REACTION OF BENZENE

- NITRATION
- SULPHONATION
- HALOGENATION
- FRIDEL CRAFT ALKYLATION & ACYLATION

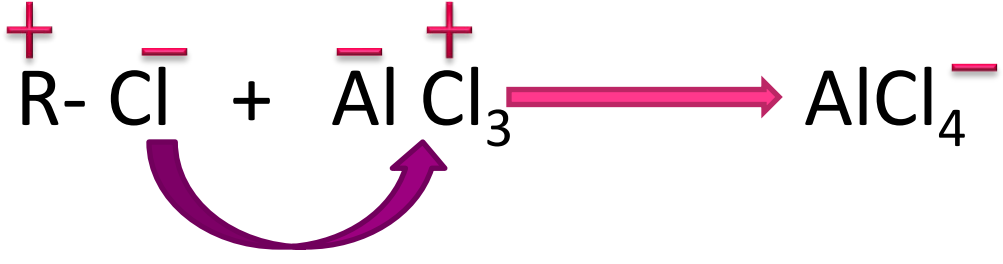
FRIEDEL CRAFT ALKYLATION

- It is a chemical reaction involving introduction of alkyl group on benzene and creating alkylbenzene.
- A Lewis acid catalyst such as $FeCl_3$ or $AlCl_3$ is employed in this reaction
- Alkyl halides are also involved

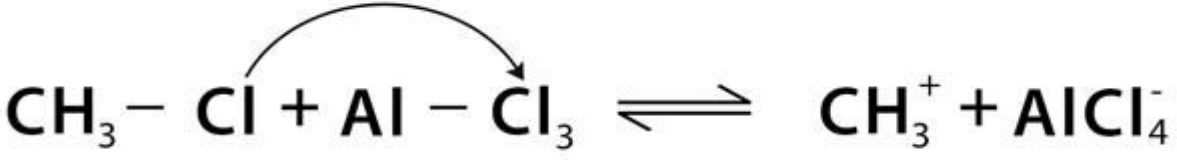
Friedel-Crafts Alkylation

MECHANISM

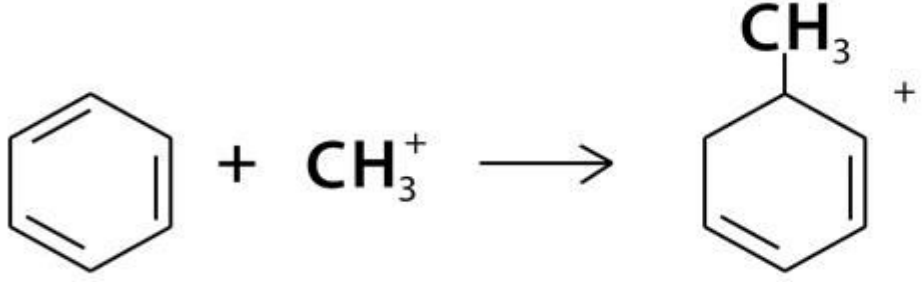
- Alkyl halide reacts with Aluminum chloride to form Tetrachloroaluminate as Cl carries negative charge hence R group is released which attacks benzene and form alkylbenzene

- 

MECHANISM

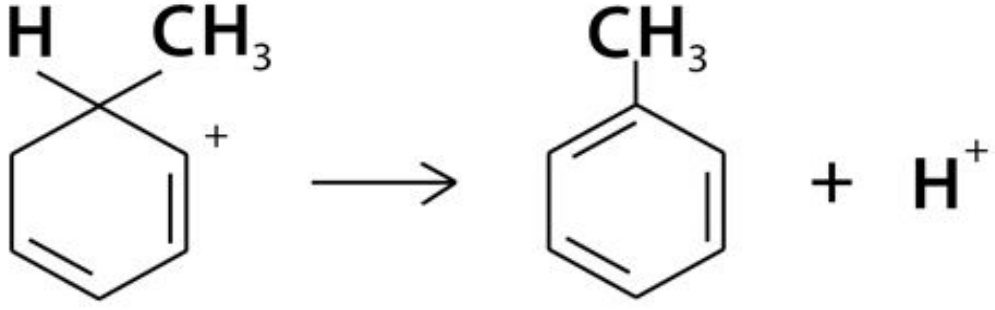


Step1: Removal of Cl from CH_3Cl to form the electrophilic species CH_3^+



Step2: CH_3^+ attacks C=C bond in benzene which loses its aromaticity to form a carbocation

