

# Chapter 12

## Reactions of Arenes:

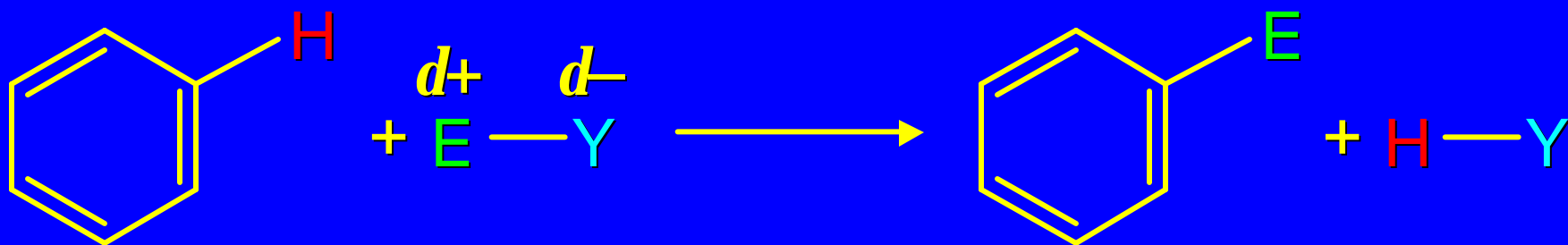
### Electrophilic Aromatic Substitution



## 12.1

# Representative Electrophilic Aromatic Substitution Reactions of Benzene





Electrophilic aromatic substitutions include:

Nitration

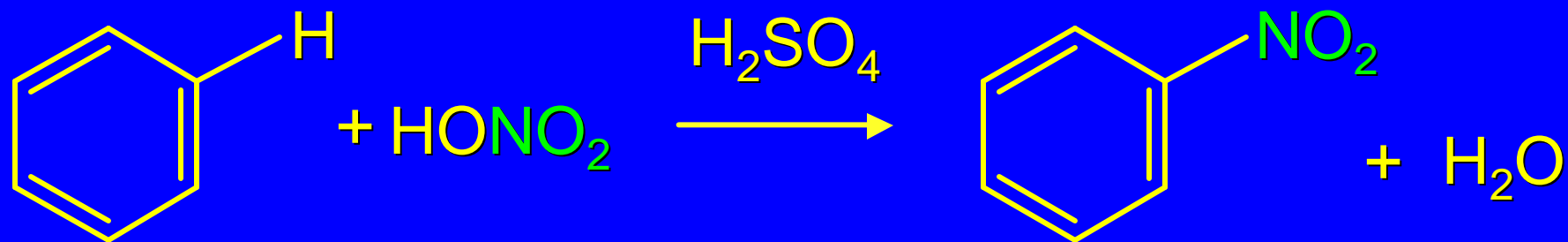
Sulfonation

Halogenation

Friedel-Crafts Alkylation

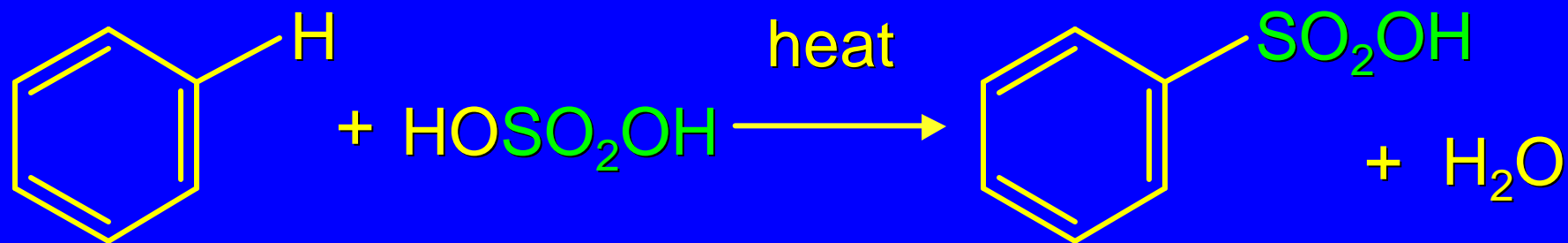
Friedel-Crafts Acylation

*Table 12.1: Nitration of Benzene*



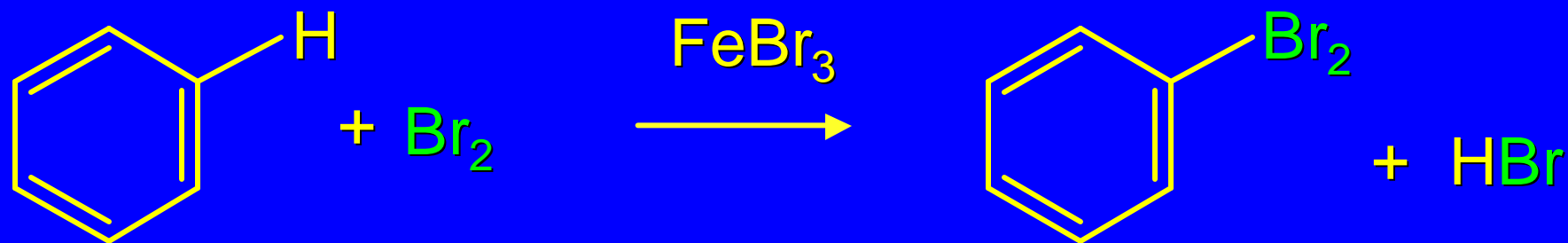
Nitrobenzene  
(95%)

*Table 12.1: Sulfonation of Benzene*



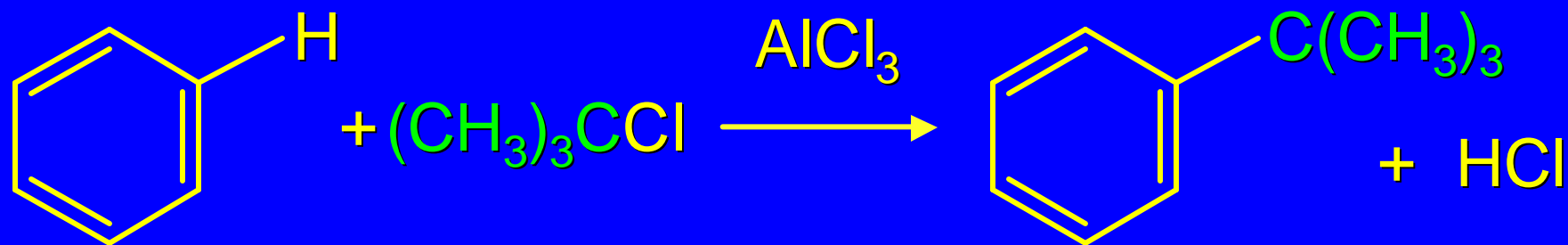
Benzenesulfonic acid  
(100%)

## Table 12.1: Halogenation of Benzene



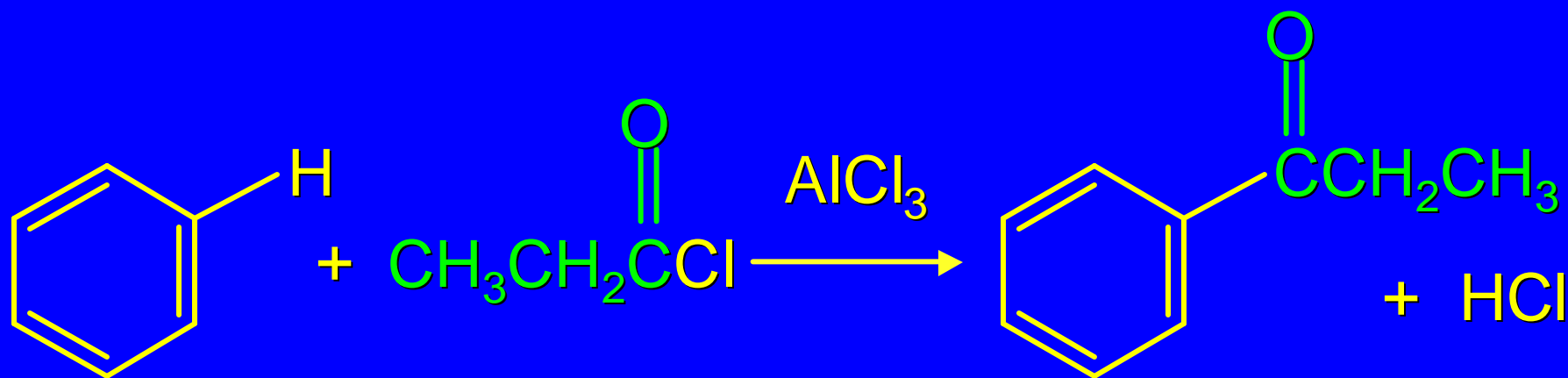
Bromobenzene  
(65-75%)

*Table 12.1: Friedel-Crafts Alkylation of Benzene*



*tert*-Butylbenzene  
(60%)

*Table 12.1: Friedel-Crafts Acylation of Benzene*

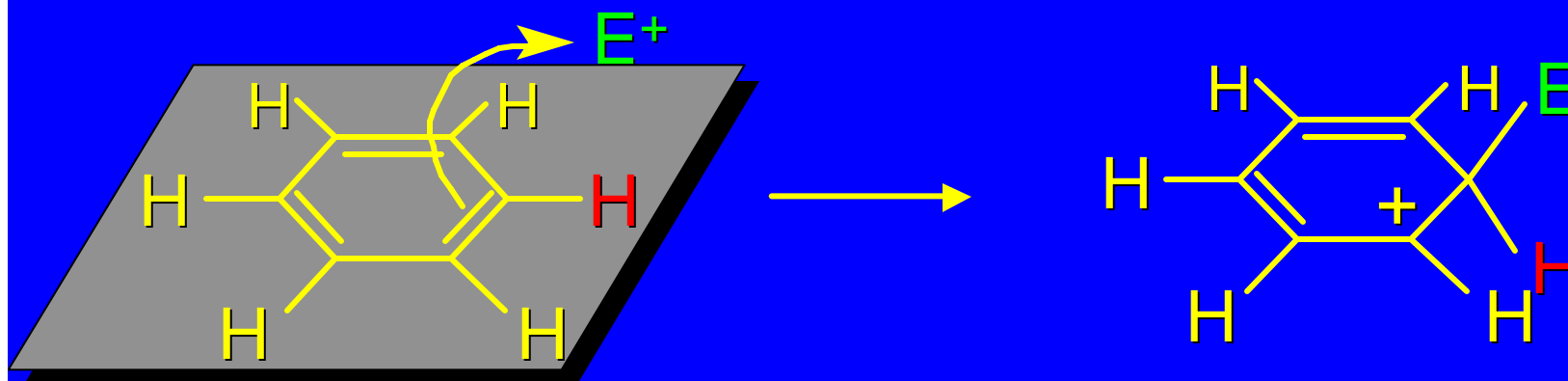


1-Phenyl-1-propanone  
(88%)



