# Organic Chemistry

# Carbonyl Compounds

by

Nurlin Abu Samah, Dr. Md. Shaheen & Dr. Nadeem Akhtar
Faculty of Industrial Sciences & Technology
nurlin@ump.edu.my

# Chapter Description

- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of carbonyl compounds
  - The students should be able to **explain** the fundamental of organic chemistry in terms of carbonyl compounds

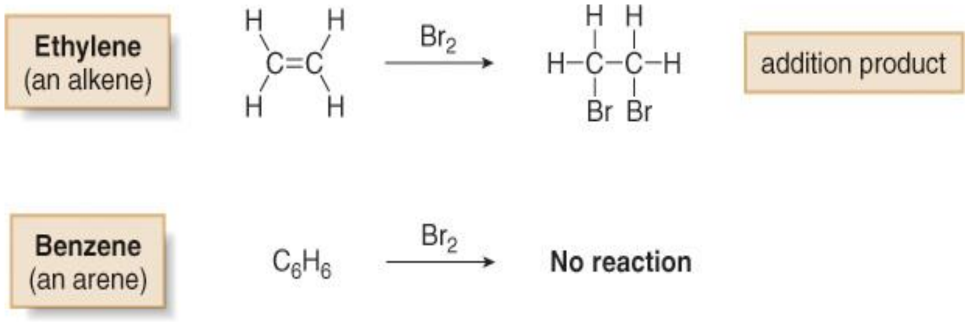
- Expected Outcomes
  - Explain the basic knowledge in carbonyl compounds
  - Describe the chemical reactions and conditions for carbonyl compounds reactions
  - Describe the carbonyl compound reactions in certain industrial application

- References
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

# Benzene and Aromatic Compounds

## Background

- Benzene ($C_6H_6$) is the simplest aromatic hydrocarbon (or arene).
- Benzene has four degrees of unsaturation, making it a highly unsaturated hydrocarbon.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.

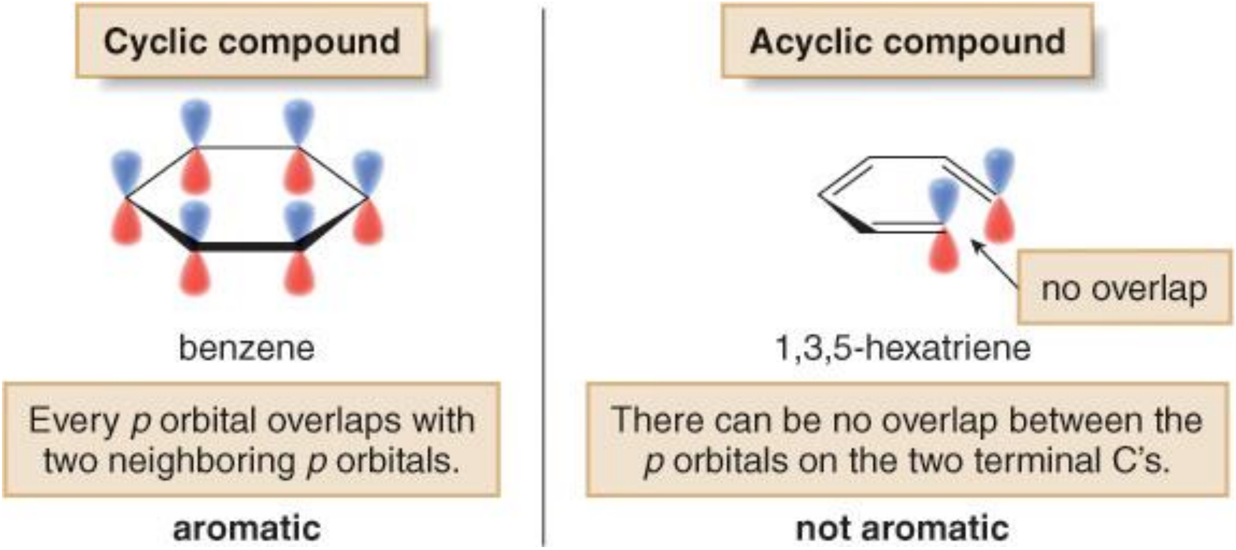


*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Benzene and Aromatic Compounds
## The Criteria for Aromaticity—Hückel's Rule

**Four structural criteria must be satisfied for a compound to be aromatic.**

**[1] A molecule must be cyclic.**



**To be aromatic, each *p* orbital must overlap with *p* orbitals on adjacent atoms.**

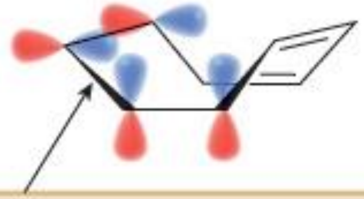
# Benzene and Aromatic Compounds
# The Criteria for Aromaticity—Hückel’s Rule

