12 Extension Topic – Organic Chemistry
Arenes

GUIDING QUESTIONS

- What determines the shape of benzene?
- How does the reactivity of benzene compare to that of alkene and why?
- Which class of reagents does benzene react with and why? What types of reactions does benzene undergo and why? How does benzene react with an electrophile?
- What types of reactions do the alkyl side-chains of arenes undergo and why?
- How does the substituent on mono-substituted arenes determine the reactivity towards, and the substitution position of an incoming electrophile?

LEARNING OUTCOMES

At the end of the chapter, you should be able to:

11.1(d) **Describe** *sp*^{3} hybridisation, as in ethane molecule, ***sp*^{2} hybridisation, as in** ethene and **benzene** molecules, and *sp* hybridisation, as in ethyne molecule.

11.1(e) **Explain the shapes of, and bond angles in**, the ethane, ethene, **benzene**, and ethyne molecules in relation to σ and π carbon-carbon bonds

11.1(f) **Predict the shapes of, and bond angles in, molecules analogous to** the ethane, ethene, **benzene**, and ethyne molecules

11.3(h) Explain, in terms of delocalisation of π electrons, the difference between benzene and alkene
- (i) reactivity towards electrophiles
- (ii) preference of benzene to undergo substitution rather than addition reaction

11.3(i) Describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene
- (i) electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalysts)
- (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Bronsted-Lowry acid catalyst)
- (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)

11.3(j)
- (i) Describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example
- (ii) Describe the effect of the delocalisation of electrons in arenes in such reactions

11.3(k) Describe the chemistry of the alkyl side chain of benzene ring as exemplified by the following reactions of methylbenzene
- (i) free-radical substitution by chlorine and by bromine
- (ii) complete oxidation to give a benzoic acid

11.3(l) Predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

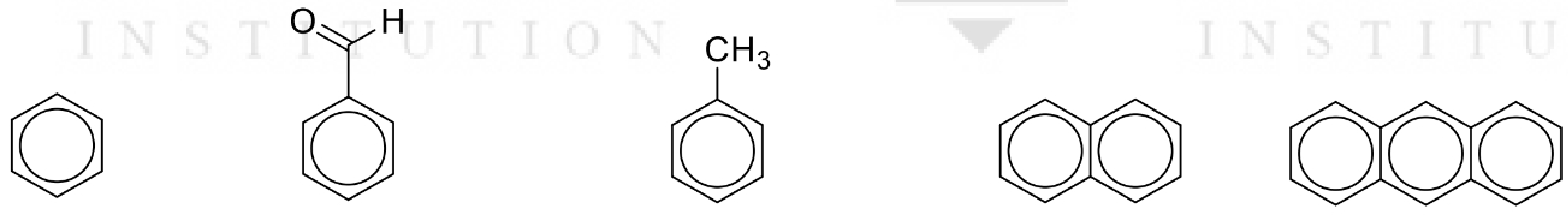
11.3(m) Apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

REFERENCES

1. Peter Cann & Peter Hughes (2002), *Chemistry for Advanced Level*, Chapter 27.
2. A. Burrows, J. Holman, A. Parsons, G, Pilling & G. Price (2009), *Chemistry^{3}*, Chapter 22.
3. John McMurry (2004), *Organic Chemistry*, Brooks/Cole, Chapters 15-16.
4. Philip S. Bailey, Jr. & Christina A. Bailey (2000), *Organic Chemistry – A Brief Survey of Concepts & Applications*, Prentice Hall, Chapter 6.
5. March’s Advanced Organic Chemistry (2007), Wiley-interscience, A John Wiley & Sons Inc. Publication, Chapter 19, Page 1745-1747.

1 INTRODUCTION

Arenes are aromatic hydrocarbons. **Aromatic compounds are those possessing the ring structure of benzene or its analogues.** The name “aromatic” originates from the past when many of the known members of the family had pleasant smells, such as benzaldehyde (from cherries, peaches and almonds) and methylbenzene (from Tolu balsam). As chemists discovered more aromatic hydrocarbons, they found that other members of the group possess unpleasant smells and are extremely carcinogenic, yet the name remained. Today, aromaticity is used to describe the extra stability of benzene and its structural relatives.



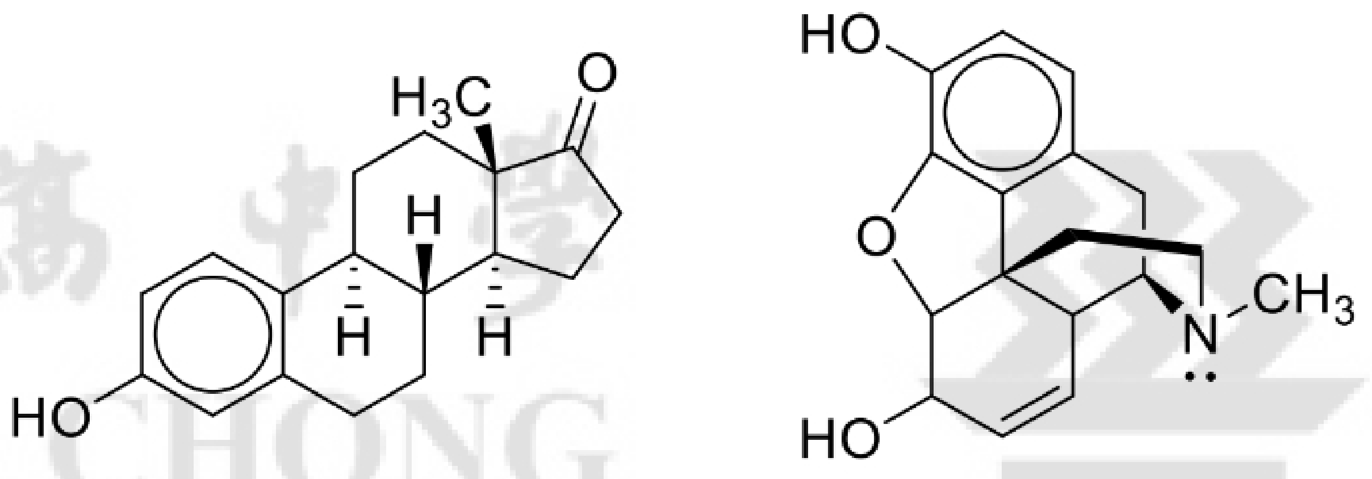
benzene benzaldehyde methylbenzene naphthalene anthracene

Figure 1. Examples of aromatic compounds.

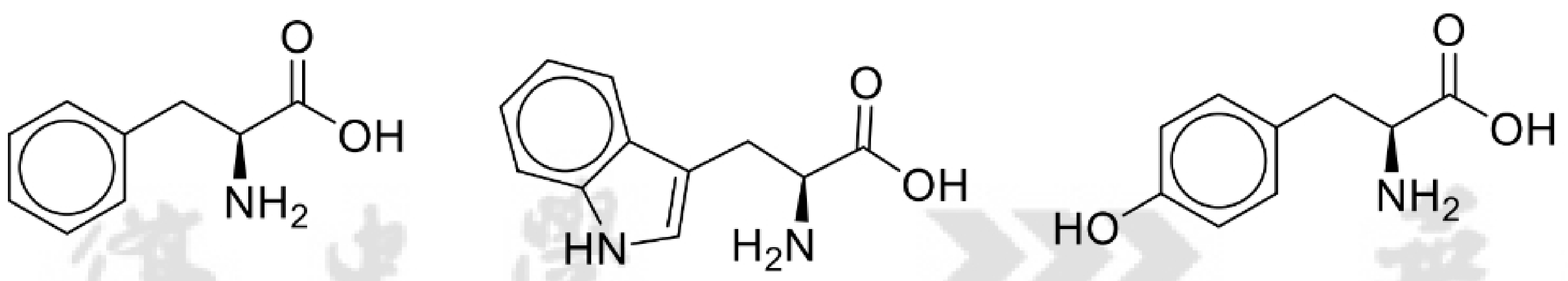
Simple aromatic compounds come from two main sources: coal and petroleum. Coal is made up primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal produces a mixture of volatile products such as benzene, methylbenzene, naphthalene, and anthracene, which are then separated using fractional distillation.

Petroleum, unlike coal, contains only a few aromatic compounds and consists largely of alkanes. However, alkanes, when passed over a catalyst at about 500 °C under high pressure, can be converted to their aromatic analogues via dehydrogenation and cyclisation (for example, heptane C_7H_{16} can be converted into methylbenzene C_7H_8).

Many compounds from natural sources as well as many synthetic drugs are aromatic in part. Similarly, each of the three aromatic amino acids phenylalanine, tryptophan, and tyrosine, also serve as the basic building blocks of proteins.



estrone (a hormone) morphine (a painkiller)



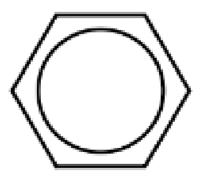
phenylalanine tryptophan tyrosine

Figure 2. Examples of compounds containing aromatic rings.

1.1 Nomenclature

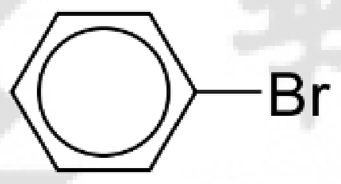
1.1.1 Benzene

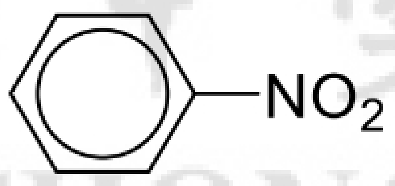
Benzene has a molecular formula of C_6H_6. The benzene ring is often represented using the skeletal formula as shown below.

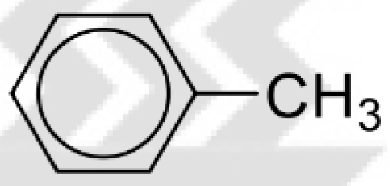

benzene

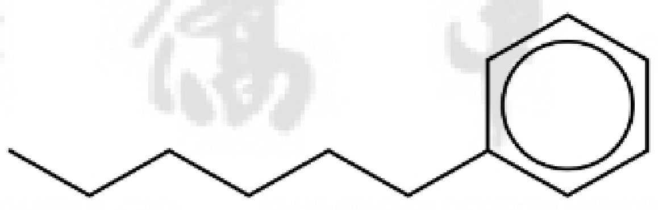
1.1.2 Mono-substituted benzenes

When one H atom of benzene is replaced by another atom or group of atoms of less or equals to 6 carbon atoms, the benzene ring is considered the **parent** and a suffix – **benzene** is employed in naming.