12.2  
Mechanistic Principles  
of  
Electrophilic Aromatic Substitution

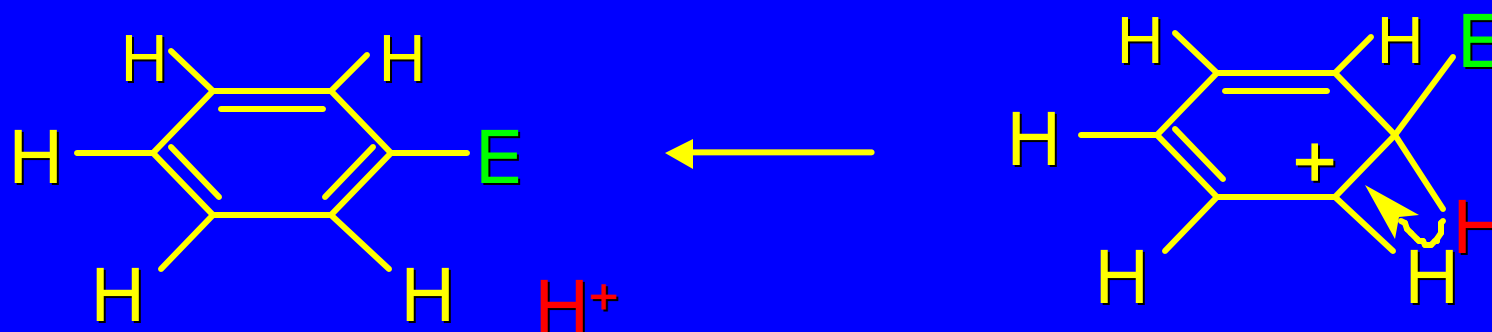
*Step 1: attack of electrophile  
on  $p$ -electron system of aromatic ring*



highly endothermic

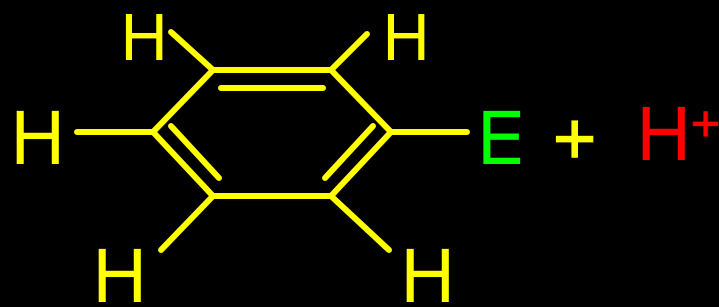
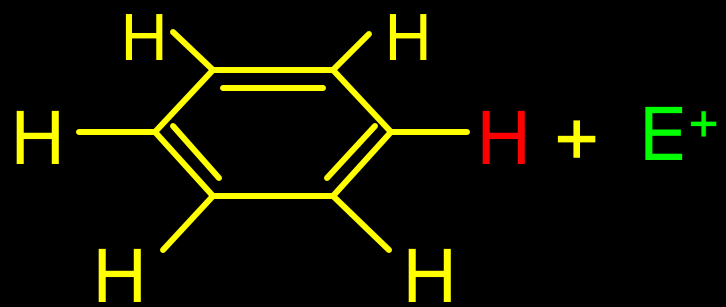
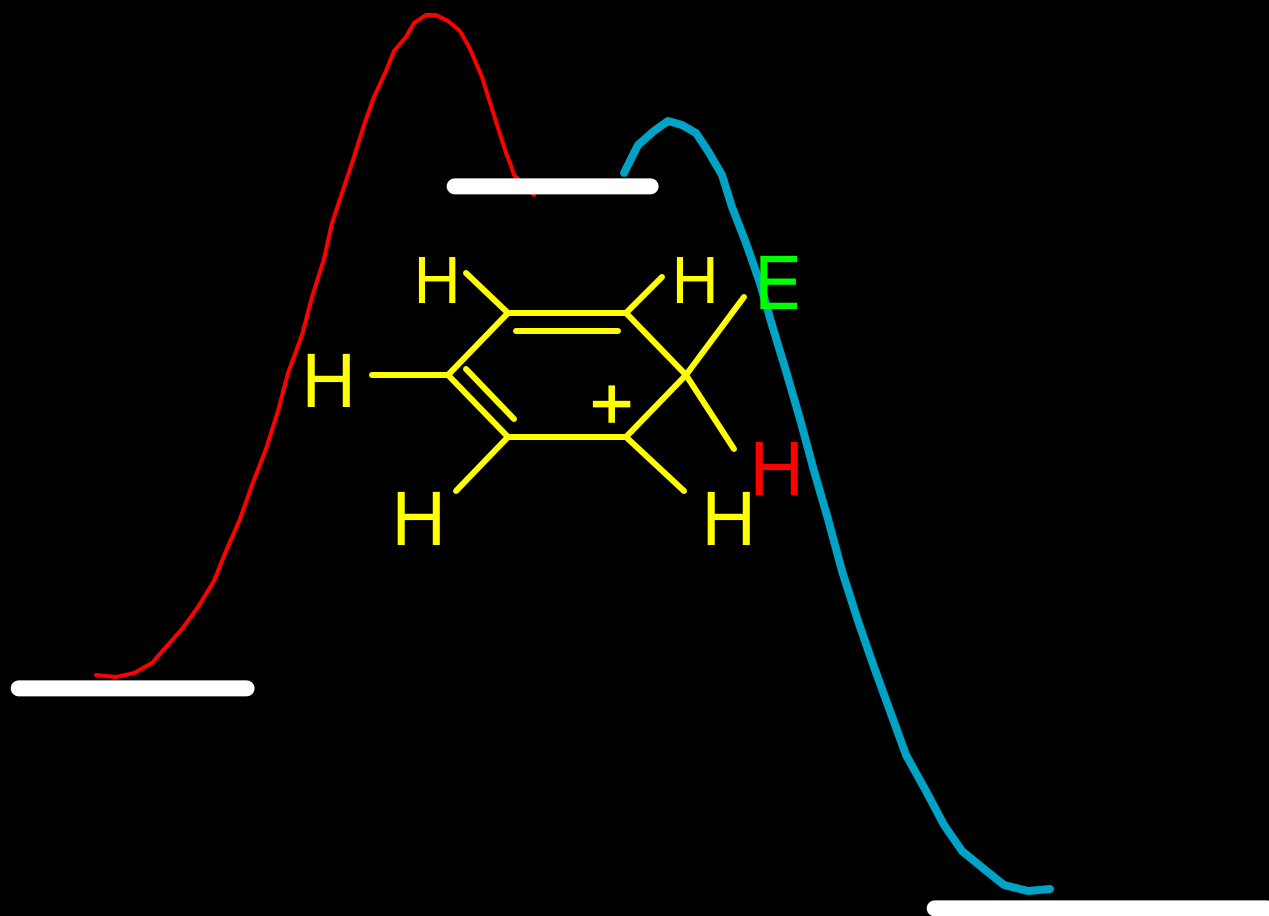
carbocation is allylic, but not aromatic

*Step 2: loss of a proton from the carbocation intermediate*



highly exothermic

this step restores aromaticity of ring

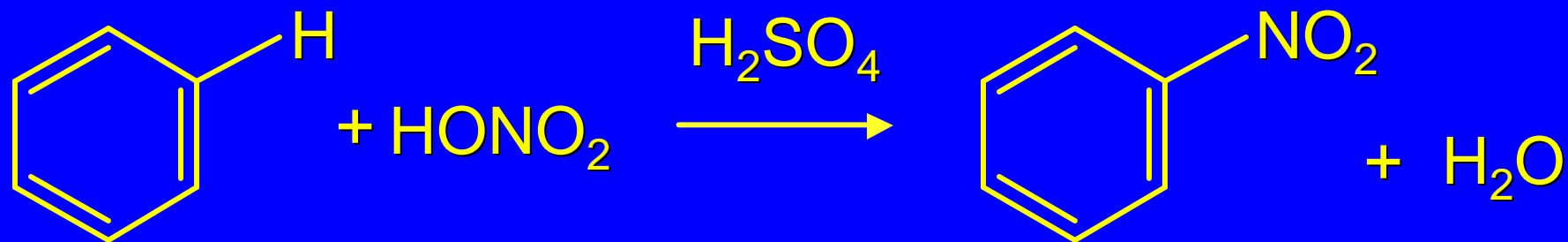


*Based on this general mechanism:*

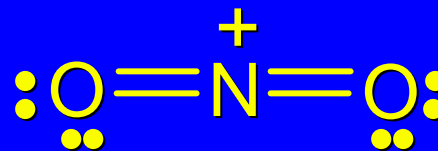
what remains is to identify the electrophile in nitration, sulfonation, halogenation, Friedel-Crafts alkylation, and Friedel-Crafts acylation to establish the mechanism of specific electrophilic aromatic substitutions