## [2] A molecule must be planar.

**All adjacent *p* orbitals must be aligned so that the $\pi$ electron density can be delocalized.**

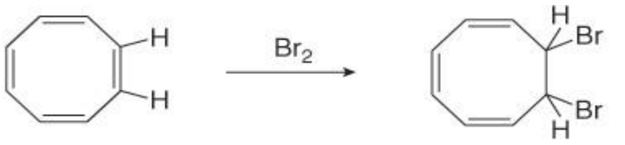
cyclooctatetraene
**not aromatic**

a tub-shaped, eight-membered ring



Adjacent *p* orbitals cannot overlap.
Electrons cannot delocalize.

**Since cyclooctatetraene is non-planar, it is not aromatic, and it undergoes addition reactions just like those of other alkenes.**



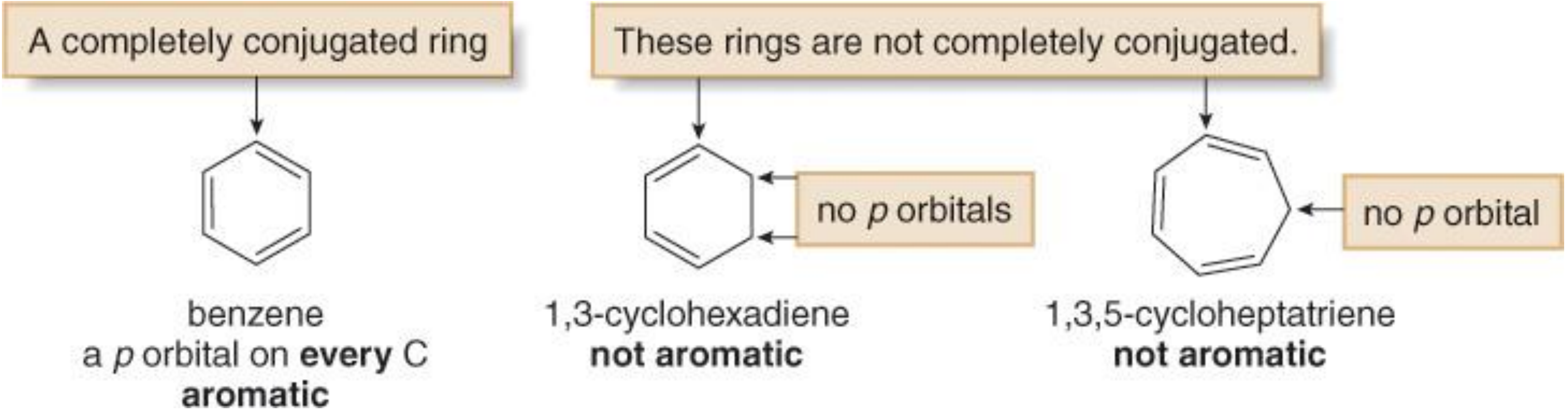
cyclooctatetraene **addition** product

*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Benzene and Aromatic Compounds
## The Criteria for Aromaticity—Hückel's Rule

**[3] A molecule must be completely conjugated.**

**Aromatic compounds must have a *p* orbital on every atom.**


A completely conjugated ring

These rings are not completely conjugated.

no *p* orbitals

no *p* orbital

benzene
a *p* orbital on **every** C
**aromatic**

1,3-cyclohexadiene
**not aromatic**

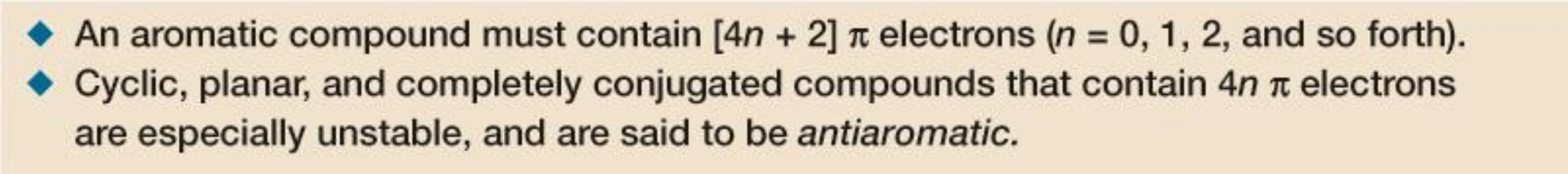
1,3,5-cycloheptatriene
**not aromatic**

*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Benzene and Aromatic Compounds
## The Criteria for Aromaticity—Hückel's Rule

