كلية العلوم التطبيقية
Faculty of Applied Sciences

قسم الكيمياء
Department of Chemistry

Electrophilic reactions of benzene ring

Chapter 3

COURSE NAME: **Chemistry of Aromatic Compounds**

COURSE CODE: **4022142-3**

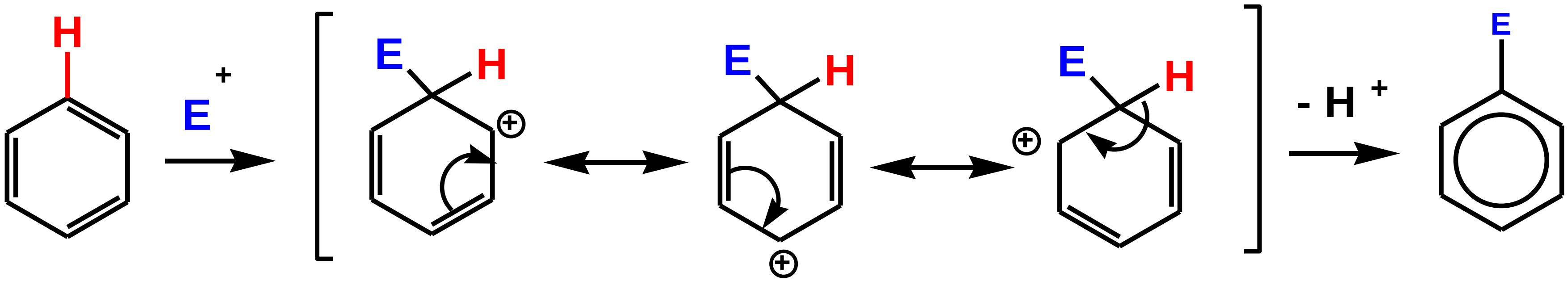
By the end of this chapter, you should understand:

1. The electrophilic substitution reactions on benzene ring
2. The substituents orientation on the benzene ring

Reactions of benzene

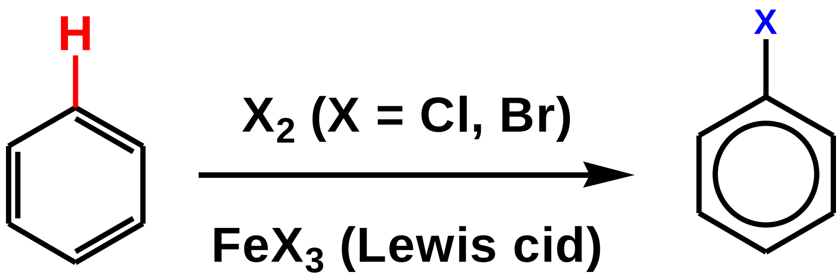
It undergoes electrophilic substitution reactions rather than addition reactions in order to preserve the delocalized π system.

A) Electrophilic substitution reactions:



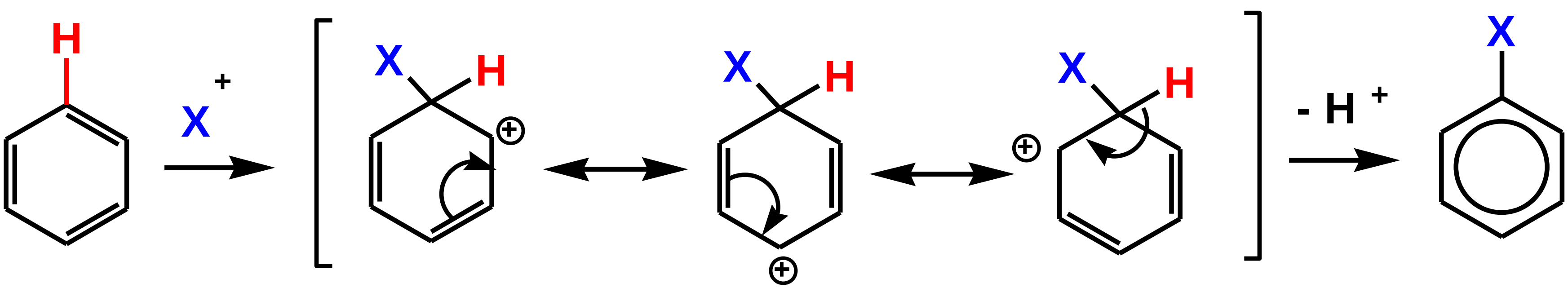
These reactions are accelerated by lewis acids to generate the electrophile

