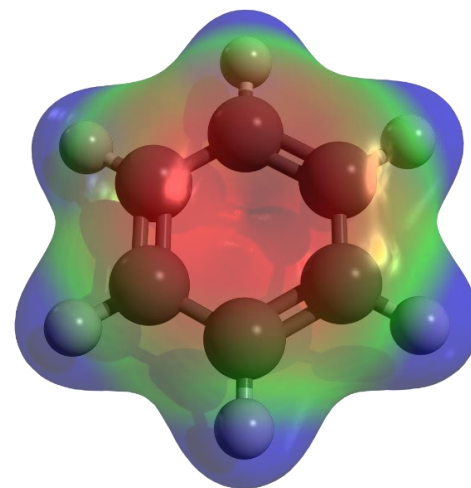
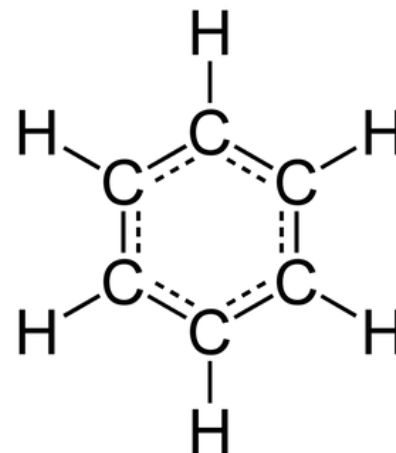


CHAPTER 6 : BENZENE & ITS DERIVATIVES

6.1 Introduction

6.2 Nomenclature

6.3 Chemical properties



Learning Outcomes

At the end of this topic, you should be able to :

6.1 Introduction (C2)

a) Describe:

- i. aromaticity;
- ii. Kekule structure; and
- iii. resonance structure of benzene.

6.2 (a) Give the name of benzene derivatives according to the IUPAC nomenclature for: (C1,C2)

- i. monosubstituted benzenes
- ii. disubstituted benzenes; and
- iii. tri and tetrasubstituted benzenes

(b) Give the structures of benzene derivatives in 6.2 (a). **(C2)**

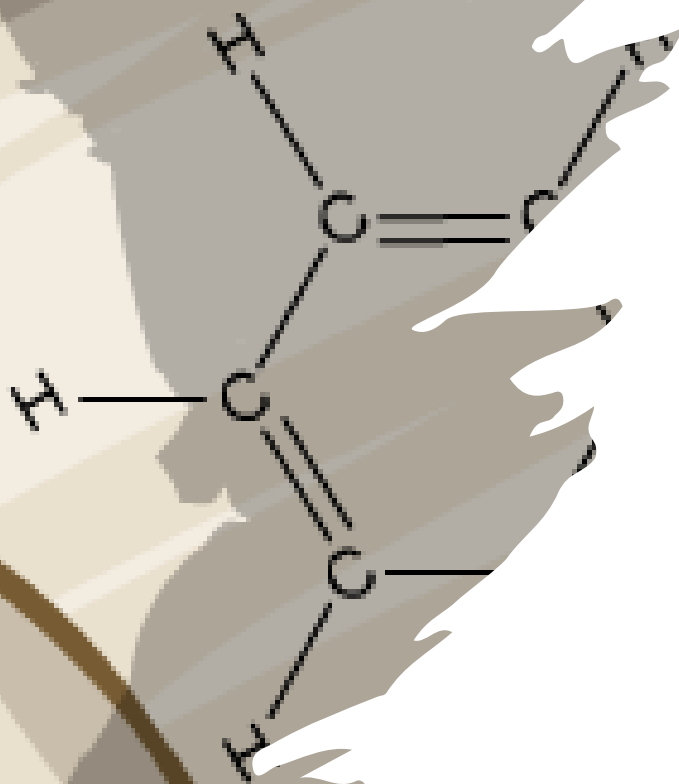
(c) Apply IUPAC rules to name compounds with C_6H_5 - phenyl or $\text{C}_6\text{H}_5\text{CH}_2$ -benzyl as substituents. **(C3)**

Learning Outcomes

At the end of this topic, you should be able to :

6.3 Chemical properties

- (a) Explain the electrophilic aromatic substitution reactions of benzene: **(C3,C4)**
 - i. Nitration
 - ii. Halogenation
 - iii. Friedel-Crafts alkylation; and
 - iv. Friedel-Crafts acylation
- (b) Illustrate the mechanism for the electrophilic aromatic substitution of benzene. **limit to reaction in 6.3(a) i,ii & iii only* **(C3,C4)**
- (c) Explain the influence of *ortho-para* and *meta* directing substituents towards electrophilic aromatic substitution reaction. **(C3)**
- (d) Predict the product of electrophilic aromatic substitution of monosubstituted benzene. **limit to reaction in 6.3(a) only* **(C3)**
- (e) Explain the following reactions of alkylbenzene: **(C3)**
 - i. oxidation with hot acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$
 - ii. halogenation (free radical substitution)



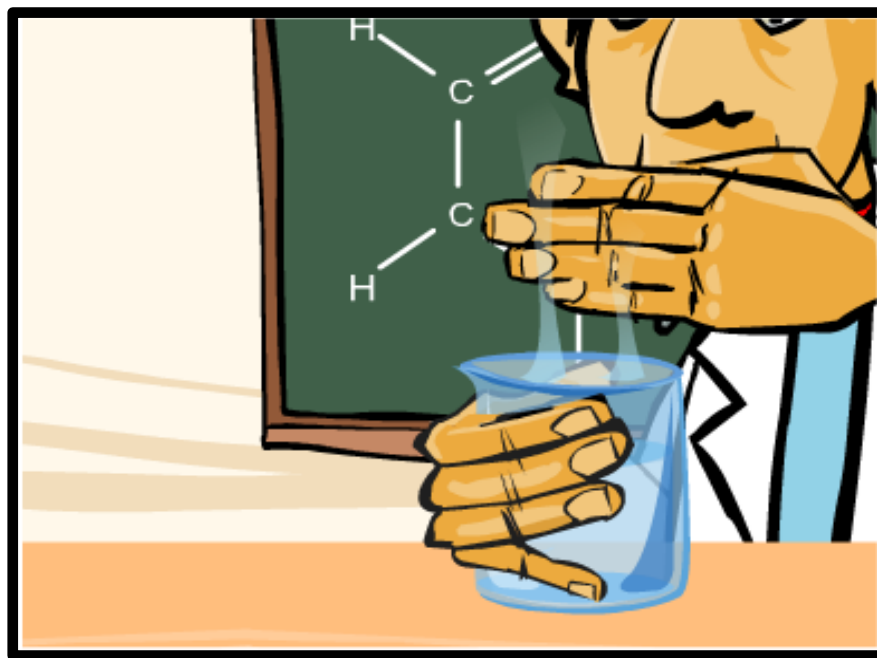
6.1 INTRODUCTION

Describe :

- Aromaticity
- Kekulé structure
- Resonance structure of benzene

Introduction

- In earlier time, compounds are called **aromatic** because of their **pleasant odours**.



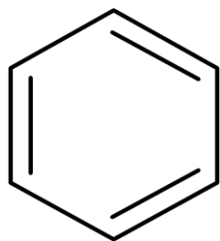
Benzene has **strong pleasant odour**...

- Today, we use the word **aromatic** to refer to **benzene** and its **structural relatives**.

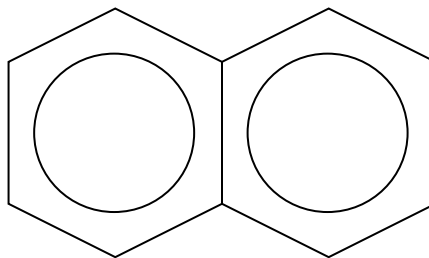
Introduction

- Arenes are aromatic hydrocarbons that contain a benzene ring as a structural unit.
- Benzene is the simplest aromatic hydrocarbon.

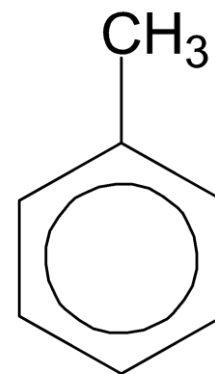
Example...



Benzene



Naphthalene

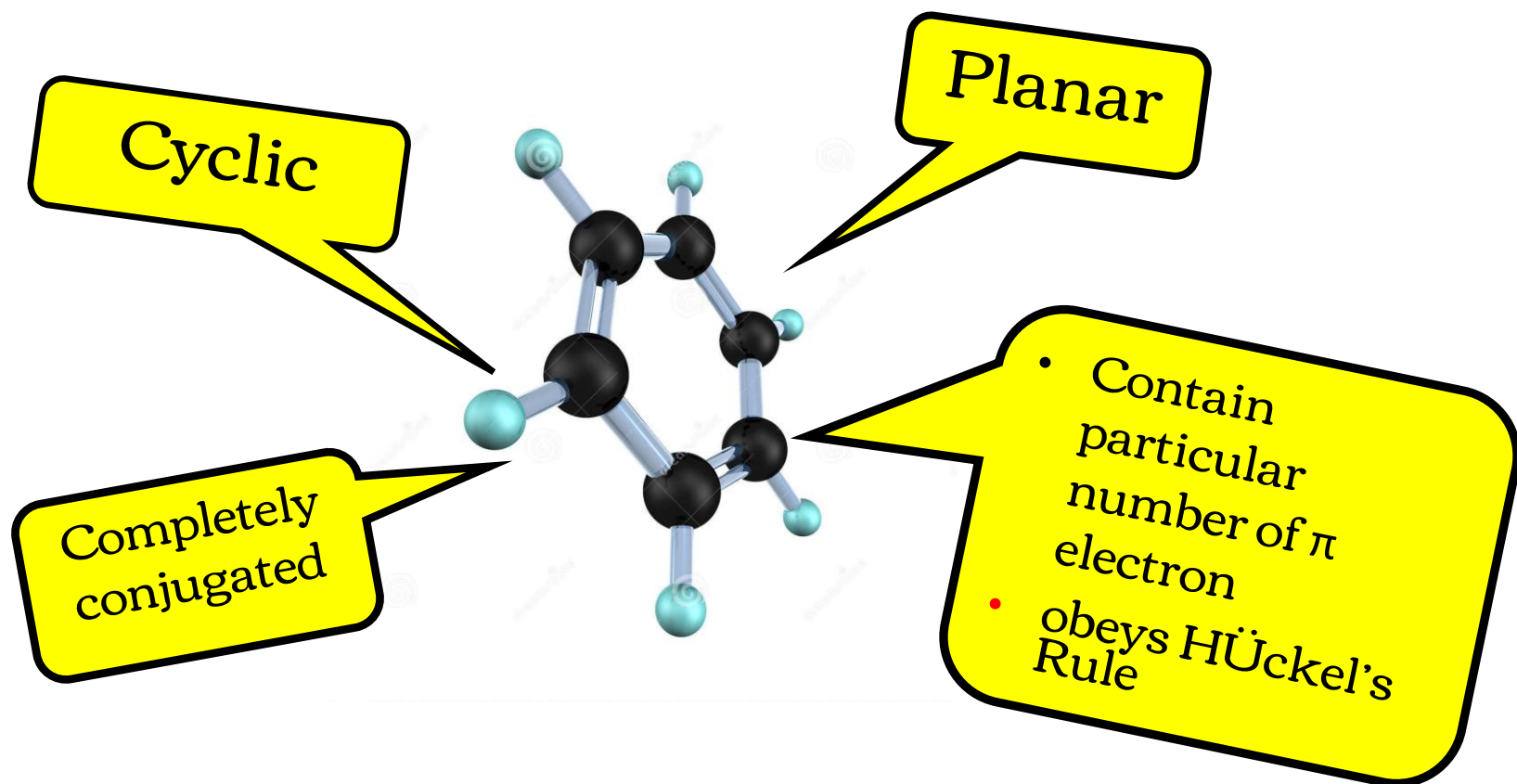


Toluene

Introduction

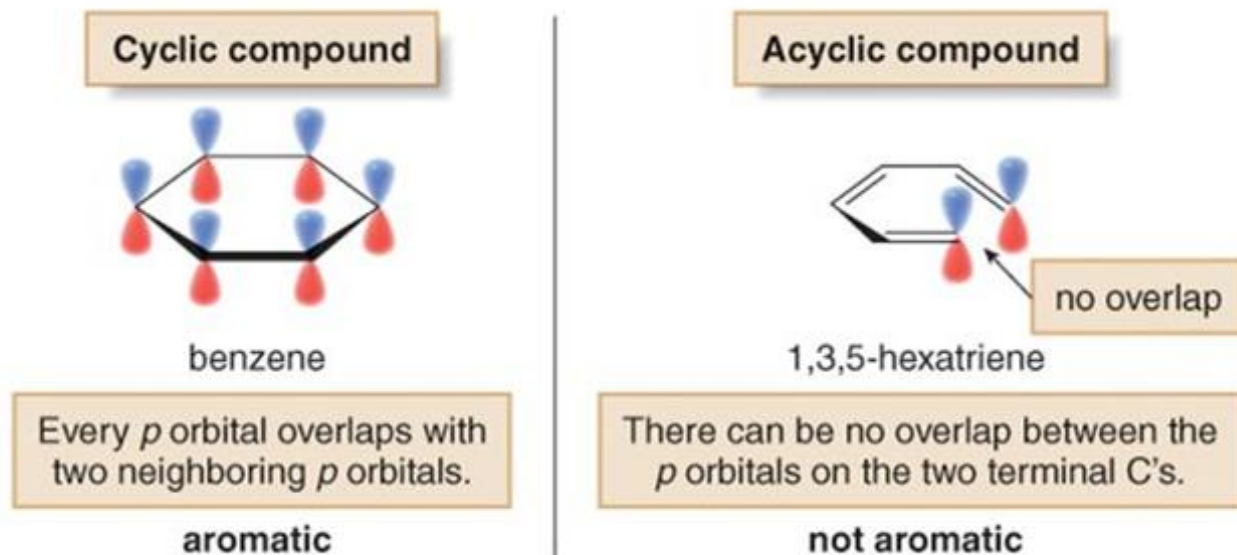
Aromaticity

4 structural criteria must be satisfied for compound to be aromatic:



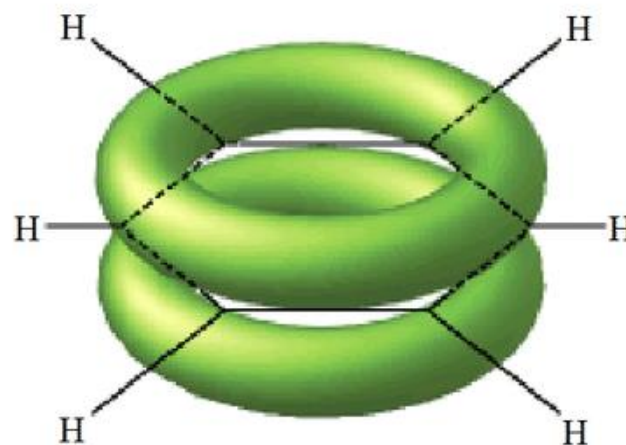
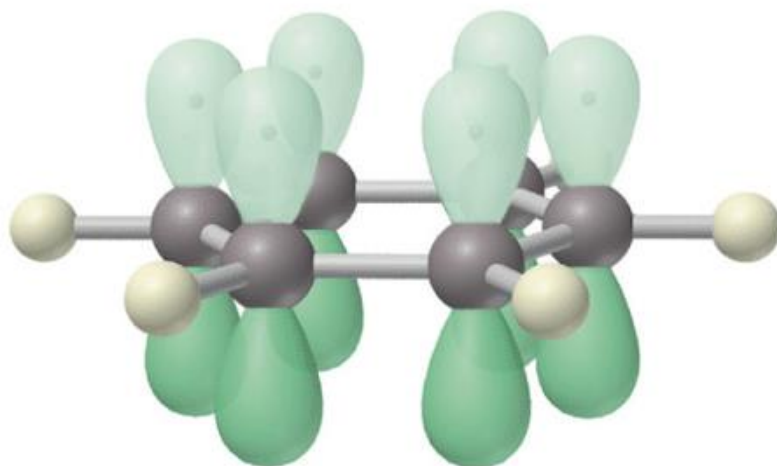
Introduction

CYCLIC



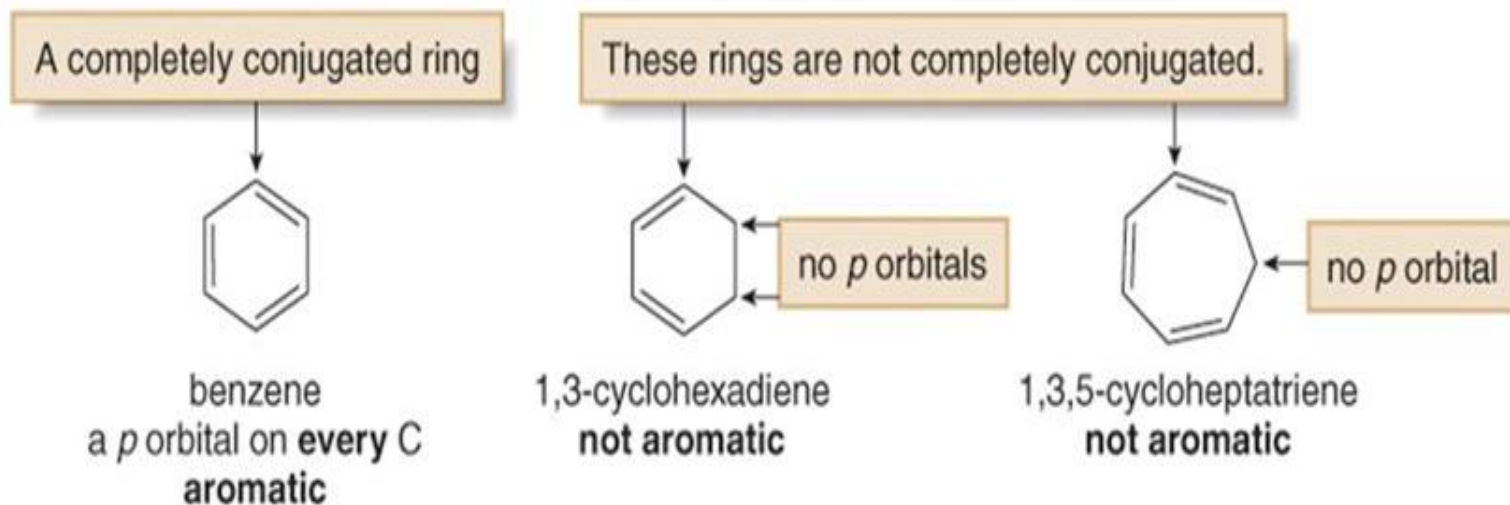
- To be aromatic, each p orbital must overlap with p orbitals on adjacent atoms.

PLANAR



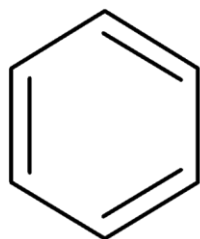
All adjacent *p* orbitals must be aligned so that the π electron density can be delocalized.

COMPLETELY CONJUGATED

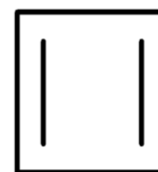


Aromatic compounds must have a p orbital on each atom.

SATISFY HUCKEL'S RULE



- 6 π electrons
- **$4n + 2 = 6$**
- Where $n = 1$
- Aromatic



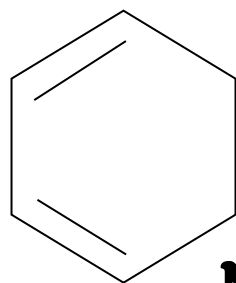
- 6 π electrons
- **$4n + 2 = 4$**
- Where $n = \frac{1}{2}$
- Not aromatic

Aromatic compounds must contain **$[4n+2]\pi$ electrons** ($n = 0, 1, 2$, and so forth).