## 12.3 Nitration of Benzene

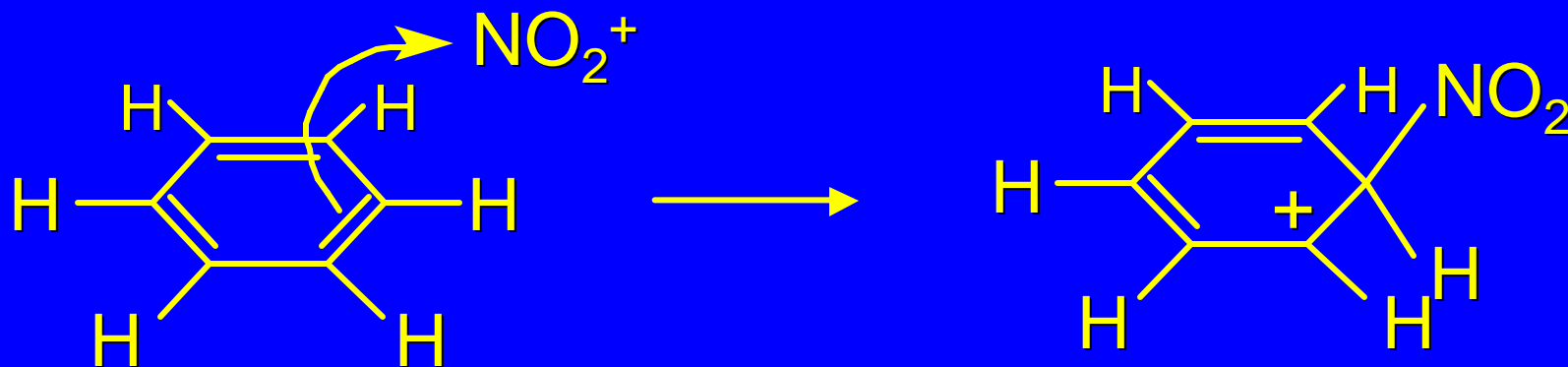
## Nitration of Benzene



Electrophile is  
nitronium ion

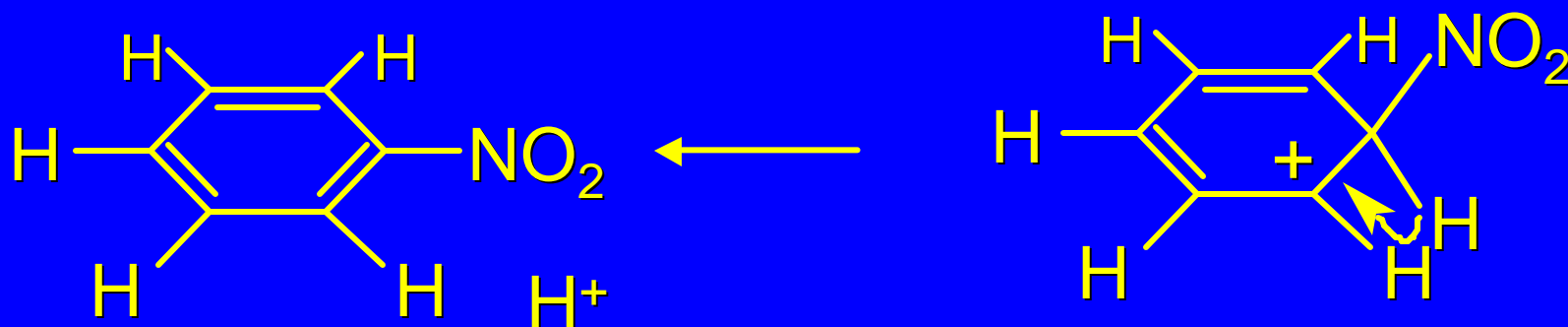


*Step 1: attack of nitronium cation  
on  $p$ -electron system of aromatic ring*

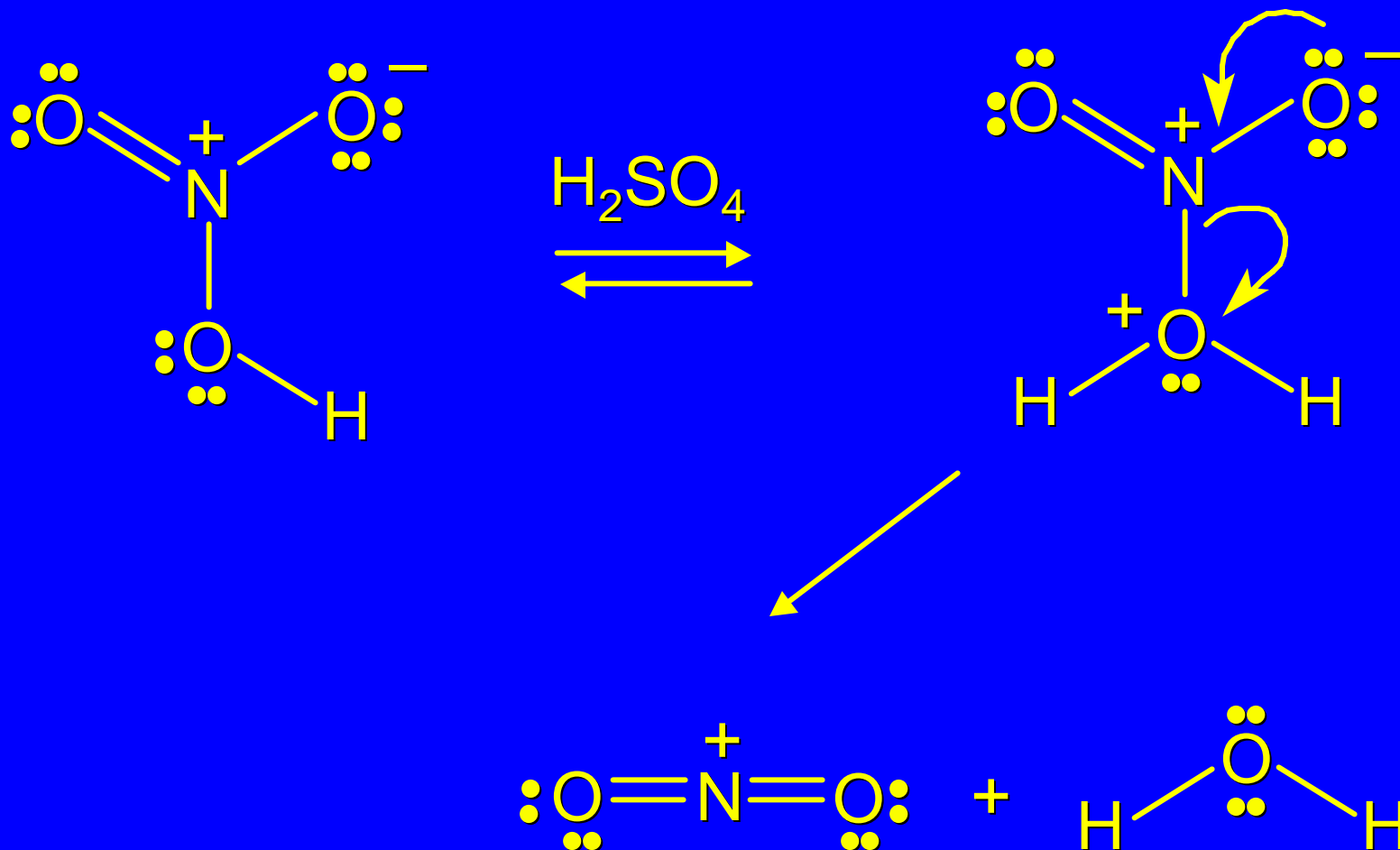




*Step 2: loss of a proton from the carbocation intermediate*

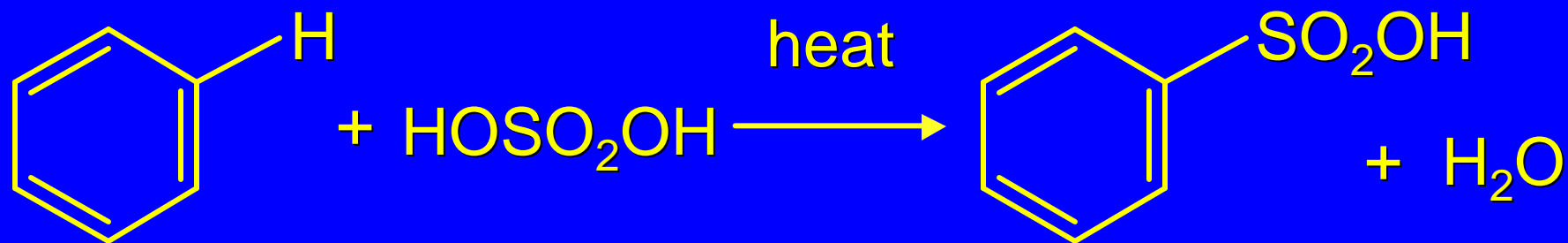


*Where does nitronium ion come from?*

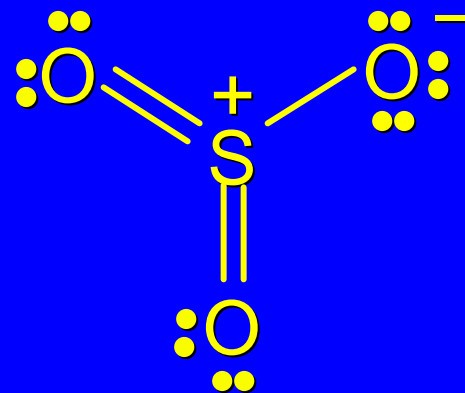


# 12.4 Sulfonation of Benzene

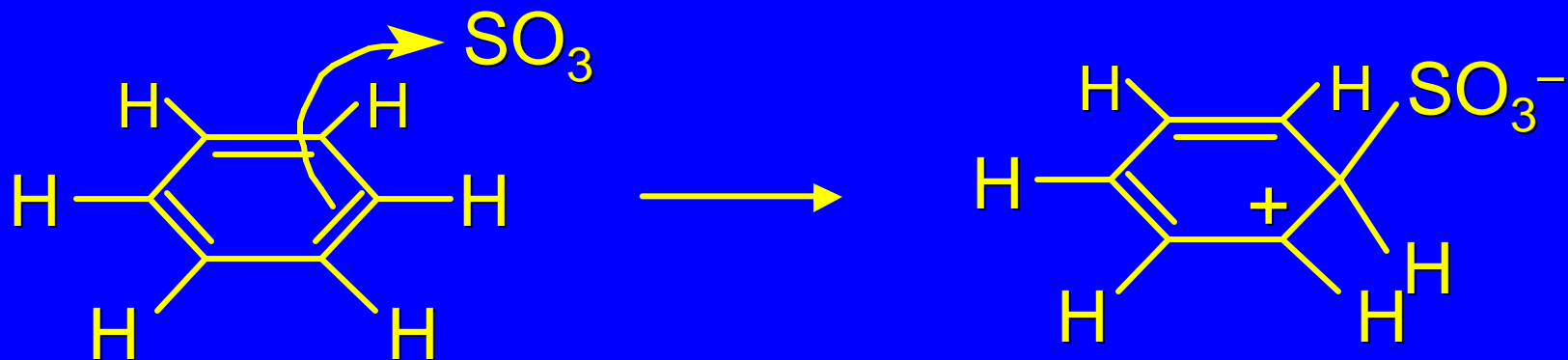
## Sulfonation of Benzene



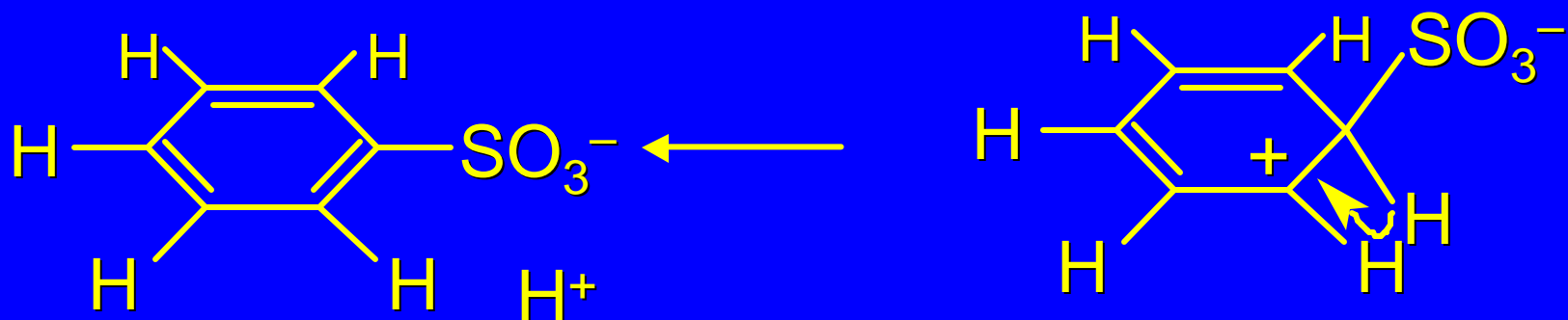
Several electrophiles present:  
a major one is sulfur trioxide