1) Halogenation



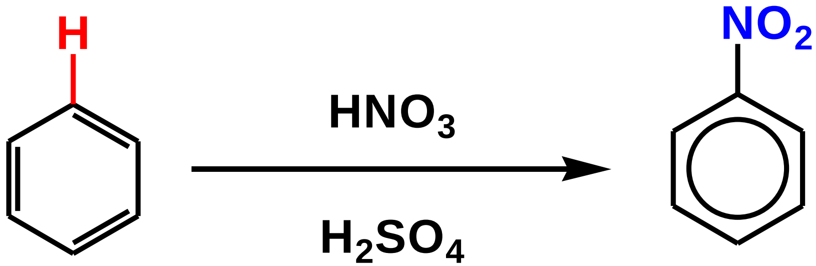
Mechanism

$$X{-}X \; + \; FeX_3 \longrightarrow [FeX_4]^{\ominus} \; + \; X^{\oplus}$$



$$H^{\oplus} \; + \; [FeX_4]^{\ominus} \longrightarrow FeX_3 \; + \; H{-}X$$

2) Nitration

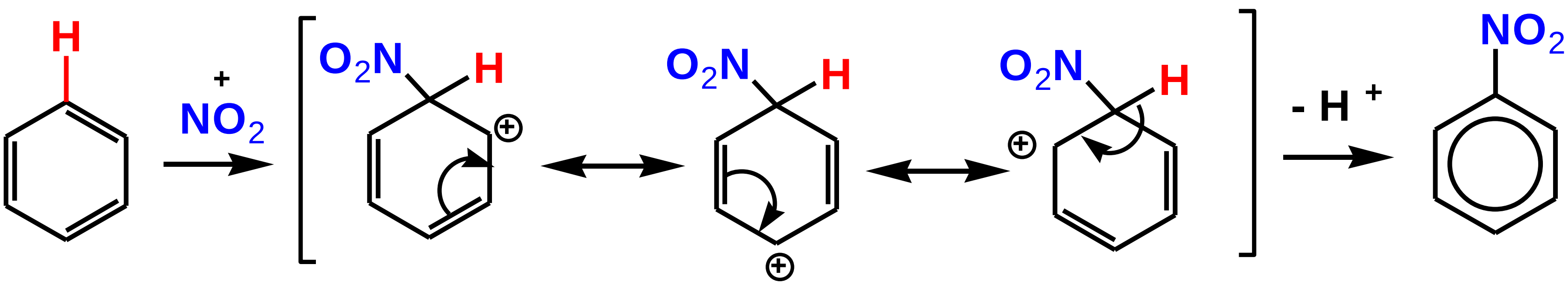


Mechanism

$HNO_3 + H_2SO_4 \longrightarrow [HSO_4]^{\ominus} + H_2NO_3^{\oplus}$

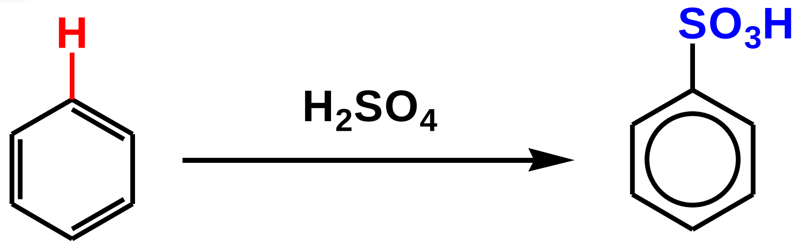
Lewis acid

$\longrightarrow H_2O + NO_2^{\oplus}$



$H^{\oplus} + [HSO_4]^{\ominus} \longrightarrow H_2SO_4$

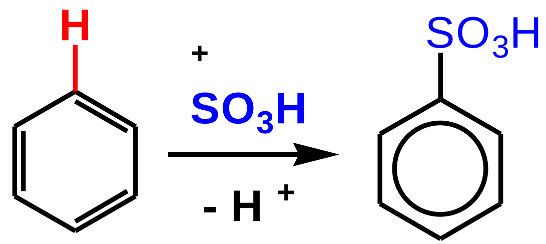
3) Sulfonation



Mechanism

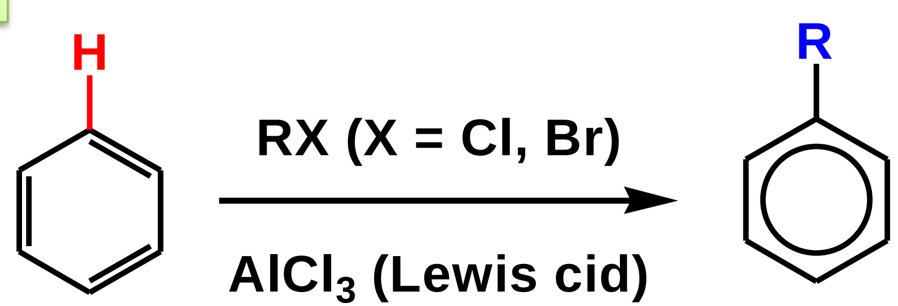
$$H_2SO_4 + \underset{\text{Lewis acid}}{H_2SO_4} \longrightarrow [HSO_4]^{\ominus} + H_3SO_4^{\oplus}$$