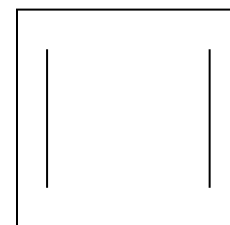
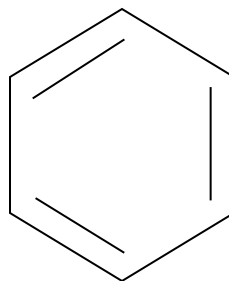
Introduction

Examples:

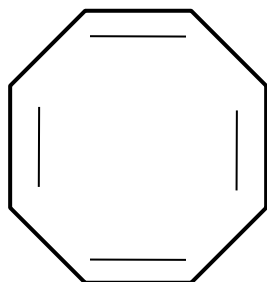
Identify the aromaticity of the compounds below:



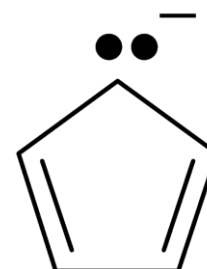
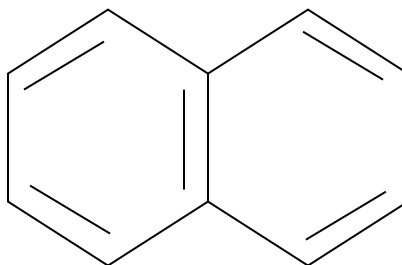
NOT
Completely
conjugated



NOT
obeys
HÜckel's
Rule



NOT
Planar



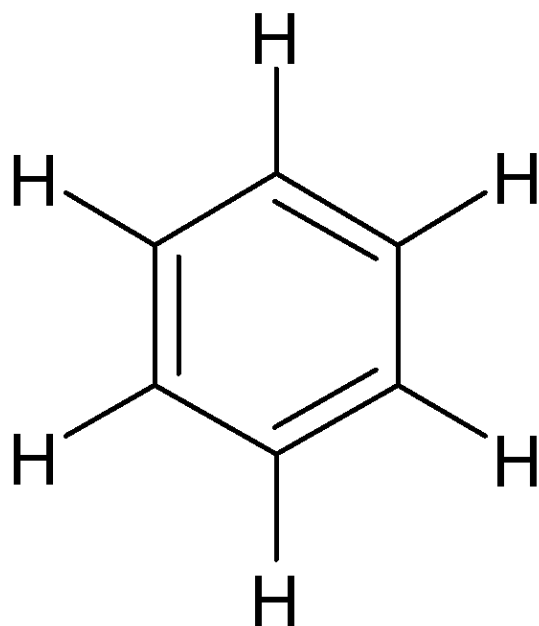
Introduction

- Aromatic compound is a cyclic conjugated unsaturated molecule or ion that is stabilised by π electron delocalisation.
- Benzene is aromatic because contain 6π electrons (obey Hückel's Rule), cyclic, planar and has a completely conjugated ring.

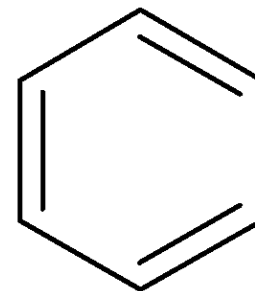
KEKULÉ STRUCTURE OF BENZENE

- August Kekulé (1872) proposed a cyclic structure for benzene.
- The Kekulé structure of benzene can be written as a six-membered ring of carbon atoms with alternating single and double bonds.
- One hydrogen atom is attached to each carbon atom.

KEKULÉ'S STRUCTURE FOR BENZENE



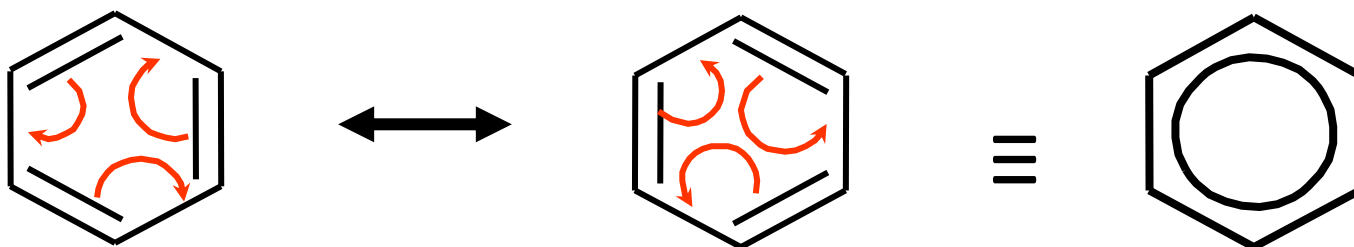
or



The benzene ring is planar and all the carbon-carbon bonds are the same length.

RESONANCE STRUCTURE

- Each carbon atom is sp^2 hybridized, thus has pure 2p orbital with single electron in it.
- The six 2p orbitals overlap to form three delocalised π bonds.
- As a result, the resonance structure of benzene is a hybrid resonance from two Kekulé structure as shown below:



- The six p electrons completely delocalized around the ring

6.2 NOMENCLATURE

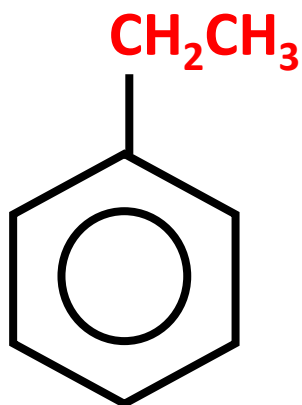
LEARNING OUTCOMES

- 6.2** (a) Give the name of benzene derivatives according to the IUPAC nomenclature for:
- i. monosubstituted benzenes
 - ii. disubstituted benzenes; and
 - iii. tri and tetrasubstituted benzenes
- (b) Give the structures of benzene derivatives in 6.2 (a).
- (c) Apply IUPAC rules to name compounds with C_6H_5 -phenyl or $\text{C}_6\text{H}_5\text{CH}_2$ -benzyl as substituents.

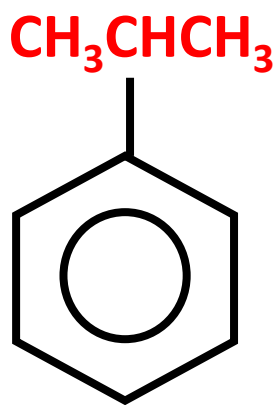
MONO SUBSTITUTED BENZENES

- To name a benzene ring with one substituent, name the substituent and add the word benzene.
- Carbon substituents are named as alkyl groups.

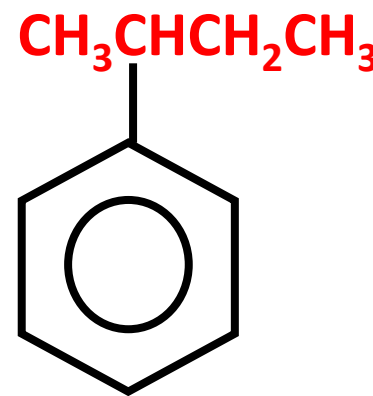
Example...



ethylbenzene



isopropylbenzene

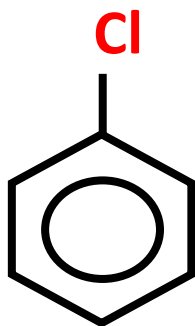


Sec-butylbenzene

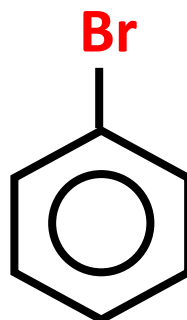
MONO SUBSTITUTED BENZENES

Halogen substituents are named as a halo, change the **-ine** ending the name of the halogen to the suffix **-o**. Eg : chlorine \rightarrow chloro

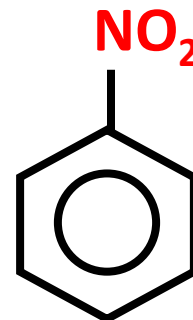
Example...



chlorobenzene



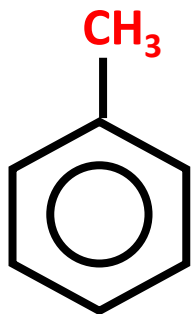
bromobenzene



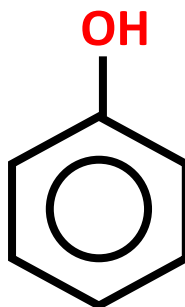
nitrobenzene

MONO SUBSTITUTED BENZENE

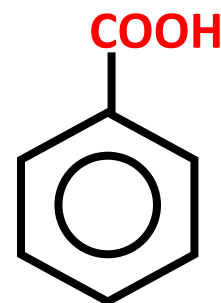
IUPAC rules allow some of the common names to be retained.



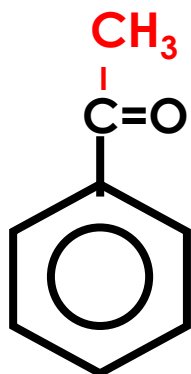
methylbenzene
(toluene)



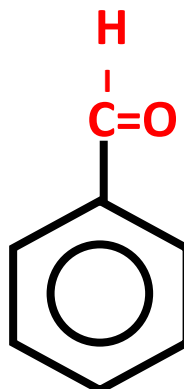
hydroxybenzene
(phenol)



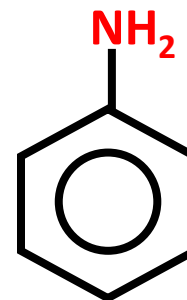
benzenecarboxylic acid
(benzoic acid)



phenylethanone
(acetophenone)



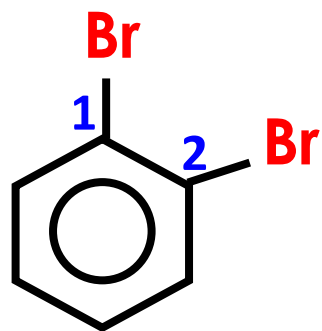
Phenylmethanal
(benzaldehyde)



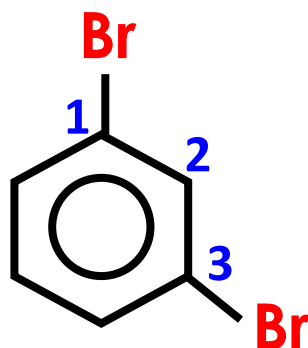
aminobenzene
(aniline)

DISUBSTITUTED BENZENE

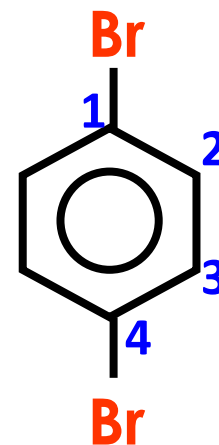
Relative position of substituents are indicated by prefixes ortho, meta, and para (*o*–, *m*–, and *p*–) or by the use of number.



1,2–dibromobenzene
or
o–dibromobenzene

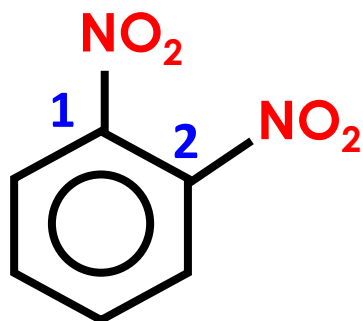


1,3–dibromobenzene
or
m–dibromobenzene

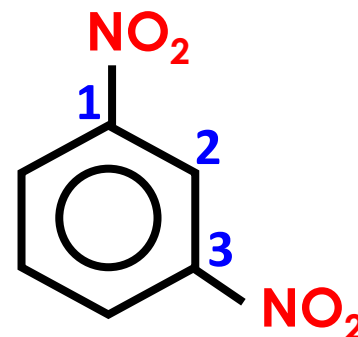


1,4–dibromobenzene
or
p–dibromobenzene

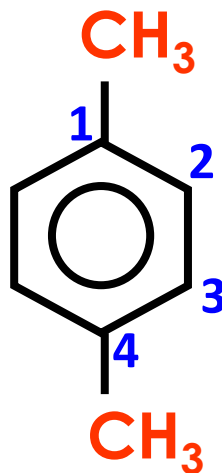
DISUBSTITUTED BENZENE



1,2-dinitrobenzene
or
o-dinitrobenzene



1,3-dinitrobenzene
or
m-dinitrobenzene

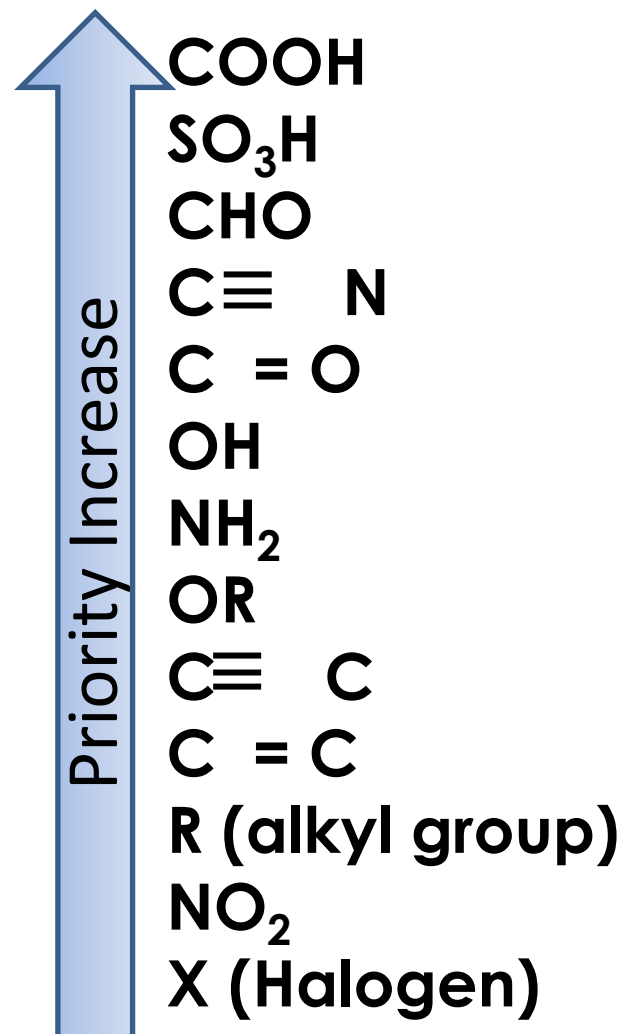


1,4-dimethylbenzene
or
p-dimethylbenzene

DISUBSTITUTED BENZENE

If two different substituents present,

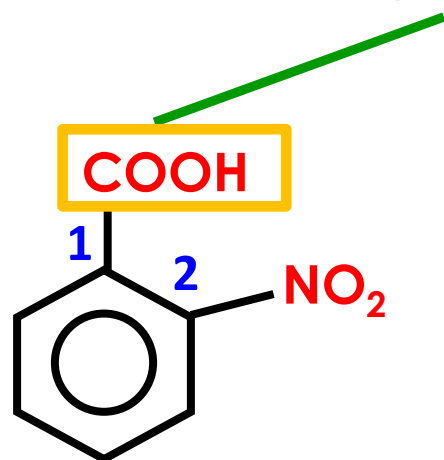
- select one of the substituent that gives new parent name.
- the **highest priority** substituent will be the **parent chain** & numbered as **C₁**.



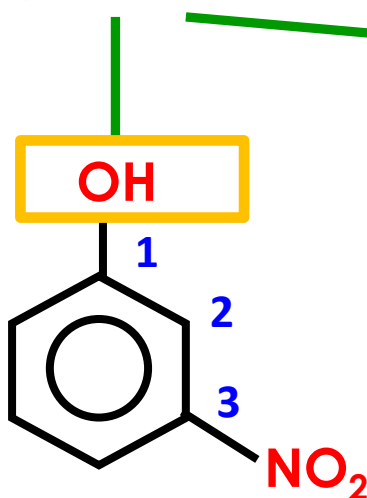
DISUBSTITUTED BENZENE

Example...

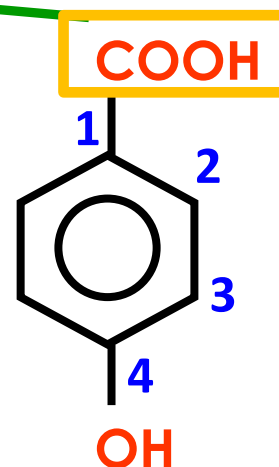
highest priority : be a parent chain



2-nitrobenzoic acid
or
o-nitrobenzoic acid

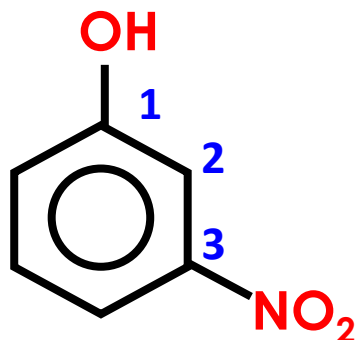


3-nitrophenol
or
m-nitrophenol

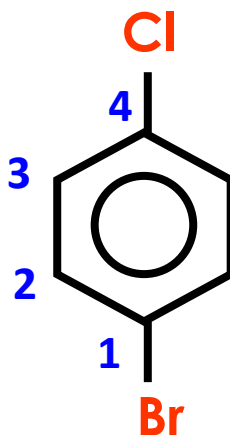


4-hydroxybenzoic acid
or
p-hydroxybenzoic acid

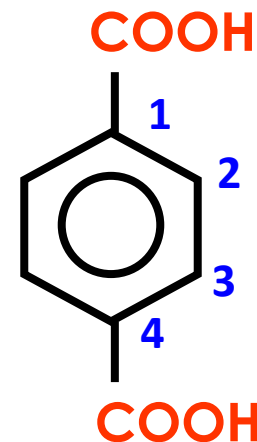
DISUBSTITUTED BENZENE



3-nitrophenol
or
m-nitrophenol



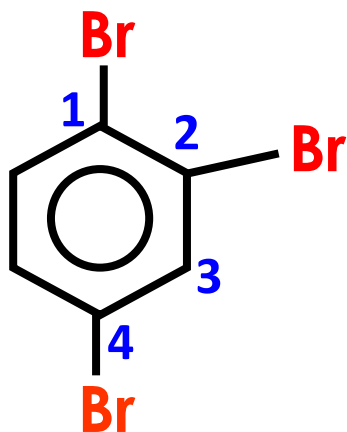
1-bromo-4-chlorobenzene



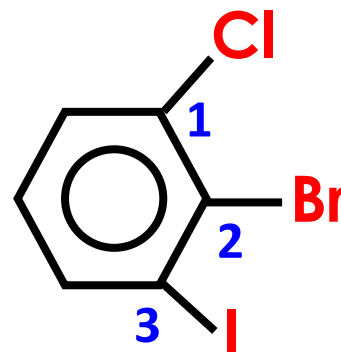
1,4-benzenedicarboxylic acid

TRI & TETRASUBSTITUTED BENZENE

- Position of substituents must be indicated by **numbers**.
- The substituents are listed **alphabetically** when writing the name.
- C atom bearing the substituent that define the **new parent's name** is numbered as **C₁**.