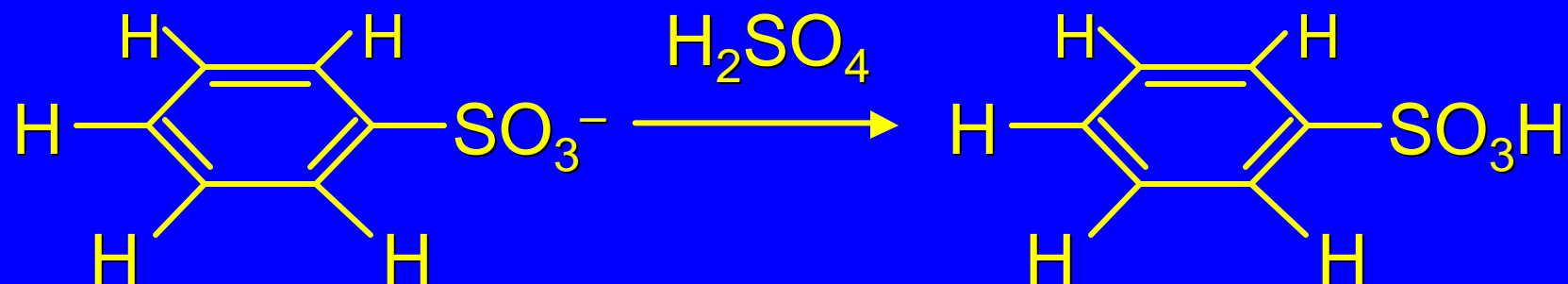
*Step 1: attack of sulfur trioxide  
on  $\pi$ -electron system of aromatic ring*



*Step 2: loss of a proton from the carbocation intermediate*



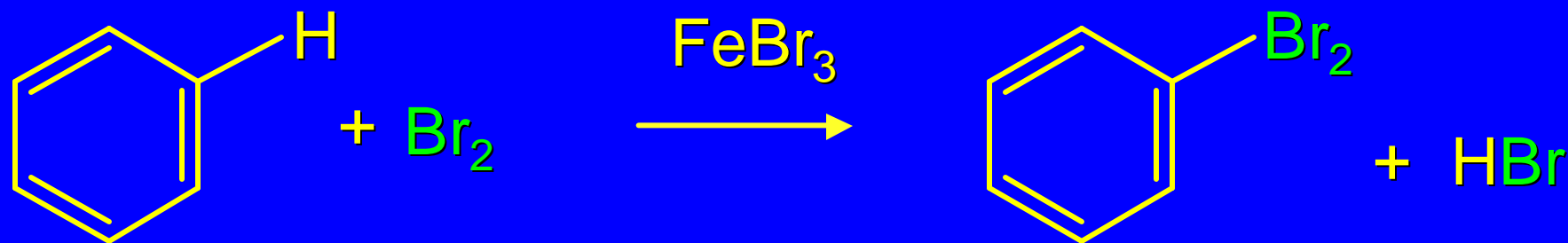
*Step 3: protonation of benzenesulfonate ion*



# 12.5 Halogenation of Benzene

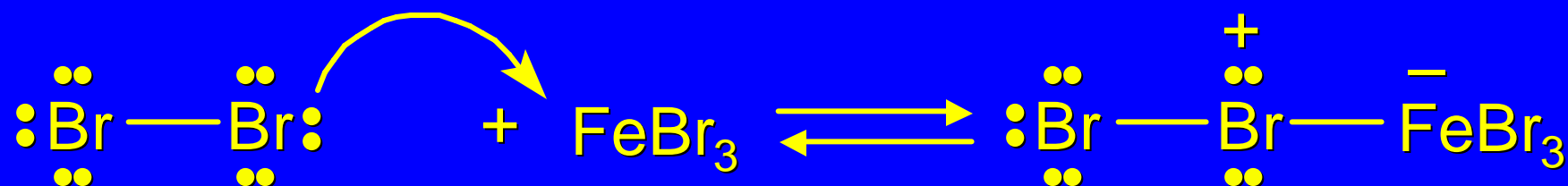


## Halogenation of Benzene



Electrophile is a Lewis acid-Lewis base complex between FeBr<sub>3</sub> and Br<sub>2</sub>.

## The $Br_2$ - $FeBr_3$ Complex



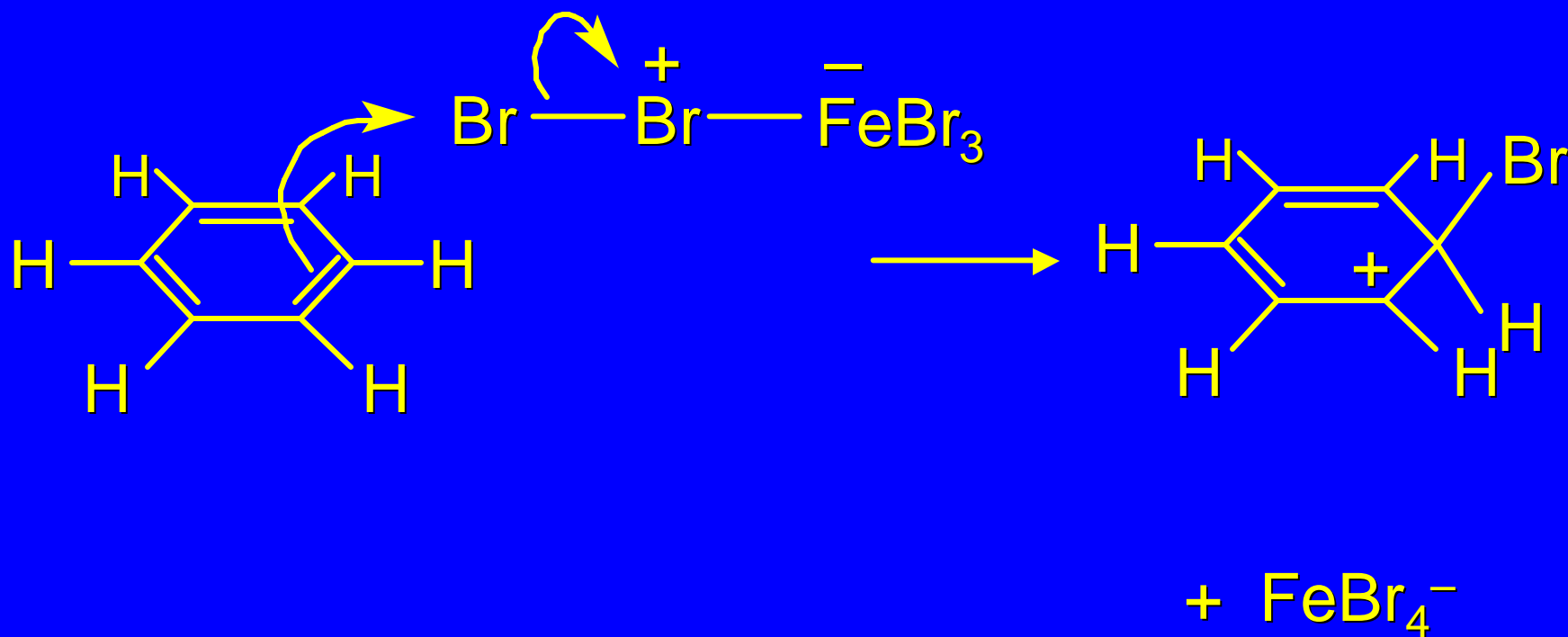
Lewis base

Lewis acid

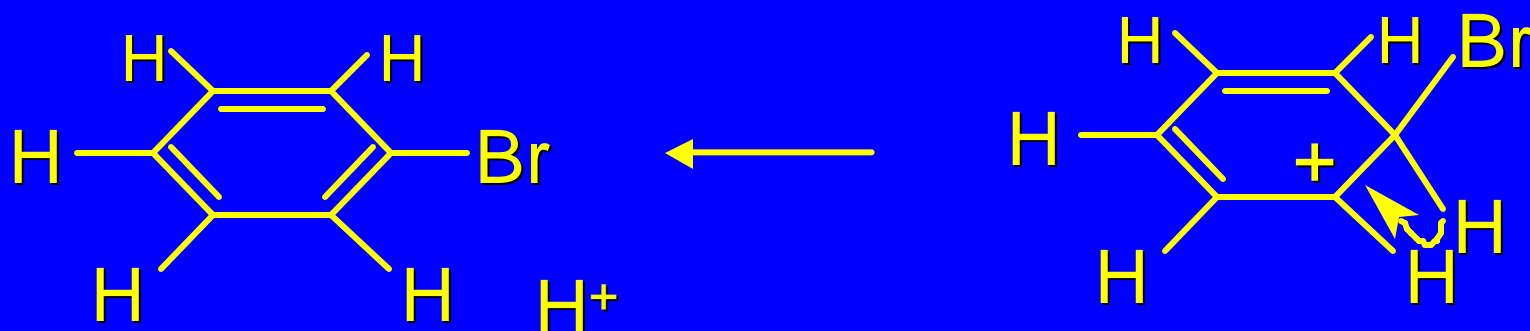
Complex

The  $Br_2$ - $FeBr_3$  complex is more electrophilic than  $Br_2$  alone.