$$H_3SO_4^{\oplus} \longrightarrow H_2O + SO_3H^{\oplus}$$



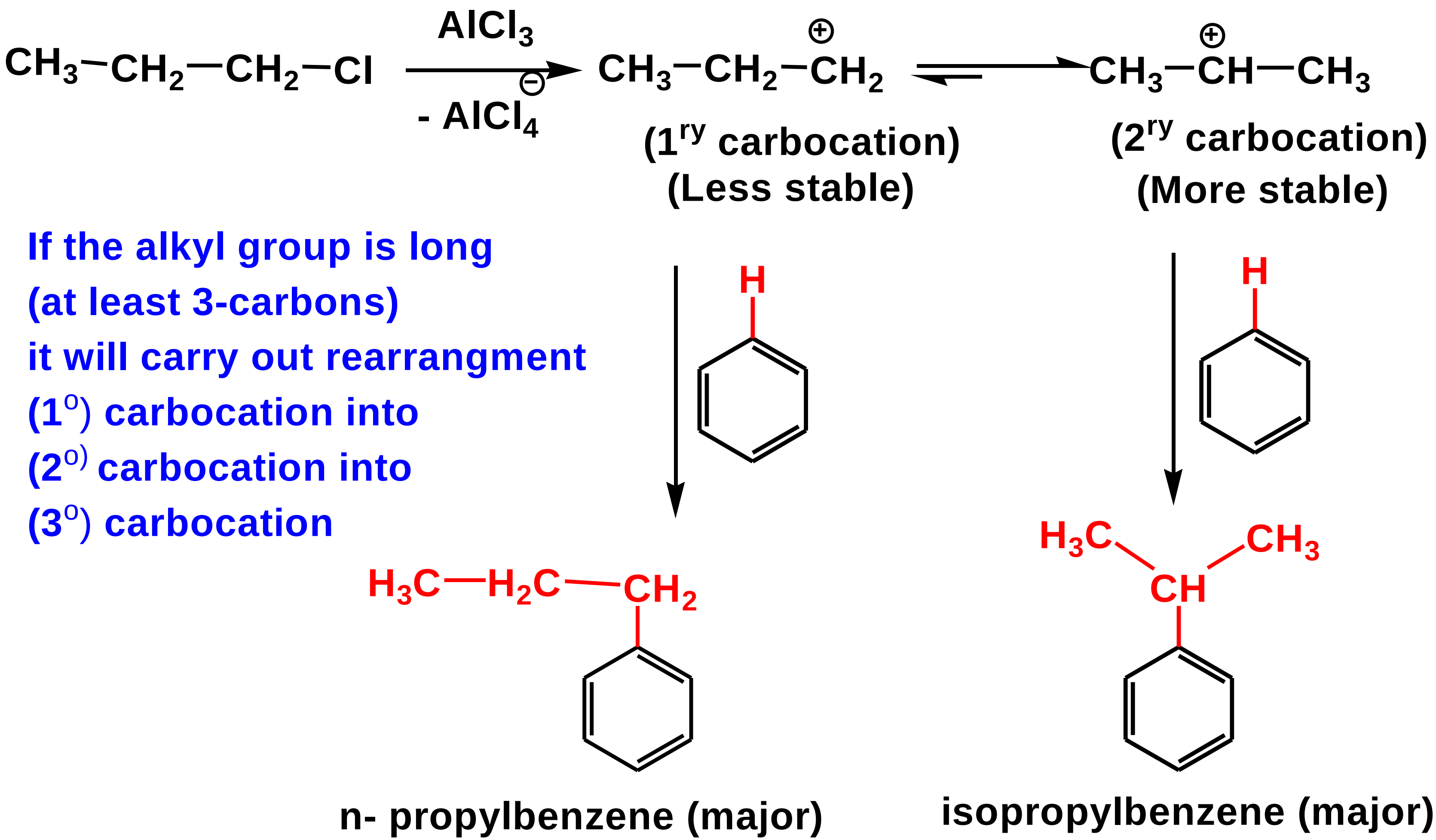
$$H^{\oplus} + [HSO_4]^{\ominus} \longrightarrow H_2SO_4$$

4) Friedel Crafts Alkylation

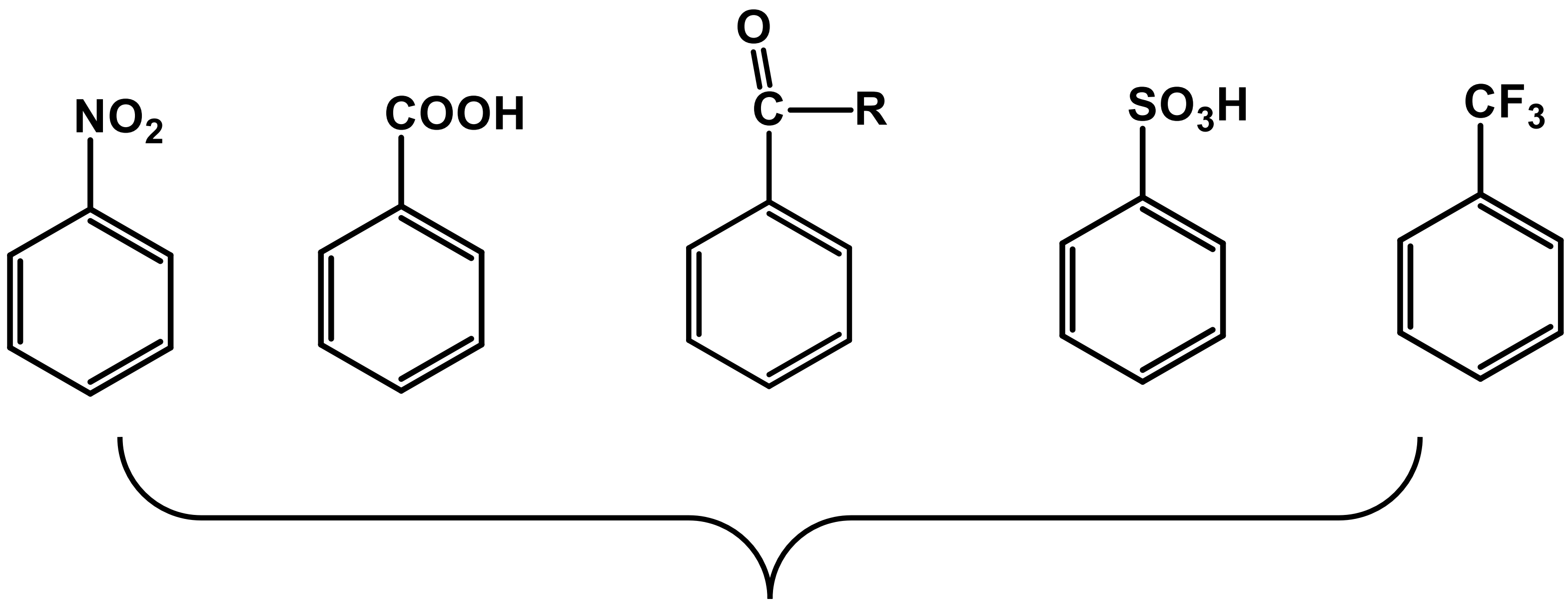


Limitation of Friedel Crafts Reaction

1) If the alkyl group is long (at least 3-carbons) it will carry out rearrangement. Primary carbocation $(R\text{-}CH_2)^+$ will convert into secondary carbocation $(R_2CH)^+$. Also, the secondary carbocation $(R_2CH)^+$ will convert into tertiary carbocation $(R_3C)^+$