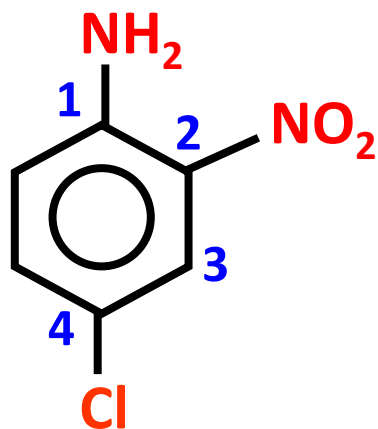


1,2,4-tribromobenzene

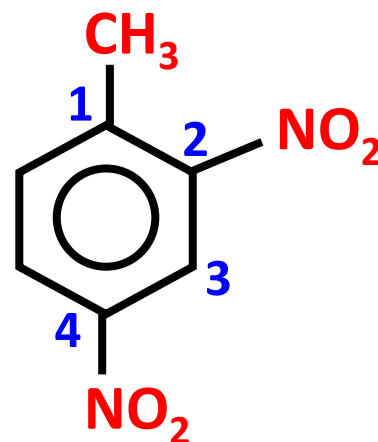


2-bromo-1-chloro-3-iodobenzene

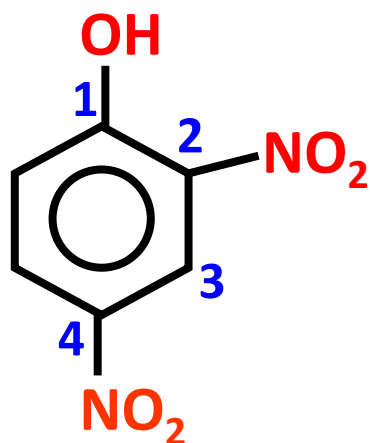
TRI & TETRASUBSTITUTED BENZENE



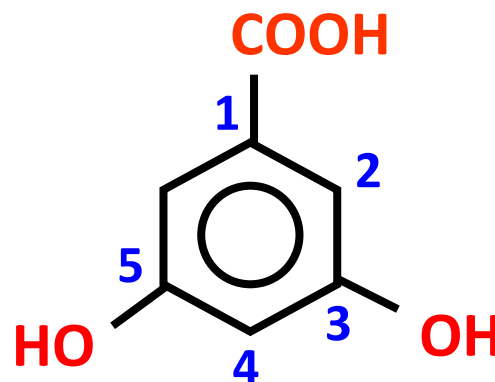
4-chloro-2-nitroaniline



2,4-dinitrotoluene

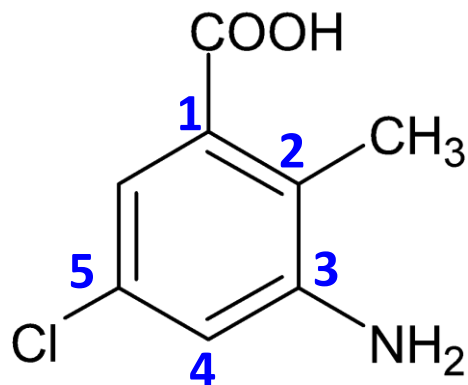


2,4-dinitrophenol

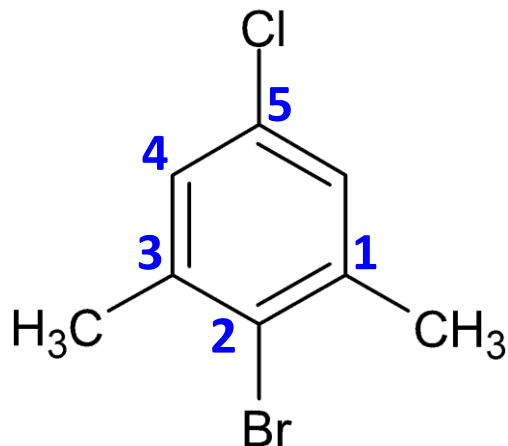


3,5-dihydroxybenzoic acid

TRI & TETRASUBSTITUTED BENZENE

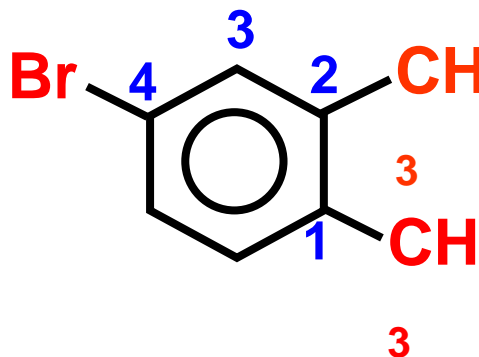


3-amino-5-chloro-2-methylbenzoic acid



2-bromo-5-chloro-1,3-dimethylbenzene

KEEP IN MIND !



4-bromo-1,2-dimethylbenzene



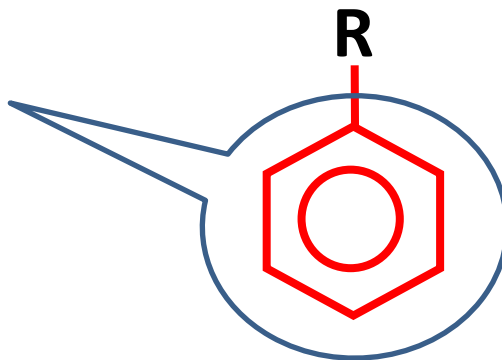
4-bromo-*o*-dimethylbenzene



o-, *m*- and *p*- naming system is used for arenes with 2 substituents only!

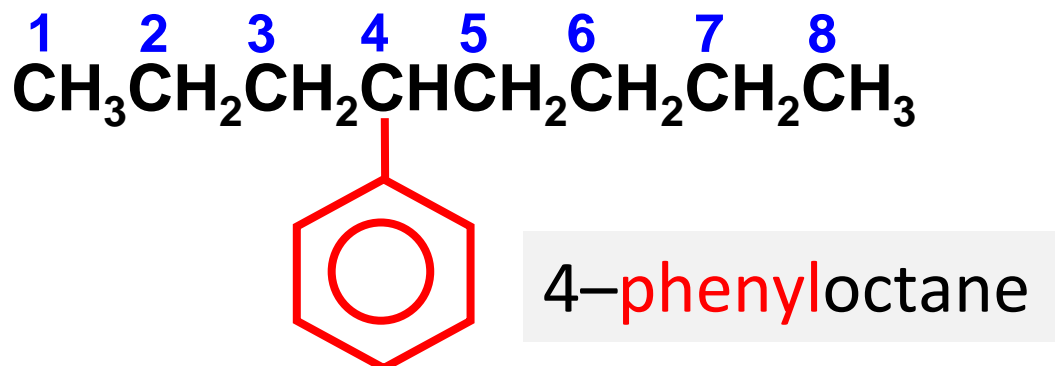
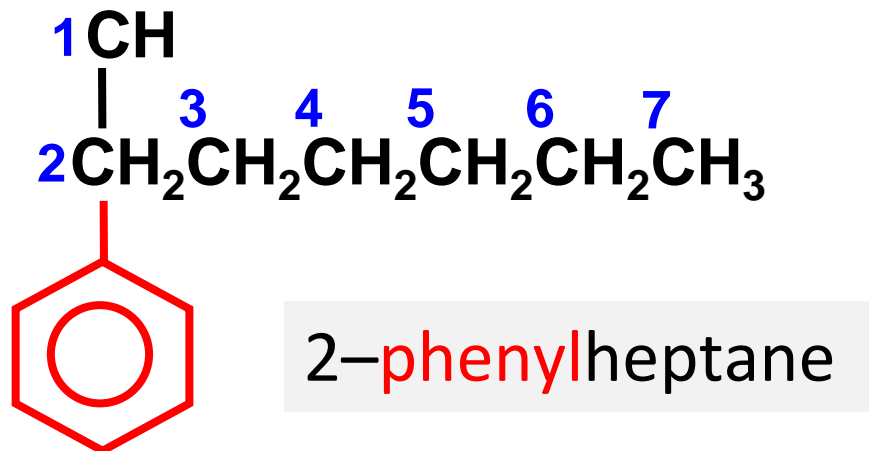
BENZENE AS A SUBSTITUENT - PHENYL

- If alkyl substituent is **larger** than the ring (**more than 6 C**), the compound is named as **phenyl-substituted alkane**.
- Benzene ring as substituent.
- Phenyl group :



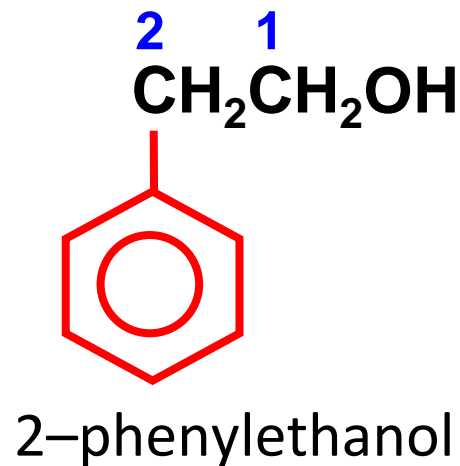
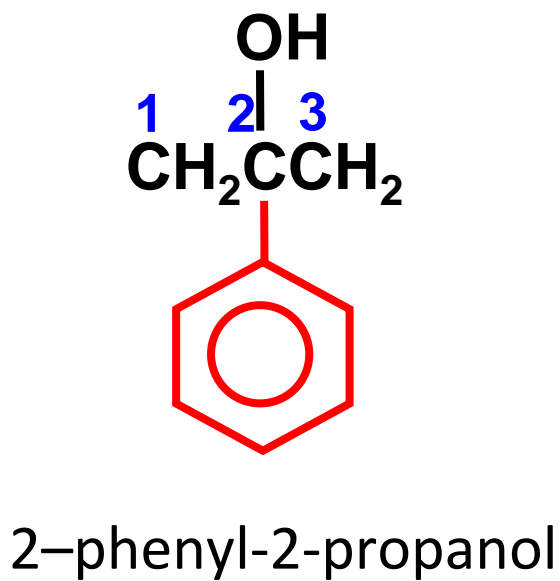
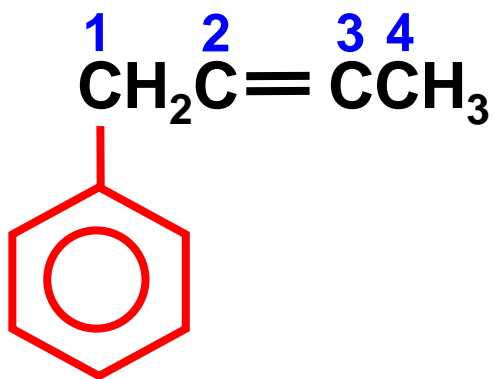
***phenyl**, Ph = C_6H_5-

BENZENE AS A SUBSTITUENT - PHENYL



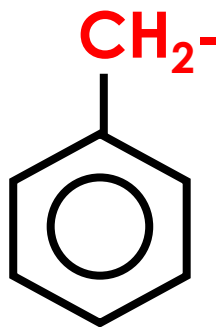
Nomenclature

- If the chain is unsaturated (have $C=C$ or $C\equiv C$) or contains important functional group, the benzene ring is considered as phenyl substituent.

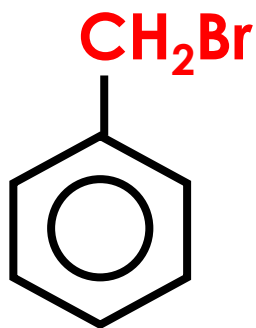


BENZENE AS A SUBSTITUENT - BENZYL

- Benzyl - the benzene ring that attach to the -CH_2 group.
- Benzyl group :



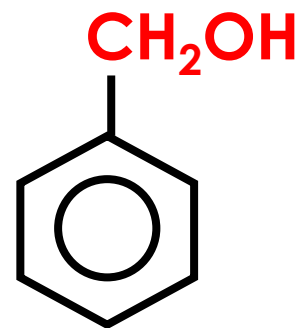
BENZENE AS A SUBSTITUENT - BENZYL



Benzylbromide

or

(bromomethyl)benzene

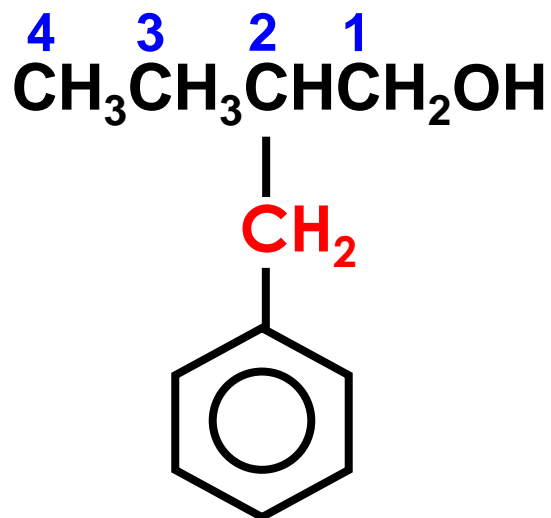


Benzylalcohol

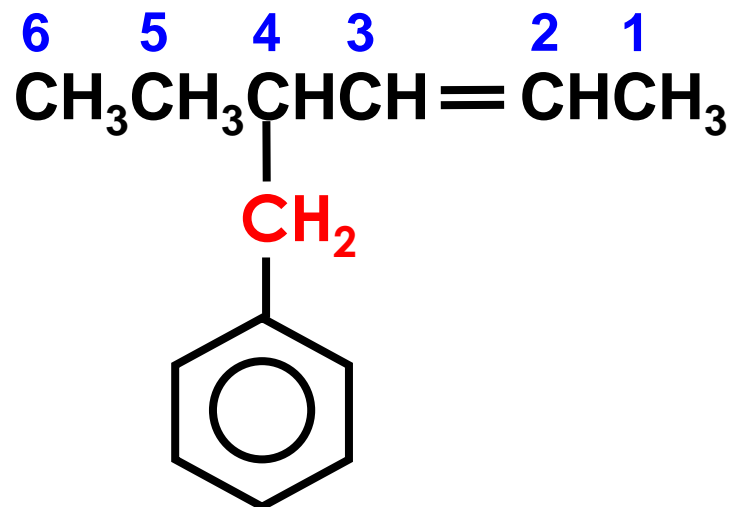
or

Phenyl methanol

Nomenclature

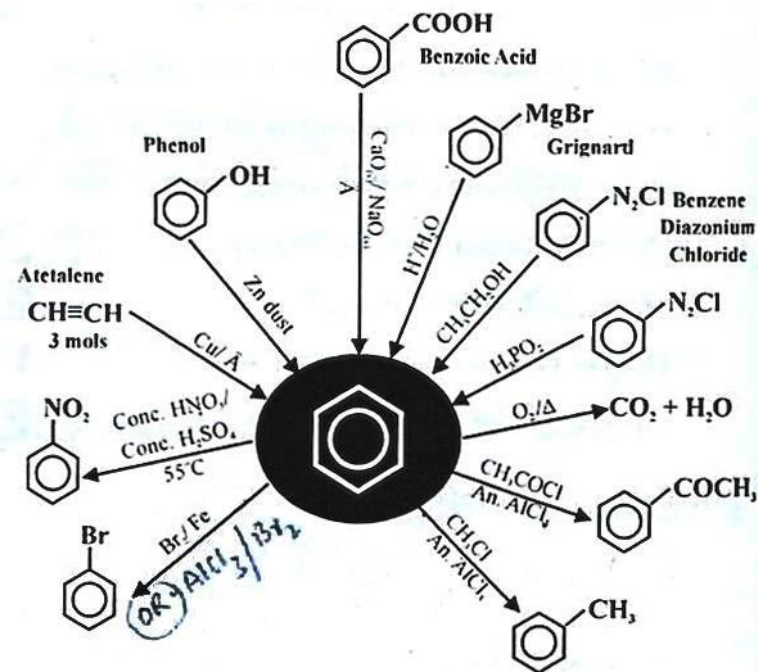


2-benzyl-1-butanol



4-benzyl-2-hexene

6.3 CHEMICAL PROPERTIES





Learning Outcomes

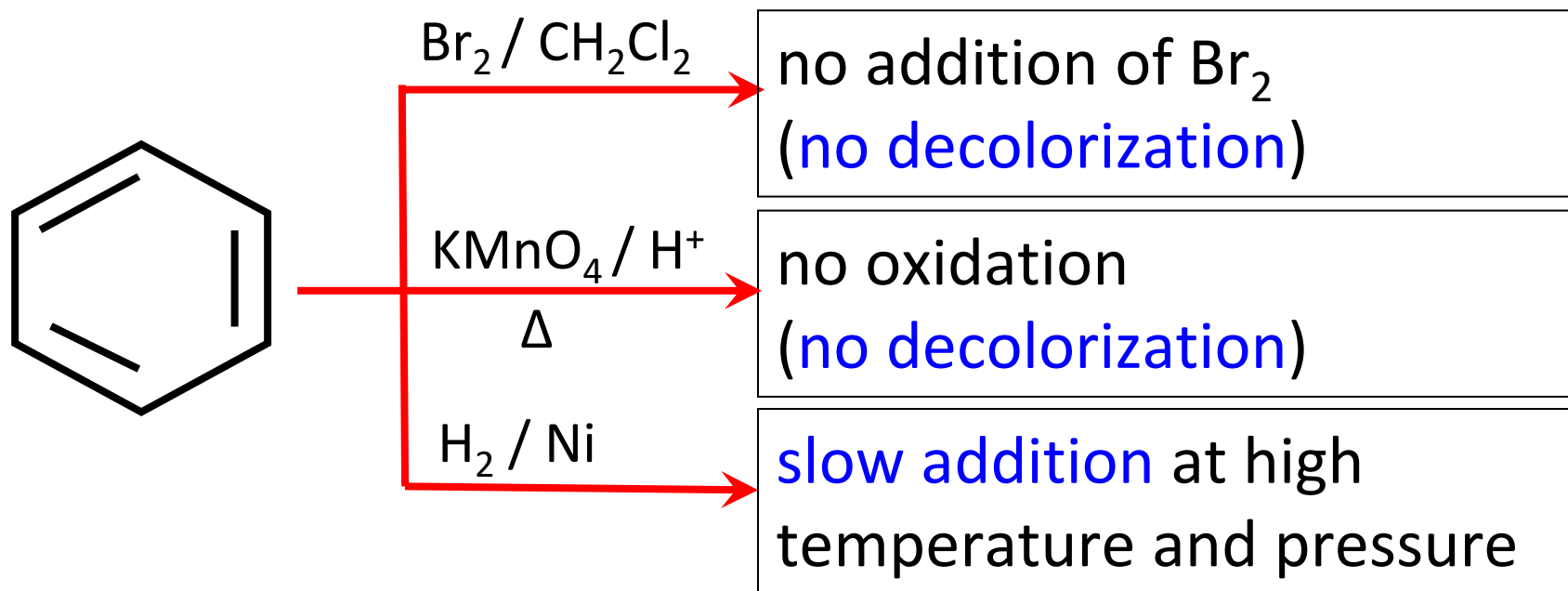
At the end of this topic, you should be able to :

6.3 Chemical properties

- (a) Explain the electrophilic aromatic substitution reactions of benzene:
 - i. Nitration
 - ii. Halogenation
 - iii. Friedel-Crafts alkylation; and
 - iv. Friedel-Crafts acylation
- (b) Illustrate the mechanism for the electrophilic aromatic substitution of benzene. *6.3 (a) i.ii & iii.
- (c) Explain the influence of *ortho-para* and *meta* directing substituents towards electrophilic aromatic substitution reaction.
- (d) Predict the product of electrophilic aromatic substitution of monosubstituted benzene.
- (e) Explain the following reactions of alkyl benzene:
 - i. oxidation with hot acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$
 - ii. halogenation (free radical substitution)