**[4] A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.**

**Hückel's rule:**



- An aromatic compound must contain [$4n + 2$] π electrons ($n = 0, 1, 2$, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*

**Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is antiaromatic and especially unstable because it contains 4 π electrons.**

Benzene
An aromatic compound

$4n + 2 = 4(1) + 2 =$
6 π electrons
aromatic

Cyclobutadiene
An antiaromatic compound

$4n = 4(1) =$
4 π electrons
antiaromatic

# Benzene and Aromatic Compounds

## The Criteria for Aromaticity—Hückel's Rule

**Considering aromaticity, a compound can be classified in one of three ways:**

1. **Aromatic—A cyclic, planar, completely conjugated compound with 4*n* + 2 π electrons.**
2. **Antiaromatic—A cyclic, planar, completely conjugated compound with 4*n* π electrons.**
3. **Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.**

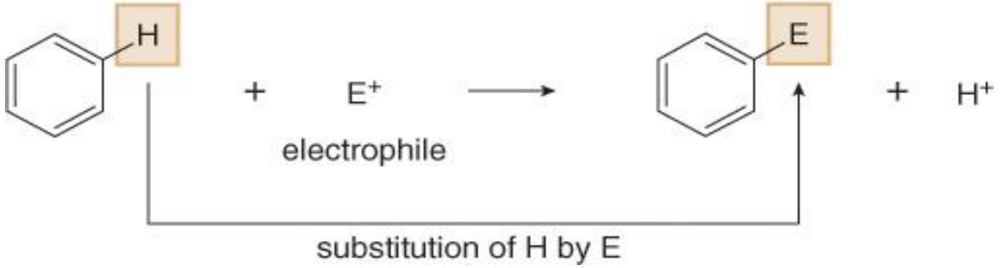
*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution Background

- **The characteristic reaction of benzene is electrophilic aromatic substitution—a hydrogen atom is replaced by an electrophile.**

- Benzene has six π electrons delocalized in six *p* orbitals that overlap above and below the plane of the ring. These loosely held π electrons make the benzene ring electron rich, and so it reacts with electrophiles.
- Because benzene's six π electrons satisfy Hückel's rule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore favored.

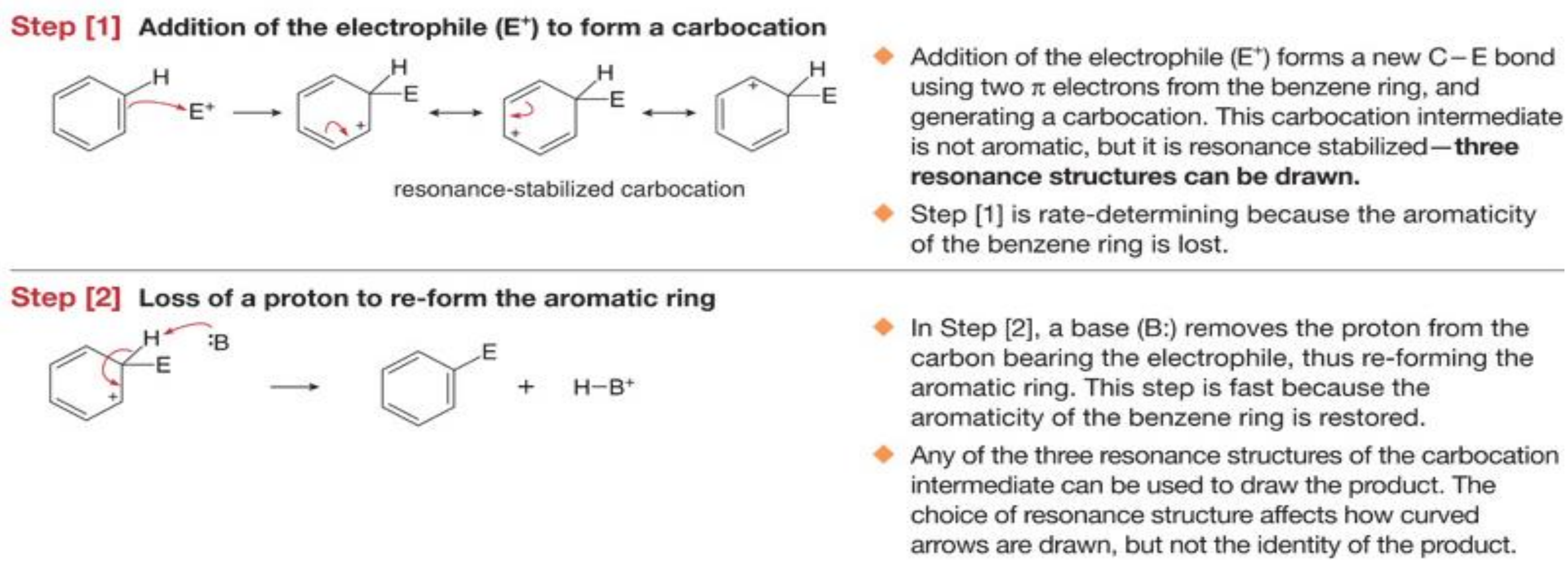
**Electrophilic aromatic substitution—General reaction**