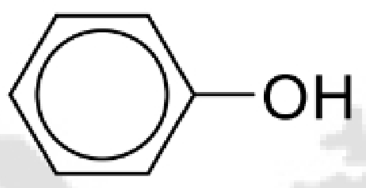

bromobenzene

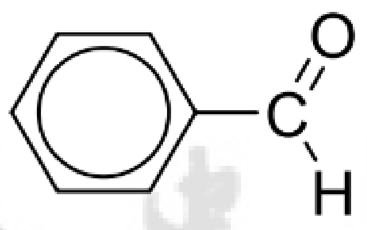

nitrobenzene

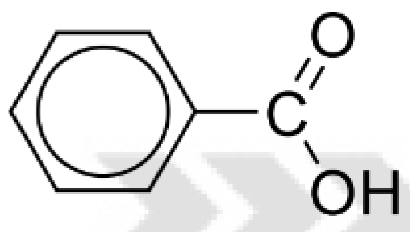

methylbenzene

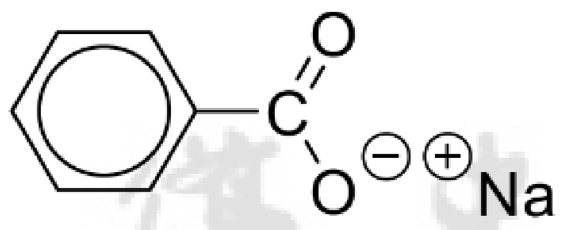

hexylbenzene

Some mono-substituted benzenes are more common such that their conventional names are used instead.

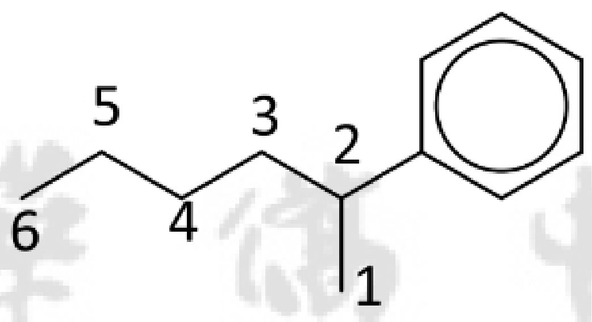

phenol


benzaldehyde

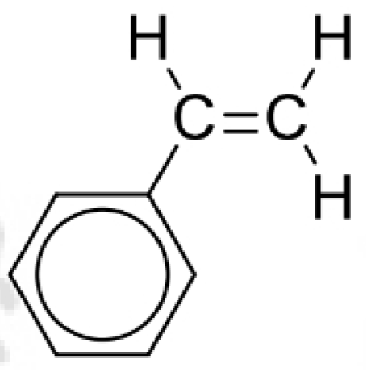

benzoic acid

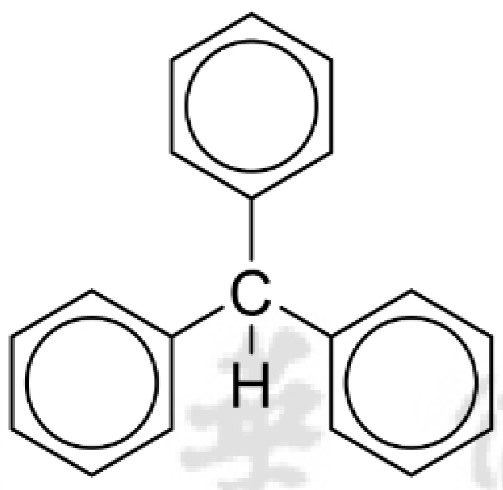

sodium benzoate

When the substituent is an alkyl group of more than 6 carbon atoms, or when it is too complex to be named conveniently as a prefix, benzene is considered as a **substituent** and named as a prefix – **phenyl**.



2-phenylhexane

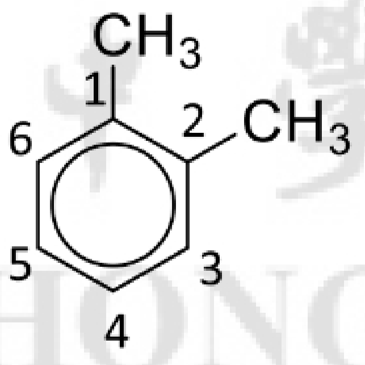

phenylethene


triphenylmethane

1.1.3 Multi-substituted benzenes

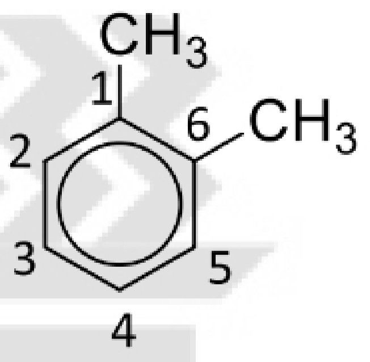
Multi-substituted benzenes are named by numbering the position of each substituent so that the lowest possible numbers are used.

E.g.



1,2-dimethylbenzene

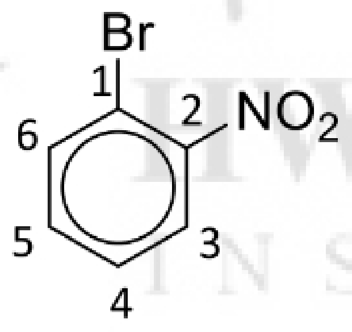
(CORRECT naming)



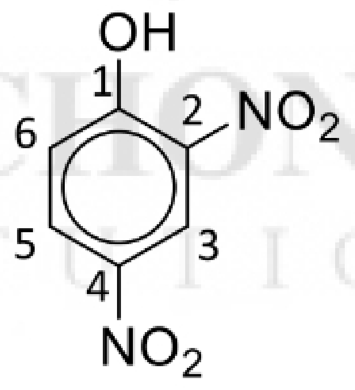
1,6-dimethylbenzene

(WRONG naming)

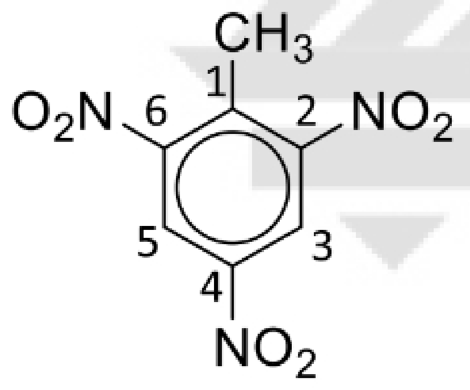
If the substituents are different, one of them is deemed the principal functional group (at position 1), in the order of precedence $-CO_2H > -OH > -CH_3 > -\text{halogen} > -NO_2$. The priority list is given in Topic 8 Introduction. The rest of the substituents are named in alphabetical order.



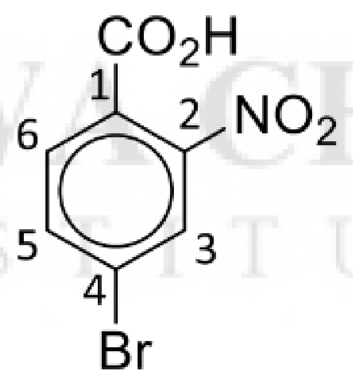
2-nitrobromobenzene



2,4-dinitrophenol



2,4,6-trinitromethylbenzene (TNT)



4-bromo-2-nitrobenzoic acid

Self-Practice 1.1

Draw the structure for each of the following compounds:

a) 4-bromo-2-nitromethylbenzene **b)** 3-methyl-2-phenylpentane

2 PHYSICAL PROPERTIES AND USES OF BENZENE

Physical properties

Benzene is a **colourless liquid** at rtp. It is toxic and carcinogenic and should therefore be handled cautiously if used in the laboratory. It is highly volatile and flammable.

Melting and boiling points

Melting point: 5.5 °C; boiling point: 80 °C
Being a non-polar molecule, only a small amount of energy is required to overcome the **weak dispersion forces** between molecules; hence benzene has **low** melting and boiling points.

Solubility

Being a non-polar molecule, benzene is **insoluble** in (or immiscible with) polar solvents (e.g. water), but **soluble** in non-polar solvents (e.g. hexane, CCl_4). It could be used as a non-polar solvent.

Uses

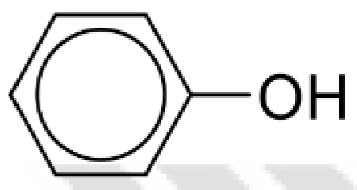
Prior to the 1920's, benzene was frequently used as an industrial solvent, especially for degreasing metal. As its toxicity became obvious, other solvents such as methylbenzene replaced benzene in most applications. By far, the largest use of benzene is as an **intermediate to make other chemicals**. The most widely produced derivatives of benzene are styrene (phenylethene), which is used to make polymers and plastics, phenol for resins and adhesives (via cumene i.e. isopropylbenzene), and cyclohexane, which is used in the manufacture of nylon.

Health effects

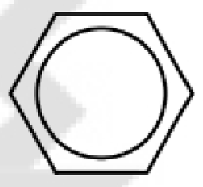
The major effect of benzene from chronic (long term) exposure is to the blood. Benzene causes harmful effects on the bone marrow and can cause a decrease in red blood cells leading to anaemia. Benzene is a known carcinogen to human beings. Long-term exposure to high levels of benzene in the air can cause leukaemia, cancer of the blood-forming organs.

Self-Practice 2.1

a) Explain the difference in the boiling point of phenol,



(bp 182 °C) with that of benzene,



(bp 80 °C).