Chemical Properties of Benzene

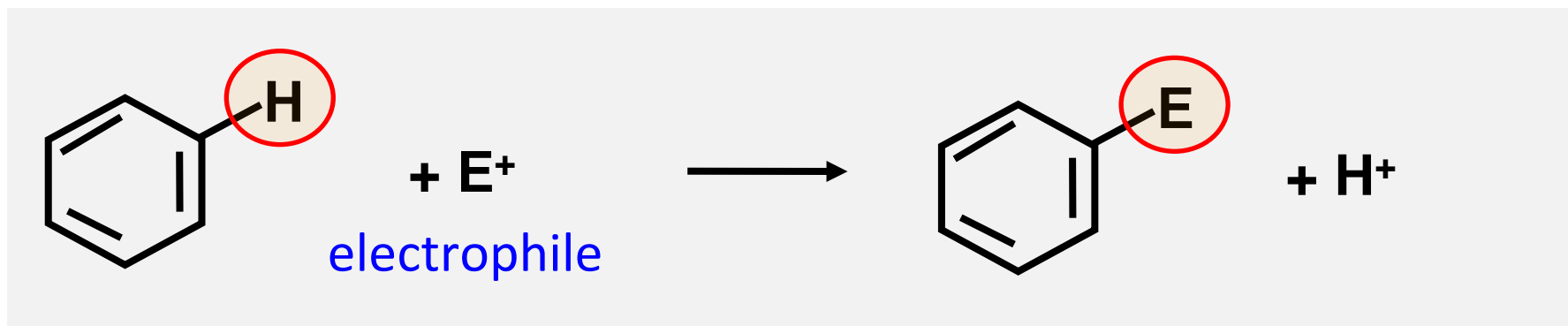
Benzeneunlike alkenes,



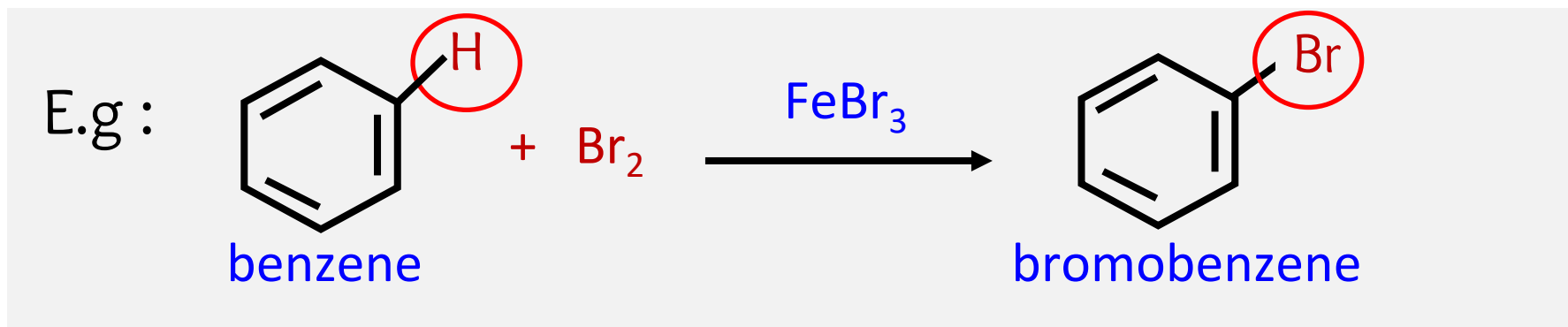
- The **stability of π electron** system will be **lost** if benzene undergo addition reactions.
- Hence, benzene and its derivative undergo **electrophilic aromatic substitution reactions.**

Chemical Properties of Benzene

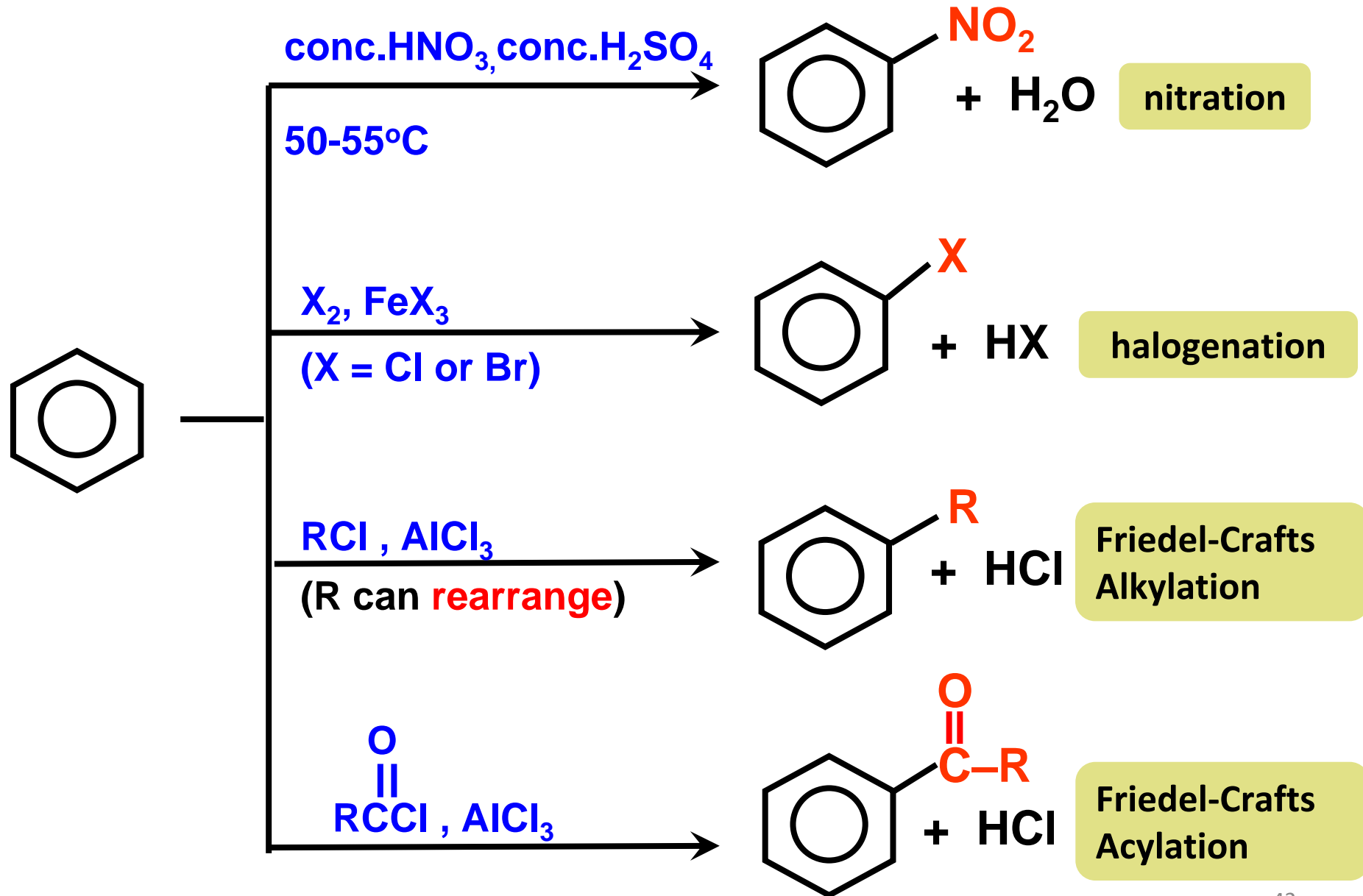
Electrophilic Aromatic Substitution Reaction



A **H atom** is **replaced** by an **electrophile**.

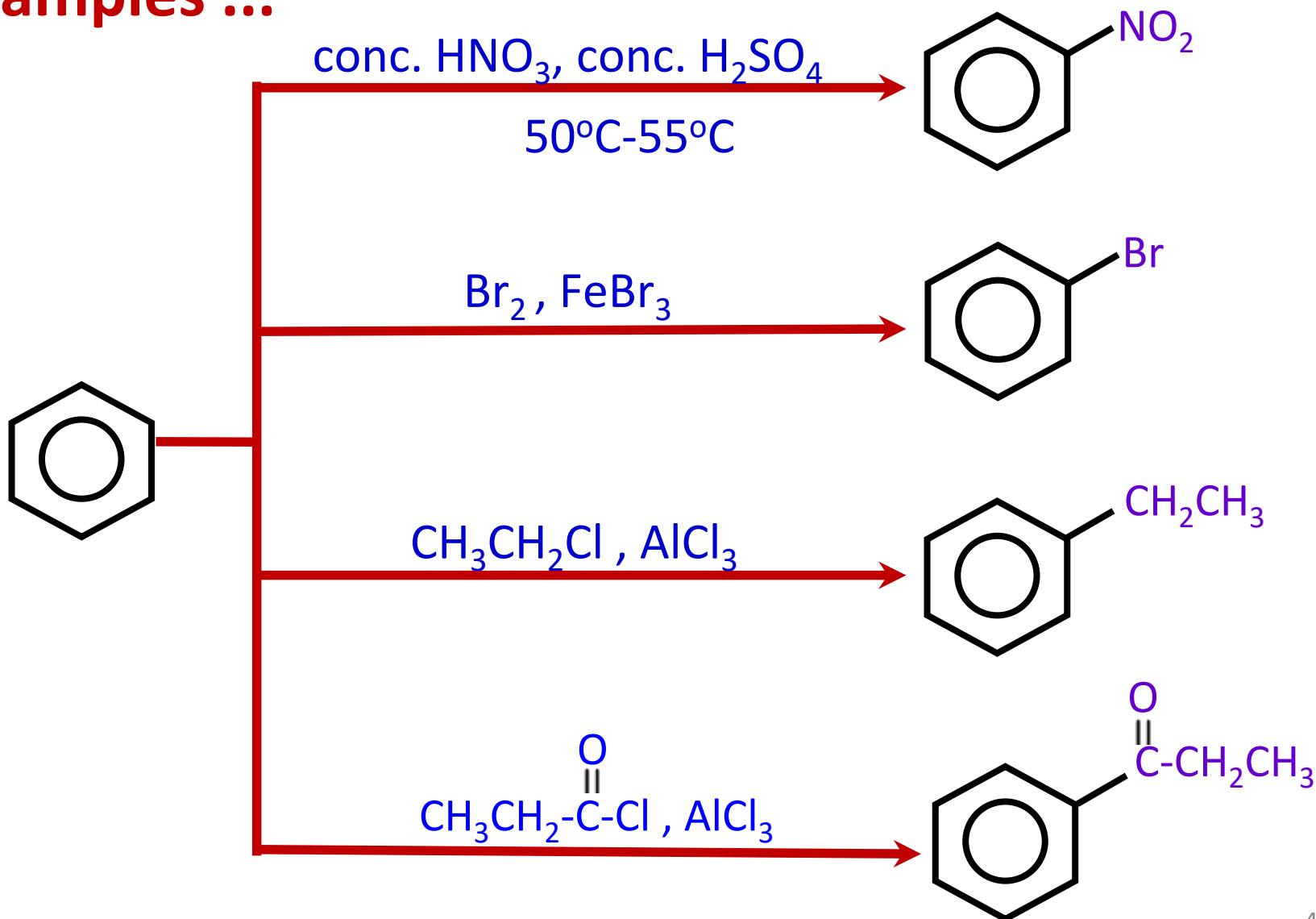


6.3 (a) Chemical Properties of Benzene



Chemical Properties of Benzene

Examples ...



6.3 (b) Mechanism for Electrophilic Aromatic Substitution of Benzene

Mechanism of benzene involves 3 steps of reaction:

Step 1 : Formation of electrophile

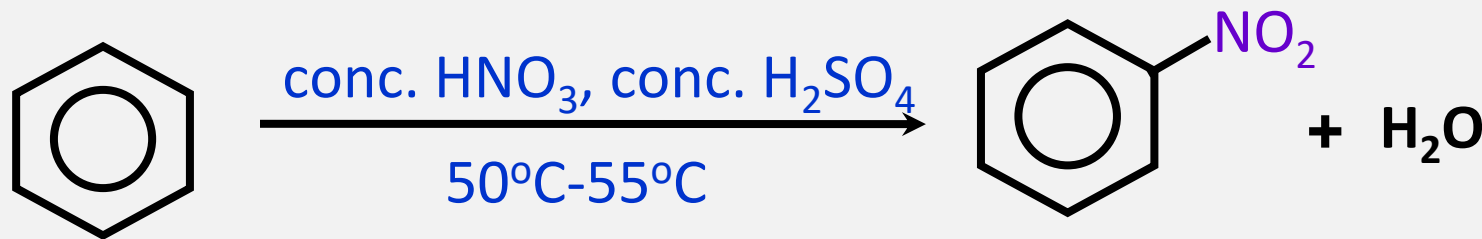
Step 2 : Formation of arenium ion

Step 3 : Deprotonation of arenium ion (lost of H^+)

(i) Nitration of Benzene

- Benzene reacts rapidly with a mixture of concentrated nitric acid and concentrated sulphuric acid to give **nitrobenzene**.

Examples ...

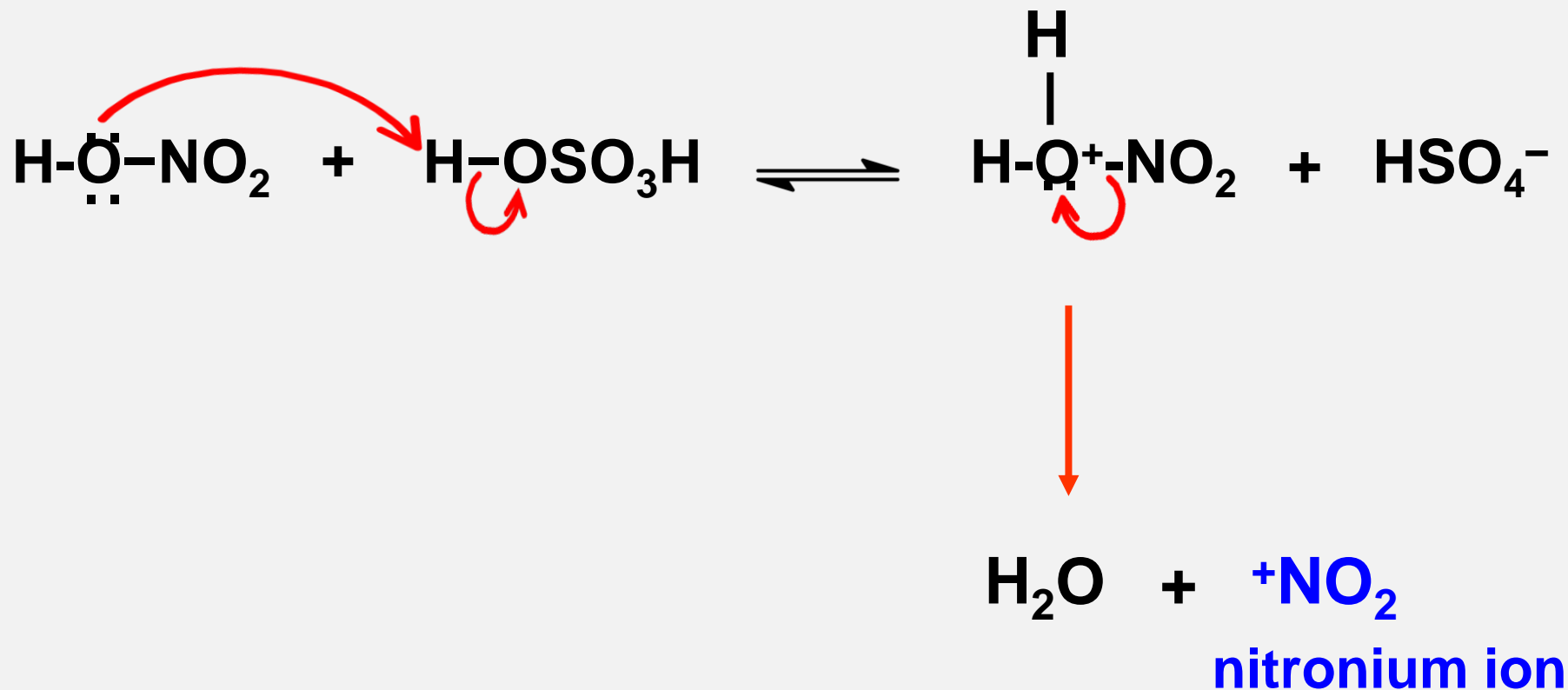


- Product : **nitrobenzene**
- Observation: **yellow oil** formed

A Mechanism For The Reaction

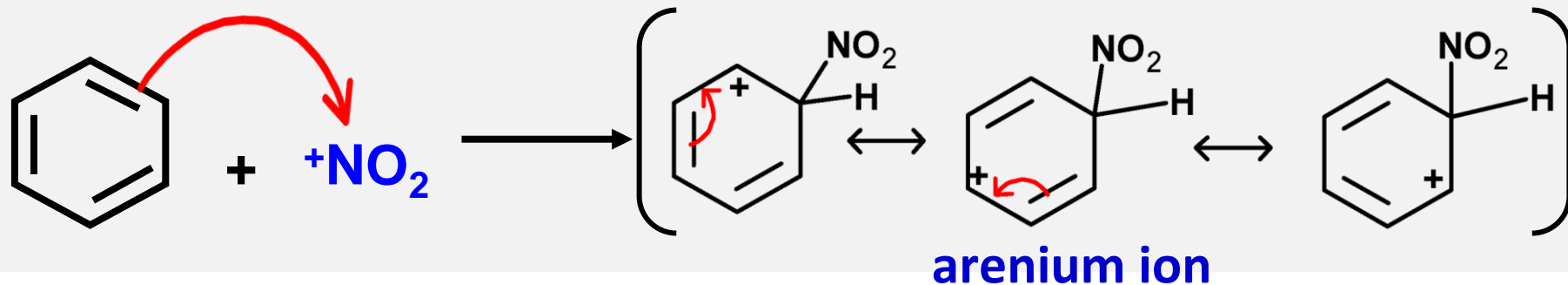
STEP 1

Formation of nitronium ion (NO_2^+)

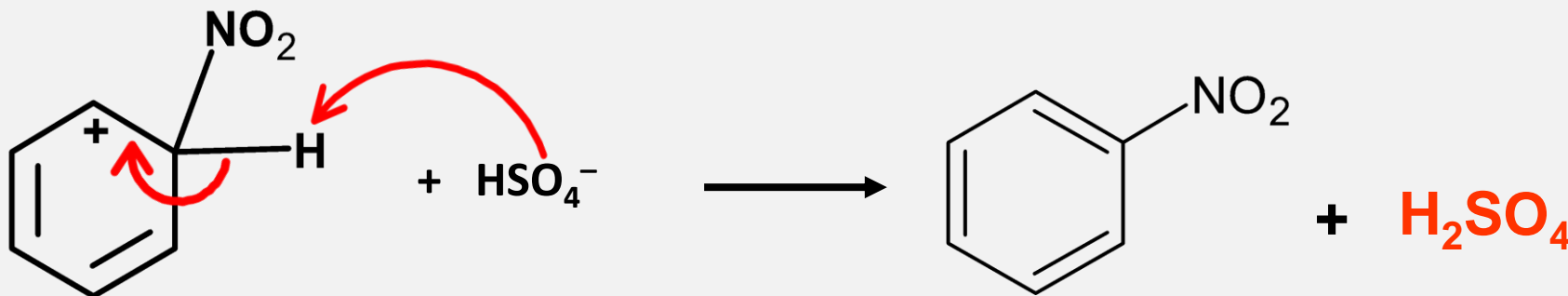


A Mechanism For The Reaction

STEP 2 Formation of arenium ion



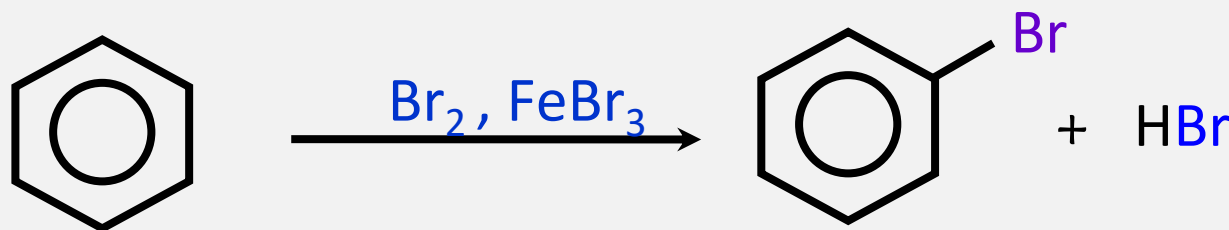
STEP 3 Loss of H^+



(ii) Halogenation of Benzene

- Benzene reacts with bromine and chlorine in the **presence of a Lewis acid**.
- The Lewis acids commonly used are FeCl_3 , AlCl_3 for chlorination and FeBr_3 for bromination.

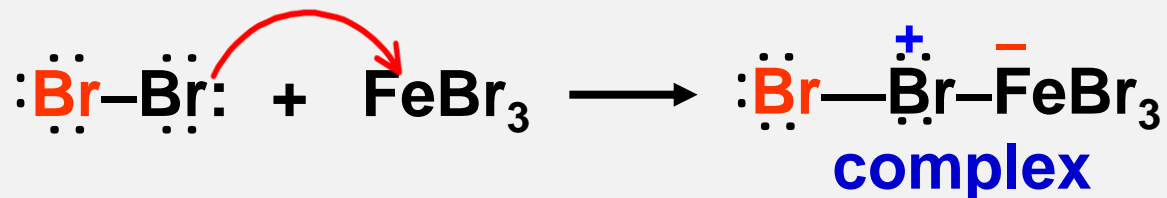
Examples ...