# Electrophilic Aromatic Substitution

## Background

- **Regardless of the electrophile used, all electrophilic aromatic substitution reactions occur by the same two-step mechanism—addition of the electrophile E⁺ to form a resonance-stabilized carbocation, followed by deprotonation with base, as shown below:**



**Step [1]** **Addition of the electrophile (E⁺) to form a carbocation**

resonance-stabilized carbocation

- Addition of the electrophile (E⁺) forms a new C–E bond using two π electrons from the benzene ring, and generating a carbocation. This carbocation intermediate is not aromatic, but it is resonance stabilized—**three resonance structures can be drawn.**
- Step [1] is rate-determining because the aromaticity of the benzene ring is lost.

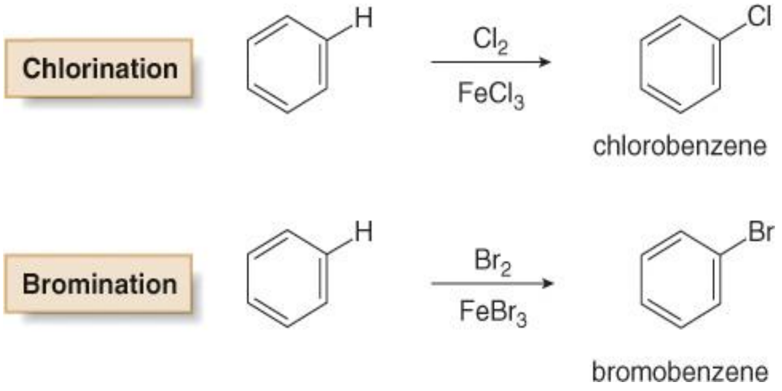
**Step [2]** **Loss of a proton to re-form the aromatic ring**

- In Step [2], a base (B:) removes the proton from the carbon bearing the electrophile, thus re-forming the aromatic ring. This step is fast because the aromaticity of the benzene ring is restored.
- Any of the three resonance structures of the carbocation intermediate can be used to draw the product. The choice of resonance structure affects how curved arrows are drawn, but not the identity of the product.