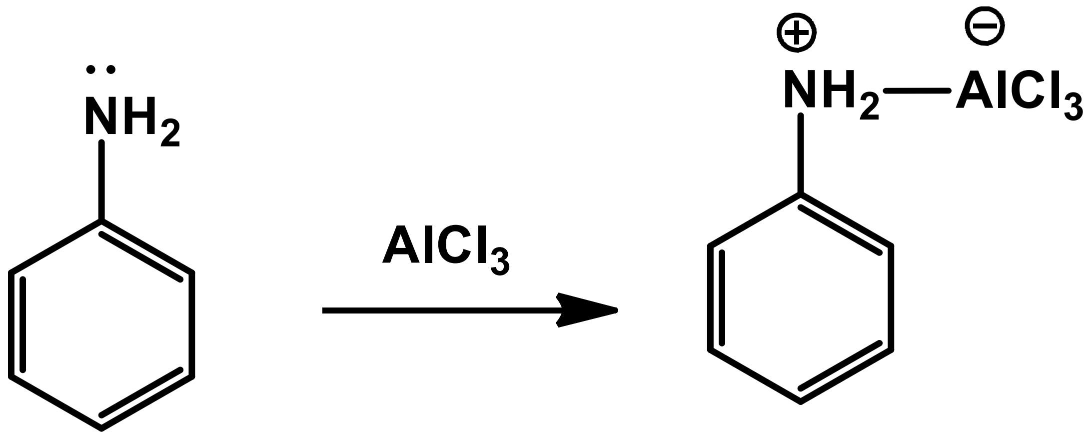
2) Friedel-Crafts reaction could not occurred when the benzene ring have strong **Electron-withdrawing groups** (**EWG**) because these groups decrease the electron density on the ring.



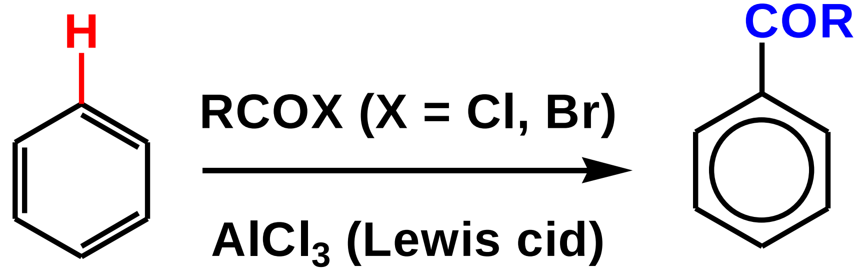
Benzene ring containing EWG

Q: How do you account for fact that:
benzene in the presence of $AlCl_3$ react with isobutyl bromide to yield *tert*-butylbenzene ?

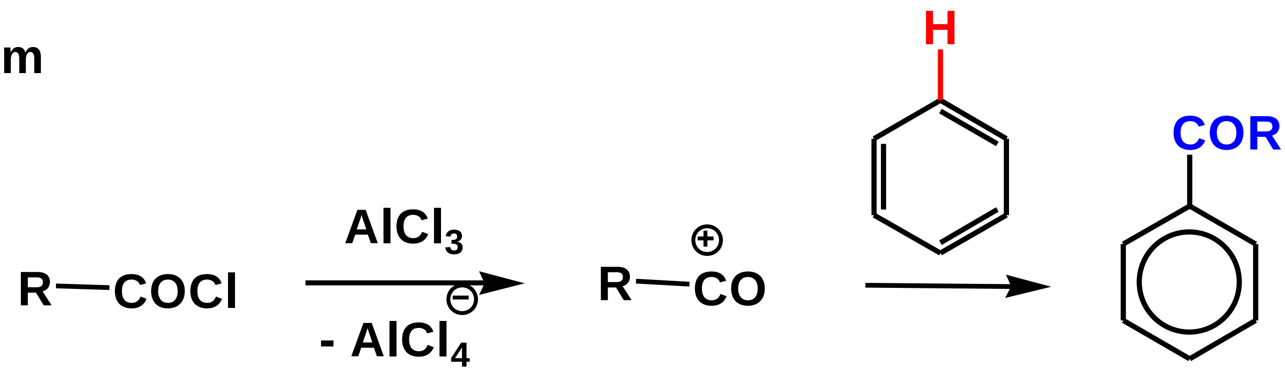
3) Friedel-Crafts reaction could not occurred when the benzene ring have NH_2- NHR- or NR_2 groups because the lone pair of electron on nitrogen atom of these groups will react with Lewis acid ($AlCl_3$) and the group will become strong **EWG** so the reaction will not proceeded.