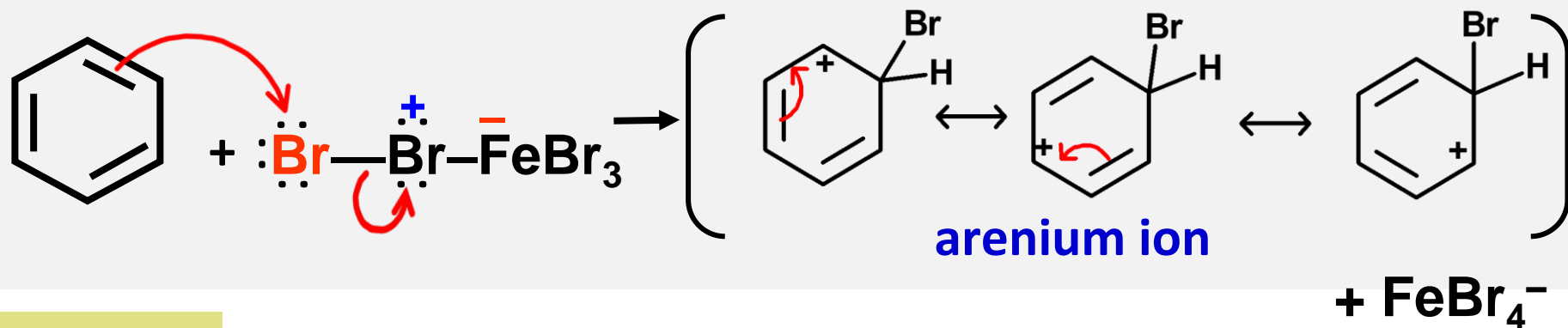
- Product : **halobenzene**
- Observation: **reddish brown** colour of bromine decolourises

A Mechanism For The Reaction

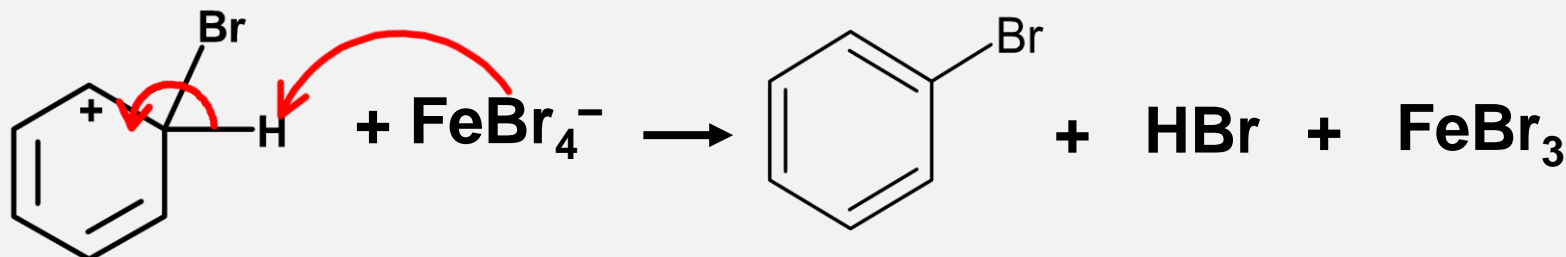
STEP 1 Bromine combines with FeBr_3 to form a complex



STEP 2 Formation of arenium ion



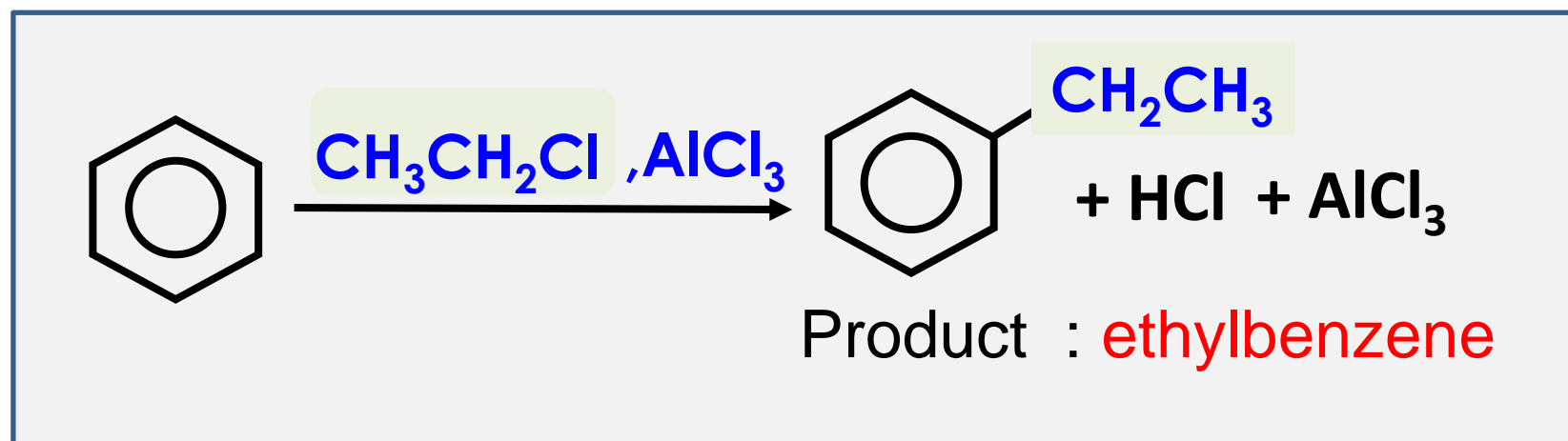
STEP 3 Loss of H^+



(iii) Friedel-Crafts Alkylation

- Benzene reacts with haloalkane in the presence of Lewis acid catalyst such as AlCl_3 or FeCl_3 to form alkylbenzene.
- For CH_3Cl and $\text{CH}_3\text{CH}_2\text{Cl}$, the Lewis acid-base complex itself serves as the electrophile for electrophilic aromatic substitution.

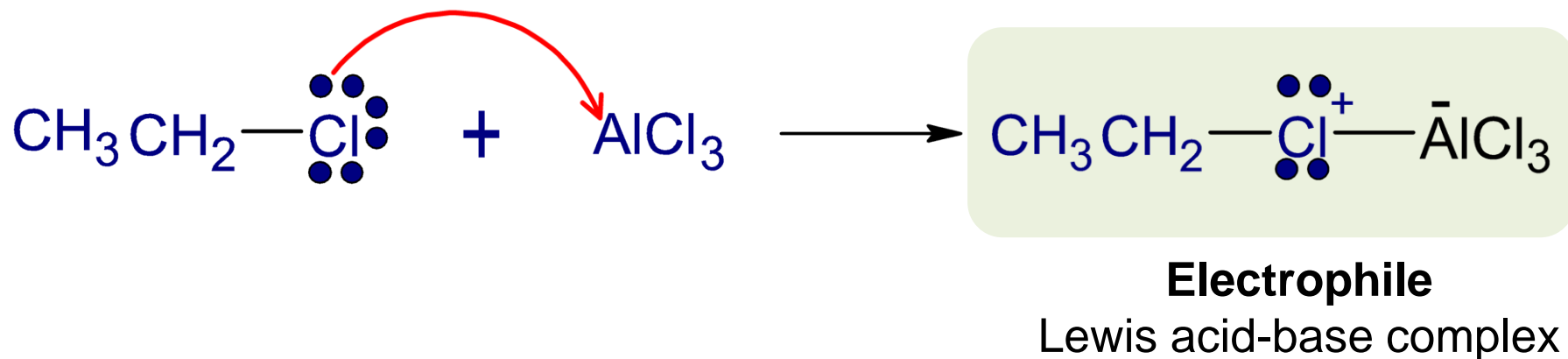
Examples 1:



A Mechanism For The Reaction

STEP 1

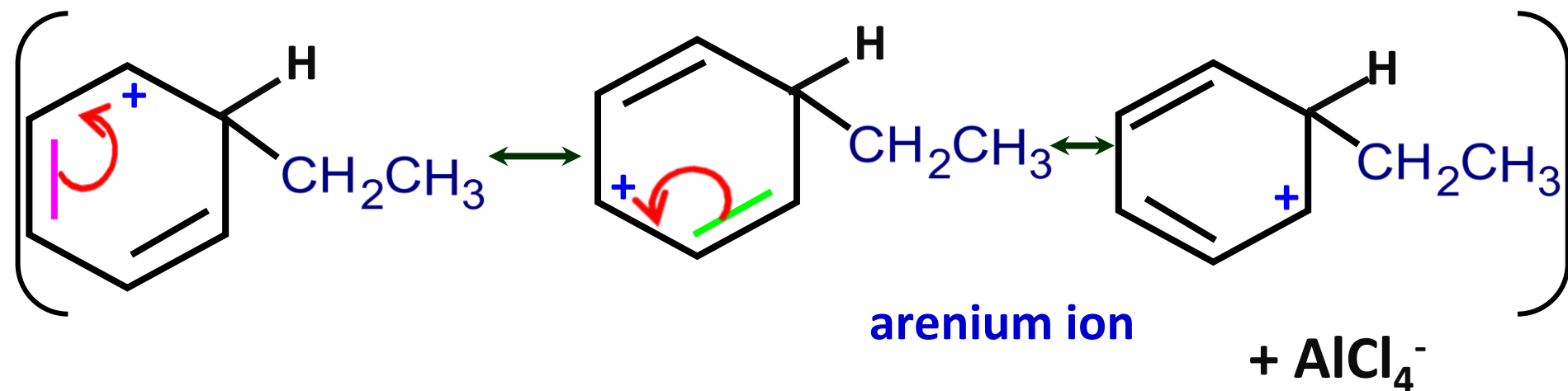
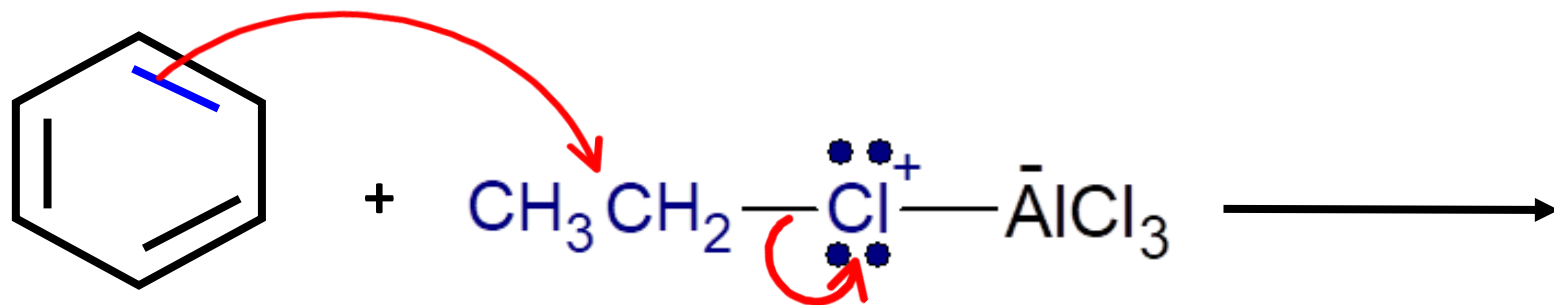
Chloroethane combines with AlCl_3 to form a complex.



A Mechanism For The Reaction

STEP 2

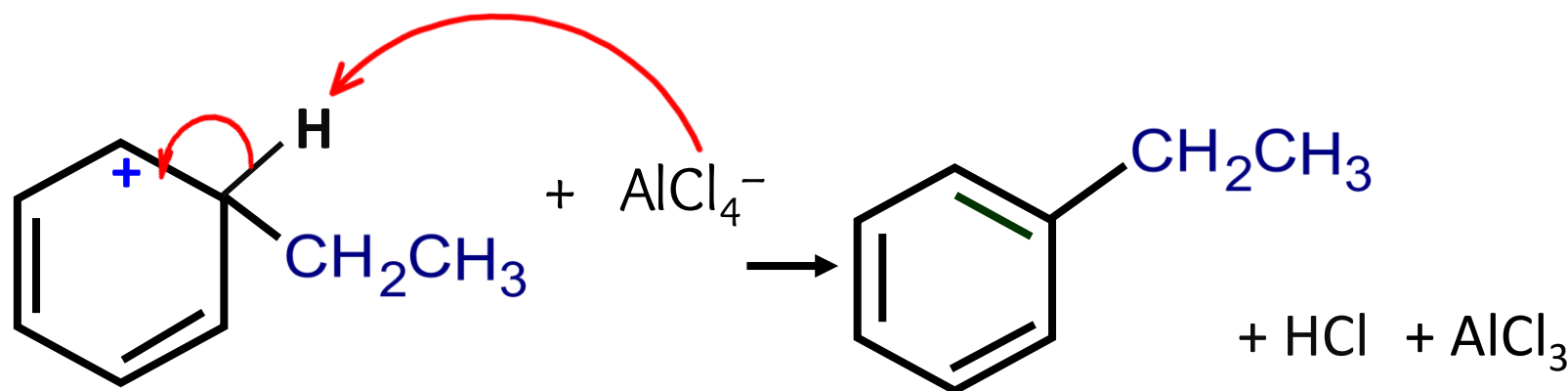
The complex react with benzene to form an arenium ion



A Mechanism For The Reaction

STEP 3

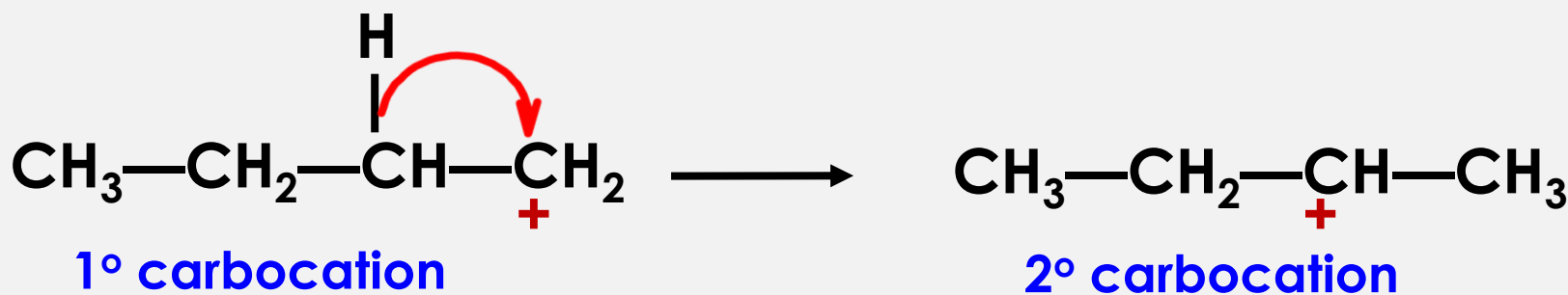
The arenium ion then loses a proton, H^+ and becomes ethylbenzene.



Friedel-Crafts Alkylation

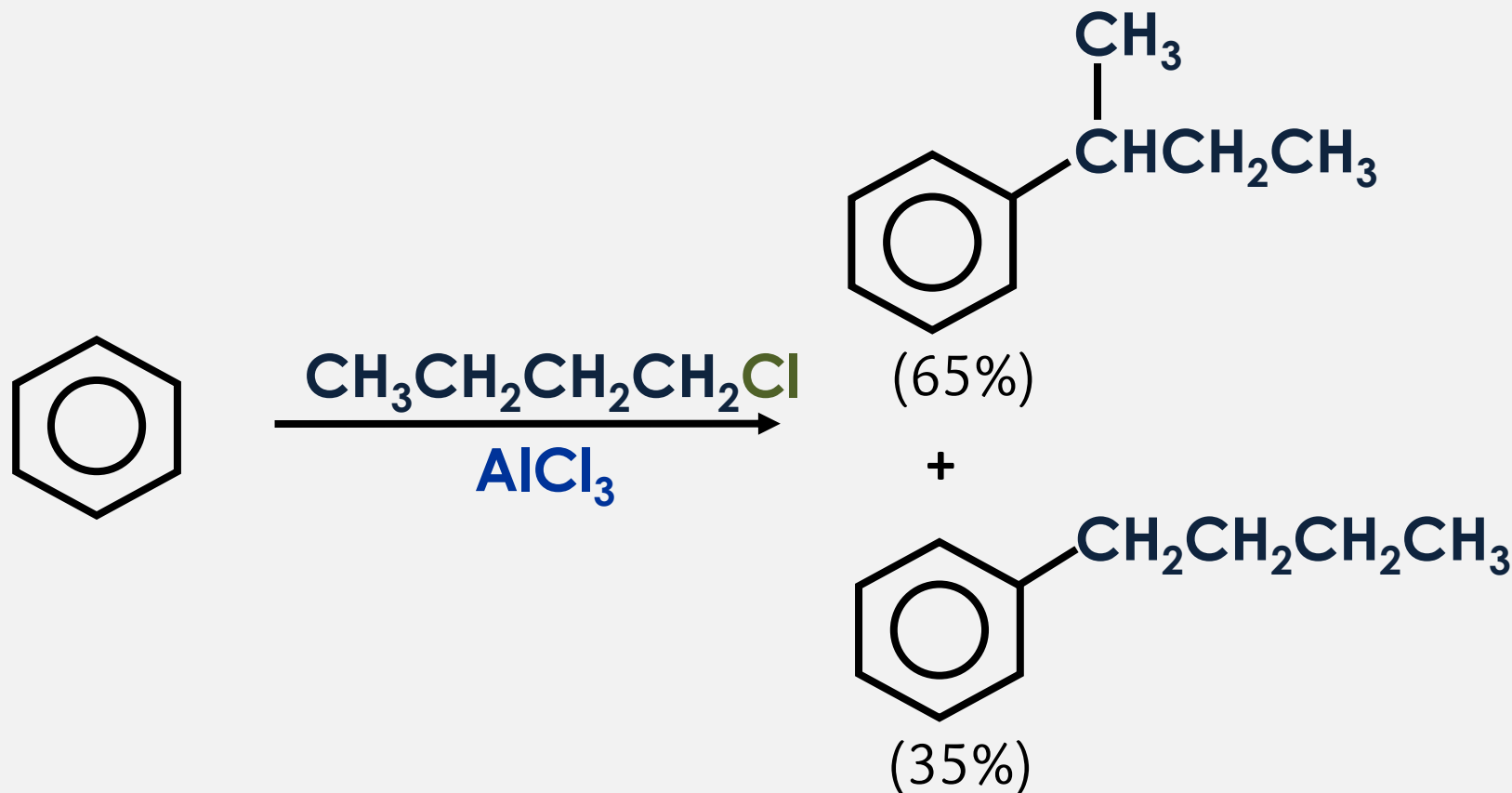
- Most Friedel - Crafts alkylation reactions involve carbocation electrophiles.
- The reaction can yield products having rearranged carbon skeletons when 1° and 2° haloalkanes are used as starting materials.