# Electrophilic Aromatic Substitution

## 1. Halogenation

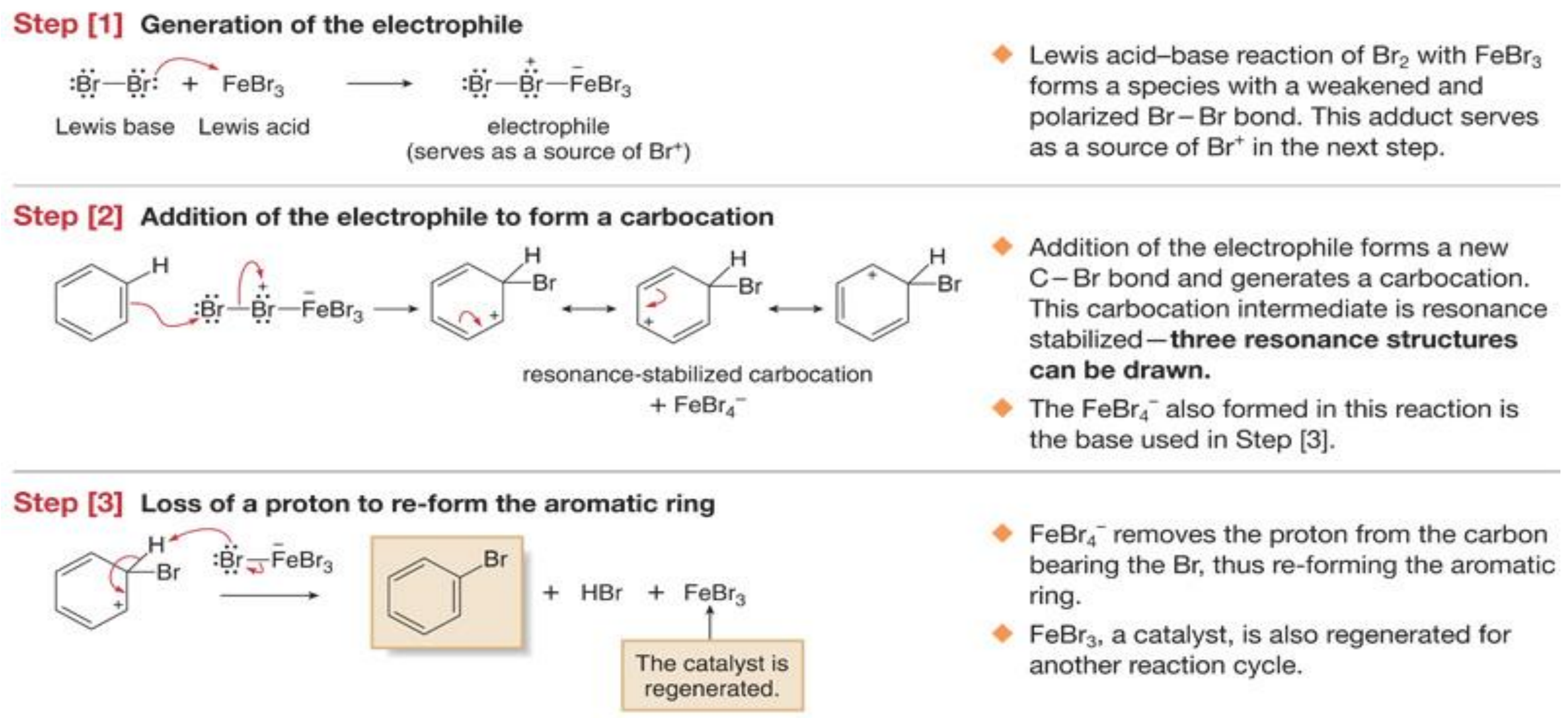
- In halogenation, benzene reacts with $Cl_2$ or $Br_2$ in the presence of a Lewis acid catalyst, such as $FeCl_3$ or $FeBr_3$, to give the aryl halides chlorobenzene or bromobenzene respectively.
- Analogous reactions with $I_2$ and $F_2$ are not synthetically useful because $I_2$ is too unreactive and $F_2$ reacts too violently.



*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution
## 1. Halogenation

- **Chlorination proceeds by a similar mechanism.**



**Step [1] Generation of the electrophile**

electrophile (serves as a source of $Br^+$)

- Lewis acid–base reaction of $Br_2$ with $FeBr_3$ forms a species with a weakened and polarized Br–Br bond. This adduct serves as a source of $Br^+$ in the next step.

**Step [2] Addition of the electrophile to form a carbocation**

resonance-stabilized carbocation + $FeBr_4^-$

- Addition of the electrophile forms a new C–Br bond and generates a carbocation. This carbocation intermediate is resonance stabilized—**three resonance structures can be drawn.**
- The $FeBr_4^-$ also formed in this reaction is the base used in Step [3].

**Step [3] Loss of a proton to re-form the aromatic ring**

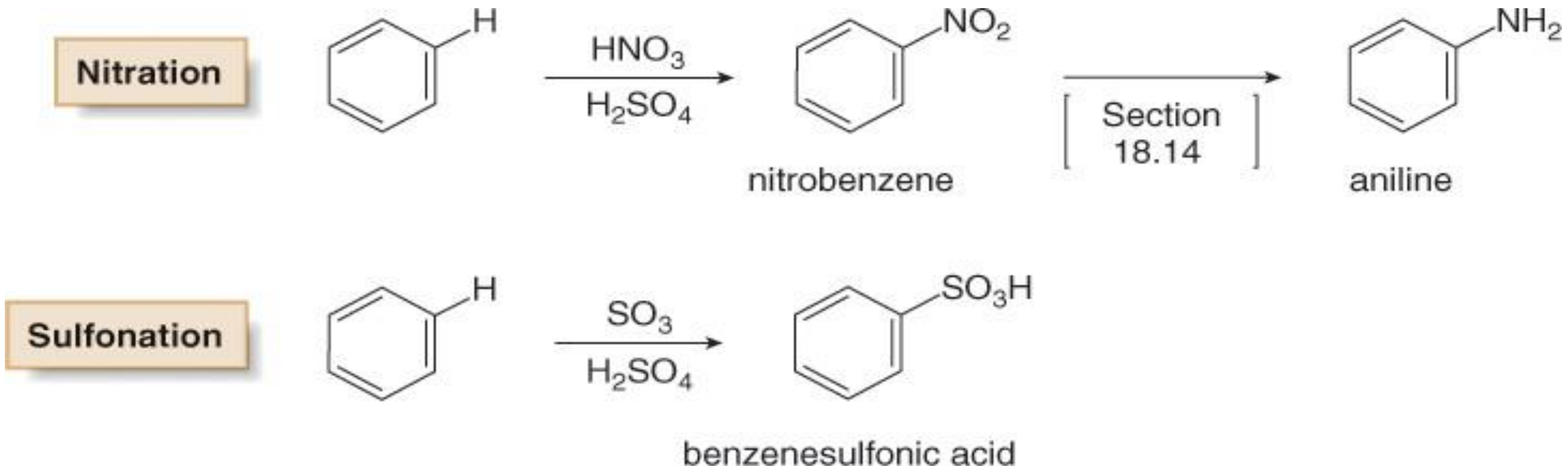
The catalyst is regenerated.