*Step 1: attack of  $Br_2-FeBr_3$  complex on  $p$ -electron system of aromatic ring*



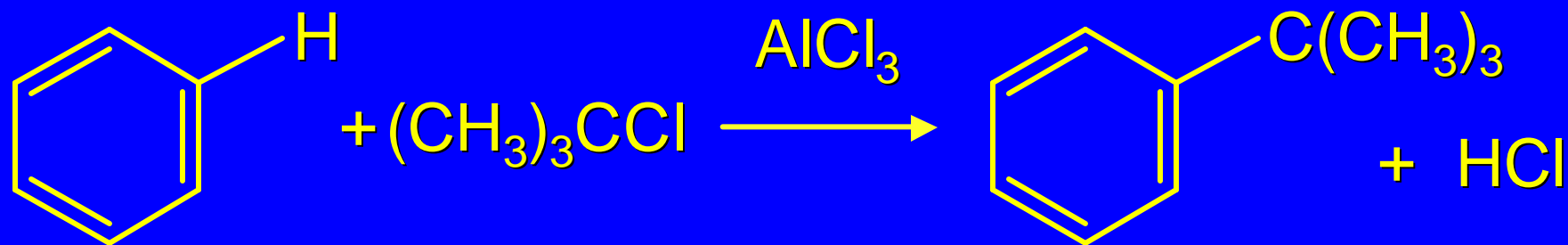
*Step 2: loss of a proton from the carbocation intermediate*



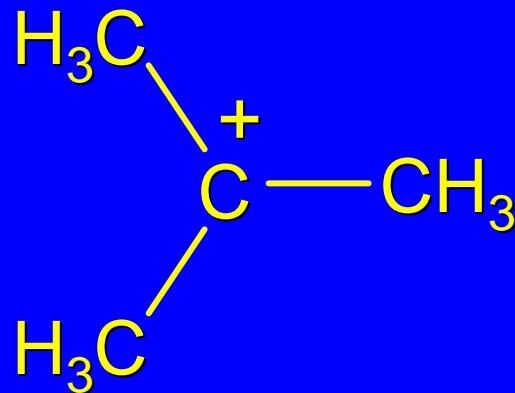
# 12.6

## Friedel-Crafts Alkylation of Benzene

## *Friedel-Crafts Alkylation of Benzene*

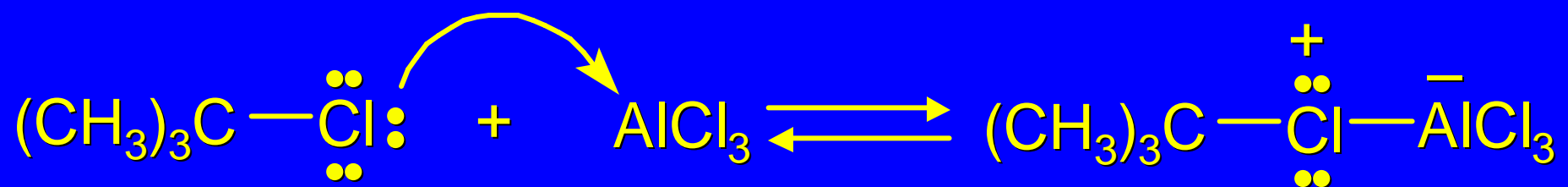


Electrophile is  
*tert*-butyl cation



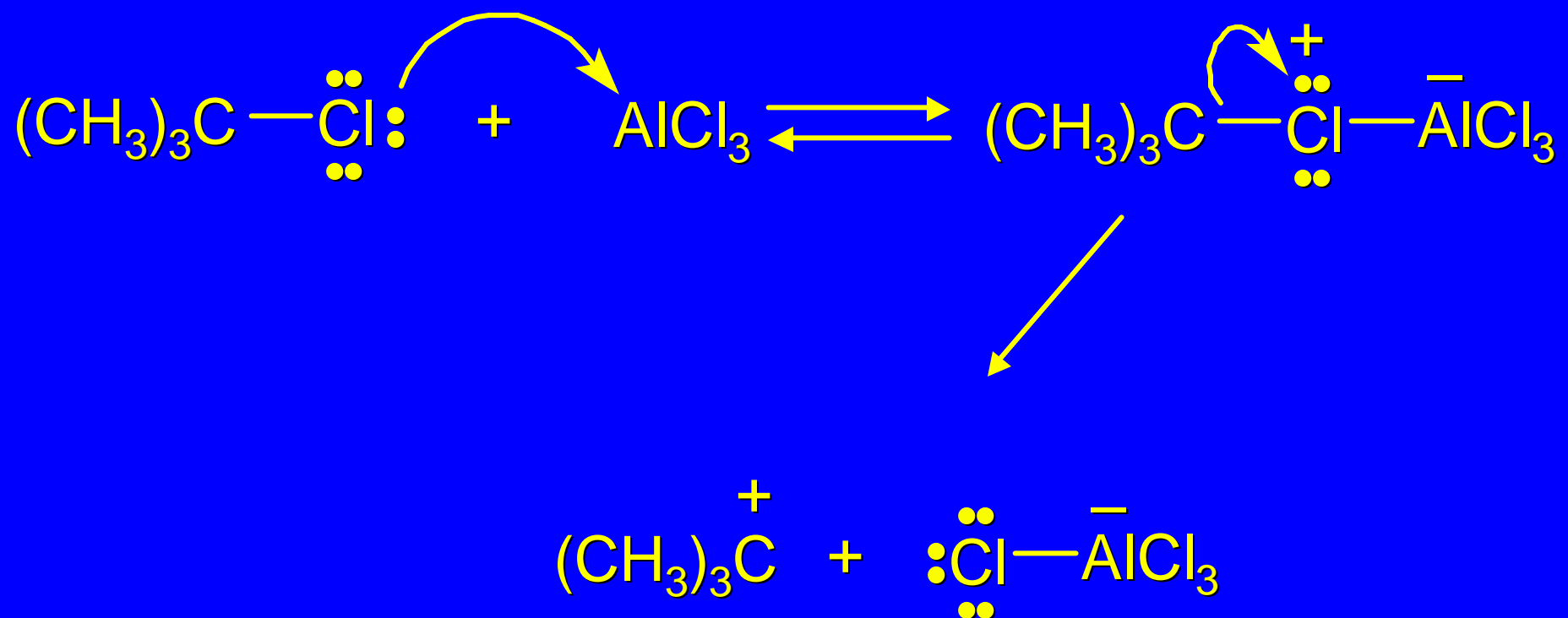
## *Role of AlCl<sub>3</sub>*

acts as a Lewis acid to promote ionization of the alkyl halide



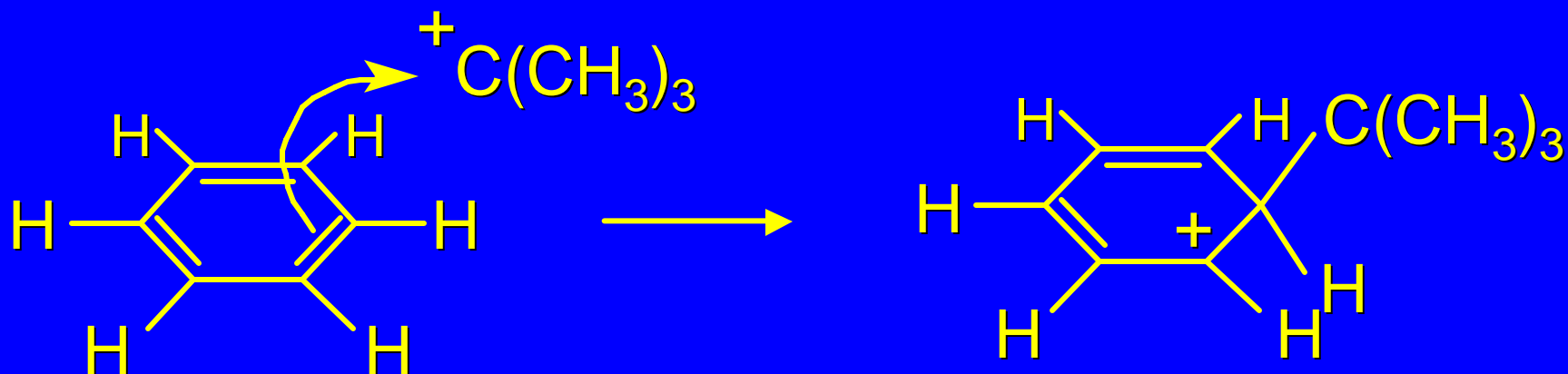
## Role of $\text{AlCl}_3$

acts as a Lewis acid to promote ionization of the alkyl halide

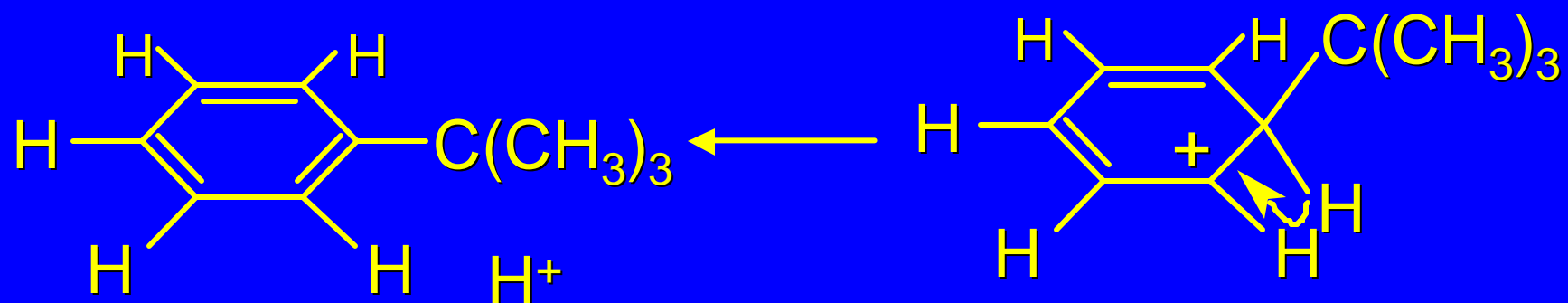




*Step 1: attack of tert-butyl cation  
on  $\pi$ -electron system of aromatic ring*