MECHANISM



Step3: Loss of proton (H^+) from the carbocation to restore the aromaticity

$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Step4: H^+ reacts with $AlCl_4^-$ to give back $AlCl_3$

Limitations

- Since the carbocations formed by aryl and vinyl halides are extremely unstable, they cannot be used in this reaction.
- The presence of a deactivating group on the aromatic ring (such as an NH_2 group) can lead to the deactivation of the catalyst due to the formation of complexes.
- An excess of the aromatic compound must be used in these reactions in order to avoid polyalkylation (addition of more than one alkyl group to the aromatic compound).
- Aromatic compounds that are less reactive than mono-halobenzenes do not participate in the Friedel-Crafts alkylation reaction.
- It is important to note that this reaction is prone to carbocation rearrangements, as is the case with any reaction involving carbocations.

Application

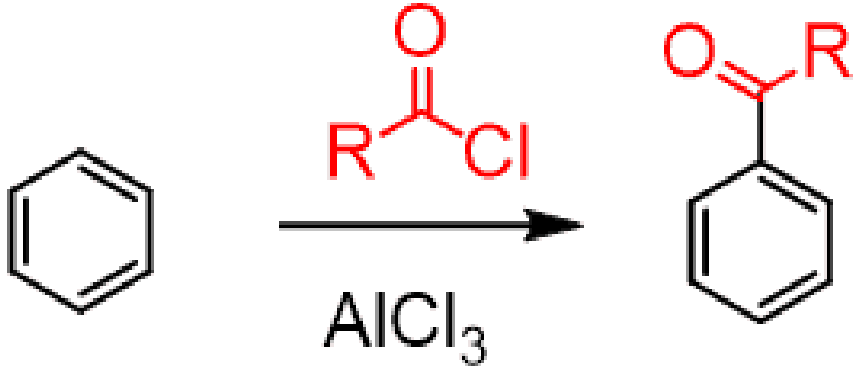
- One common application is in the production of alkylated aromatic compounds, which are used in the manufacturing of pharmaceuticals, fragrances, and dyes.
- It can also be used to synthesize polymers with specific properties. Additionally, Friedel-Crafts alkylation plays a crucial role in the synthesis of various organic intermediates and fine chemicals.
- It's a versatile reaction that allows chemists to introduce alkyl groups onto aromatic rings, expanding the range of compounds that can be synthesized.

FRIEDEL CRAFT ACYLATION

- The Friedel-Crafts acylation reaction involves the addition of an acyl group to an aromatic ring.
- Typically, this is done by employing an acid chloride (R-(C=O)-Cl) and a Lewis acid catalyst such as $AlCl_3$.
- In a Friedel-Crafts acylation reaction, the aromatic ring is transformed into a ketone.

