two reactions differ very much as one regenerates the original structure with a substituent, i.e., a substituted product is formed, whereas the other gives an addition product and thus, the original structure (presence of double bond) is destroyed. It is because the regenerated benzene nucleus, by a loss of proton, stabilizes itself by resonance whereas there is no such comparable large resonance stabilisation in the case of alkenes which thus tend to add the nucleophilic reagent.

4. Friedel Craft's reactions: The reaction of an alkyl halide or acyl halide with benzen in the presence of Lewis acid, generally AlCl₃, is known as Friedel Craft's reaction; so it can be divided into alkylation and acylation.

Alkylation: The alkylation of benzene, at least with primary alkyl halides, takes place with the formation of a polar addition compound between aluminium chloride and alkyl halide. Thus, the function of AlCl₃ is to supply the electron deficient species in the following manner.

However, the alkylation reaction suffers from the following defects.

(i) Since the alkyl groups are o, p-directing, they further facilitate the substitution and hence the reaction always leads to polyalkylation, e.g.,

$$+ CH_3CI \stackrel{AlCl_3}{\rightleftharpoons} CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

(ii) Sometimes the rearranged product is obtained, e.g., alkylation with n-propyl chloride gives isopropylbenzene.

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{Denzene} \end{array}$$

It is due to the fact that the less stable primary carbonium ion from the alkyl halide has a tendency

With sec. and ter-halides the carbon atom having halogen is progressively more able to accommodate the positive charge and thus, here carbonium ion (R⁺) can be formed.

² Stable addition compound of this type has been isolated, viz. CH₃Br.AlBr₃ and CHCl₃CaCl₂.

to rearrange to a more stable secondary carbonium ion.

$$CH_{3}CH_{2}CH_{2}CI + AICI_{3} \rightleftharpoons CH_{3}CH_{2}CH_{2}AICI_{4} \longrightarrow CH_{3}-CHCH_{2} \xrightarrow{C_{6}H_{6}} C_{6}H_{5}CH_{2}CH_{2}CH_{3}$$

$$Primary \ carbonium \ ion \qquad Normal \ product \ (Propylbenzene)$$

$$CH_{3}.CH.CH_{3} \xrightarrow{C_{6}H_{6}} C_{6}H_{5}.CH \xrightarrow{CH_{3}}$$

$$CH_{3}.CH.CH_{3} \xrightarrow{C_{6}H_{6}} CG_{6}H_{5}.CH \xrightarrow{CH_{3}}$$

$$Secondary \qquad Rearranged \ product \ (Cumene)$$

(iii) Alkylated products often isomerise and disproportionate to give different products, e.g.,

$$\begin{array}{c}
CH_3 \\
CH_3
\end{array}$$

Alkylation may also be carried out with alkenes, alcohols, ethers and esters in the presence of acids, viz. BF₃. The latter is responsible for the production of carbonium ion in the following manner.

$$CH_3.CH = CH_2 \xrightarrow{H^+} CH_3.CH.CH_3 \xrightarrow{C_6H_6} C_6H_5CH(CH_3)_2$$

$$(CH_3)_2CHOH \xrightarrow{H^+} (CH_3)_2CHOH_2 \xrightarrow{-H_2O} (CH_3)_2CH \xrightarrow{C_6H_6} C_6H_6CH(CH_3)_2$$

Acylation: Acylation of benzene may be brought about with acid chorides or anhydrides in the presence of Lewis acids. The reaction takes place as below.

$$CH_{3}COCI + AICI_{3} \longrightarrow CH_{3}CO + AICI_{4}^{-}$$

$$H \longrightarrow COCH_{3} \longrightarrow COCH_{3}$$

$$+ CH_{3}CO \longrightarrow + AICI_{3}^{-} \longrightarrow + AICI_{3} + HCI$$

The acylation process differs from the alkylation in the following points.

- (i) Acylation is usually carried out in a solvent, commonly CS₂ or nitrobenzene.
- (ii) Acylation requires more catalyst than alkylation because much of the catalyst is removed by the formation of a complex with the product (ketone).

$$C_6H_5COCH_3 + AlCl_3 \rightleftharpoons C_6H_5 C=O$$
—AlCl₃

(iii) In acylation, rearragement products are not formed, but if the acid halide is highly branched then alkylated, rather than expected acylated, product may be formed as follows.

(CH₃)₃C
$$\xrightarrow{\uparrow}_{C}$$
 Carbonium ion

Carbonium ion

Carbonium ion

Carbonium ion

(iv) Unlike alkylation, acylation is easily controlled to produce monosubstituted product since as one acyl group is introduced in the ring, it is very difficult to introduce the second acyl group in the same ring (see further); for this reason monosubstituted alkylated benzenes are generally prepared by acylation process, rather than alkylation, in the following manner.

Moreover, by this method no rearranged alkylated product (viz. cumene) is formed.