Friedel Crafts Reaction

The reaction used for the introduction of alkyl or an acyl group into an aromatic compound in the presence of lewis acid catalyst. The most commonly used lewis acid catalyst is anhydrous AlCl₃ while other catalyst which have been used are BF₃, FeCl₃, SnCl₄ etc.

(a) Friedel Crafts Alkylation

Benzene and other aromatic compound react with alkyl halide in the presence of anhydrous aluminium chloride to form alkyl benzenes.

\[
\text{C}_6\text{H}_5\text{Cl} + \text{H}_3\text{C}-\text{Cl} \xrightarrow{\text{Anhyd. AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{H-Cl}
\]

Mechanism:

This reaction has one big disadvantage, namely that the product is more nucleophilic than the reactant due to the electron donating alkyl-chain. Therefore, another hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule. Also, if the chloride is not on a tertiary carbon or secondary carbon, then the carbocation formed (R⁺) will undergo a carbocation rearrangement reaction.

(b) Friedel Crafts Acylation:

Benzene and other aromatic compound react with acid halide or acid anhydride in the presence of anhydrous aluminium chloride to form ketones.
Mechanism of Friedel - Crafts Reaction

Mechanism:

Friedel–Crafts acylation is the acylation of aromatic rings with an acyl chloride using a strong Lewis acid catalyst. Friedel–Crafts acylation is also possible with acid anhydrides. Reaction conditions are similar to the Friedel–Crafts alkylation mentioned above. This reaction has several advantages over the alkylation reaction. Due to the electron-withdrawing effect of the carbonyl group, the ketone product is always less reactive than the original molecule, so multiple acylations do not occur. Also, there are no carbocation rearrangements, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen.

In a simple mechanistic view, the first step consists of dissociation of a chloride ion to form an acyl cation (acylium ion)

```
        O
       /\    
      /  \   
     /    \  
    R     Cl
   (Cl+) AlCl3
```

In some cases, the Lewis acid binds to the oxygen of the acyl chloride to form an adduct. Regardless, the resulting acylium ion or a related adduct is subject to nucleophilic attack by the arene:

```
        O+  [AlCl4]−
       /   /    
      /    |    
     R    C
   (Cl−)  (Cl−)
```

Finally, chloride anion (or AlCl4−) deprotonates the ring (an arenium ion) to form HCl, and the AlCl3 catalyst is regenerated:

```
       O
      /  \   
     /    \  
    R     
```

If desired, the resulting ketone can be subsequently reduced to the corresponding alkane substituent by either Wolff–Kishner reduction or Clemmensen reduction. The net result is the same as the Friedel–Crafts alkylation except that rearrangement is not possible.