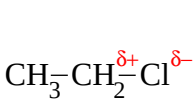
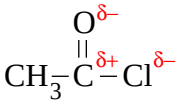
FRIEDEL-CRAFTS REACTIONS - AN OVERVIEW

General thoughts

- Friedel-Crafts reactions involve **electrophilic substitution** of benzene (aromatic) rings
- There are two types - **Alkylation** and **Acylation**
- Alkylation involves the substitution of alkyl groups such as CH_3, C_2H_5 and C_3H_7
- Acylation involves the substitution of acyl groups such as $CH_3C{=}O$
- In both cases a catalyst is needed
- This is because the attacking species isn't a strong enough electrophile
- It hasn't enough positive character to persuade benzene to react
- Haloalkanes and acyl chlorides have polar bonds but the C isn't positive enough



a haloalkane

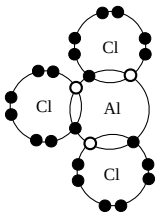


an acyl chloride

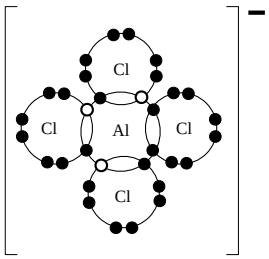
- The catalyst makes the attacking species more positive
- **Anhydrous** aluminium chloride is the catalyst
- It works because it is a **Lewis acid**
- In $AlCl_3$ the aluminium is **electron deficient** - it only has 6 electrons in its outer shell
- In both cases the reagent has a polar C-Cl bond
- The carbon atom has a $\delta+$ charge but it isn't enough to tempt the benzene
- The aluminium chloride increases the charge so that benzene become interested

Action of $AlCl_3$

- The aluminium atom is electron deficient with only 6 in its outer shell
- It acts as a Lewis acid as it can accept a lone pair to make up its octet



BEFORE
incomplete octet
trigonal planar *shape*



AFTER
complete octet
tetrahedral *shape*

- It can do this by attracting a chlorine atom away from a C-Cl bond
- The more the Cl is attracted by the $AlCl_3$ the more polar the C-Cl bond gets
- In the extreme case it pulls the chlorine right off leaving a C^+ behind

Alkylation $\quad RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$

Acylation $\quad RCOCl + AlCl_3 \rightleftharpoons AlCl_4^- + RCO^+$

- The aromatic benzene ring will now attack and electrophilic substitution takes place

Alkylation substitutes an alkyl (e.g. methyl, ethyl) group

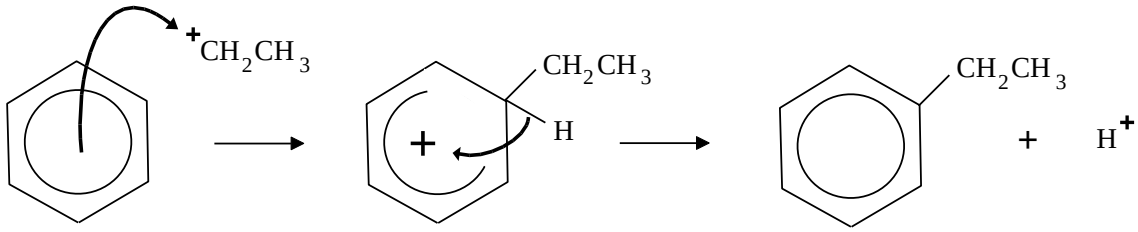
reagents a haloalkane (RX) and anhydrous aluminium chloride $AlCl_3$

conditions room temperature; dry inert solvent (ether)

electrophile a carbocation R^+ (e.g. CH_3^+)

equation **C_6H_6 + C_2H_5Cl ———> $C_6H_5C_2H_5$ + HCl**

mechanism



Industrial method The industrial preparation of similar compounds is slightly different
Alkenes are used instead of haloalkanes - see other notes

Acylation substitutes an acyl (e.g. ethanoyl) group
the aluminium chloride catalyst acts in the same was as with alkylation

reagents an acyl chloride (RCOCl) and anhydrous $AlCl_3$

conditions reflux 50°C; dry inert solvent (ether)

electrophile $RC^+{=}O$ (e.g. CH_3C^+O)

product carbonyl compound (aldehyde or ketone)

equation **C_6H_6 + CH_3COCl ————> $C_6H_5COCH_3$ + HCl**

mechanism