- $FeBr_4^-$ removes the proton from the carbon bearing the Br, thus re-forming the aromatic ring.
- $FeBr_3$, a catalyst, is also regenerated for another reaction cycle.

*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution
## 2. Nitration and Sulfonation

- **Nitration and sulfonation introduce two different functional groups into the aromatic ring.**
- **Nitration is especially useful because the nitro group can be reduced to an $NH_2$ group.**

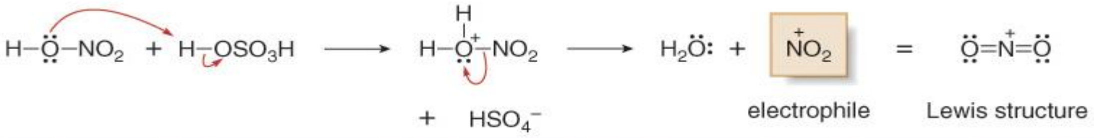


# Electrophilic Aromatic Substitution

## 2. Nitration and Sulfonation

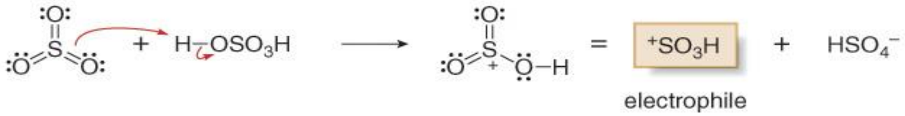
- **Generation of the electrophile in both nitration and sulfonation requires strong acid.**

**Formation of the Nitronium Ion ($^+NO_2$) for Nitration**



In **sulfonation,** protonation of sulfur trioxide, $SO_3$, forms a positively charged sulfur species ($^+SO_3H$) that acts as an electrophile.

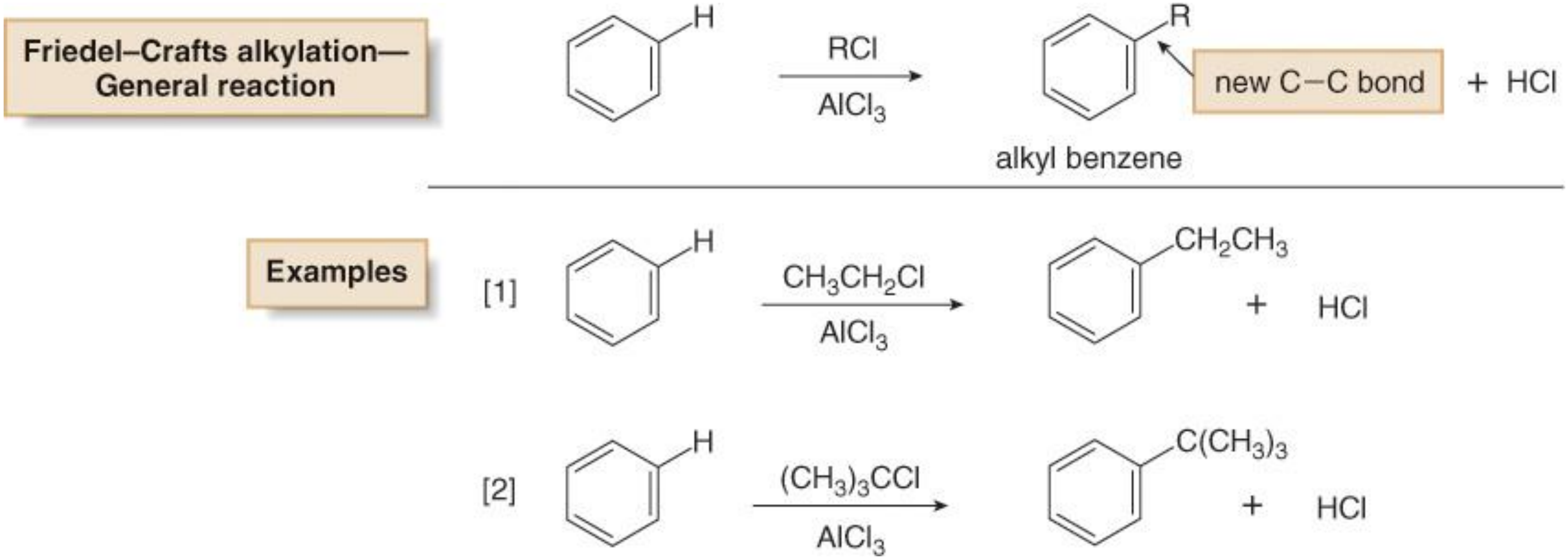
**Formation of the Electrophile $^+SO_3H$ for Sulfonation**