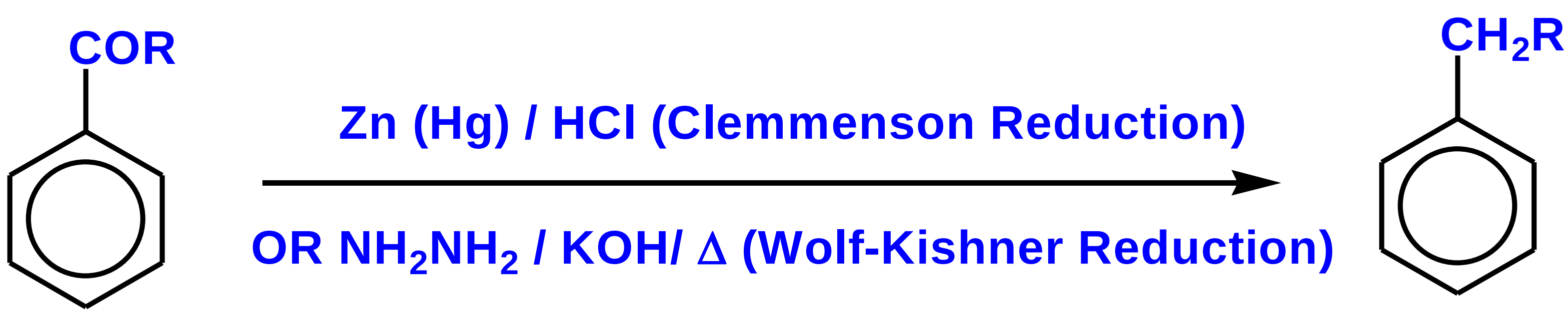
5) Friedel Crafts Alkylation



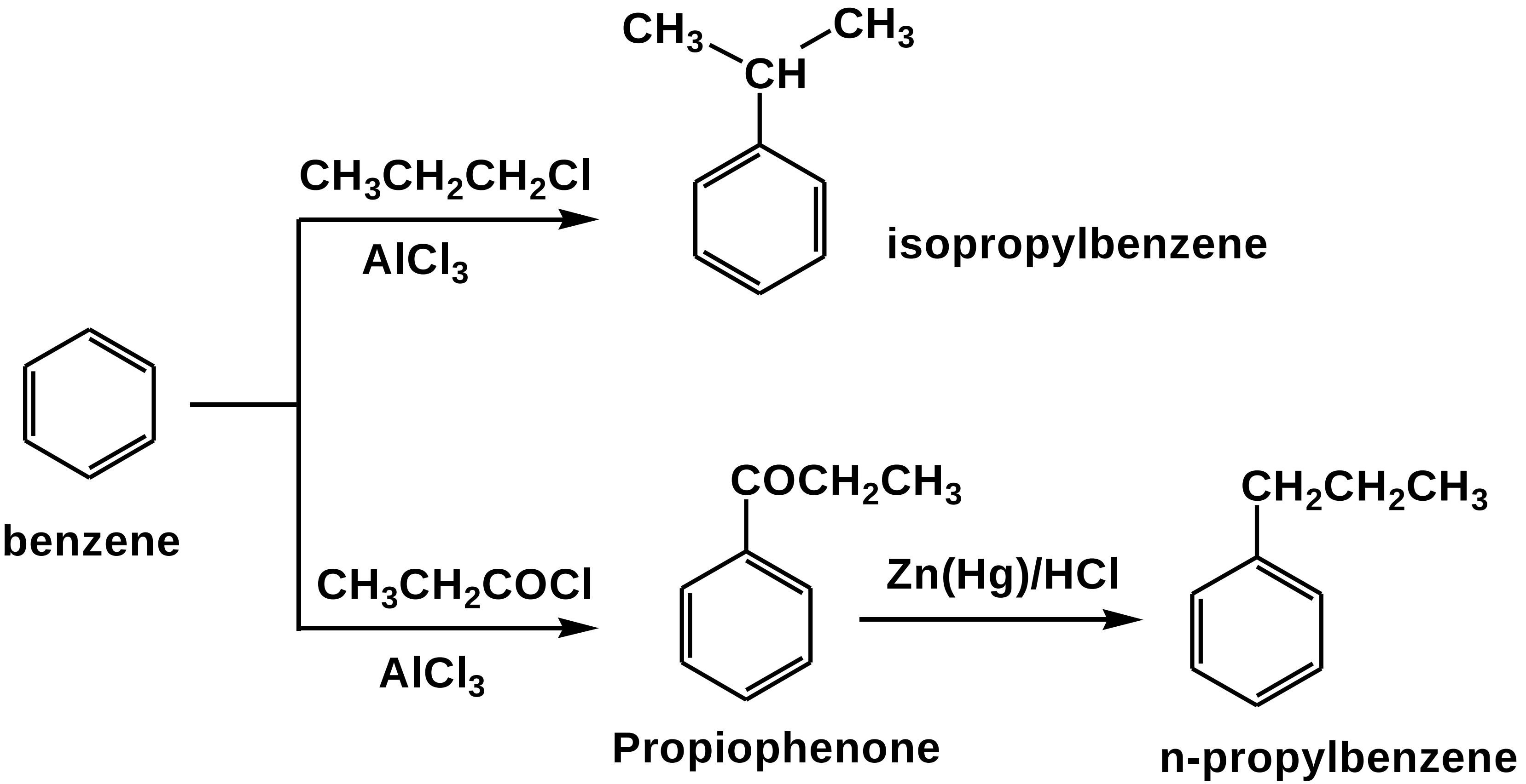
Mechanism



Acylbenzenes have many uses in organic chemistry as precursors for the preparation of n-alkylbenzenes withought rearrangement



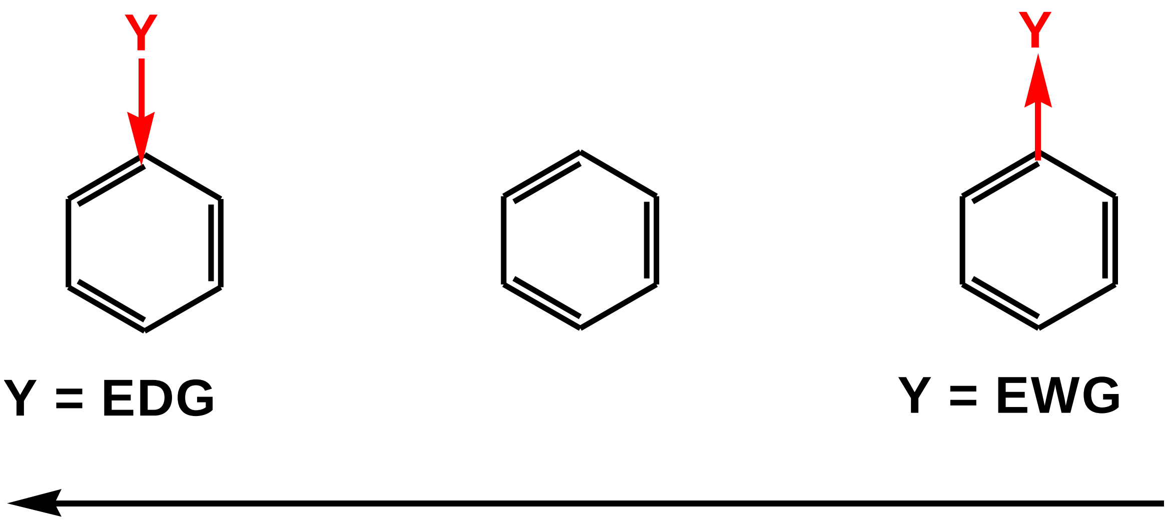
Strarting from benzene, show how can you prepare
i) iso-propyl benzene ii) n-propyl benzene



Effect of substituent on the reactivity of benzene ring

Electron donating group such as NH_2, OH, OR and Cl will increases the electron density on benzene ring so the rate of electrophilic substitution reaction will increase.

