

I. ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

- A. There are five general types of electrophilic aromatic substitution reactions.
1. Halogenation of benzene with Br_2 , Cl_2 or I_2 occurs through the same mechanism.
 - a. Bromination of benzene occurs upon treatment with Br_2 and FeBr_3 .
 - b. Chlorination of benzene occurs upon treatment with Cl_2 and FeCl_3 .
 - c. Iodination of benzene occurs upon treatment with I_2 and CuCl_2 .
 2. Nitration of benzene occurs through treatment with a nitronium ion, ${}^+\text{NO}_2$.
 - a. The nitronium ion can be generated from nitric acid and sulfuric acid.
 - b. The nitronium ion can be generated from nitronium tetrafluoroborate.
 - c. Nitration of benzene occurs through the same mechanism as halogenation.
 3. Sulfonation of benzene occurs through treatment with fuming sulfuric acid.

The reaction is reversible and products depend on the reaction conditions.

 - a. In strong acid, sulfonation is favored.
 - b. In hot, dilute acid, desulfonation is favored.
 - c. Sulfonation of benzene occurs through the same mechanism as halogenation & nitration.
 4. Alkylation (Friedel-Crafts Alkylation) of benzene involves substituting a hydrogen atom on a benzene ring with an alkyl group. This reaction occurs by treatment of benzene with a stable carbocation and aluminum trichloride. There are a number of problems with alkylation of an aromatic ring using the Friedel-Crafts reaction.
 - a. Only alkyl halides can be used to generate the carbocation.
 - b. Benzene rings substituted with electron-withdrawing groups are not reactive.
 - c. The monosubstituted product initially formed is more reactive than the starting material
 - d. Rearrangements can occur with unstable carbocations.
 - e. Amino substituted benzenes do not undergo Friedel-Crafts reactions.
 5. Acylation (Friedel-Crafts Acylation) of benzene involves substitution of a hydrogen atom on the benzene ring with an acyl group. This reaction occurs by treatment of benzene with an acid chloride and aluminum trichloride.
 - a. Acylation of aromatic rings occurs through the same mechanism as alkylation, sulfonation, nitration and halogenation.
 - b. Amino substituted benzenes do not undergo Friedel-Crafts reactions.

II. REACTIVITY OF SUBSTITUTED AROMATIC RINGS IN ELECTROPHILIC AROMATIC SUBSTITUTIONS

1. There are two types of substituents that affect the reactivity of aromatic rings in electrophilic aromatic substitutions.
 - a. Activating groups make the ring more electron rich and thus more reactive. (Electron-donating groups)
 - b. Deactivating groups make the ring electron poor and thus less reactive. (Electron-withdrawing groups)
2. The activating or deactivating ability of a substituent can be described in two ways.
 - a. The inductive effect of a substituent depends on the polarity of the substituent relative to the benzene ring.
 - b. The resonance effect of a substituent depends on the group's ability to delocalize electrons.
3. Reaction on a monosubstituted aromatic ring can occur in three possible positions on the ring relative to the initial substituent, i.e., ortho-, meta- and/or para-. Different substituents can direct the reaction to specific positions on the ring and can be classified according to their directing ability.
 - a. Ortho-/para-directing activators direct reaction to ortho- and para positions.
 - b. Ortho-/para-directing deactivators direct reaction to ortho- and para positions.
 - c. Meta-directing deactivators direct reaction to the meta position.
4. To predict the reactivity of a di- or trisubstituted benzene refer to the following rules.
 - a. If substituents direct the reaction to the same position then reaction will occur at that position.
 - b. If substituents direct reactivity to different positions then the more powerful director will dominate.
 - c. In a meta-disubstituted benzene, reaction at the site ortho to both substituents does not occur due to steric hindrance.

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