# Electrophilic Aromatic Substitution

## 3. Friedel-Crafts Alkylation and Friedel-Crafts Acylation

- **In Friedel-Crafts alkylation, treatment of benzene with an alkyl halide and a Lewis acid ($AlCl_3$) forms an alkyl benzene.**

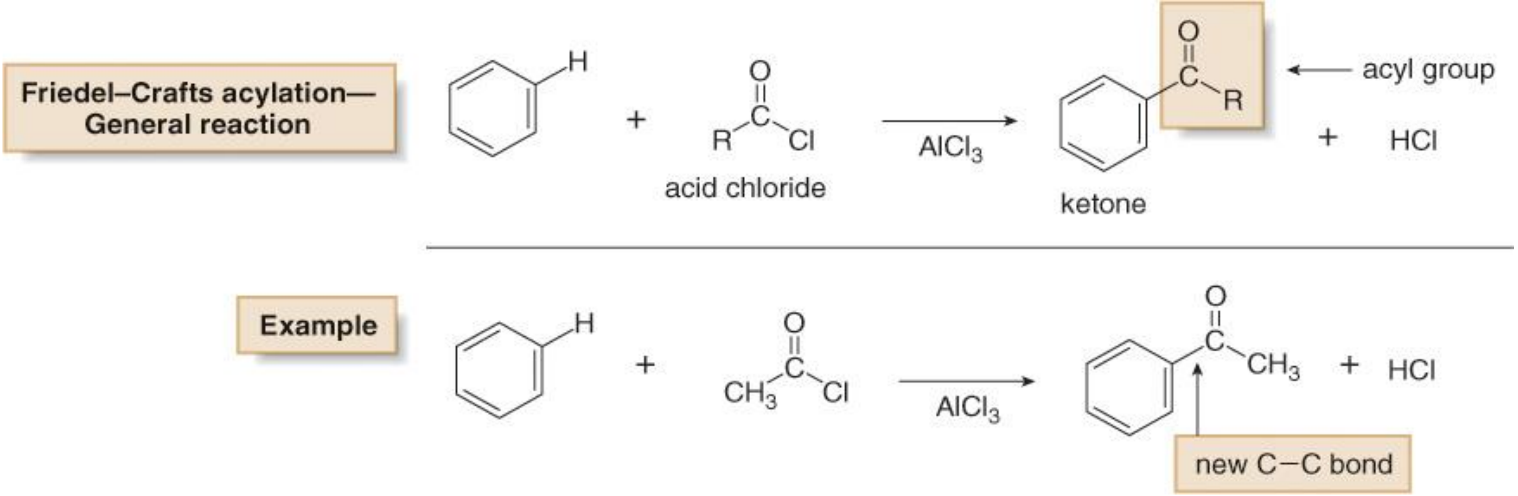


*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution

## 3. Friedel-Crafts Alkylation and Friedel-Crafts Acylation

- **In Friedel-Crafts acylation, a benzene ring is treated with an acid chloride (RCOCl) and $AlCl_3$ to form a ketone.**
- **Because the new group bonded to the benzene ring is called an acyl group, the transfer of an acyl group from one atom to another is an acylation.**