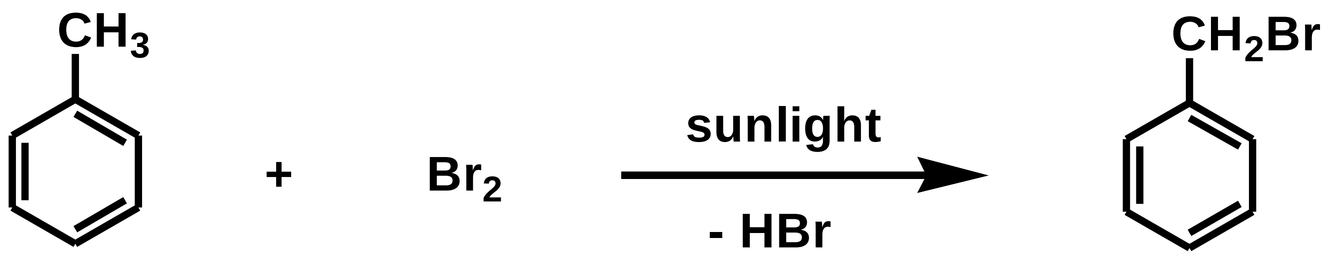
While, **Electron withdrawing group such as C=O, NO_2, SO_3H and COOH** will decreases the electron density on benzene ring so the rate of electrophilic substitution reaction will decrease.