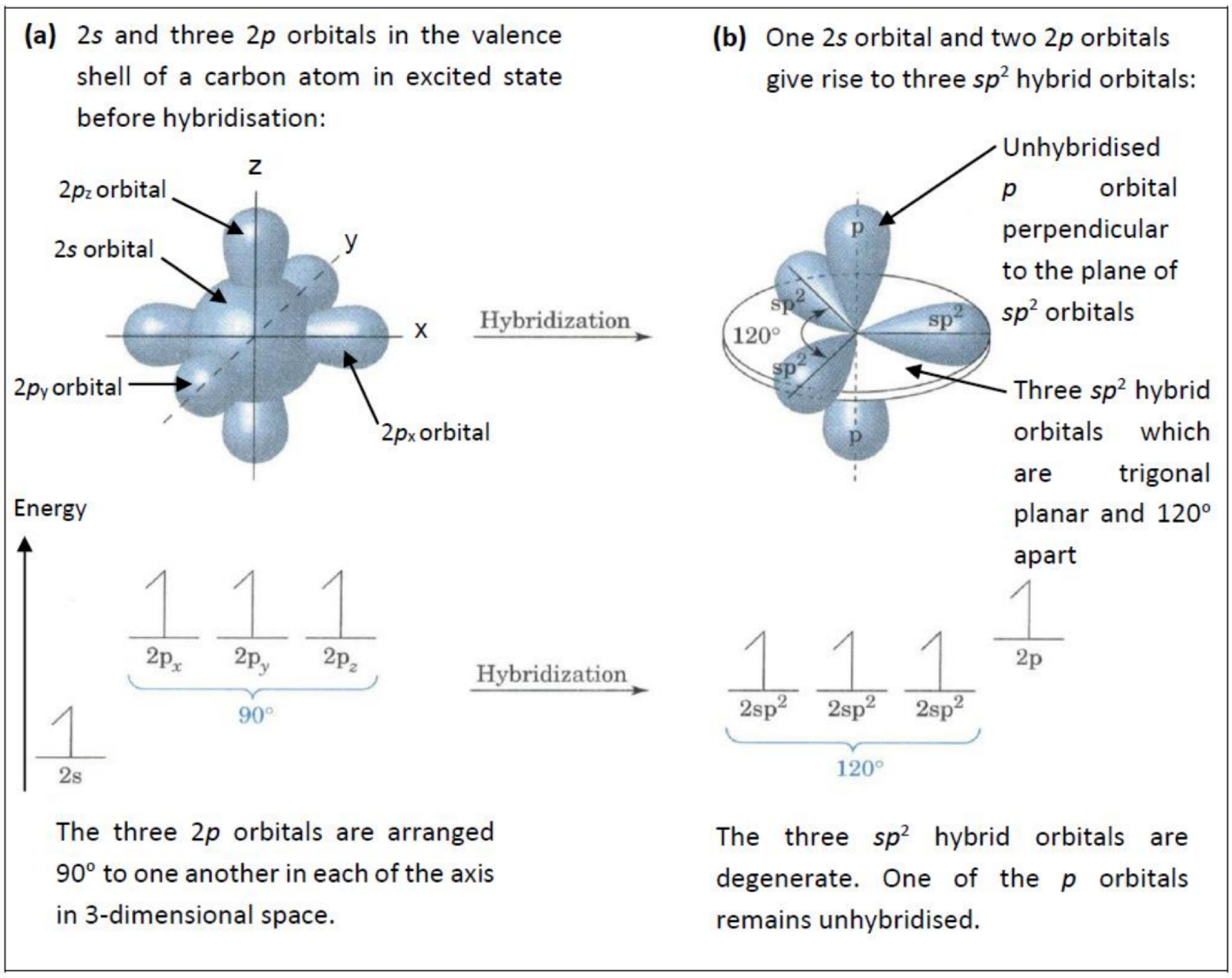
b) Explain, in terms of intermolecular forces and energy, why benzene is insoluble in water. (You may refer to Topic 2 Chemical Bonding for the discussion on solubility.)

3 BENZENE

3.1 Structure of benzene

Benzene is a **planar**, aromatic molecule where all carbon atoms that make up the benzene ring are ***sp*^{2} hybridised**. Recall from Topic 2 Chemical Bonding where you also learnt about *sp*^{2} hybridisation in the ethene molecule.

In benzene, each carbon is bonded to two other carbons and one hydrogen. The geometry around **each carbon atom in benzene is trigonal planar with C–C–C bond angle of 120°**. The hybridisation theory proposes that one electron in the 2*s* orbital (of carbon) is promoted to the empty 2*p* orbital to give 4 unpaired electrons in an excited state. Mixing one s and two p orbitals gives three *sp*^{2} hybrid orbitals directed at 120° to each other. All three *sp*^{2} hybrid orbitals are identical in shape and energy.



(a) 2*s* and three 2*p* orbitals in the valence shell of a carbon atom in excited state before hybridisation:

(b) One 2*s* orbital and two 2*p* orbitals give rise to three *sp*^{2} hybrid orbitals:

The three 2*p* orbitals are arranged 90° to one another in each of the axis in 3-dimensional space.

The three *sp*^{2} hybrid orbitals are degenerate. One of the *p* orbitals remains unhybridised.

Figure 3. (a) 2s and three 2p orbitals in a carbon atom in excited state before hybridisation (b) sp^2 *hybridisation of carbon in benzene.*

Carbon atoms in the ring are bonded to one another and to their hydrogen atoms by **σ bonds**. The σ bond formed between two carbon atoms occurs via the head-on overlap between one sp^2 hybrid orbital of one carbon atom with one sp^2 hybrid orbital of the adjacent carbon atom. The σ bond formed between one carbon atom and one hydrogen atom occurs via the head-on overlap between one sp^2 hybrid orbital of one carbon atom with the 1*s* orbital of the adjacent hydrogen atom.

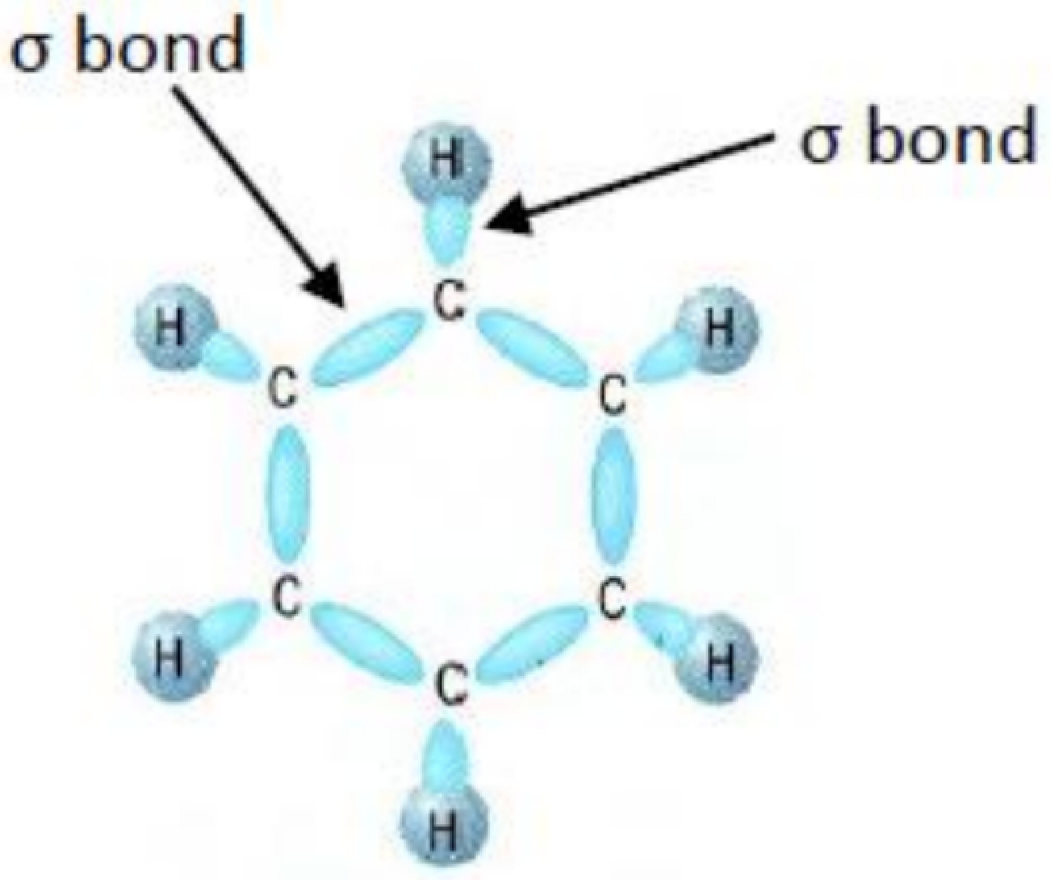
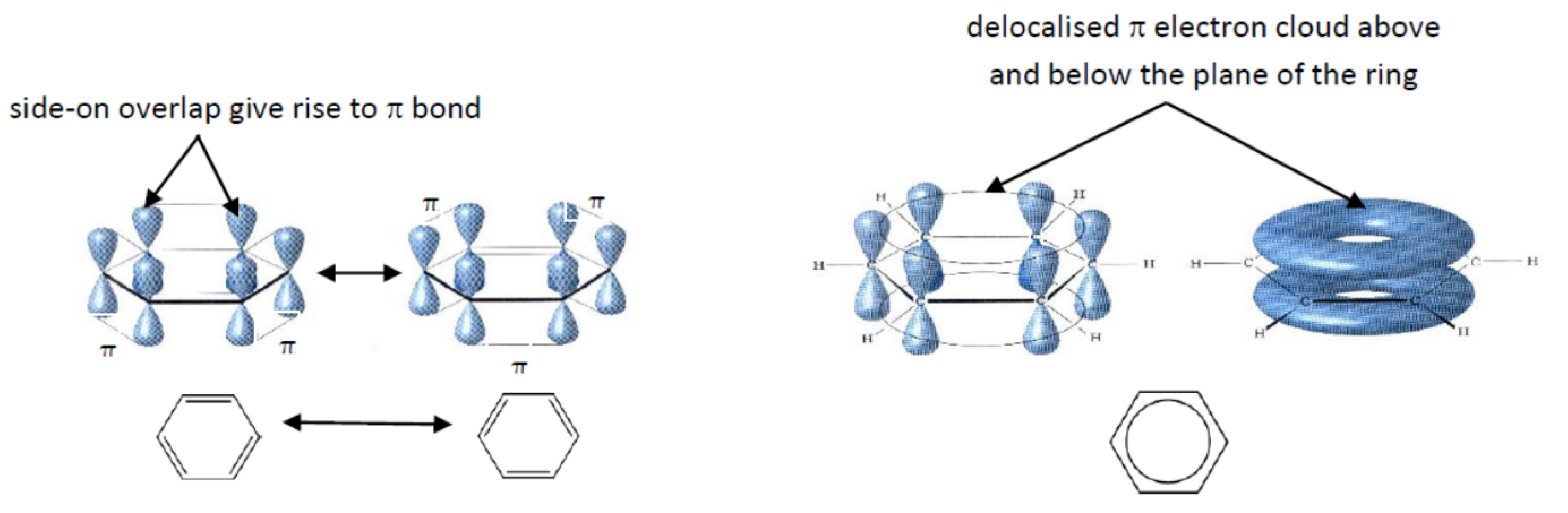


Figure 4. σ bonds between two carbon atoms and between carbon and hydrogen atoms in benzene.

The unhybridised *p* orbital that is perpendicular to the plane of the ring overlaps side-on with the unhybridised *p* orbitals on adjacent carbon atoms. The overlapping *p* orbitals produce two continuous rings of π electrons above and below the plane of the benzene ring, known as the **delocalised π electron cloud**. The six electrons found in these delocalised π electron cloud are free to move throughout the entire π electron cloud, so the electrons are said to be delocalised.



Two resonance structures of benzene

Each individual resonance structure seems to imply that benzene has alternating single and double carbon-carbon bonds, but neither resonance structure is the correct structure of benzene by itself.