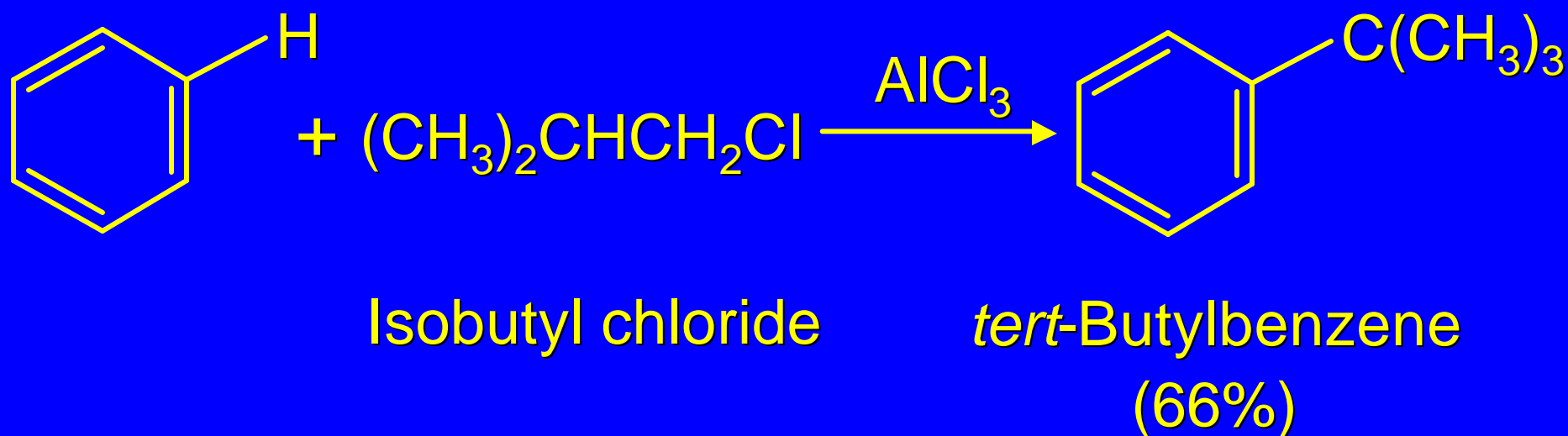
*Step 2: loss of a proton from the carbocation intermediate*



## Rearrangements in Friedel-Crafts Alkylation

Carbocations are intermediates.

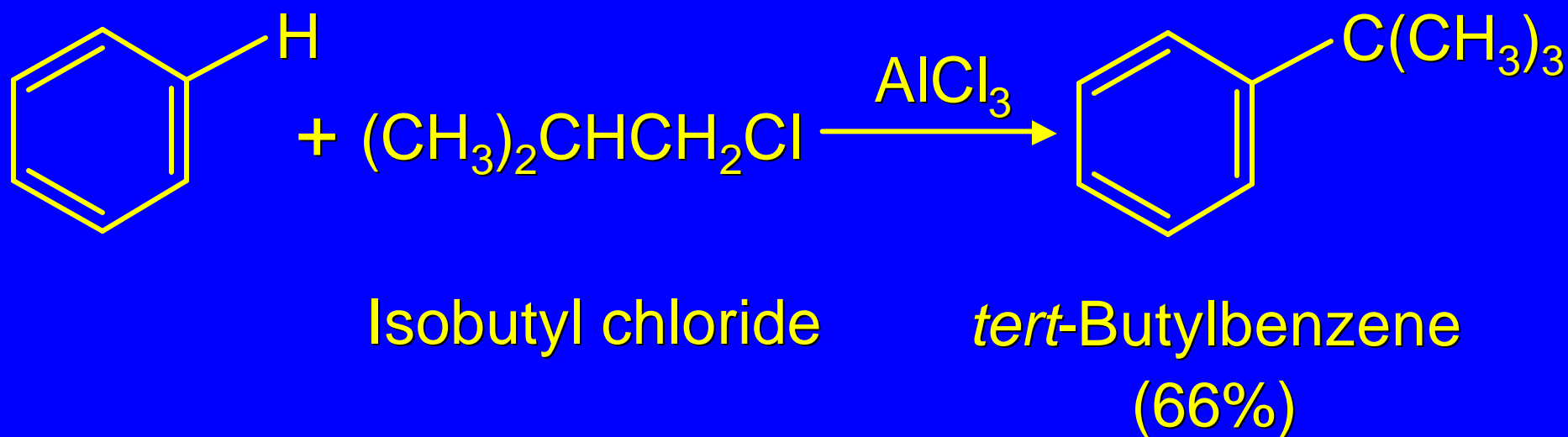
Therefore, rearrangements can occur



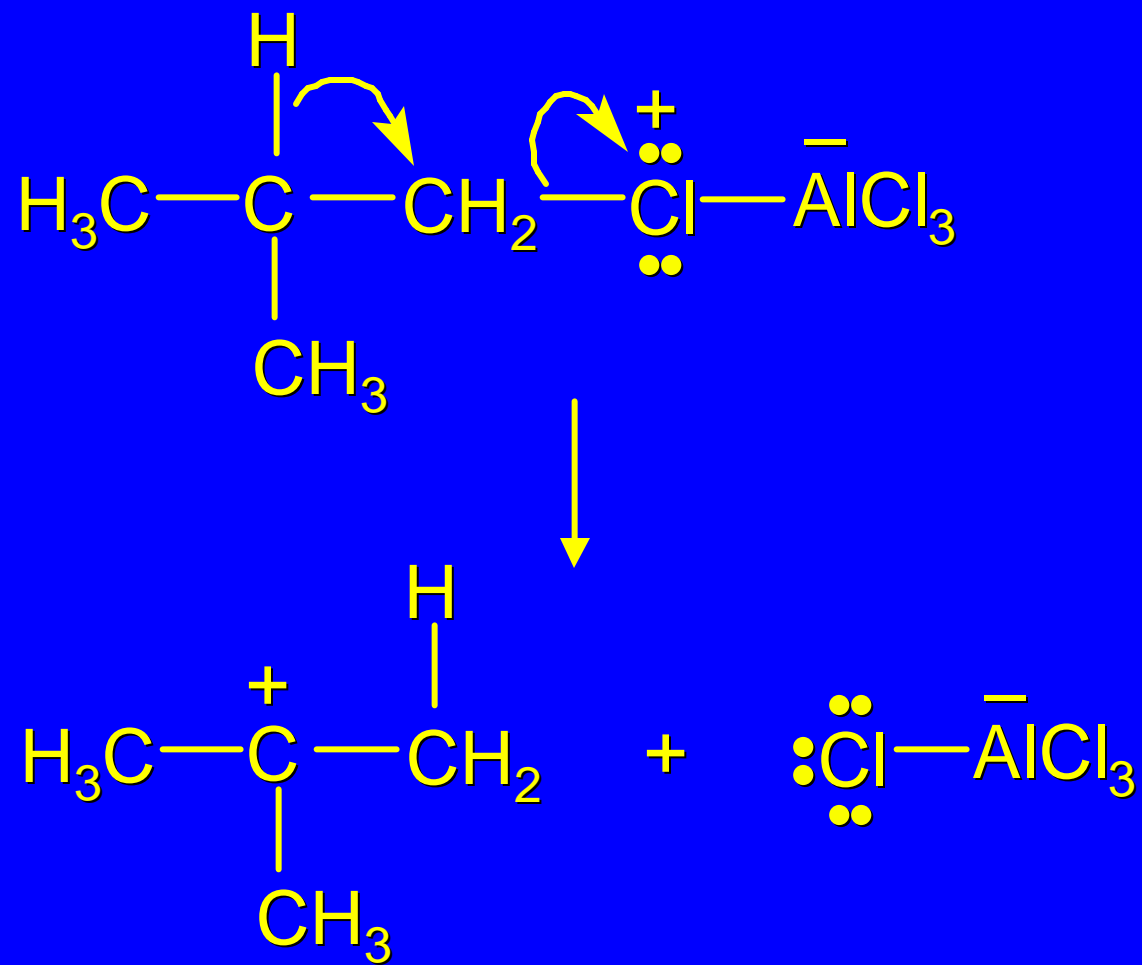
## Rearrangements in Friedel-Crafts Alkylation

Isobutyl chloride is the alkyl halide.

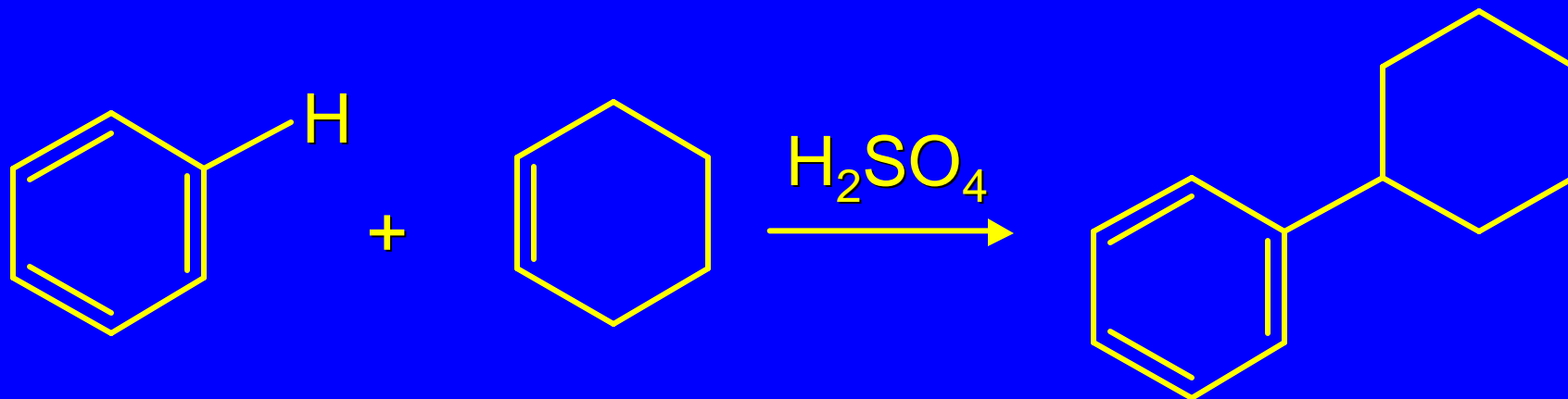
But *tert*-butyl cation is the electrophile.