DEPTH OF BIOLOGY

FRIEDEL CRAFT ACYLATION

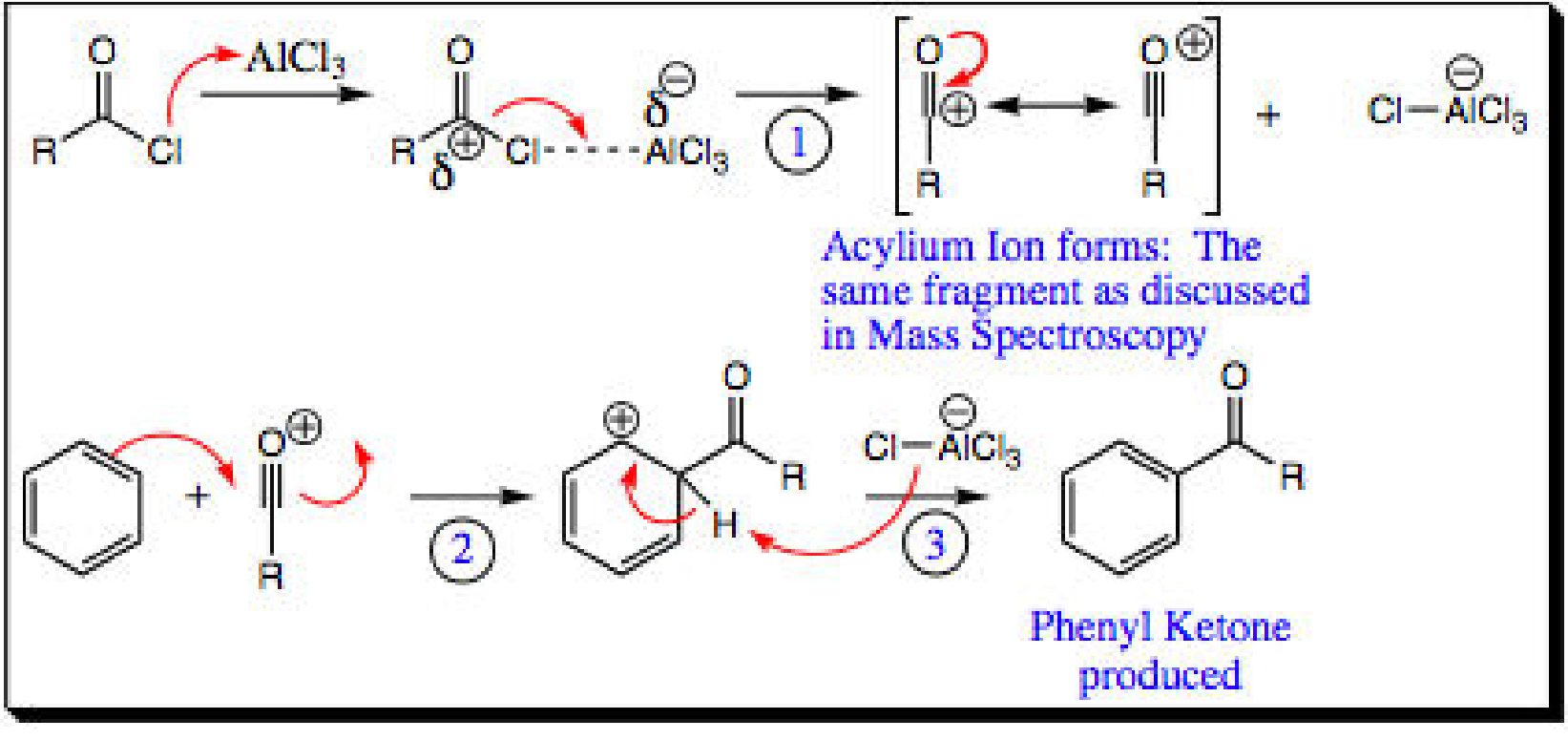


Friedel-Crafts Acylation

MECHANISM

- Al will donate electron to Cl and create a negative charge on it hence $AlCl_4$ formation will take place
- R-(C=O) will remain and get attached to benzene

MECHANISM


AlCl3
R
Cl
δ
δ
Cl
AlCl3
1
O
R
+
Cl—AlCl3
Acylium Ion forms: The same fragment as discussed in Mass Spectroscopy
+
2
H
Cl—AlCl3
3
Phenyl Ketone produced

LIMITATION

- Despite overcoming some limitations of the related alkylation reaction (such as carbocation rearrangement and polyalkylation), the Friedel-Crafts acylation reaction has a few shortcomings.
- The acylation reaction only yields ketones. This is because formyl chloride (H(C=O)Cl) decomposes into CO and HCl when exposed to these conditions.
- The aromatic compound cannot participate in this reaction if it is less reactive than a mono-halobenzene.
- Aryl amines cannot be used in this reaction because they form highly unreactive complexes with the Lewis acid catalyst.
- The acylations can take place on the nitrogen or oxygen atoms when amine or alcohols are used.

APPLICATION

- One specific application of Friedel-Crafts acylation is in the synthesis of aspirin, also known as acetylsalicylic acid. The acylation of salicylic acid with acetic anhydride using a Lewis acid catalyst, such as sulfuric acid, results in the formation of aspirin.
- Without Friedel-Crafts reactions we wouldn't be able to extend aromatic compounds into larger molecules, with more carbon atoms. So, we would be able to form the individual rings for DNA but we wouldn't be able to connect them together to fully form DNA.