Accepted structural formula

True structure of benzene is a hybrid of the resonance structures where all six carbon-carbon bonds are equivalent.

The delocalised π electron cloud is represented as a circle.

Figure 5. Delocalised π electron clouds in benzene.

3.2 Implications of π electron cloud delocalisation (Independent Learning subtopic)

Due to the delocalised π electron cloud in benzene, **all carbon-carbon bond lengths in benzene are equal**. This creates a planar, regular hexagonal shape. X-ray measurements of benzene showed that all the carbon-carbon bonds are identical in length and is intermediate between a carbon-carbon single bond length and a carbon-carbon double bond length. The bond energy of carbon-carbon bond in benzene is also between a carbon-carbon single bond energy and a carbon-carbon double bond energy.

carbon-carbon bond	bond length / nm	bond energy / kJ mol^{-1}
C–C bond	0.154	350
carbon-carbon bond in benzene	**0.139**	**520**
C=C bond	0.134	610

Table 1. Different types of carbon-carbon bond lengths and bond energies.

The delocalisation of the π electron cloud results in **resonance stabilisation**, giving rise to the **extra stability of benzene**. This extra stability of benzene is also known as the aromaticity of benzene. We can get a quantitative idea of benzene's stability from the comparison of various enthalpy change of hydrogenation. The experimentally determined enthalpy change of hydrogenation of cyclohexene is −118 kJ mol^{-1}. The experimentally determined enthalpy change of hydrogenation of cyclohexa-1,4-diene is −232 kJ mol^{-1}, which is approximately twice of the experimentally determined enthalpy change of hydrogenation of cyclohexene. Hence the theoretical prediction for benzene's enthalpy change of hydrogenation, based on the model of 3 alternating C–C and C=C bonds (i.e. hypothetical cyclohexatriene), is –354 kJ mol^{-1} (−118 kJ mol^{-1} × 3). However, the experimentally determined enthalpy change of hydrogenation of benzene was found to be –205 kJ mol^{-1}. Hence, benzene is estimated to be more stable than the hypothetical cyclohexatriene by about 354 – 205 = 149 kJ mol^{-1}. The stabilisation of 149 kJ mol^{-1} is known as the stabilisation energy, the delocalisation energy or the resonance energy.

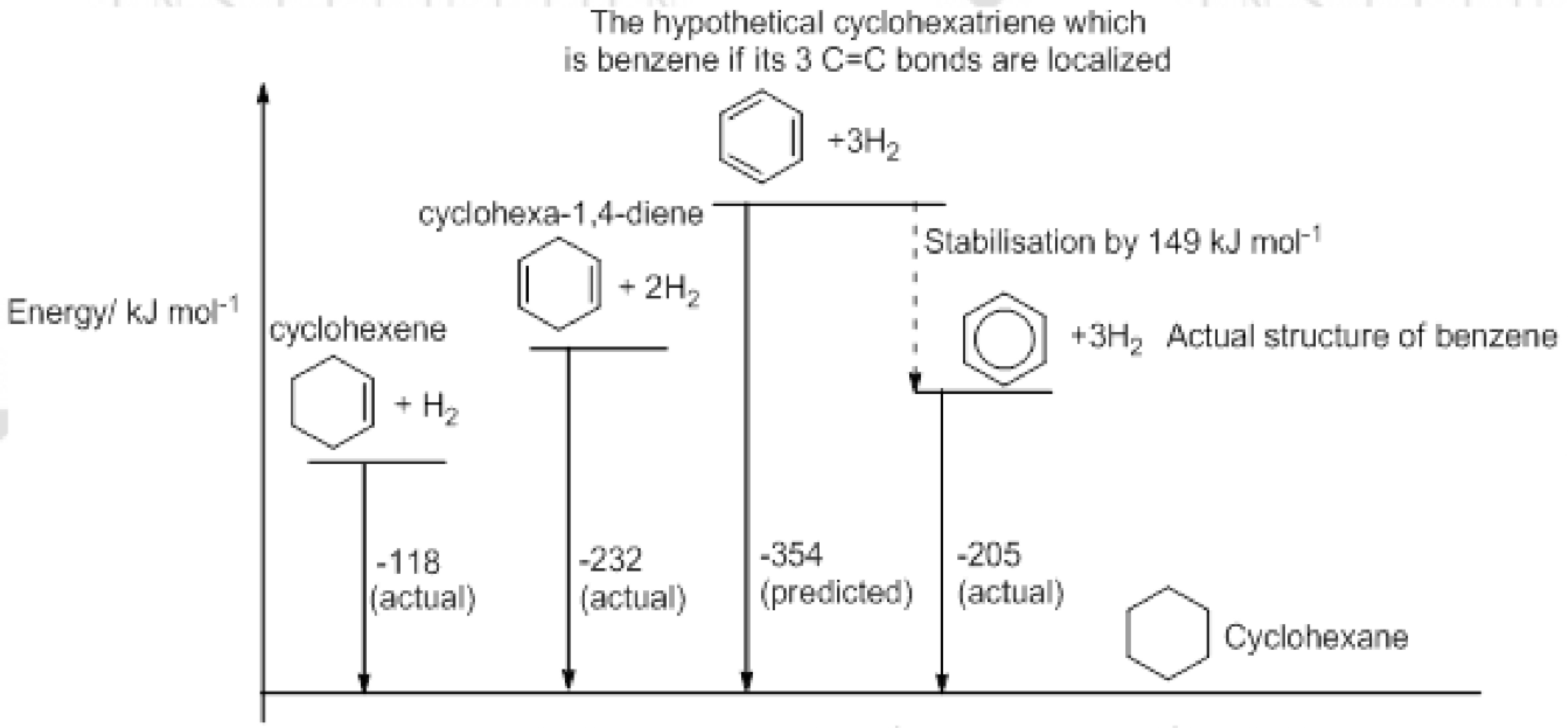
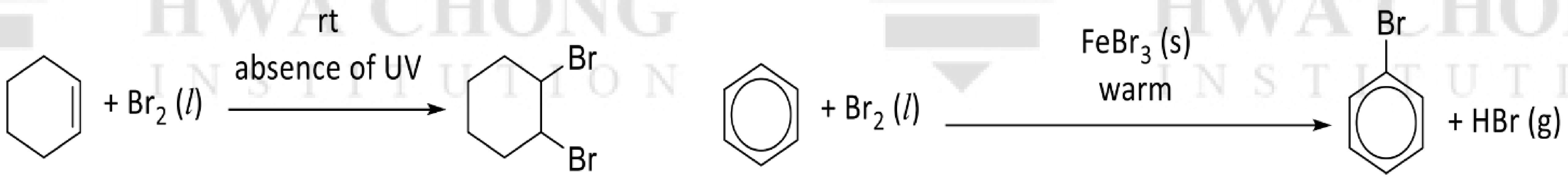


Figure showing energy level diagram for hydrogenation of cyclohexene, cyclohexa-1,4-diene, the hypothetical cyclohexatriene and actual benzene

Figure 6. Energy level diagrams for hydrogenation of cyclohexene, cyclohexa-1,4-diene, the hypothetical cyclohexatriene and actual benzene

Similar to electron-rich alkenes, π electrons in benzene attracts electrophiles (electron-deficient species). Although benzene is unsaturated, it does not undergo electrophilic addition like alkenes. As a result of the resonance stabilisation due to the delocalisation of the π electron cloud, **benzene undergoes electrophilic substitution** where one or more hydrogen atoms can be substituted by electrophiles. Electrophilic addition destroys the delocalised π electron cloud and this requires a significant amount of energy, which is highly unfavourable. Benzene preferentially undergoes electrophilic substitution reactions, which preserve its aromaticity. The following shows an example of the electrophilic addition in alkenes and the electrophilic substitution in arenes, respectively.



Due to resonance stabilisation from π electron cloud delocalisation, **π electron cloud in benzene is less susceptible to attack by electrophiles than C=C in alkenes. As a result, benzene requires a stronger electrophile to react as compared to alkenes.** For example, electrophilic addition of cyclohexene using liquid bromine as electrophile can be carried out at room temperature and without a catalyst, whereas electrophilic substitution of benzene with liquid bromine requires warming, and $FeBr_3$ as a Lewis acid catalyst to generate strong electrophile Br^+ (Refer to Section 4.2). In the slow step of electrophilic substitution, the addition of electrophile Br^+ to benzene give a carbocation intermediate which requires high activation energy due to the loss of aromatic stability. Hence benzene reacts with electrophile slower than alkenes.

Self-Practice 3.1

a) Consider cyclohexane, cyclohexene and methylbenzene, is methylbenzene the only compound that contains *sp*^{2} hybridised carbon atoms? Explain your answer.

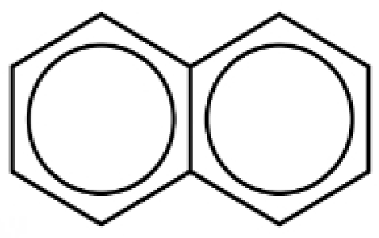
[Modified from PromoHCI09/I/16]

b) Which property does benzene have as a consequence of the delocalised electrons present in the molecule?

A It is a good conductor of electricity.
B It is susceptible to attack by nucleophilic reagents.
C Addition reactions of benzene take place more readily than substitution.
D The carbon-carbon bond length is between that of a C–C bond and a C=C bond.

[PromoHCI09/I/19]

c) Naphthalene is an aromatic compound with the following structure.



i) How many π electrons does naphthalene have?
ii) Is naphthalene a planar molecule? Explain your answer.

iii) Draw all the hydrogen atoms on naphthalene.