Examples 2:



Friedel-Crafts Alkylation

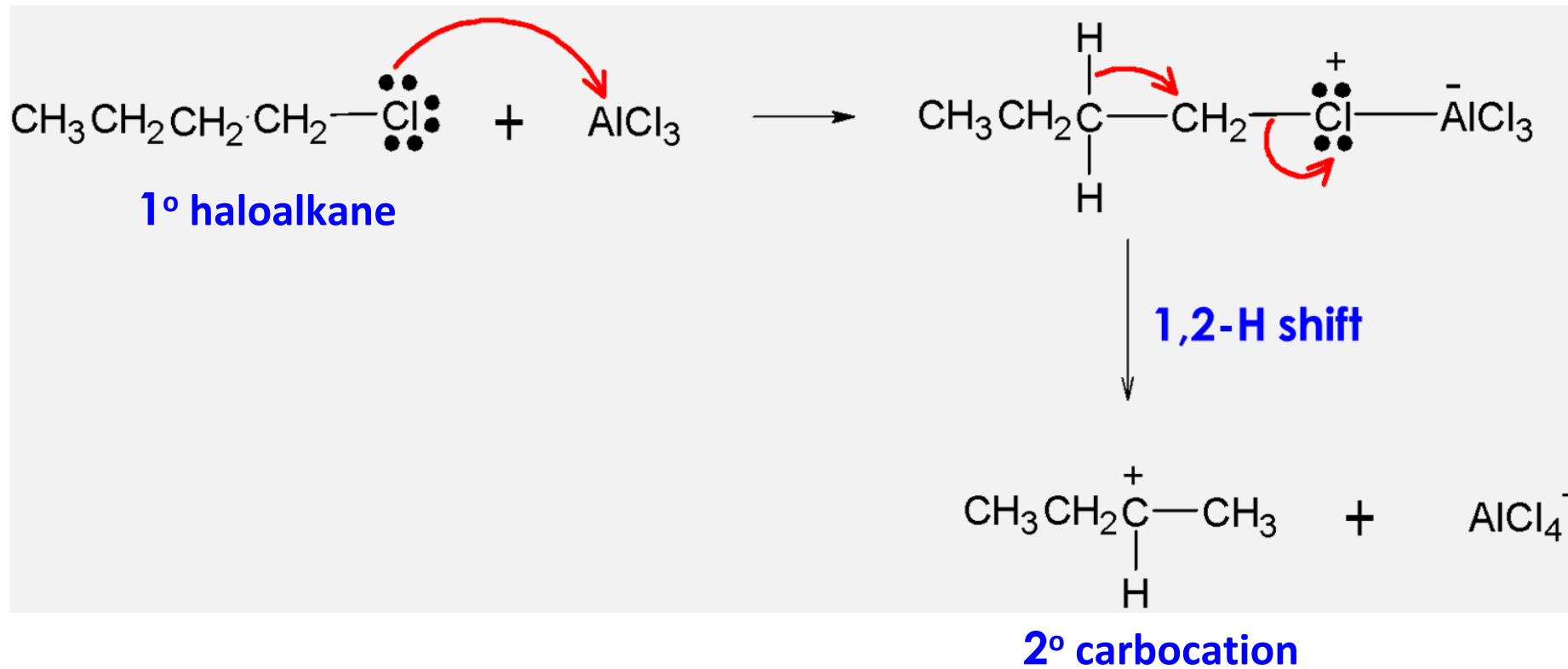
Examples 2



Product : alkylbenzene

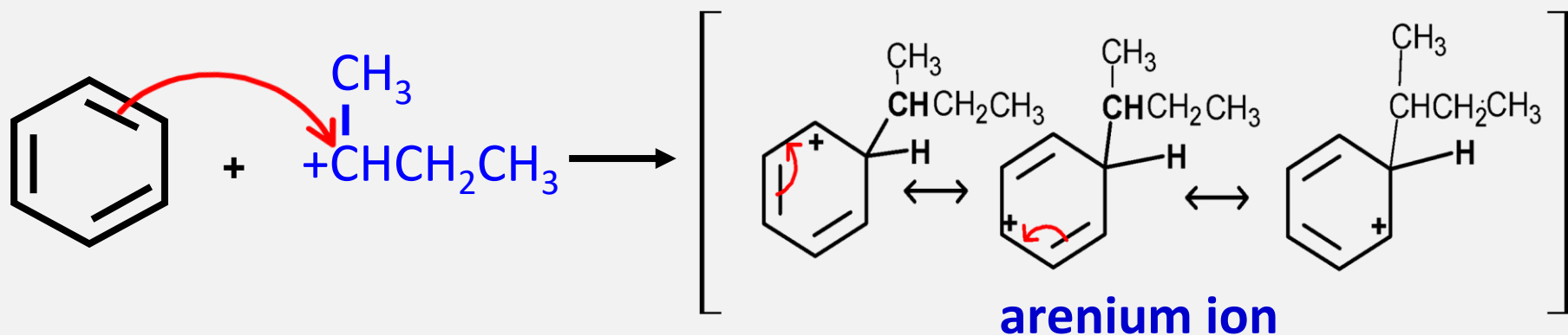
A Mechanism For The Reaction

STEP 1 Formation of carbocation

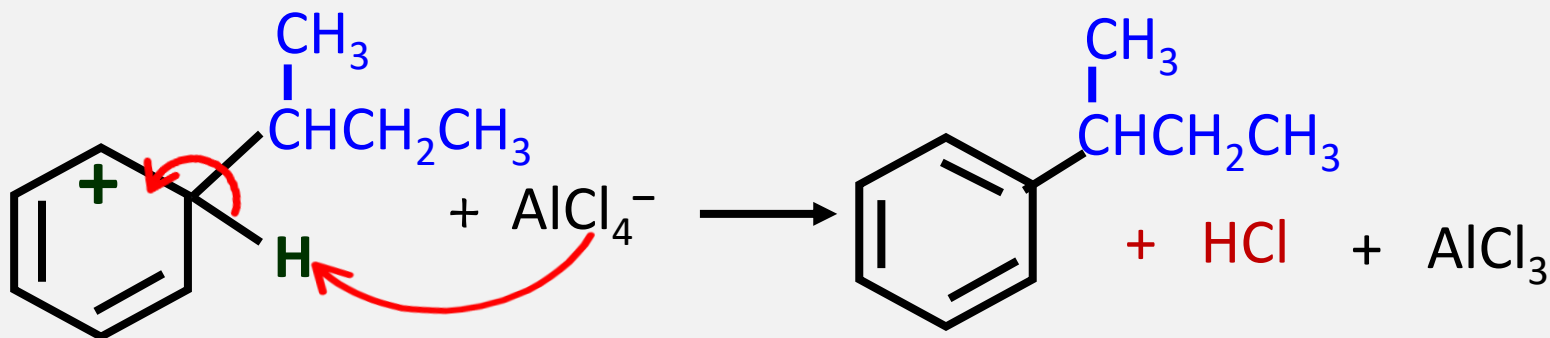


A Mechanism For The Reaction

STEP 2 Formation of arenium ion

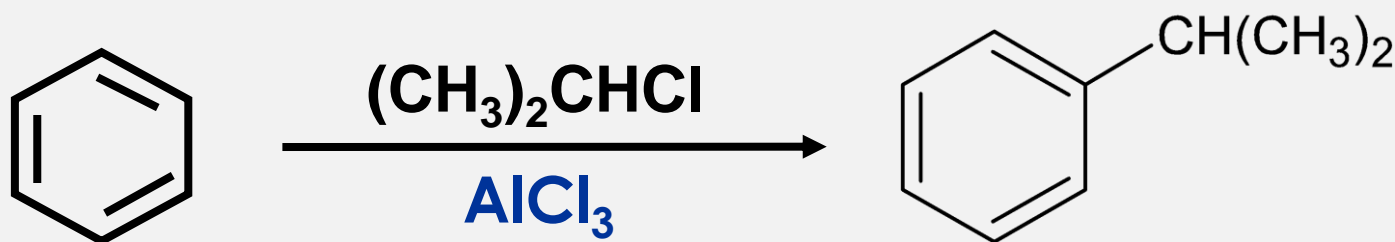


STEP 3 Loss of H^+



Friedel-Crafts Alkylation

Examples 3

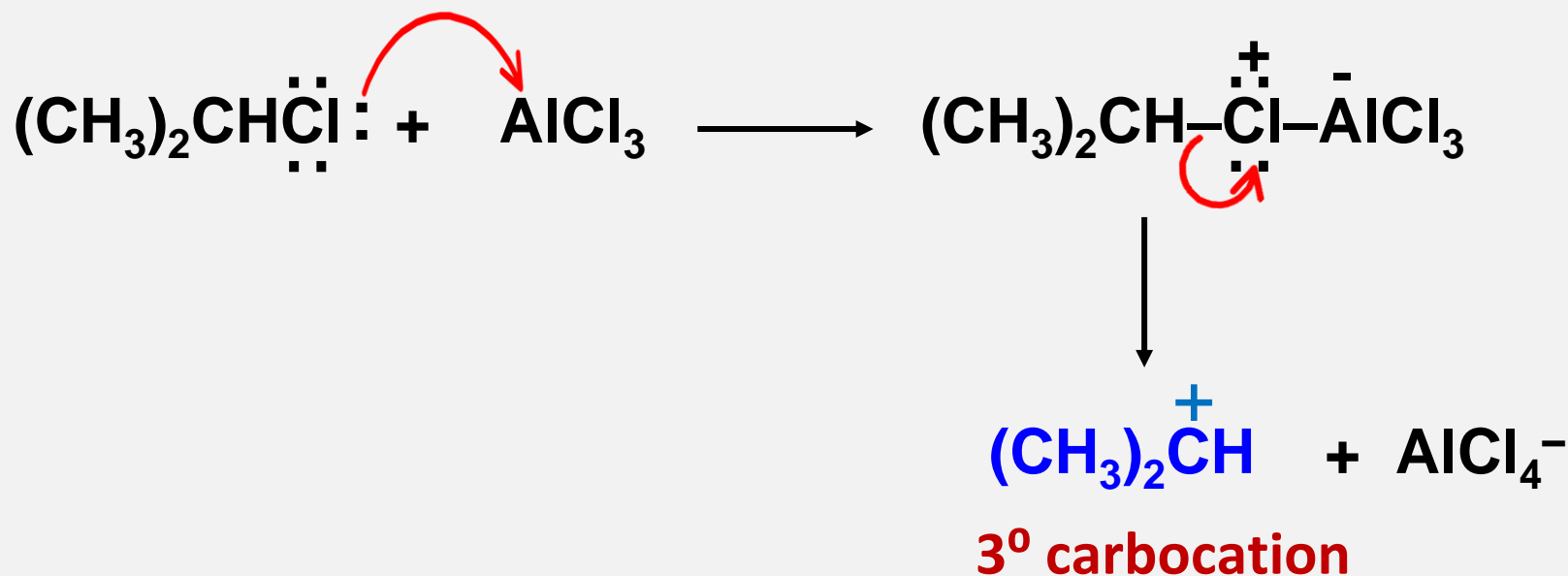


Reagent : 3° Haloalkane

Product : **alkylbenzene**

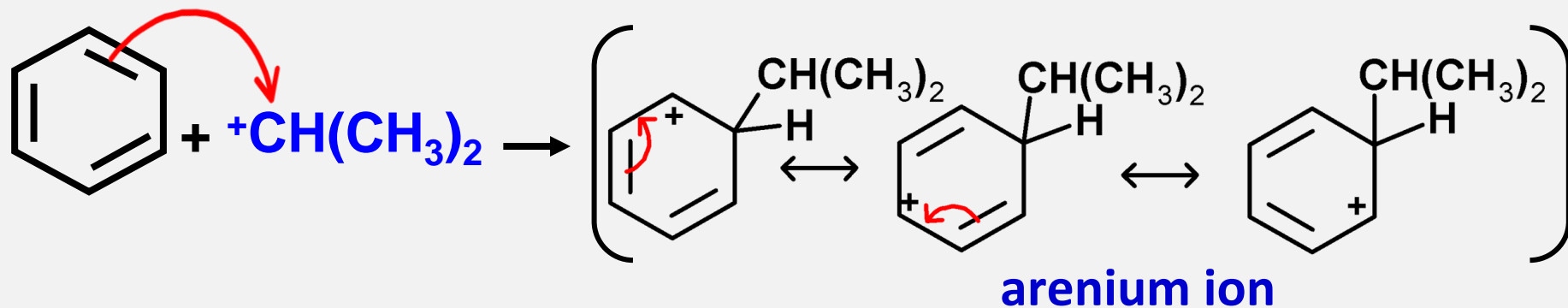
A Mechanism For The Reaction

STEP 1 Formation of carbocation

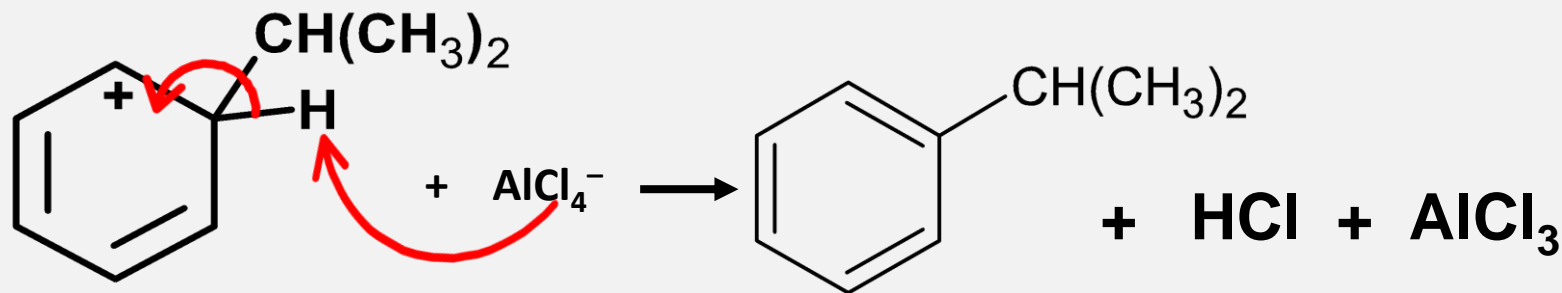


A Mechanism For The Reaction

STEP 2 Formation of arenium ion



STEP 3 Loss of H⁺

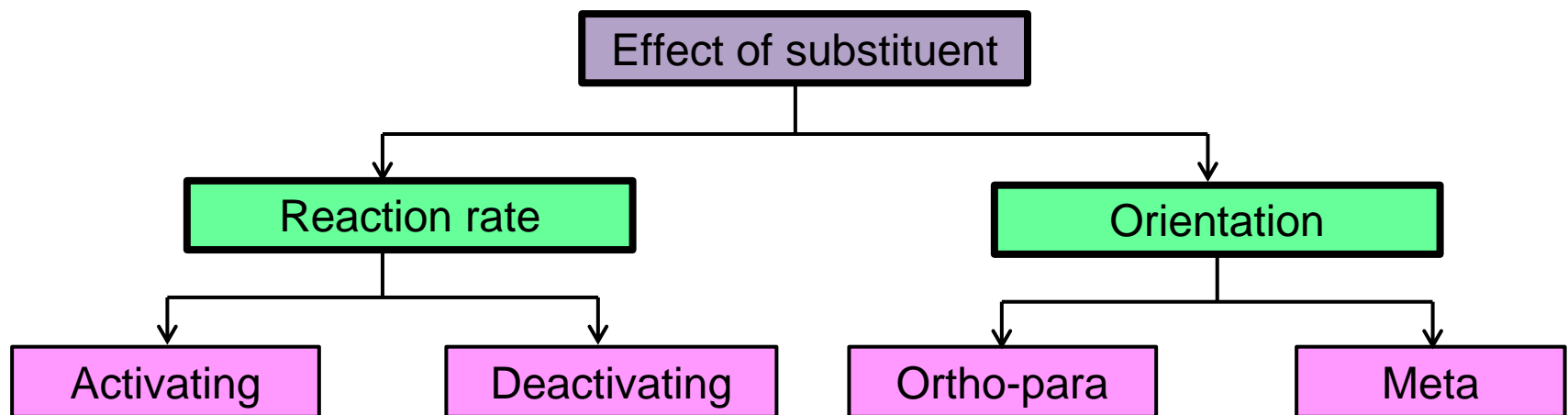


6.3 (c) The influence of *ortho*-*para* and *meta* directing substituents towards electrophilic aromatic substitution reaction.

i. Effect of Substituents on Electrophilic Aromatic Substitution

A substituent on the benzene ring affects 2 aspects of electrophilic aromatic substitution :

- a) Reaction rate
- b) Orientation



i. Reaction Rate

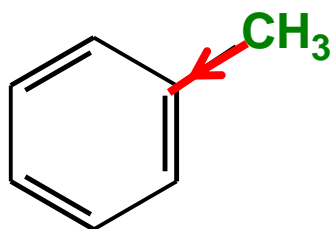
- A substituted benzene reacts **faster** or **slower** towards further substitution.
- Example: **more reactive** or **less reactive**

i. Activating Groups (activators)

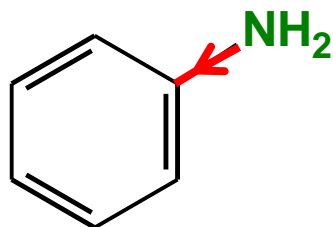
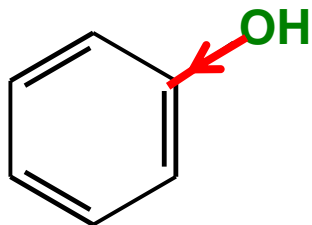
- **Activate** the benzene ring towards electrophilic attack, making it **more reactive** than benzene via Inductive Effect or Resonance Effect.
- **Electron-donating groups / electron-releasing groups** are activating groups

Example

Benzene rings that contain an **electron-donating group (activating group)**:



Alkyl group activates the benzene ring via Inductive Effect



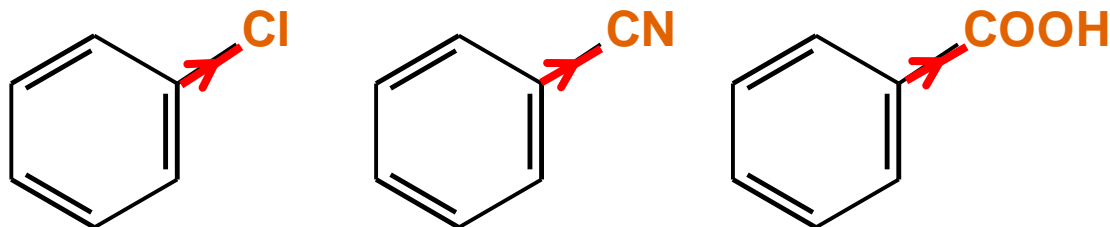
Hydroxy and amino groups activate the benzene ring via Resonance Effect

ii. Deactivating Groups (deactivators)

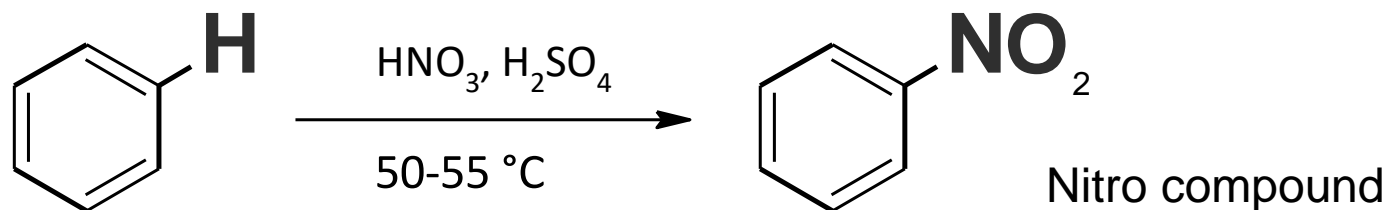
- Deactivate a benzene ring towards electrophilic attack, making it less reactive than benzene.
- Electron-withdrawing groups are deactivating groups.

