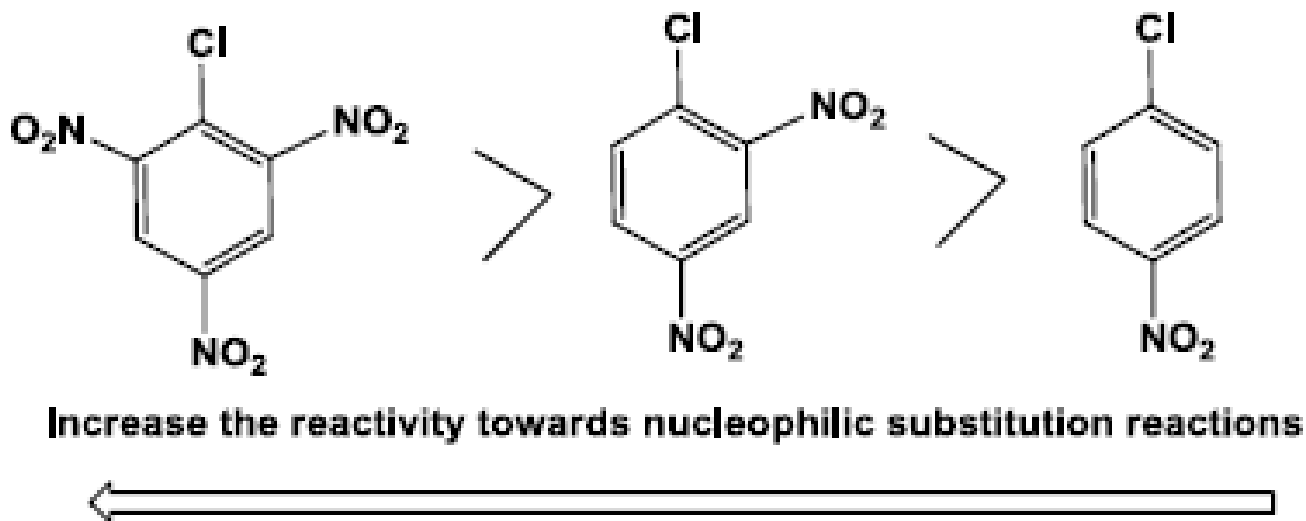


V) The Addition-Elimination Mechanism

In this case, the benzene ring which has halogen atom must contain strong electron-withdrawing group(s) in ortho- and para- position with respect to the halogen atom. This group(s) will stabilize the anion formed after addition of nucleophile as shown in the given mechanism

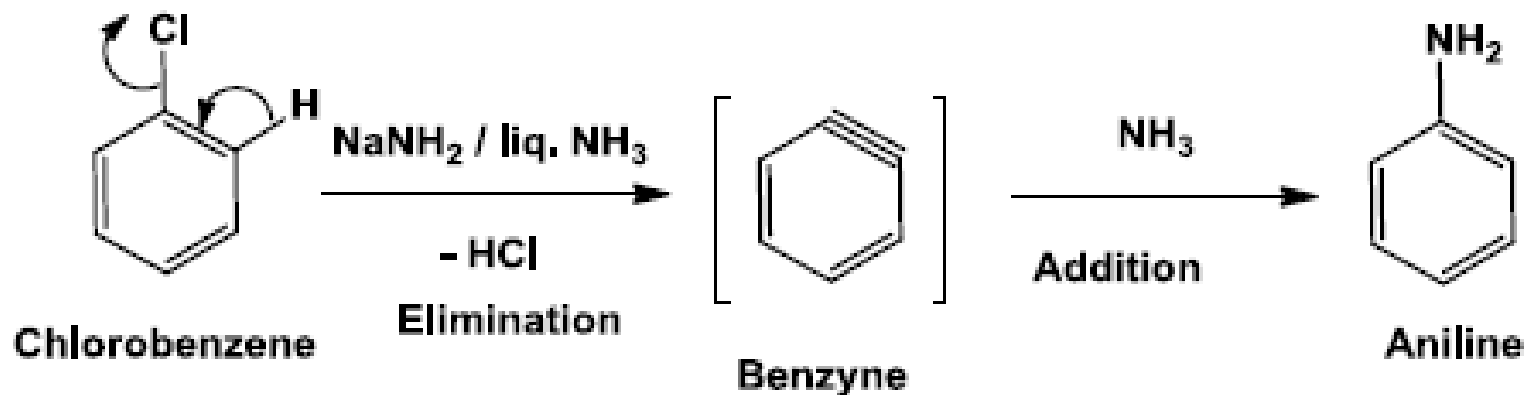


As the number of electron-withdrawing groups on benzene ring increase (especially in ortho- and para- position with respect to the halogen atom), the reactivity towards nucleophilic substitution reaction will also increase and the vice-versa.