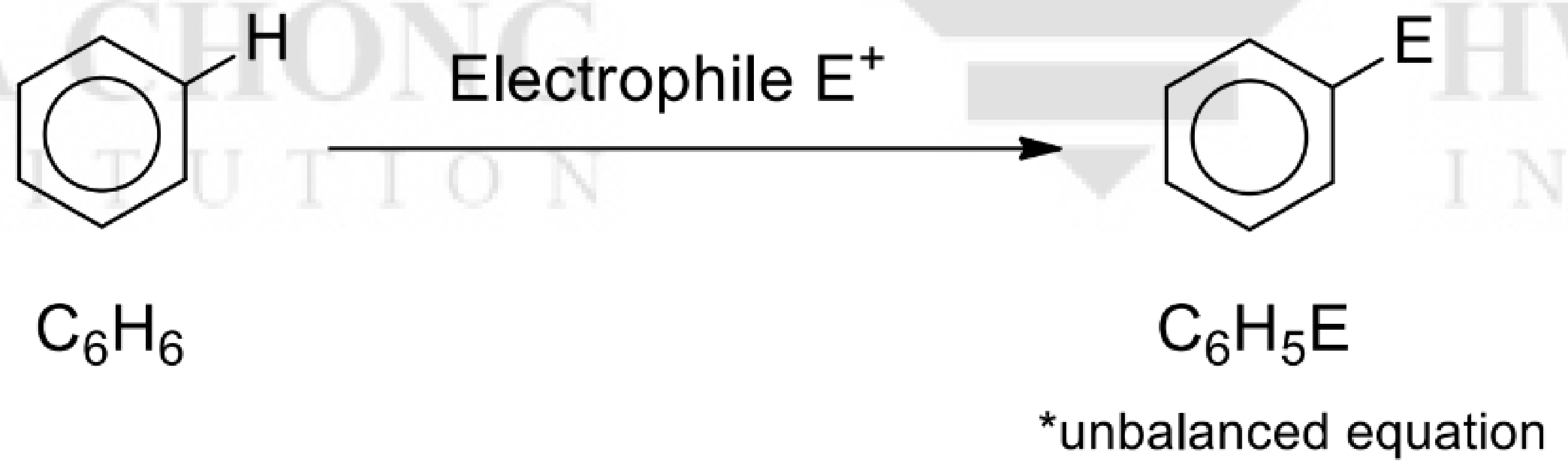
[Modified from PrelimRI12/I/21]

4 Reactions of Benzene

4.1 Electrophilic substitution reaction

Aromatic compounds like benzene undergo electrophilic substitution reactions where a hydrogen atom bonded to the benzene ring is substituted by an electrophile.

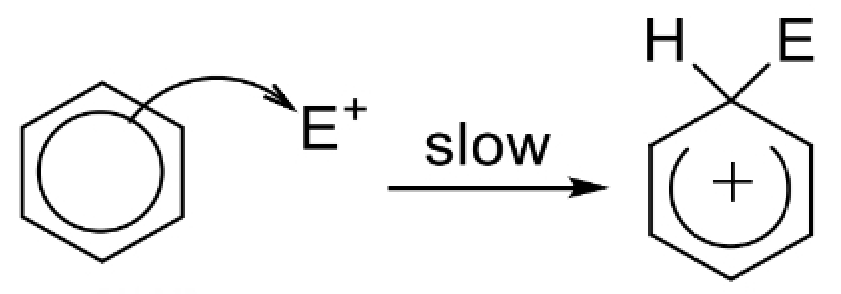
The overall reaction for an electrophilic substitution can be represented as:



Examples of electrophiles that can react with benzene include Br^+, NO_2^+ and R^+ (R = alkyl group).

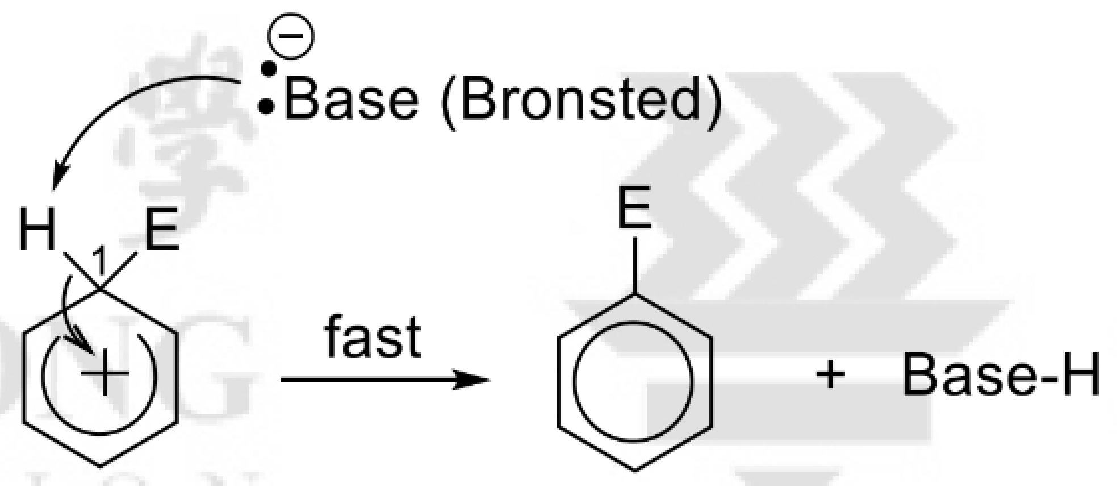
4.1.1 General Mechanism

Step 1:



- Initial attack by the π electrons of the aromatic system on the electrophile, forming a carbocation intermediate with a positive charge delocalised across only five carbon atoms.
- The movement of two π electrons means that the stability conferred by the delocalisation of the six π electrons of the ring is disrupted, so the process has high activation energy. Hence, this is the **slow step** i.e. rate-determining step.

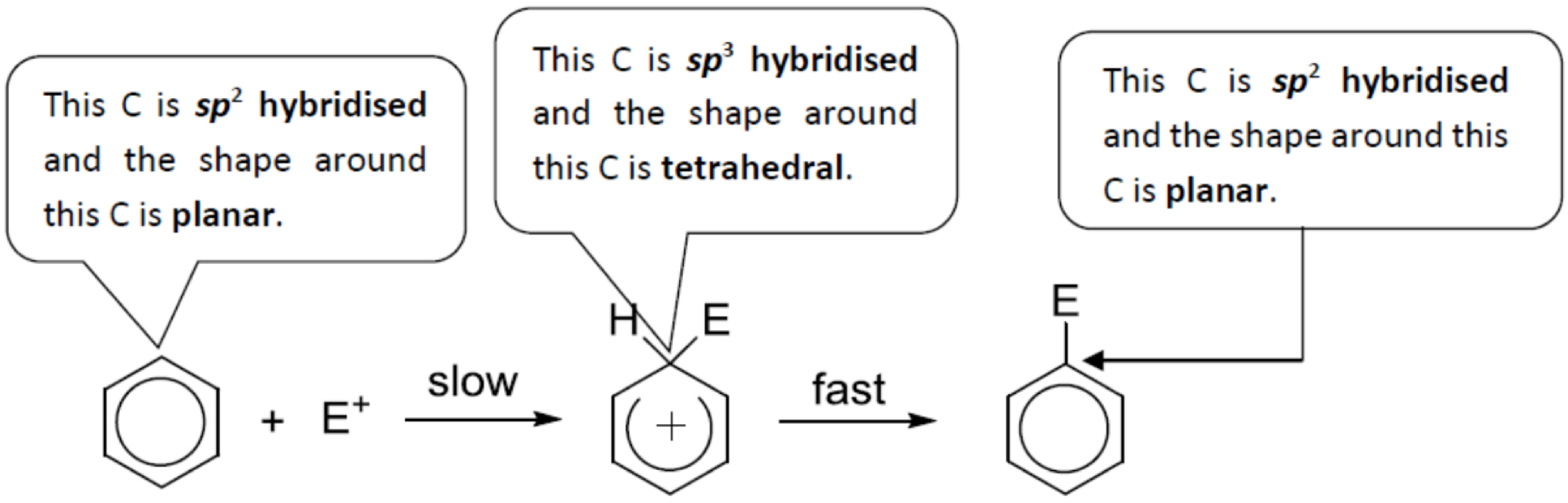
Step 2:



- The proton i.e. H^+ on the carbon-1 of the intermediate will be removed by a Bronsted base.
- Once the proton is removed, the delocalised π system and the planar shape of the molecule is restored.
- A stable substitution product results, and aromaticity is restored.

4.1.2 Shape of molecule and intermediate

The hybridisation and shape of the following carbon atom changes in each step of the mechanism.



This C is *sp*^{2} **hybridised** and the shape around this C is **planar**.

This C is *sp*^{3} **hybridised** and the shape around this C is **tetrahedral**.

This C is *sp*^{2} **hybridised** and the shape around this C is **planar**.

planar benzene molecule

non-planar carbocation intermediate

planar benzene ring (aromaticity restored)

4.2 Electrophilic substitution with chlorine or bromine (chlorination or bromination)

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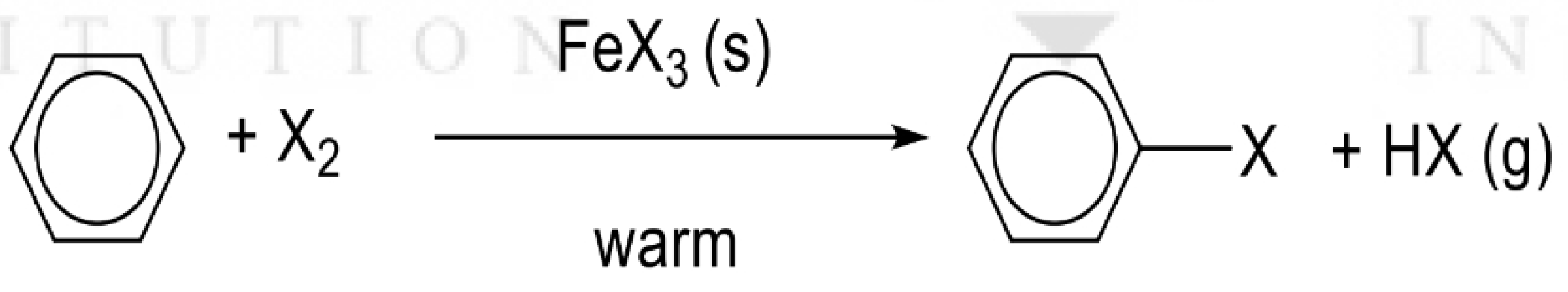
<tr><td colspan="2"> </td></tr>
<tr><td>X = Cl</td><td>X = Br</td></tr>
<tr><td>Reagents & Conditions:
Cl_2 (g), $FeCl_3$ (s) as Lewis acid catalyst, warm
OR
Cl_2 (g), Fe (s), warm</td><td>Reagents & Conditions:
Br_2 (<i>l</i>), $FeBr_3$ (s) as Lewis acid catalyst, warm
OR
Br_2 (<i>l</i>), Fe (s), warm</td></tr>
<tr><td>Observations:
decolourisation of greenish-yellow Cl_2 (g)
and white fumes of HCl (g)</td><td>Observations:
decolourisation of reddish-brown Br_2 (<i>l</i>)
and white fumes of HBr (g)</td></tr>
<tr><td colspan="2">Note
• Fe (s) is not the Lewis acid catalyst for electrophilic substitution.
• Lewis acid catalyst FeX_3 (s) is generated <i>in situ</i> from X_2 and Fe (s).
• The reaction conditions must be anhydrous (absence of moisture or water).
• Aluminium analogues such as $AlCl_3$ (s), $AlBr_3$ (s), and Al (s) can also be used in place of their respective iron counterparts.</td></tr>
</table>