## Rearrangements in Friedel-Crafts Alkylation



## Reactions Related to Friedel-Crafts Alkylation



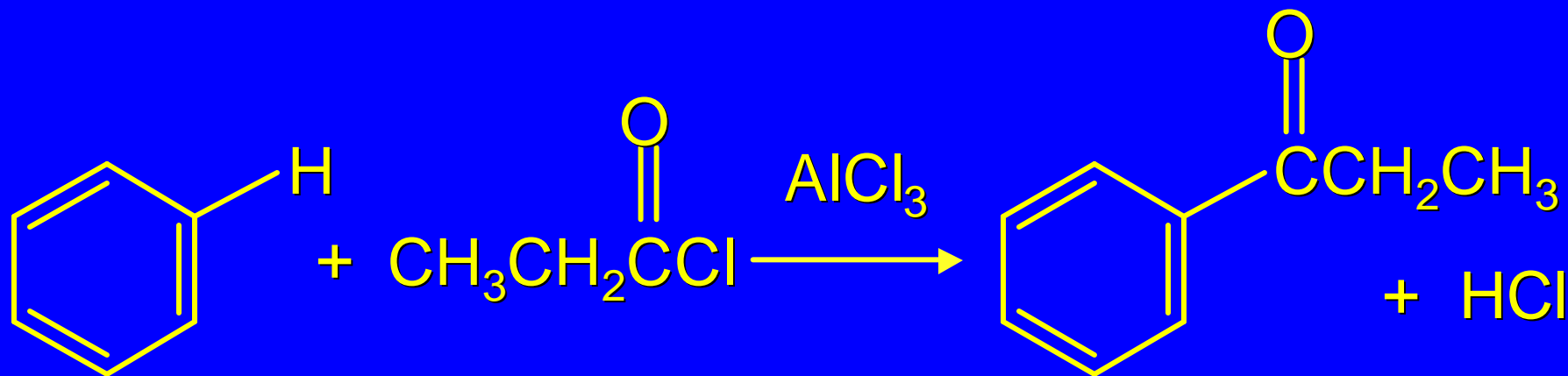
Cyclohexylbenzene  
(65-68%)

Cyclohexene is protonated by sulfuric acid, giving cyclohexyl cation which attacks the benzene ring

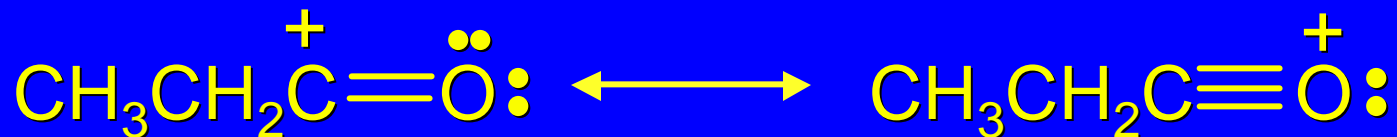
# 12.7

## Friedel-Crafts Acylation of Benzene

## Friedel-Crafts Acylation of Benzene

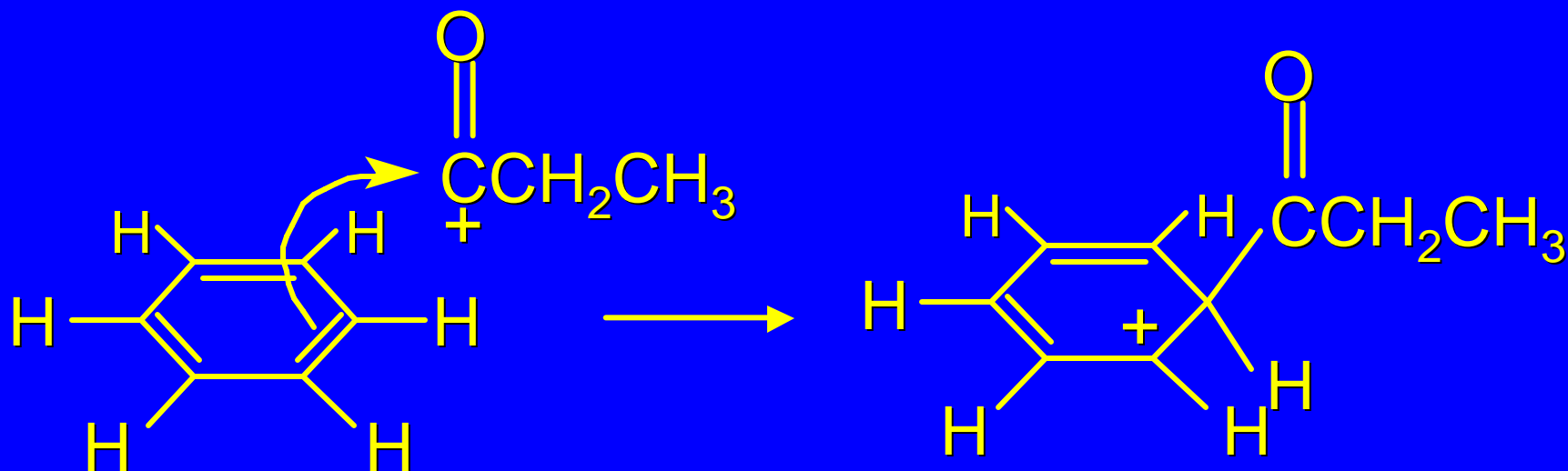


Electrophile is an acyl cation

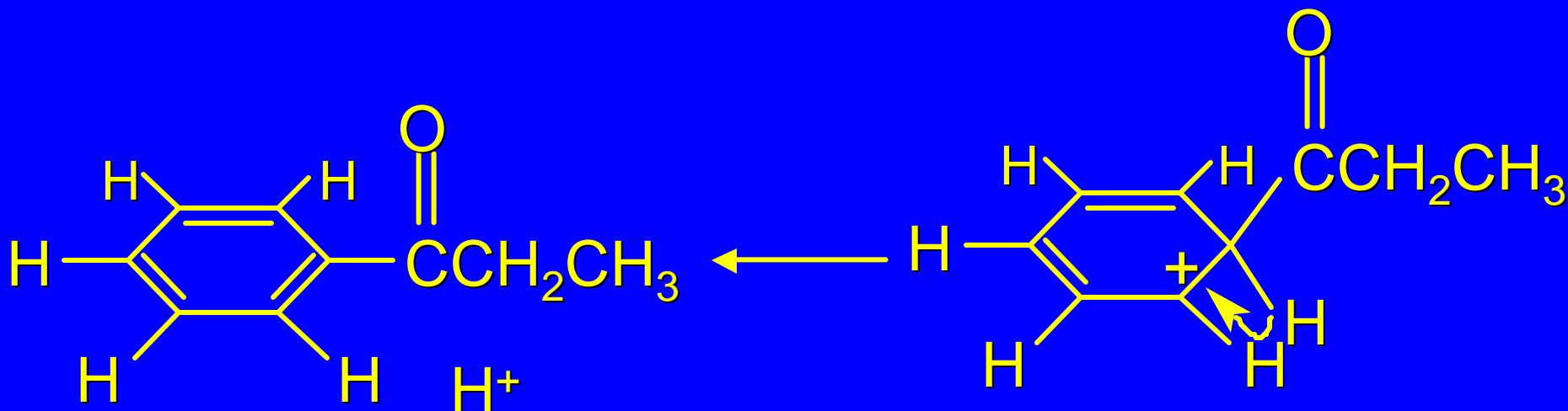




*Step 1: attack of the acyl cation  
on  $\pi$ -electron system of aromatic ring*