Increase in the rate of electrophilic substitution reactions

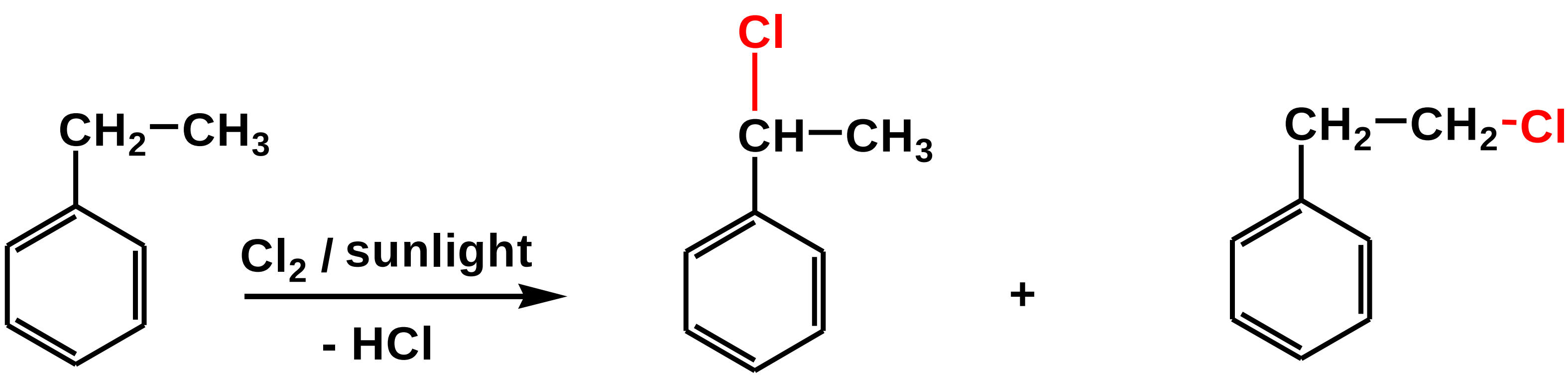
Reaction of alkyl side chain

1) Halogenation



Toluene

Benzyl bromide

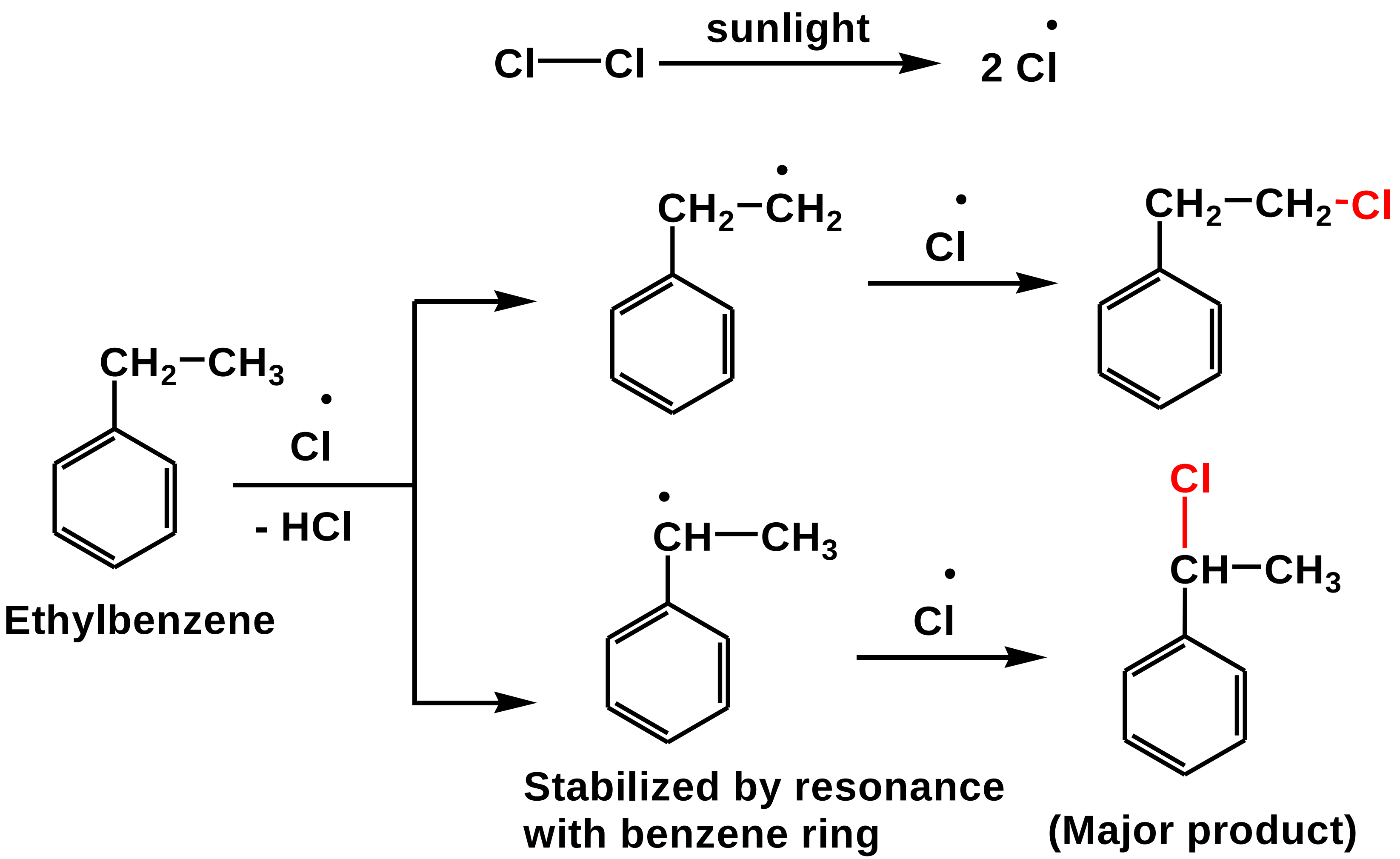


Ethylbenzene

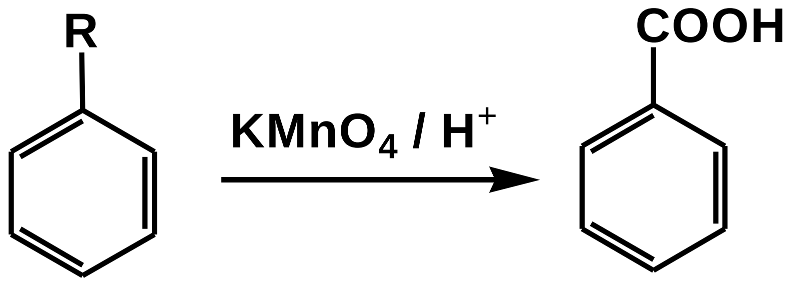
(1-Chloro-1-phenylethane)
(Major product)

(1-Chloro-2-phenylethane)
(Minor product)

Free Radical Mechanism

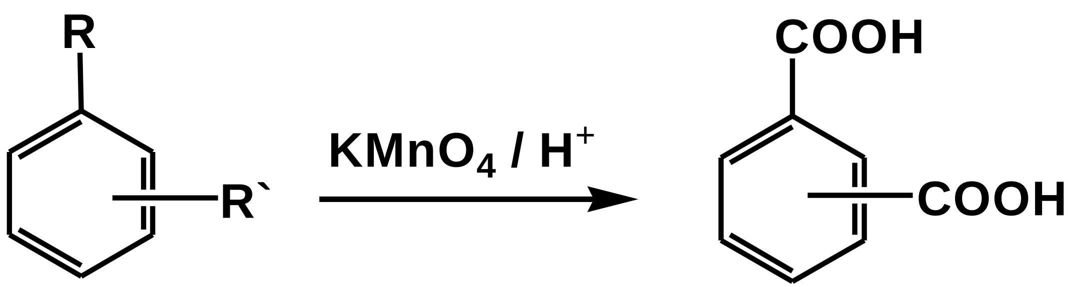


2) Oxidation of alkyl side-chain



Alkylbenzene Benzoic acid

R = CH_3, CH_3CH_2, ...



Dialkylbenzene Dicarboxylic acid

R, R` = CH_3, CH_3CH_2, ...