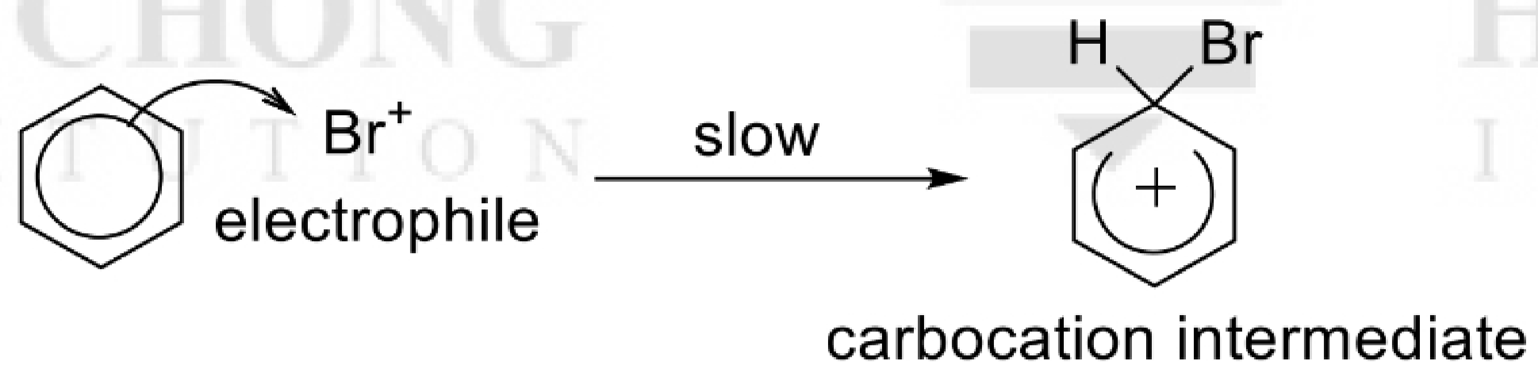
Mechanism: Electrophilic substitution

Formation of electrophile Br^+

$$FeBr_3 + Br_2 \longrightarrow \underset{\text{electrophile}}{Br^+} + [FeBr_4]^-$$

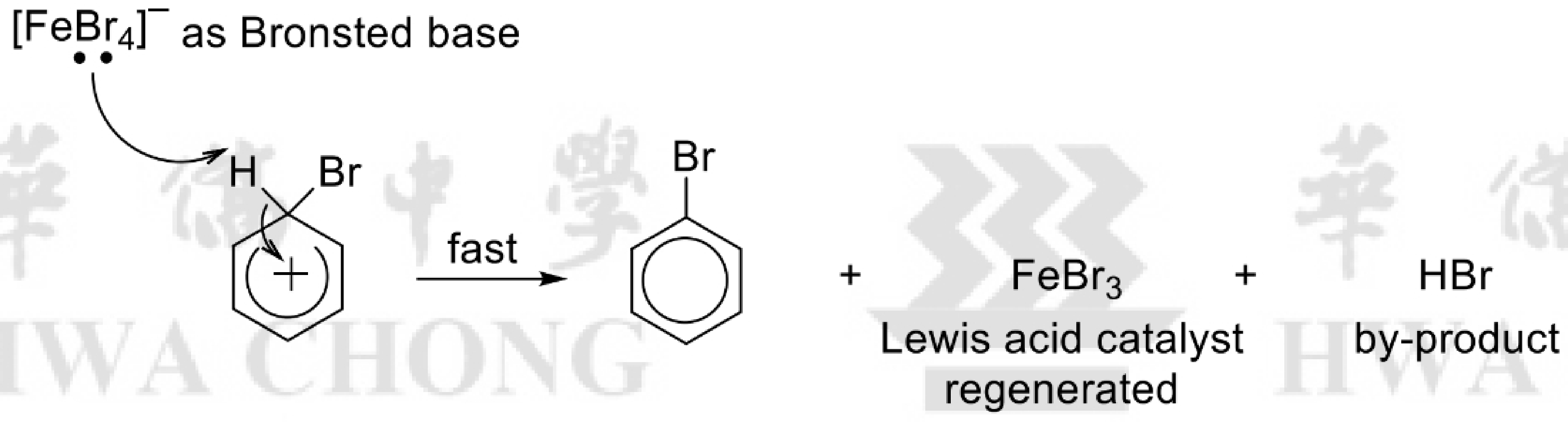
Reaction between $FeBr_3$ (s) and Br_2 (*l*) generates a strong electrophile Br^+.

Step 1: Delocalised π electron cloud attacks the electrophile.



Electrophile Br^+ adds onto the benzene ring forming a carbocation (an intermediate). The positive charge on this intermediate is delocalised over the 5 carbon atoms which are not bonded to the bromine group. The delocalised π system is disrupted in this step thus it has fairly high activation energy; kinetics studies indicate that this is the rate-determining step (slow step). Notice that E_{A1} is larger than E_{A2} in Figure 7 as step 1 is the slow step.

Step 2: The intermediate loses a proton and aromaticity is restored.



$[FeBr_4]^-$ acts as a Bronsted base and deprotonates the carbocation intermediate, producing the product bromobenzene, by-product HBr, and regenerating the Lewis acid catalyst $FeBr_3$.

The energy profile diagram of bromination of benzene via electrophilic substitution is as follows:

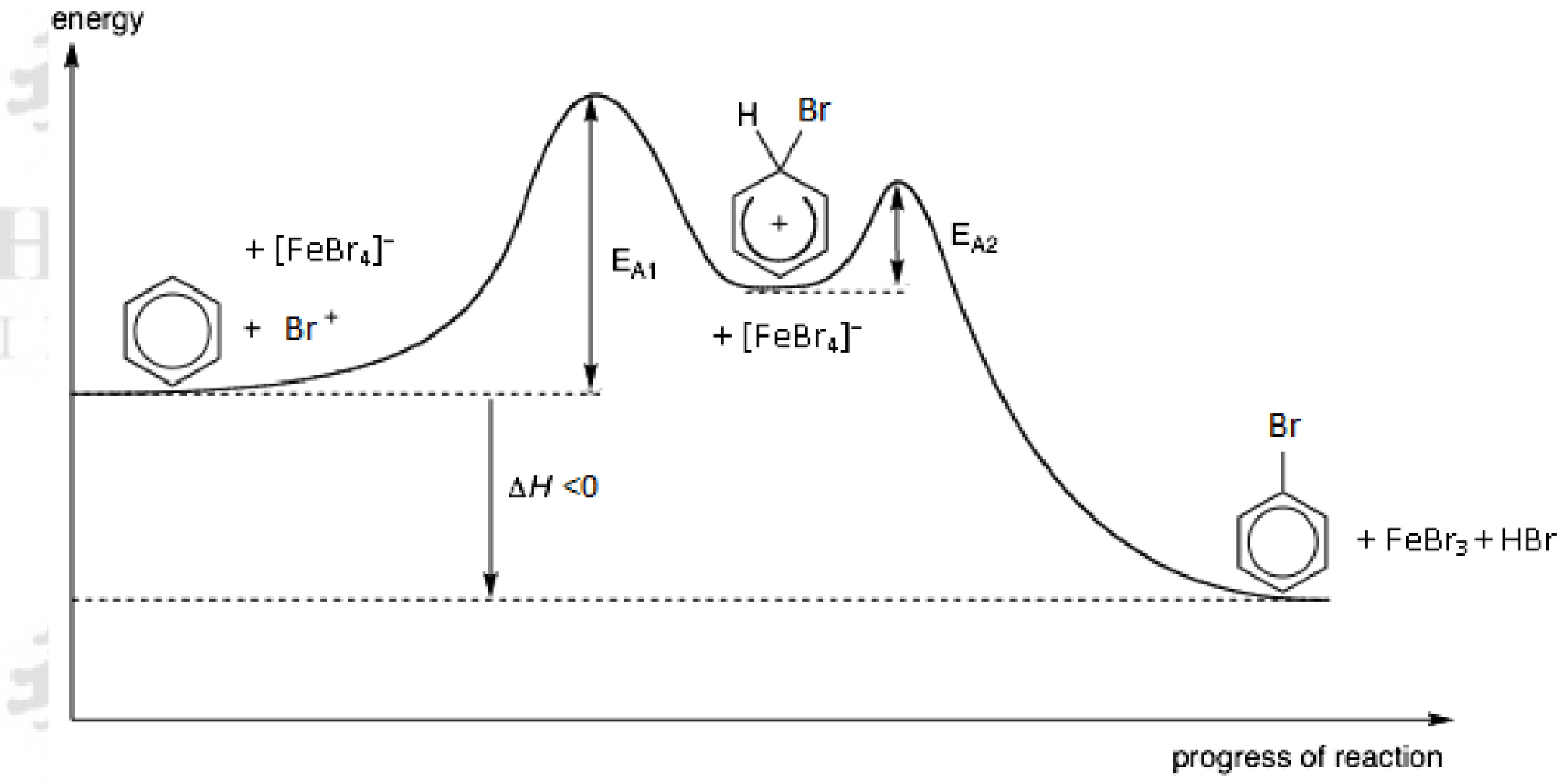


Figure 7. Energy profile diagram of bromination of benzene via electrophilic substitution.

Note

1. Fe in FeX_3 (s) or A*l* in AlX_3 (s) can accept a lone pair of electrons from the halogen X_2. Hence FeX_3 (s) or AlX_3 (s) are called the **Lewis acid** (electron pair acceptors) catalyst.