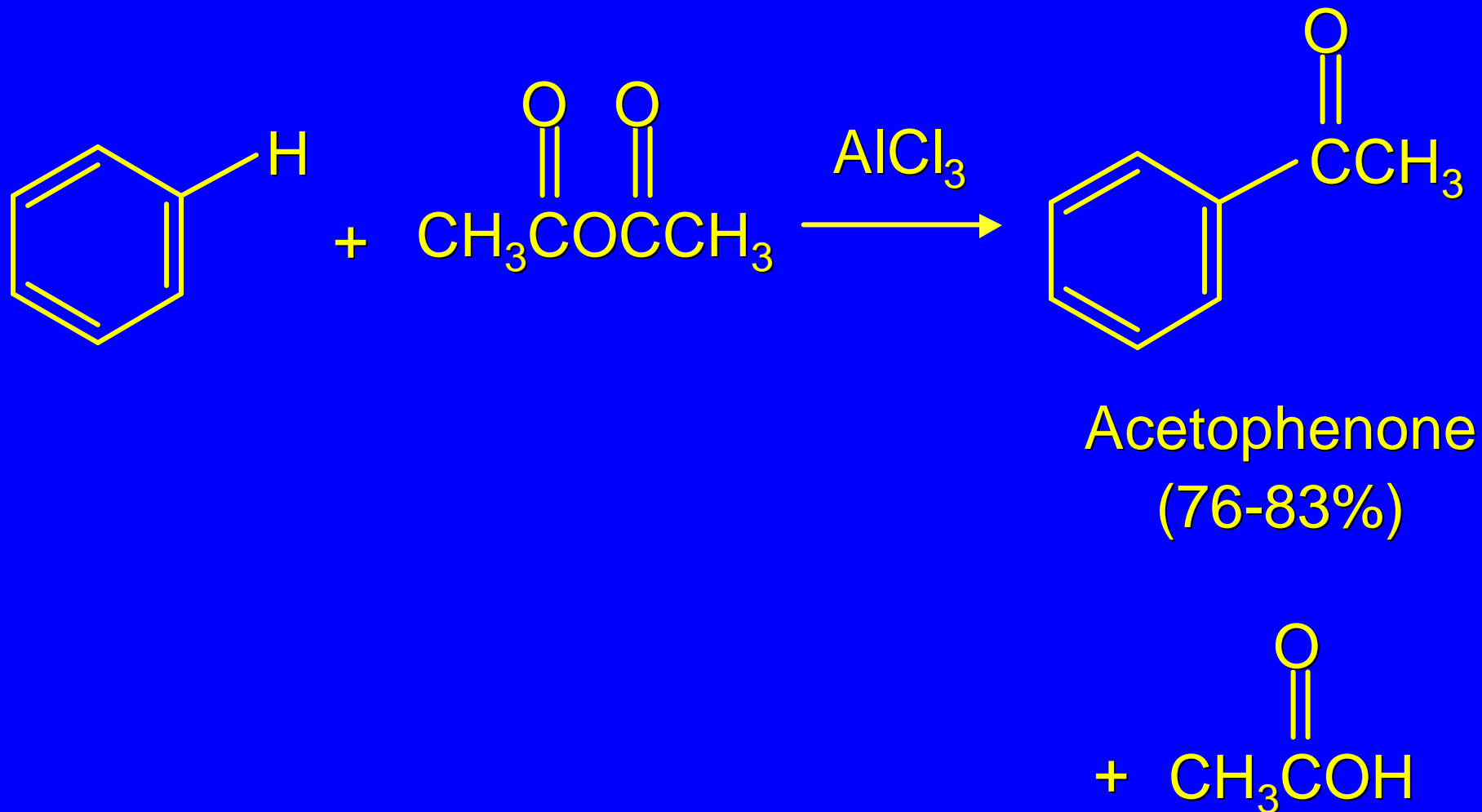


*Step 2: loss of a proton from the carbocation intermediate*



## Acid Anhydrides

can be used instead of acyl chlorides

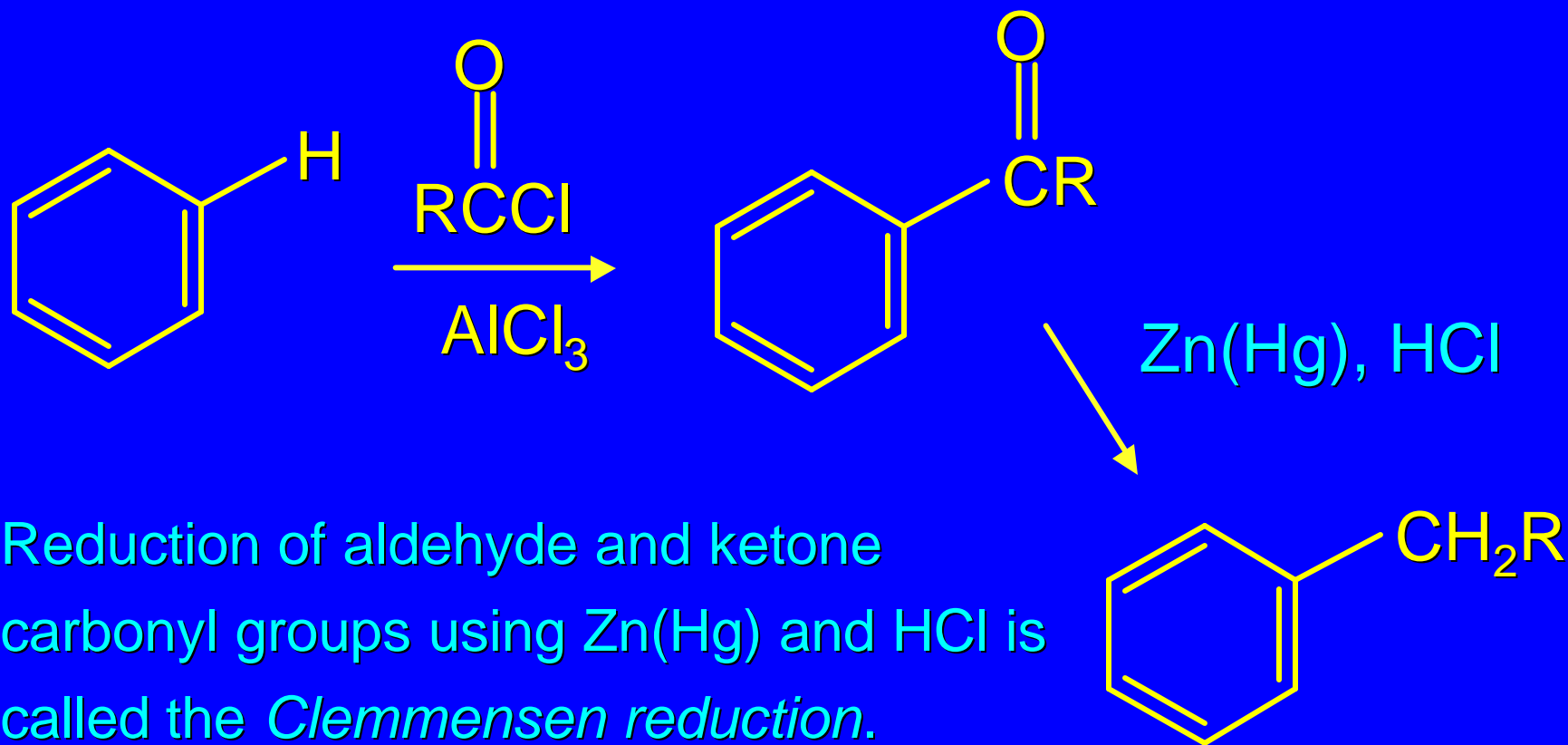


# 12.8

## Acylation-Reduction

## Acylation-Reduction

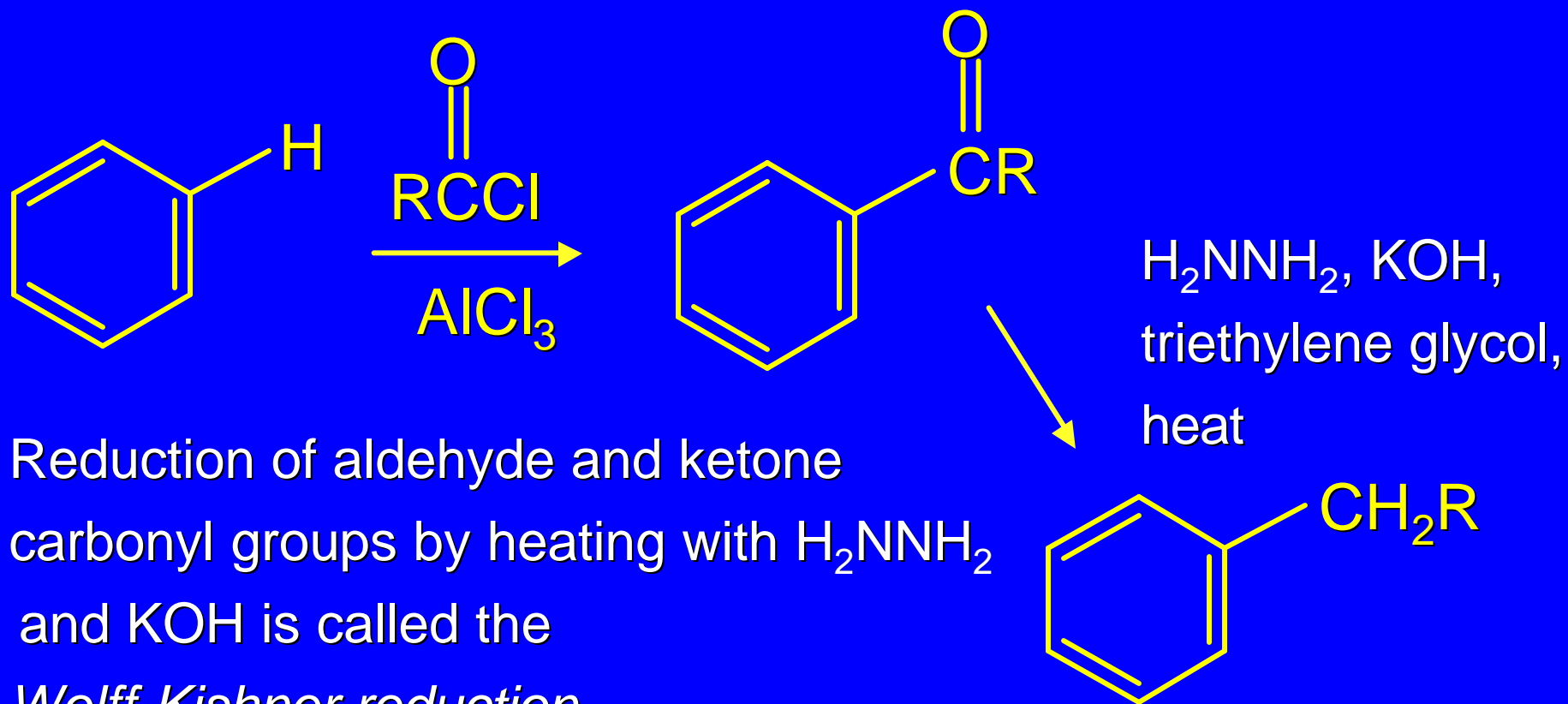
permits primary alkyl groups to be attached to an aromatic ring



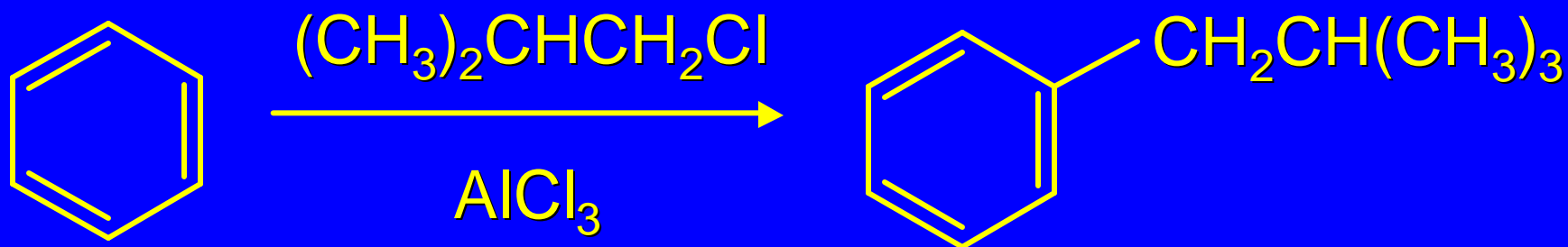
Reduction of aldehyde and ketone carbonyl groups using Zn(Hg) and HCl is called the *Clemmensen reduction*.

## Acylation-Reduction

permits primary alkyl groups to be attached to an aromatic ring

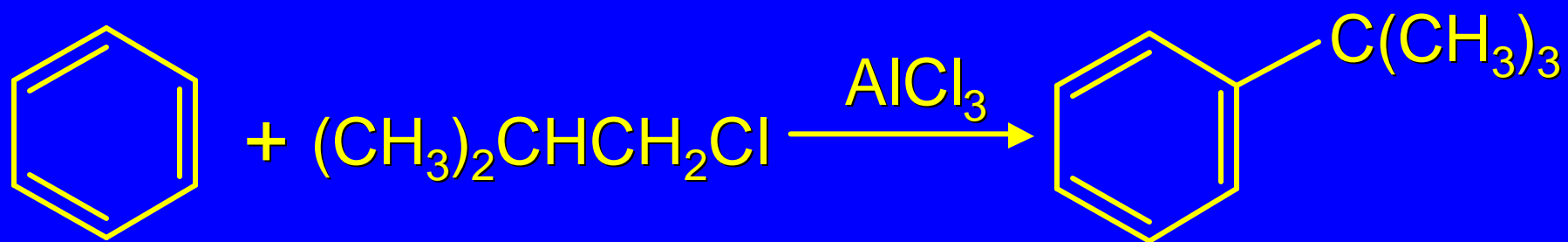


*Example: Prepare isobutylbenzene*



No! Friedel-Crafts alkylation of benzene using isobutyl chloride fails because of rearrangement.

*Recall*



Isobutyl chloride

*tert*-Butylbenzene  
(66%)



*Use Acylation-Reduction Instead*