Example

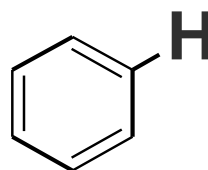
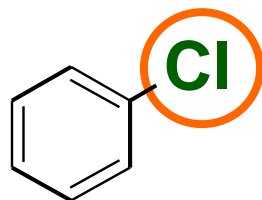
Benzene rings that contain an electron-withdrawing group (deactivating group):



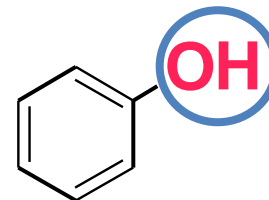
Example



Deactivating group



Activating group



Relative rate
of nitration

0.033

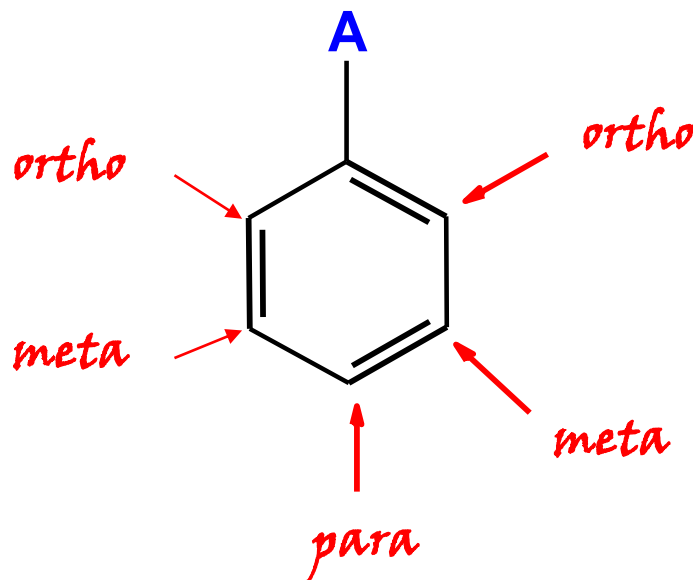
1

1000

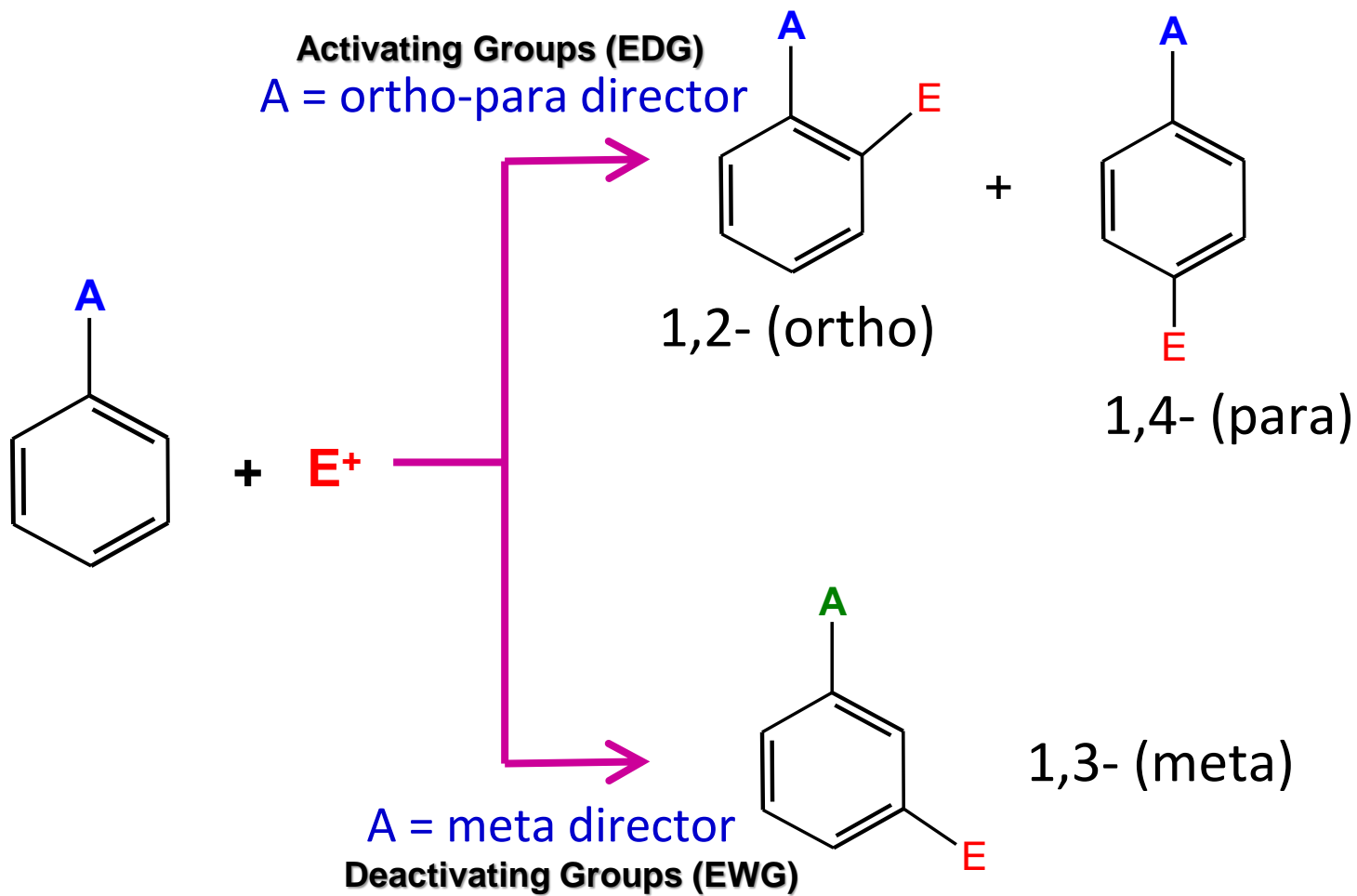
reactivity

ii. Orientation

The existing substituent on the benzene ring determines the **position of the second substituent**.

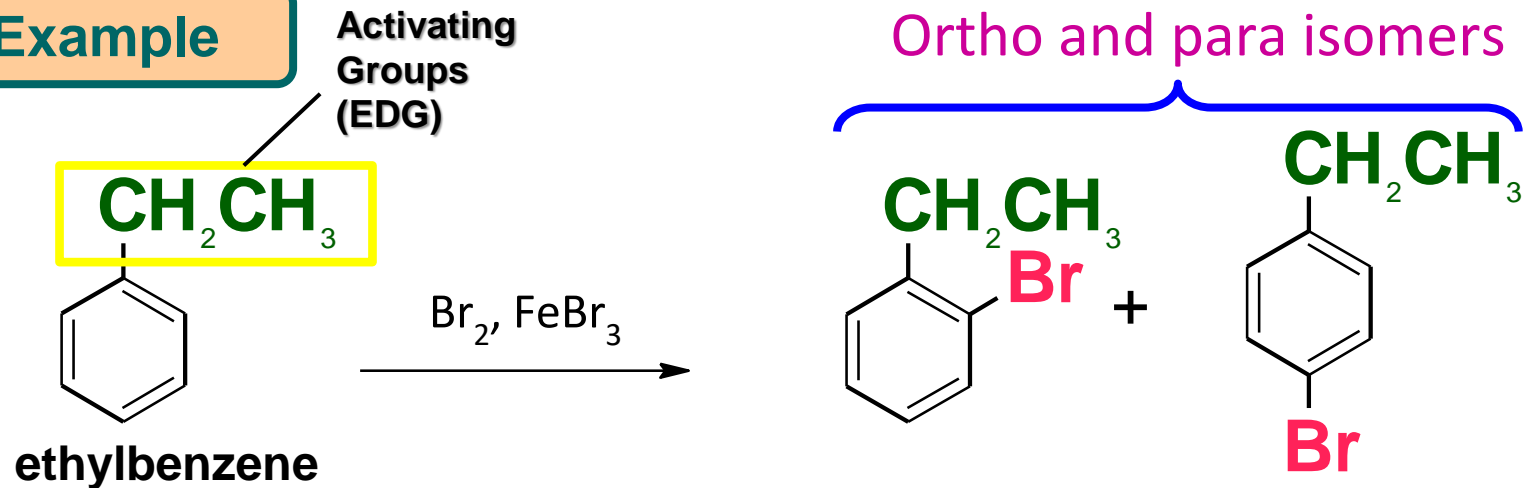


A = substituent

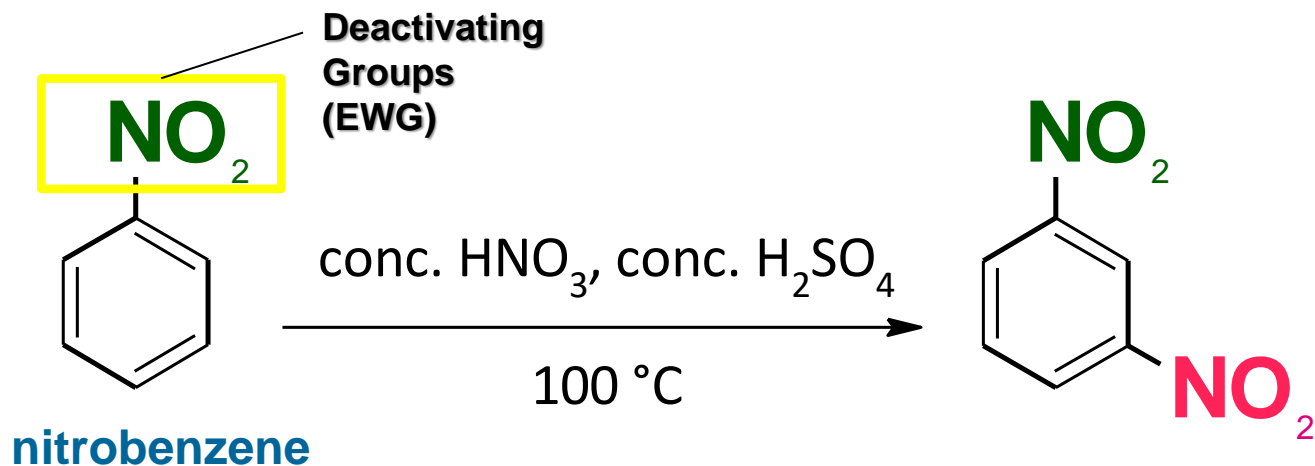


a) Ortho-para director

Example



ii. Meta director

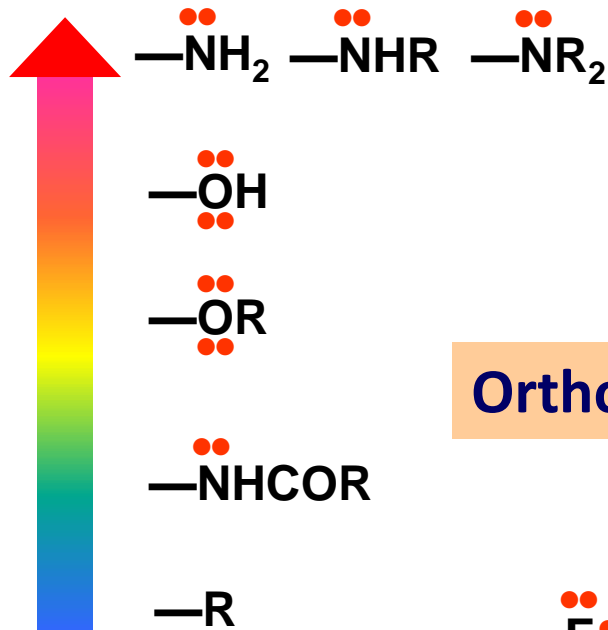


Thus,

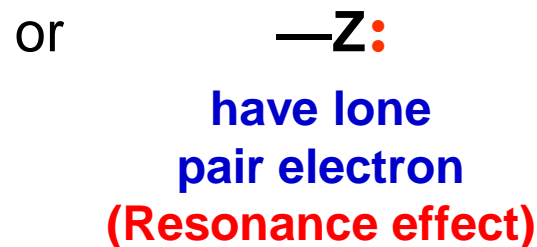
1. All ortho-para directors (except halogens) \Rightarrow activating groups.
2. All meta directors \Rightarrow deactivating groups.
3. The halogens are ortho-para directors but deactivating groups.

Ortho-para directors which are activating groups

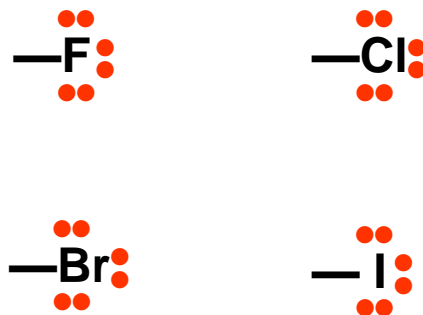
Increasing ring activation



General structure



Ortho-para directors which are deactivating groups



General structure :



Meta director which are deactivating groups



—CHO

—COR

—COOR

—COOH

—CN

—SO₃H

—NO₂

⁺
—NR₃

General structure:
—Y (δ^+ or +)

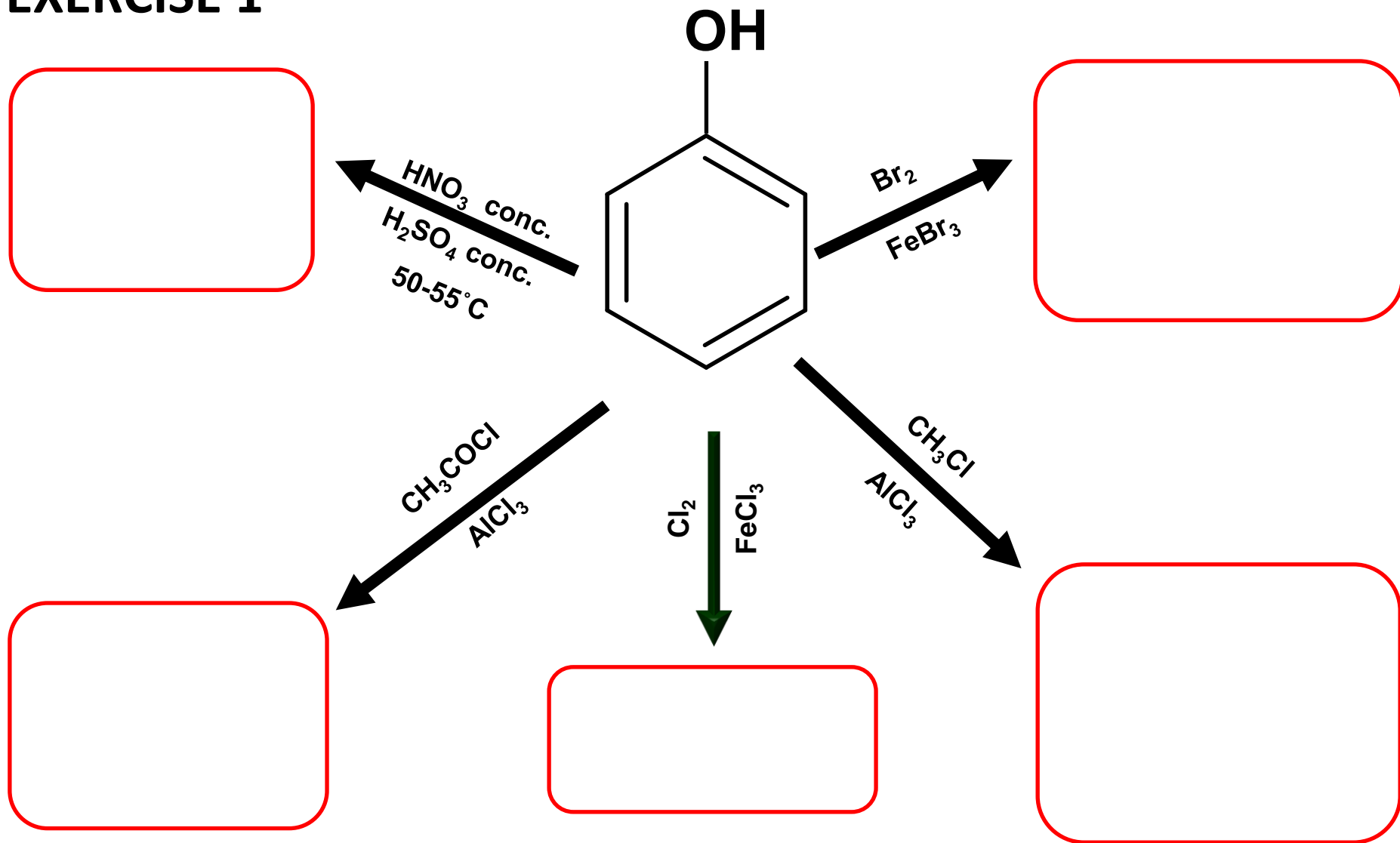
partial
charge

full
charge

Increasing ring deactivation

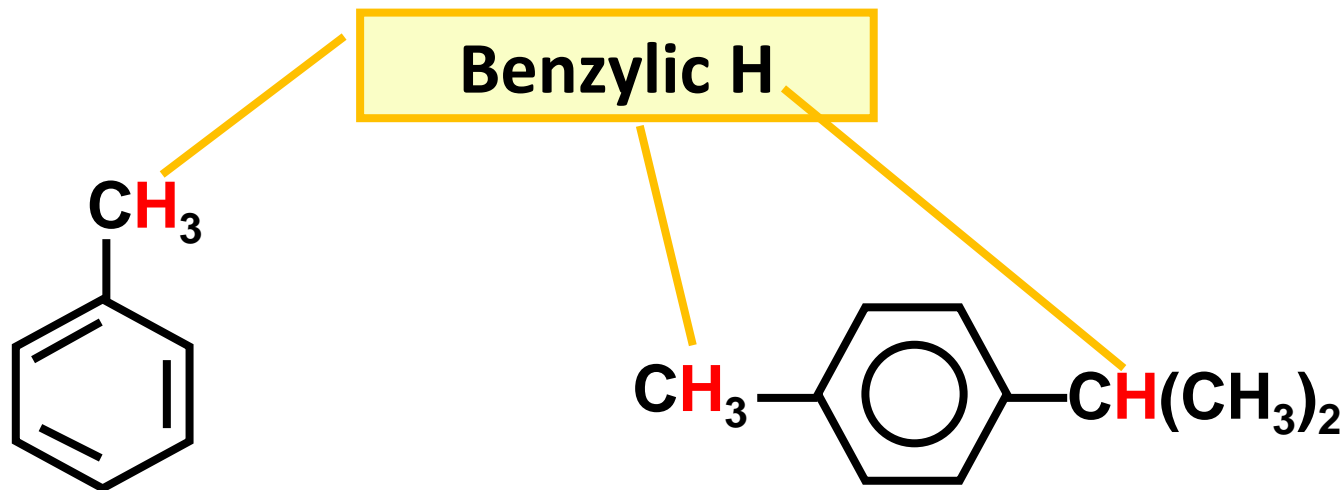
6.3 (d) Predict the product of electrophilic aromatic substitution of monosubstituted benzene.

EXERCISE 1



6.3 (e) Reactions of Alkylbenzene

(i) OXIDATION WITH HOT ACIDIFIED KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$

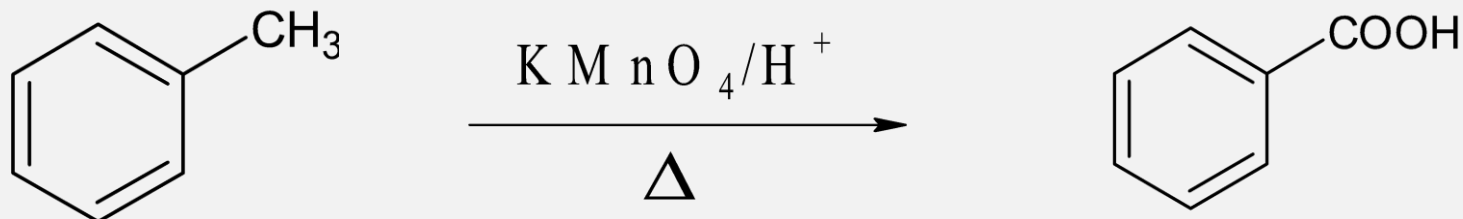


Benzylic hydrogen

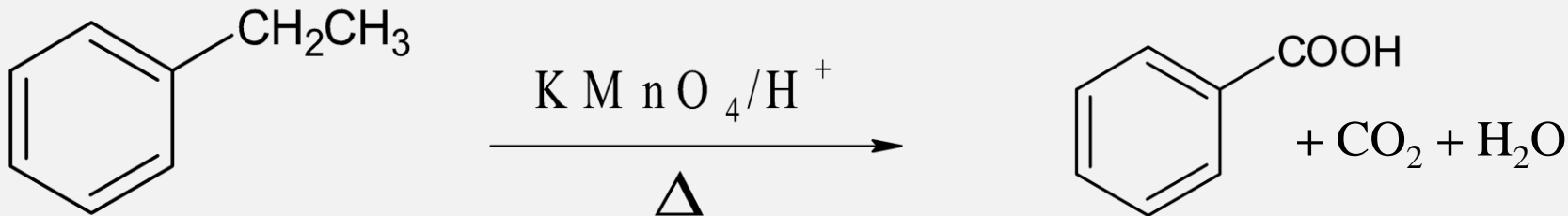
Hydrogen atom bonded to **a sp^3 hybridized carbon atom** that bonded to a benzene ring.