2. FeX_3 (s) or AlX_3 (s) catalyses the electrophilic substitution because they react with halogen X_2 (where X = C*l* or Br) to generate a **strong electrophile** (Cl^+ or Br^+).

$$FeCl_3 + Cl_2 \longrightarrow Cl^+ [FeCl_4]^-$$
$$FeBr_3 + Br_2 \longrightarrow Br^+ [FeBr_4]^-$$

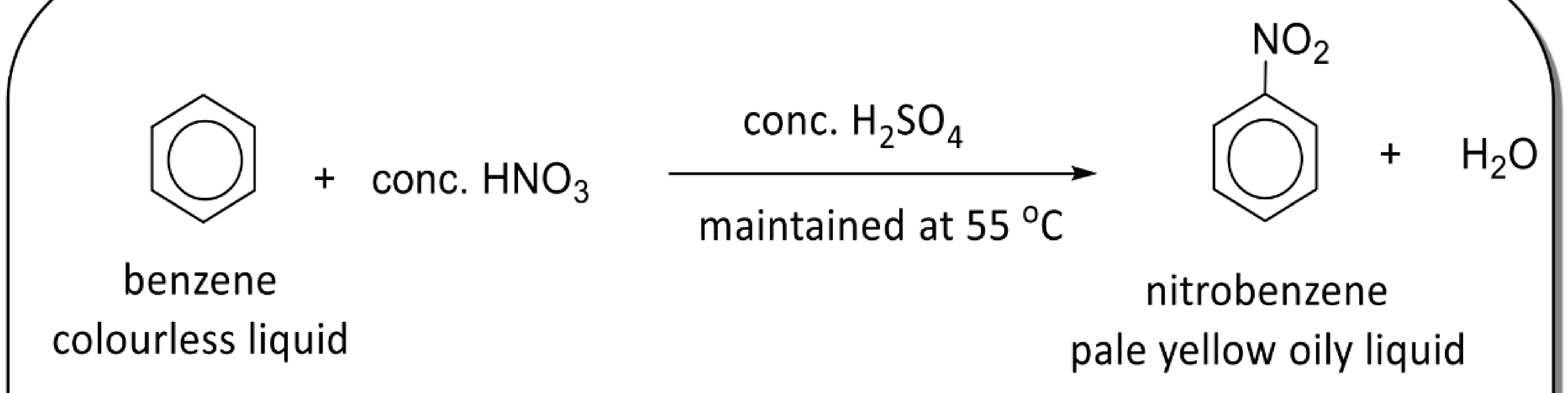
3. In the **absence** of the Lewis acid catalyst, reaction between benzene and halogen **cannot** take place. This is because halogen molecule Cl_2 (g) or Br_2 (*l*) is a **weak electrophile**, unable to activate the resonance-stabilised benzene ring.

4. The reaction conditions must be **anhydrous**. This is because in the presence of water, FeX_3 (s) or AlX_3 (s) will accept lone pair of electrons from water instead, and hence can no longer accept lone pair of electrons from halogen X_2 to generate the strong electrophile X^+.

5. Fe (s) can also be used instead of FeX_3 (s). This is because when Fe(s) comes into contact with X_2, Lewis acid catalyst FeX_3 (s) is generated *in situ* according to the redox reaction shown below.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$
$$2Fe(s) + 3Br_2(l) \longrightarrow 2FeBr_3(s)$$

4.3 Electrophilic substitution with concentrated nitric acid (nitration)



Reagent: concentrated HNO_3

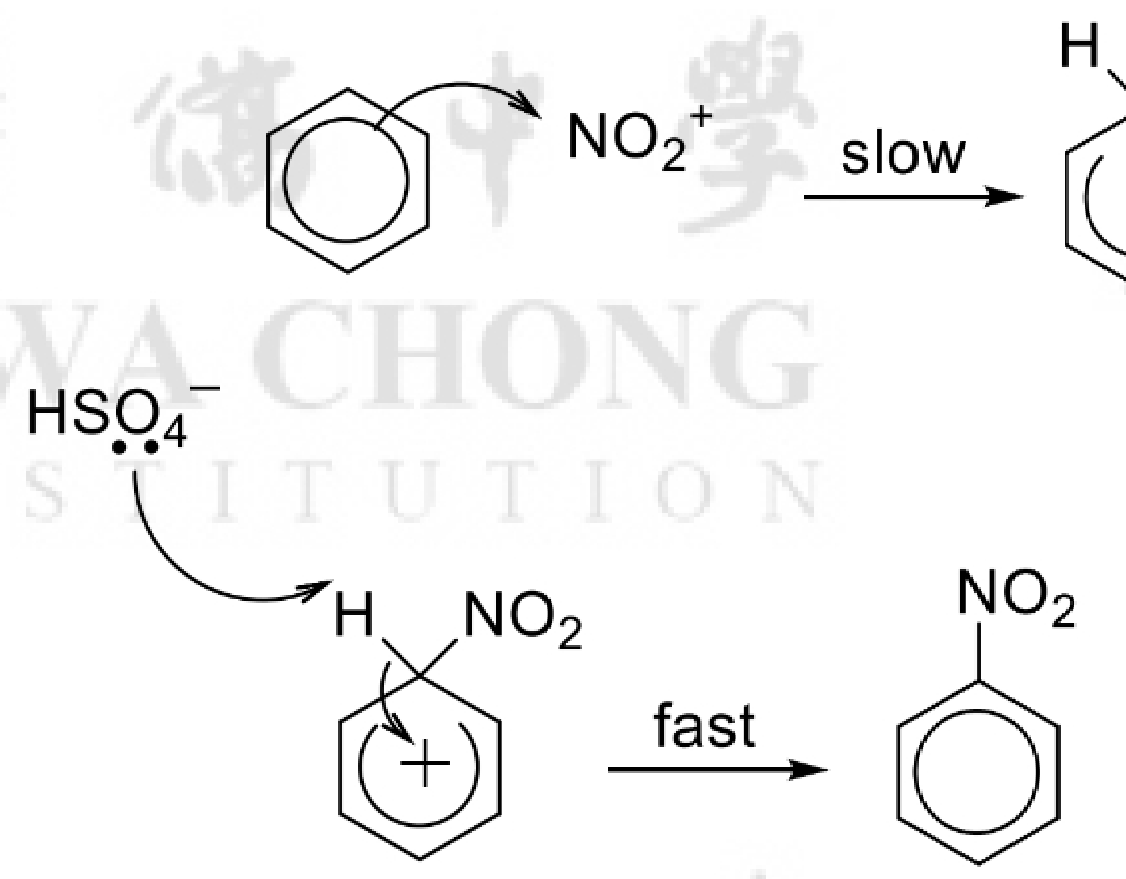
Conditions: concentrated H_2SO_4 as Bronsted-Lowry acid catalyst, maintained at 55 °C

Observation: pale yellow oily liquid formed

Mechanism

Electrophilic substitution

$$2H_2SO_4 + HNO_3 \longrightarrow \underset{\text{electrophile}}{NO_2^+} + H_3O^+ + 2HSO_4^-$$



+ H_2SO_4
Bronsted-Lowry acid catalyst regenerated

Note

1. Sulfuric acid is a **stronger Bronsted-Lowry acid** than nitric acid hence sulfuric acid protonates nitric acid, eventually generating strong electrophile nitronium ion NO_2^+.

For your information

Sulfuric acid protonates nitric acid

$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + H_2NO_3^+$

The protonated nitric acid loses a water molecule to give nitronium ion

$H_2NO_3^+ \longrightarrow H_2O + NO_2^+$

The water molecule lost is protonated by another molecule of sulfuric acid to give hydronium ion

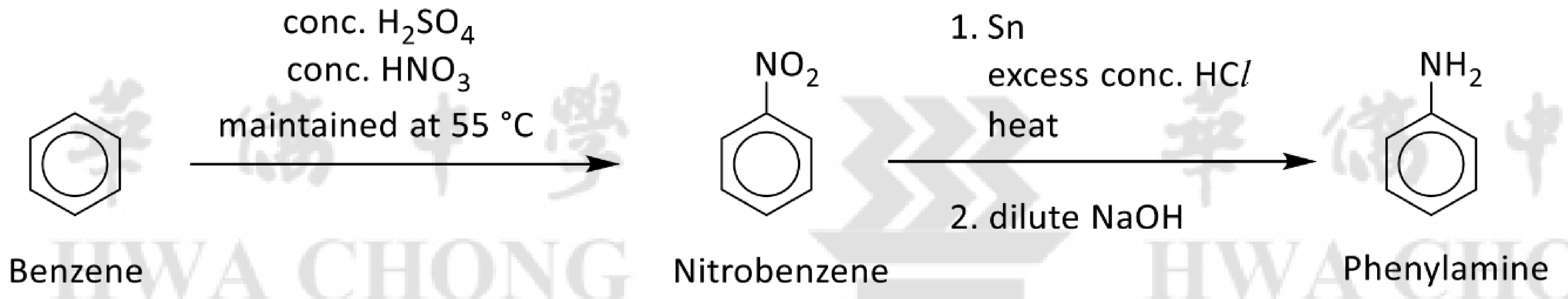
$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+$

Overall equation is therefore $2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + NO_2^+$

2. The reaction does not occur in the absence of concentrated sulfuric acid.

3. Under more rigorous conditions (e.g. prolonged heat or heating at a higher temperature), nitrobenzene can be further nitrated to give 1,3-dinitrobenzene or 1,3,5-trinitrobenzene. After mononitration, as the nitro substituent is strongly deactivating (Refer to Section 5.4.3), more rigorous conditions are required to result in further nitration. After mononitration, as the nitro substituent is 3-directing (Refer to Section 5.5), it directs incoming electrophile NO_2^+ to 3-position to give 1,3-dinitrobenzene.

4. Nitration of benzene is an important first step on the way to a variety of compounds in organic synthesis. For example:



Lecture Exercise 4.1

1. Which set of conditions will bring about the transformation shown below?

A $Cl_2(g)$ in the presence of UV
B $Cl_2(g)$ in the presence of $AlCl_3(aq)$
C $Cl_2(g)$ in the presence of Fe(s)
D Concentrated HCl with heat

[Modified from PrelimRI12/I/20]

2. What is the main reason for adding concentrated sulfuric acid to concentrated nitric acid in the preparation of nitrobenzene?

$$C_6H_6(l) + HNO_3(l) \rightarrow C_6H_5NO_2(l) + H_2O(l)$$

A It acts as an inert solvent for the benzene and nitric acid.
B It removes protons from nitric acid, thus forming NO_3^- ions.
C It donates protons to the nitric acid, thus forming NO_2^+ ions.
D It removes the water, thus preventing equilibrium being established.

[J99/3/23]

3. Will benzene decolourise liquid bromine when warmed in the presence of anhydrous iron(III) chloride? Explain your answer.

[Modified from PrelimVJC12/I/37]

4. Draw the organic product when benzene is warmed with $BrCl$ and anhydrous iron(III) chloride.

[Modified from PrelimTJC12/I/21]

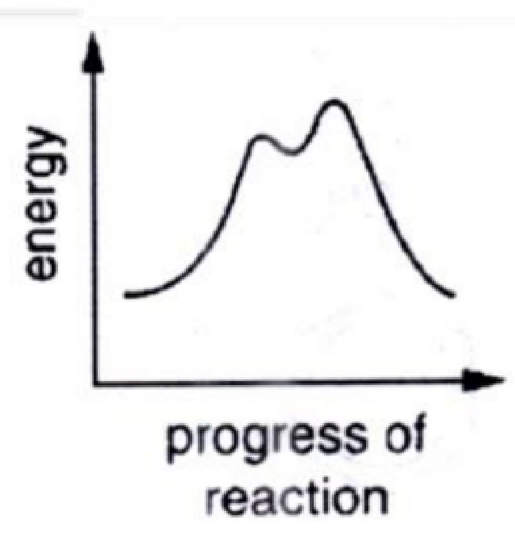
Self-Practice 4.1

The bromination of benzene in the presence of $AlBr_3$ can be represented by the following mechanism. The enthalpy change of reaction for the bromination of benzene is **−43 kJ mol^{-1}**.