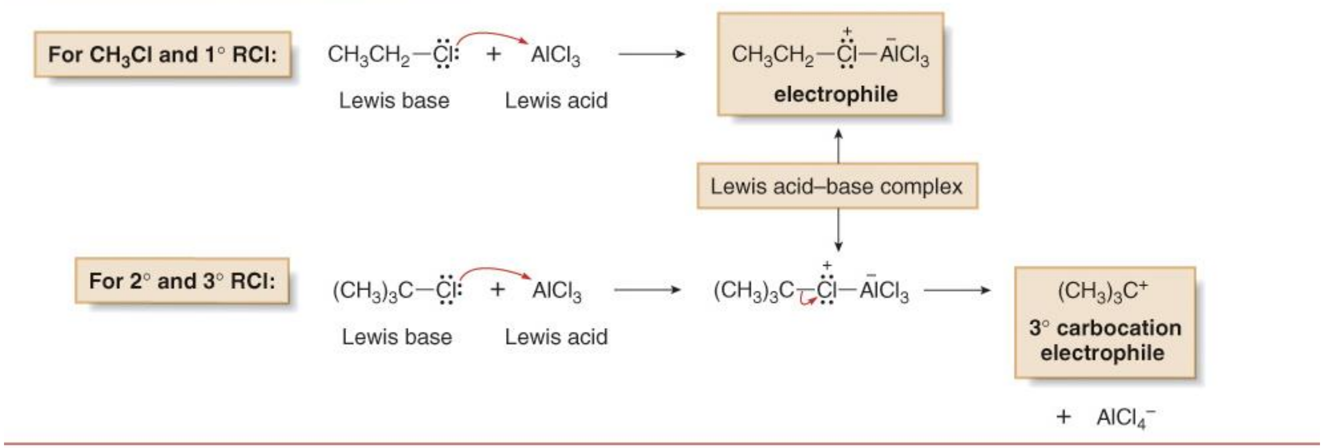


*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution

## 3. Friedel-Crafts Alkylation and Friedel-Crafts Acylation

**Formation of the Electrophile in Friedel–Crafts Alkylation—Two Possibilities**



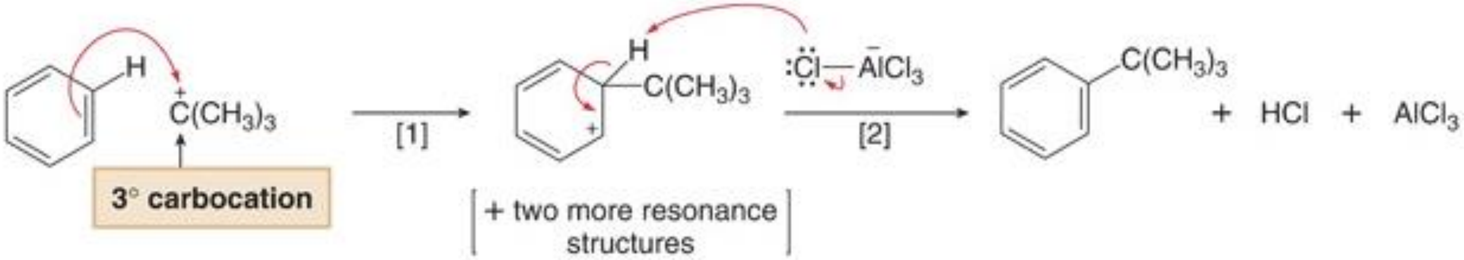
- For $CH_3Cl$ and 1° RCl, the Lewis acid–base complex itself serves as the electrophile for electrophilic aromatic substitution.
- With 2° and 3° RCl, the Lewis acid–base complex reacts further to give a 2° or 3° carbocation, which serves as electrophile. Carbocation formation occurs only with 2° and 3° alkyl chlorides, because they afford more stable carbocations.

*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Electrophilic Aromatic Substitution

## 3. Friedel-Crafts Alkylation and Friedel-Crafts Acylation

**Friedel–Crafts Alkylation Using a 3° Carbocation**



Addition of the electrophile (a 3° carbocation) forms a new carbon–carbon bond in Step [1].

$AlCl_4^-$ removes a proton on the carbon bearing the new substituent, thus re-forming the aromatic ring in Step [2].

# Conclusion of The Chapter

- Conclusion #1
  - The fundamental of carbonyl compounds with its nomenclature were understandable.
- Conclusion #2
  - The fundamental of carbonyl compounds included its reactions involves were practically explained.
- Conclusion #3
  - The fundamental of carbonyl compounds reaction was practically shown in industrial application such as Friedel-Crafts alkylation reaction.

*Carbonyl compounds*
*by Nurlin Abu Samah*
*http://ocw.ump.edu.my/course/view.php?id=491*

# Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

nurlin@ump.edu.my