Reactions of Alkylbenzene

Example...

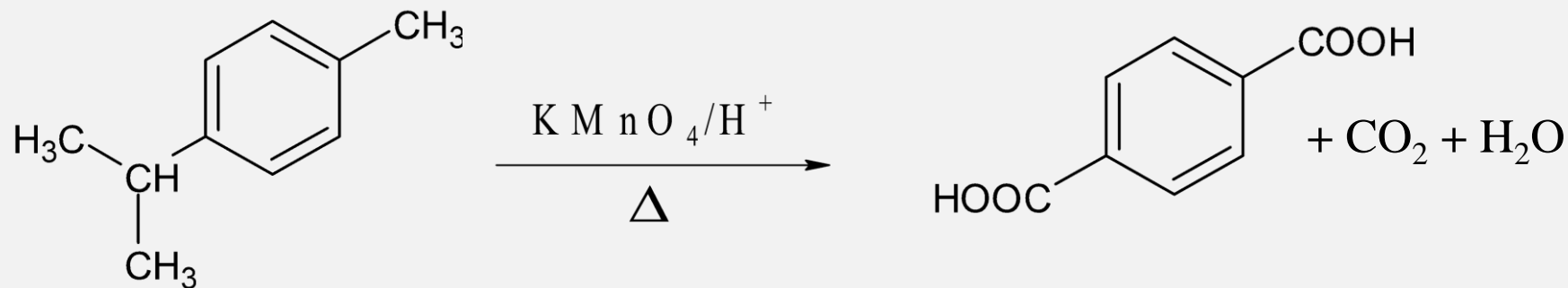


The alkylbenzenes with alkyl groups **other than methyl** will produce **benzoic acid, carbon dioxide and water**.

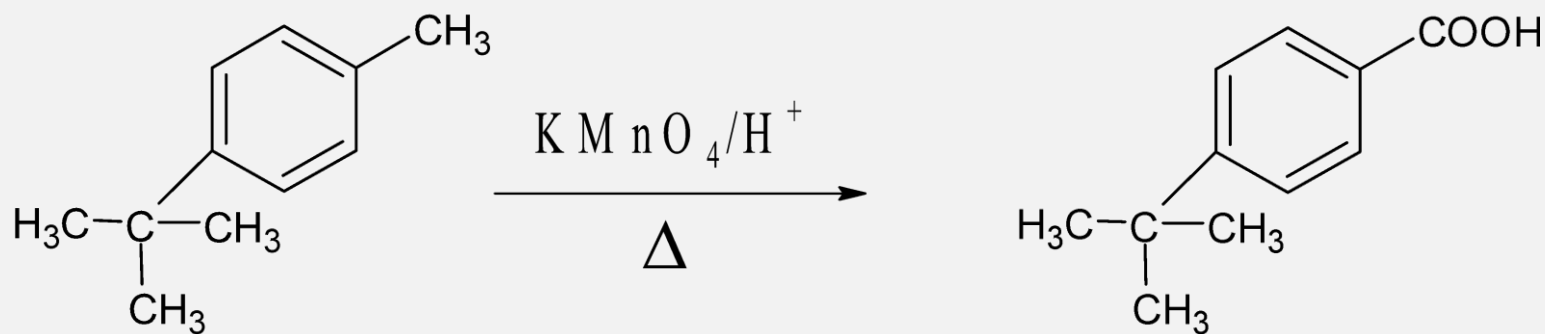


Reactions of Alkylbenzene

Example...



Compounds **without a benzylic H** are inert to oxidation.

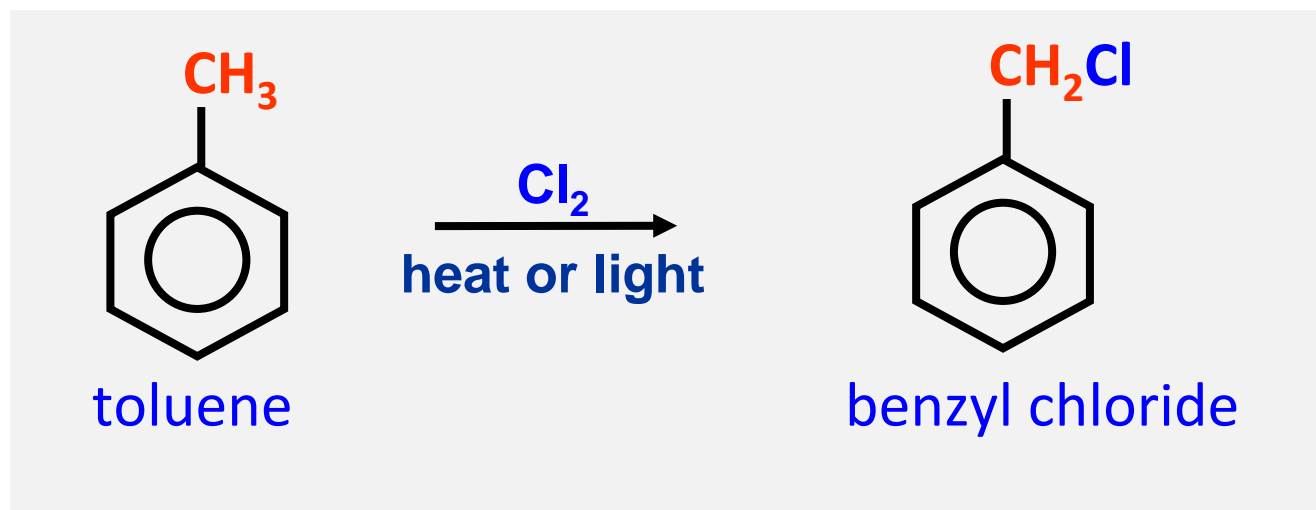


Reactions of Alkylbenzene

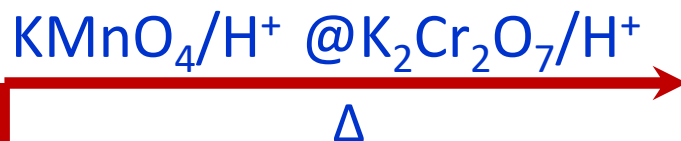
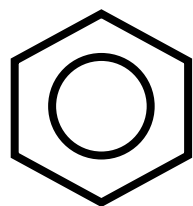
(ii) Halogenation (free radical substitution)

- Take place at **high temperature** or in the presence of **uv light**.
- Mechanism: **free-radical substitution**.
- Cl or Br replaces H atom of alkyl group.

Example...



Benzene vs Alkylbenzene



no reaction occur
benzene cannot undergo
oxidation



Where X: $\text{Cl}_2 @ \text{Br}_2$

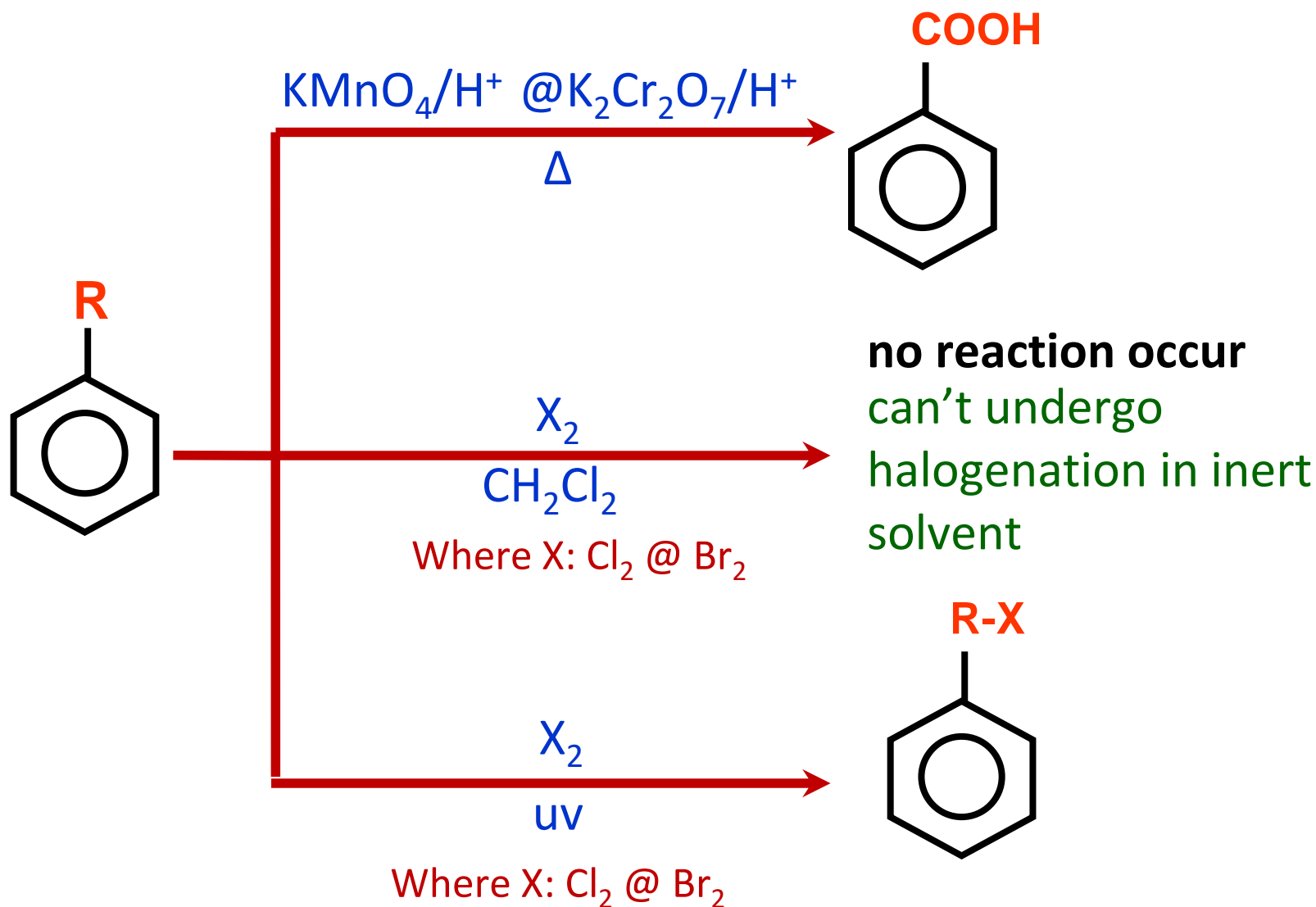
no reaction occur
benzene cannot undergo
halogenation in inert
solvent



Where X: $\text{Cl}_2 @ \text{Br}_2$

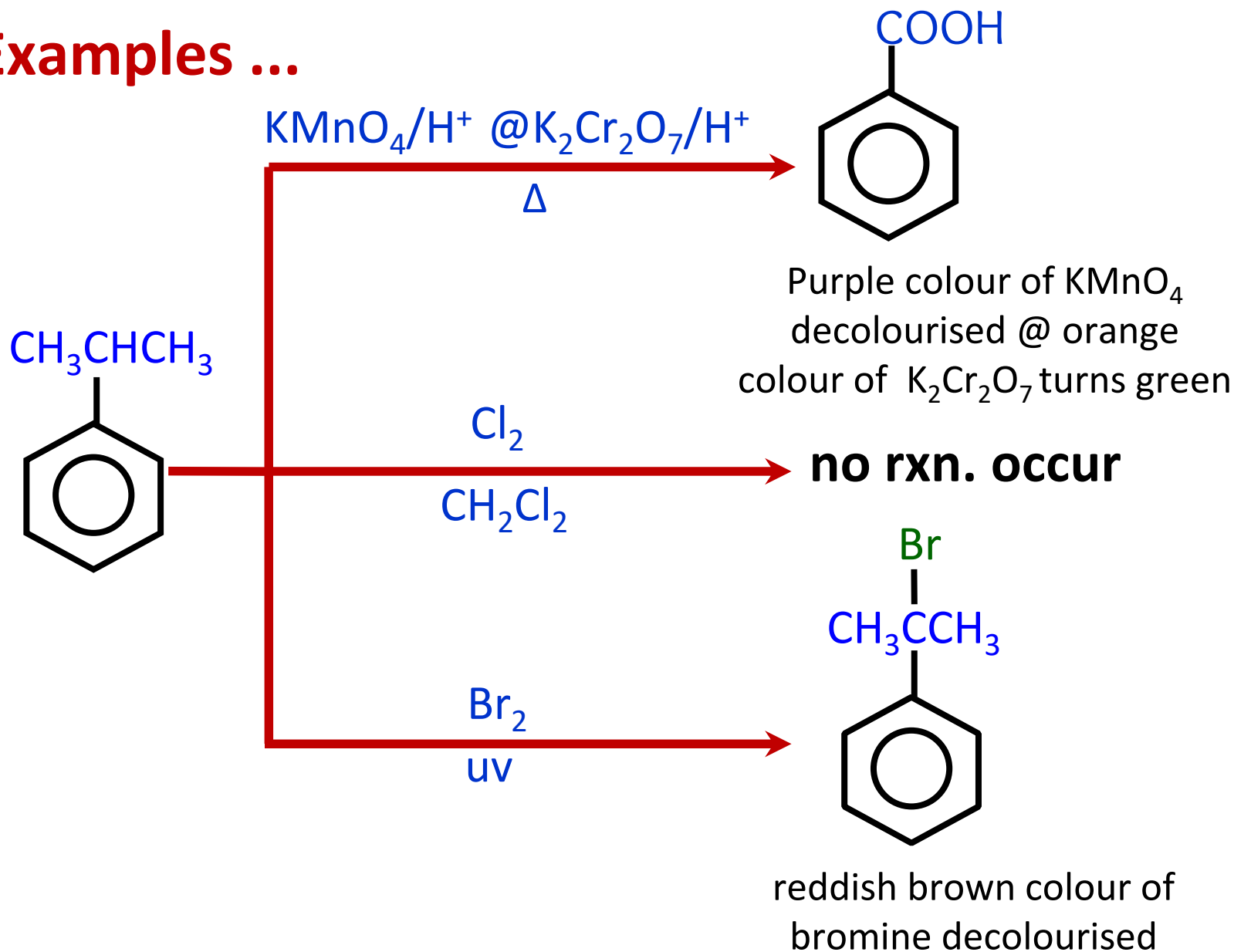
no reaction occur
benzene cannot undergo
halogenation under
sunlight

Benzene vs Alkylbenzene



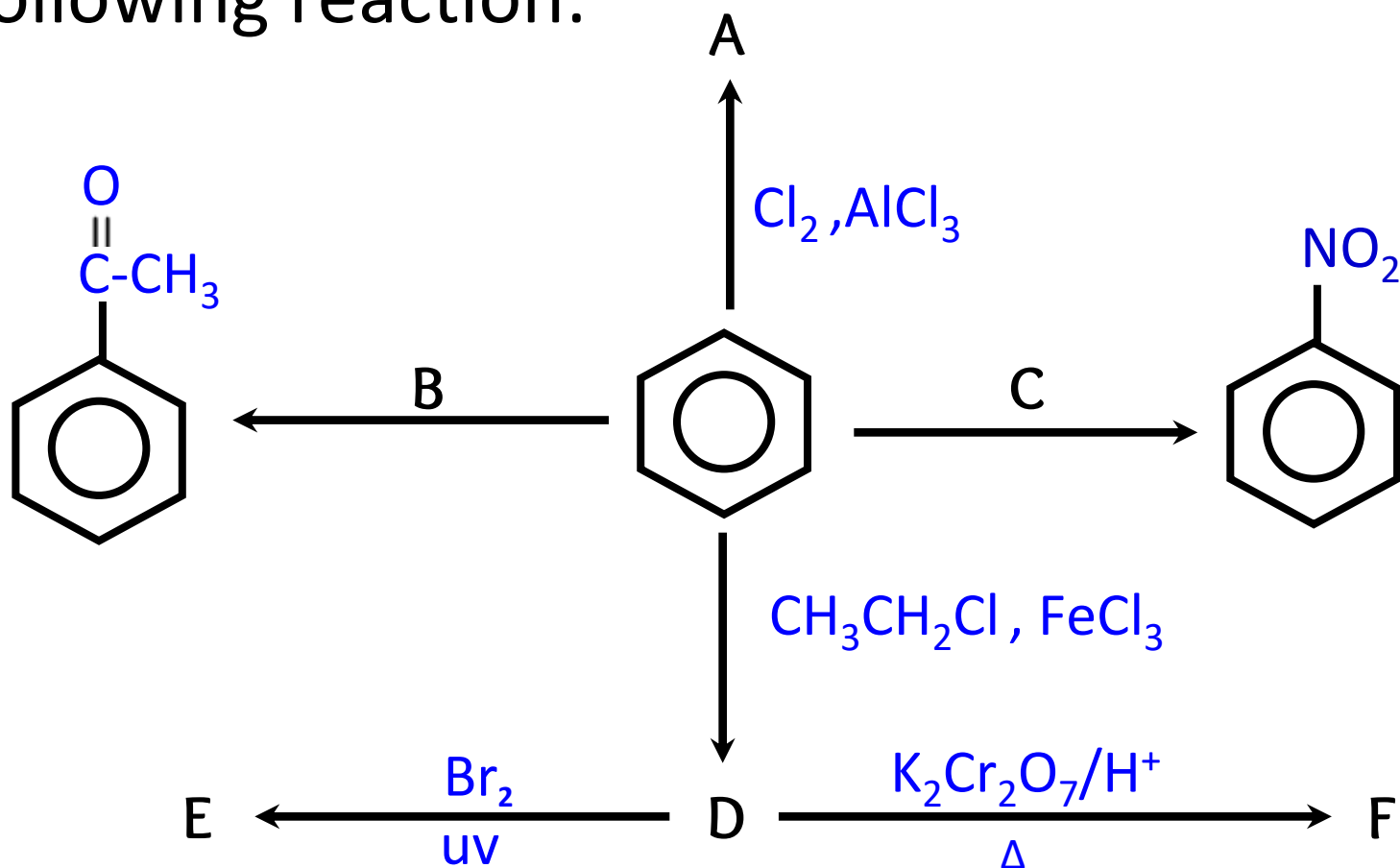
Benzene vs Alkylbenzene

Examples ...



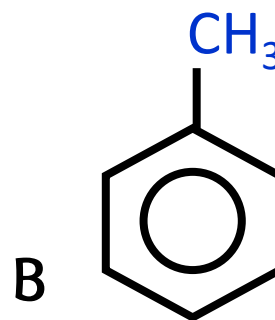
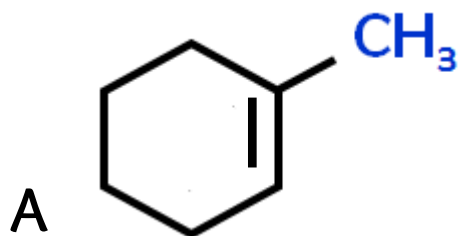
Exercise 1

Suggest the reagents and products formed for the following reaction:



Exercise 2

Compound **A** and **B** are hydrocarbon with the structural formula:



Name the compound **A** and **B**



Write the equation for the reaction between **B** and bromine under sunlight



The product of bromination of **B** depends on the reaction conditions. State the conditions and the product formed.

CHAPTER 6 : BENZENE AND ITS DERIVATIVES

BIL	TERM	DEFINITION
1.	Kekule structure	The carbons are arranged in a hexagon, suggested alternating double and single bonds between them. Each carbon atom has a hydrogen attached to it
2.	Aromaticity	A property of the conjugated cycloalkenes which enhances the stability of a molecule due to the delocalization of electrons present in the π - π orbitals.
3.	Electrophilic aromatic substitution	Organic reactions where an electrophile replaces an atom which is attached to an aromatic ring
4.	Friedel-Crafts alkylation	The replacement of an aromatic proton with an alkyl group.
5.	Friedel-Crafts acylation	The reaction of an arene with acyl chlorides or anhydrides using a strong Lewis acid catalyst.
6.	Monosubstituted benzene	When one of the positions on the ring has been substituted with another atom or group of atoms.