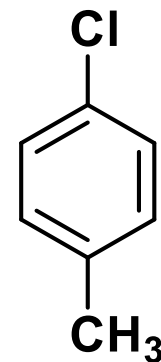
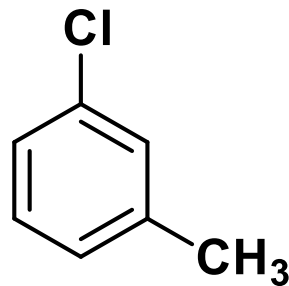
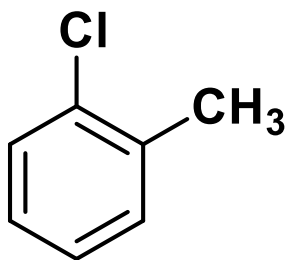


VI) The Elimination-Addition Mechanism

Reaction of halobenzene with strong base such as, sodium amide in liquid ammonia, ($\text{NaNH}_2 / \text{liq. NH}_3$) will give aniline derivative. The reaction is proceeded by **benzyne intermediate** as shown.

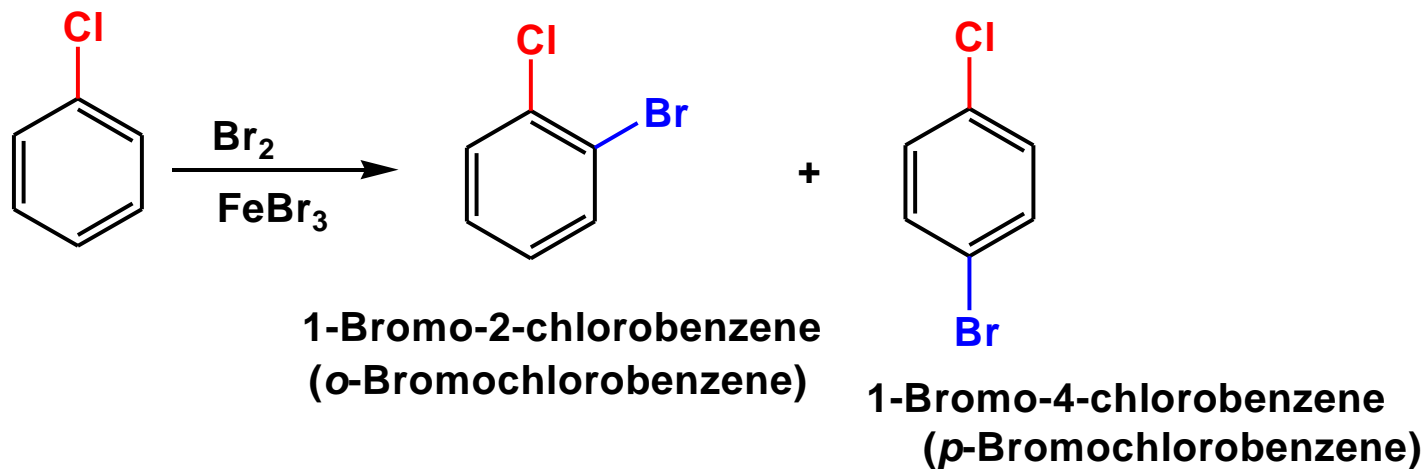


Q. What are the products of the following compounds when reacted with $\text{NaNH}_2/\text{liq. NH}_3$?

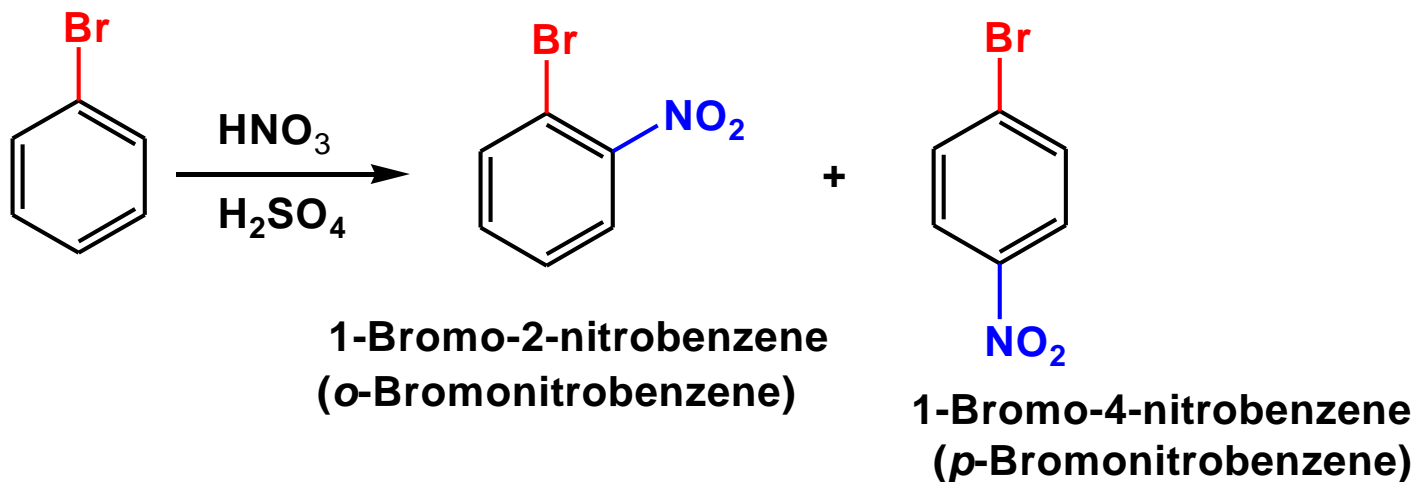


VII) Electrophilic substitution reactions

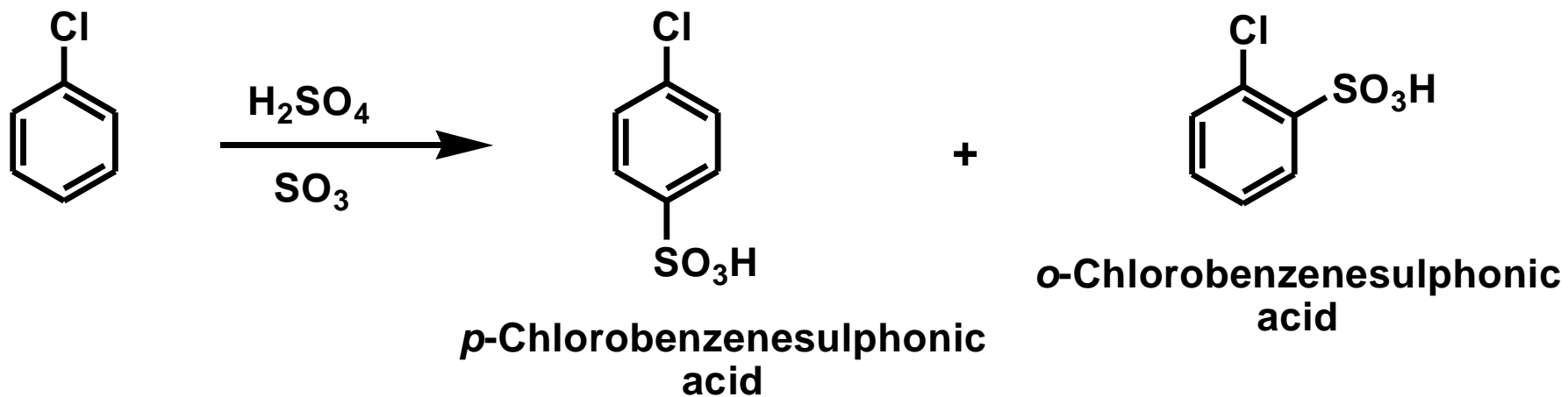
1) Halogenation