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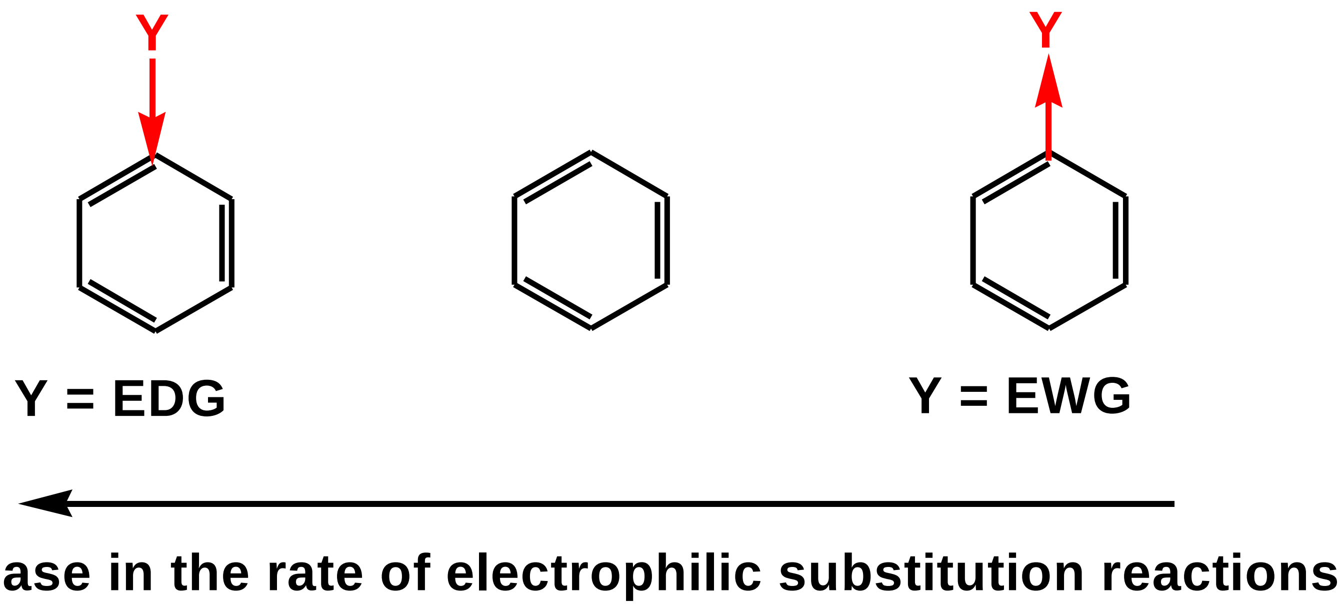
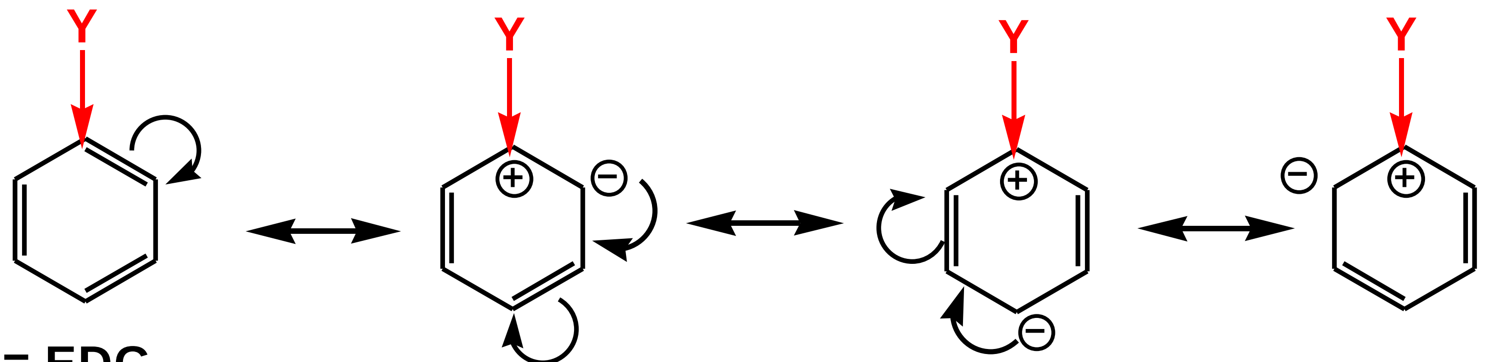


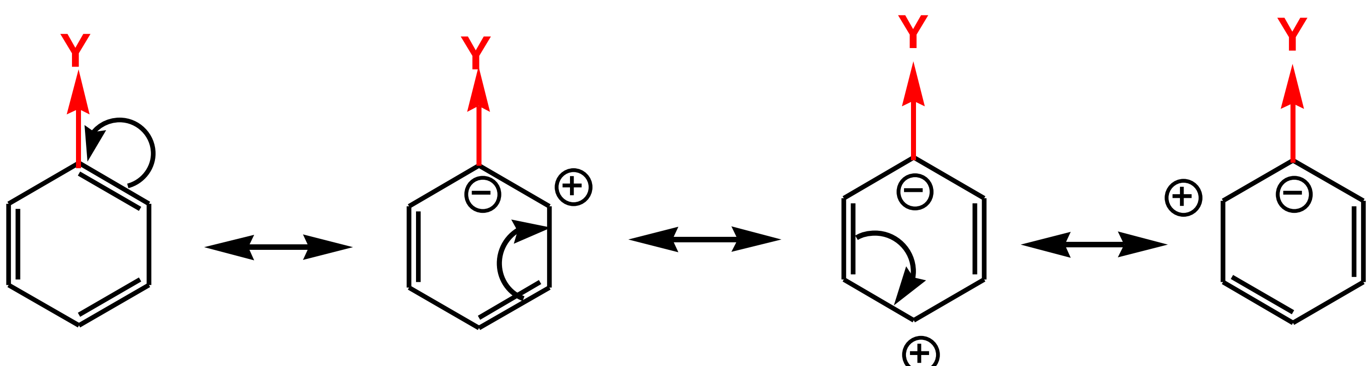
Effect of substituent on the orientation in benzene ring

Electron-Donating Group (ortho and para directing group) will increase the electron density on the benzene ring specially on ortho and para positions.



Y = EDG

Electron-Withdrawing Group (meta directing group) will decrease the electron density on the benzene ring specially on ortho and para positions.



Y = EWG

Substituent	Orientation effect	Effect on reactivity
$-NH_2$, $-NHR$, $-NR_2$ -OH, -OR	ortho-para directing	Strongly activating
-NHCOR, -OCOR,	ortho-para directing	Moderatley activating
-R, -Ar, $-CH=CR_2$	ortho-para directing	Weakly activating
-F, -Cl, -Br, -I	ortho-para directing	Weakly deactivating
-CHO, -COR, -COCl -COOH	meta directing	Moderately deactivating
-CN, $-^{+}SO_3H$, $-^{+}NH_3$ $-^{+}NH_2R$, $-^{+}NHR_2$, $-^{+}NR_3$ $-NO_2$	meta directing	Strongly deactivating

Q:How can you prepare the following compounds from benzene (assume that a pure para isomer can be separated from an ortho, para mixture)?

1) p-nitrotoluene
2) p-bromonitrobenzene
3) p-bromobenzoic acid
4) m-bromobenzenesulfonic acid
5) p-chlorophenol

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