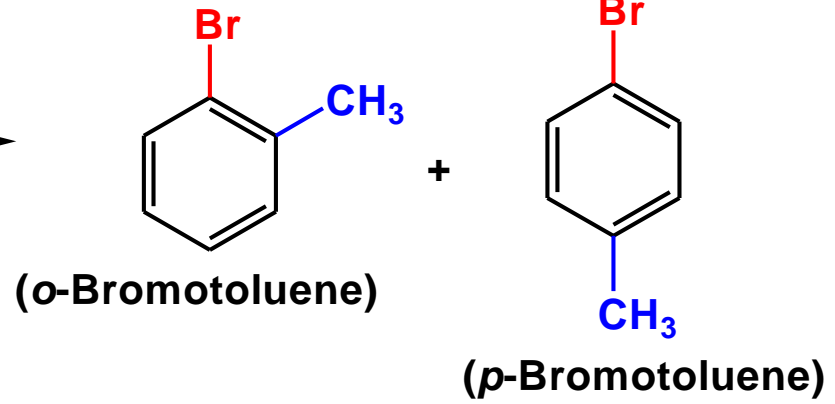
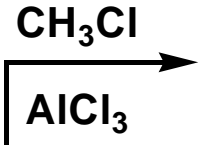
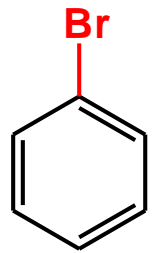
2) Nitration



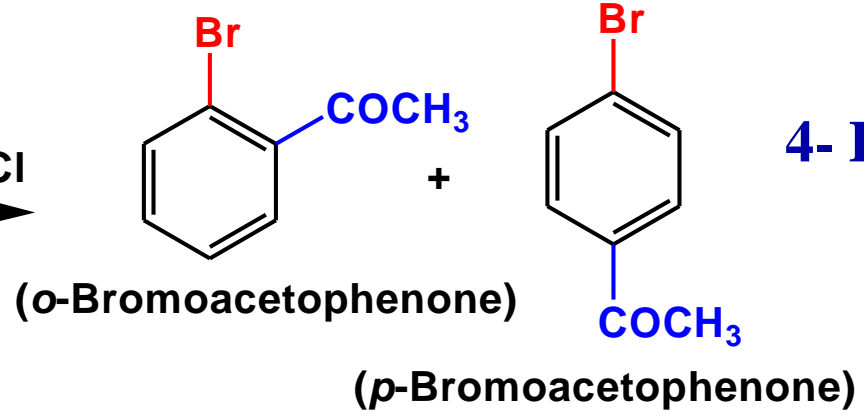
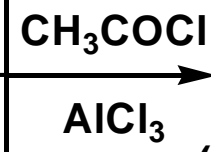
3) Sulphonation



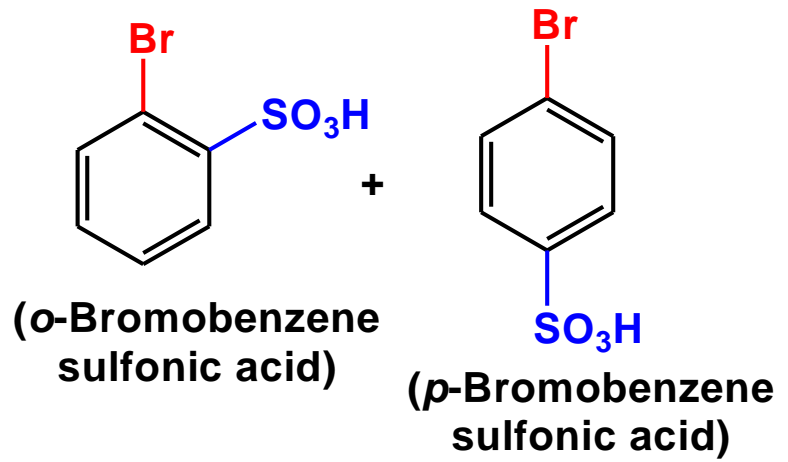
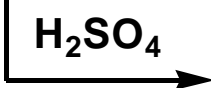
3- Friedel Crafts Alkylation



4- Friedel Crafts Acylation

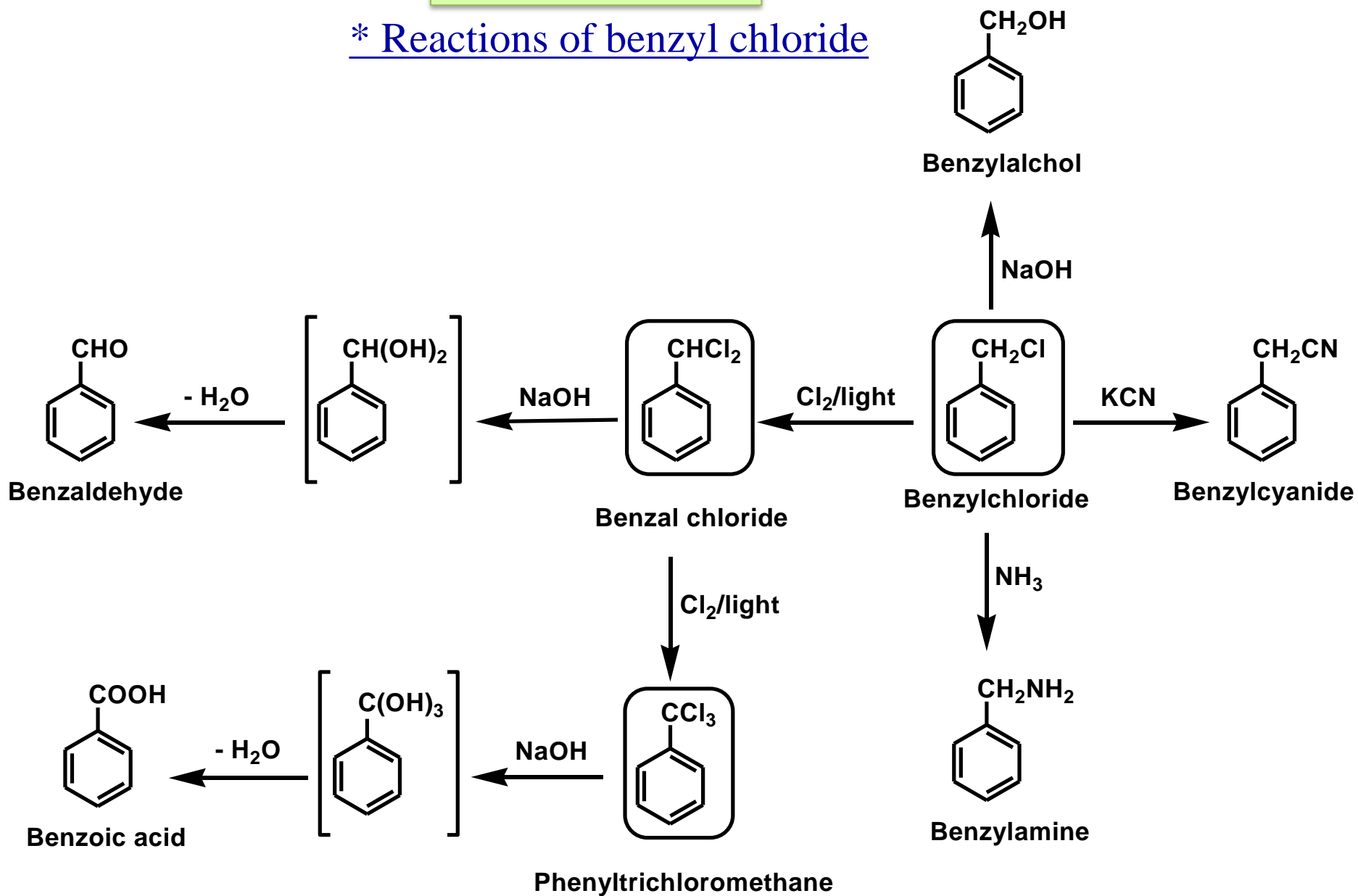


5- Sulphonation



Aralkyl halides

* Reactions of benzyl chloride



REFERENCES

1. J. D. Hepworth, D. R. Waring and M. J. Waring. “*Aromatic Chemistry*”, RSC 2002, ISBN: 0-85404-662-3.
2. J. McMurry. “*Organic Chemistry*”, 9th Edition, Cengage Learning, 2015