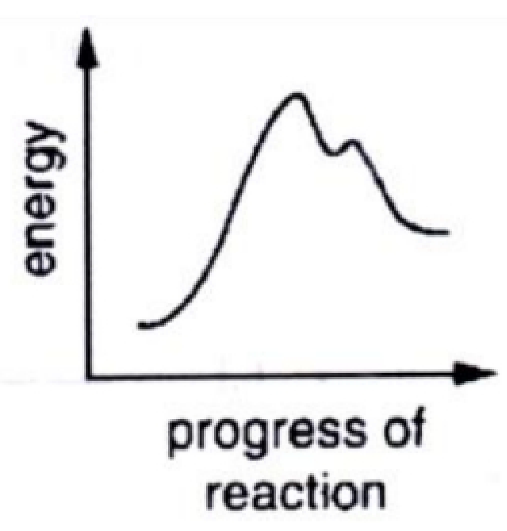
$$C_6H_6 + Br_2 \xrightleftharpoons{AlBr_3} C_6H_6Br^+ + AlBr_4^- \longrightarrow C_6H_5Br + HBr + AlBr_3$$

Which of the following reaction profiles correctly represents this mechanism?

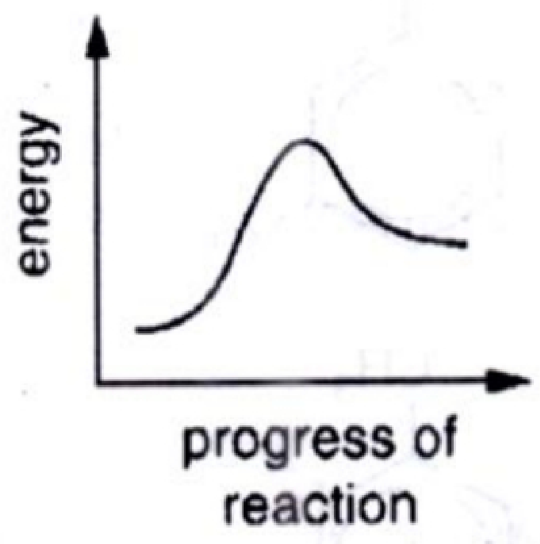
A



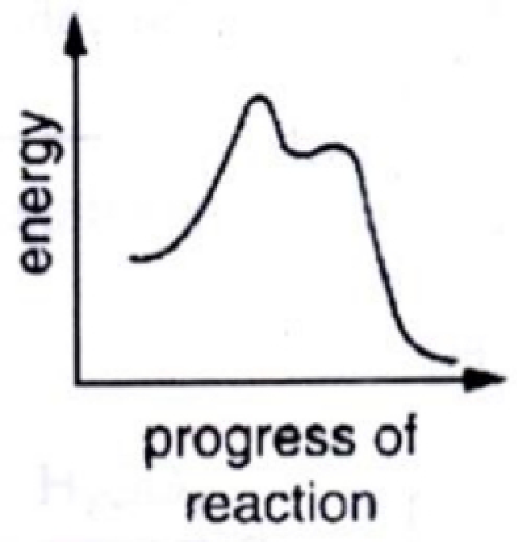
B



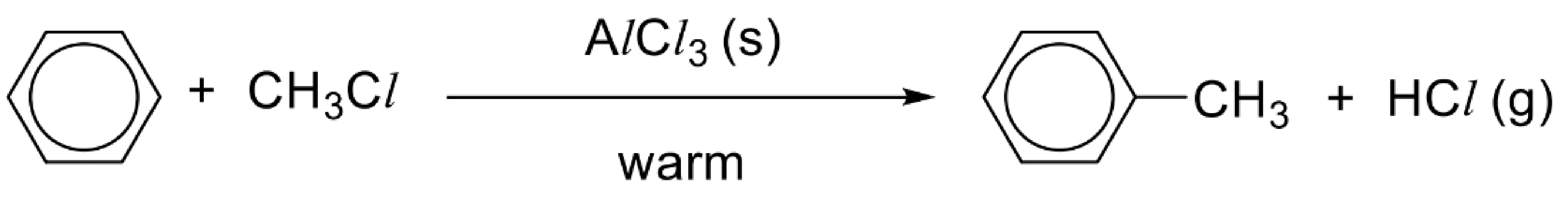
C



D



4.4 Electrophilic substitution with halogenoalkanes (Friedel-Crafts alkylation)



Reagent: chloroalkane

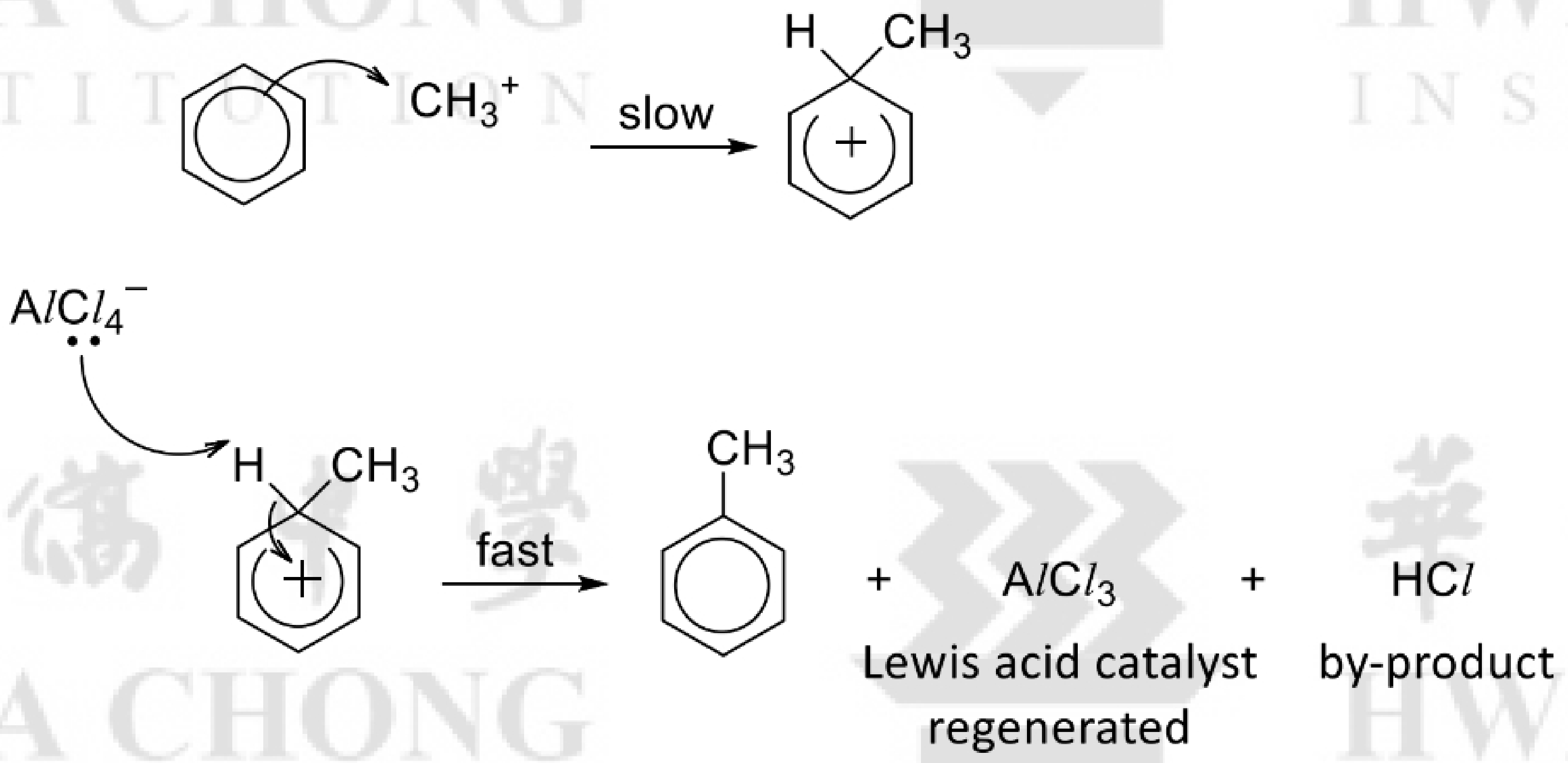
Conditions: $AlCl_3$ (s) as Lewis acid catalyst, warm

Observation: white fumes of HCl (g)

Mechanism

Electrophilic substitution

$$CH_3Cl + AlCl_3 \longrightarrow \underset{\text{electrophile}}{CH_3^+} + AlCl_4^-$$



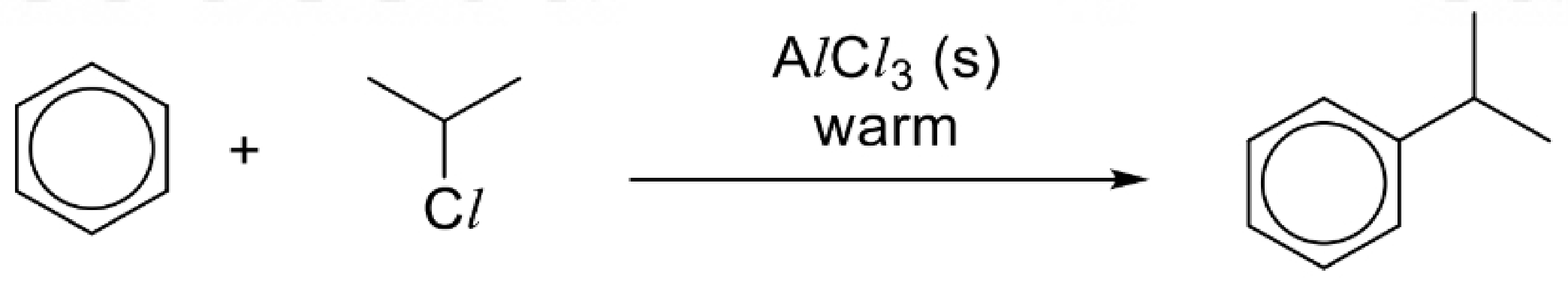
Note

1. Similar to electrophilic substitution using halogen, A*l*C*l*$_3$ (s) acts as the **Lewis acid catalyst**.

2. Friedel-Crafts alkylation only works with **alkyl halides as reagents** like chloroalkane, bromoalkane and iodoalkane, and not aryl halides (like chlorobenzene) as reagents. Later in Topic 13 Halogen Derivatives, you will learn that the C–X bond in aryl halides cannot be broken easily.

Lecture Exercise 4.2

Describe the mechanism for the following reaction scheme.



5 METHYLBENZENE AND OTHER SUBSTITUTED BENZENES

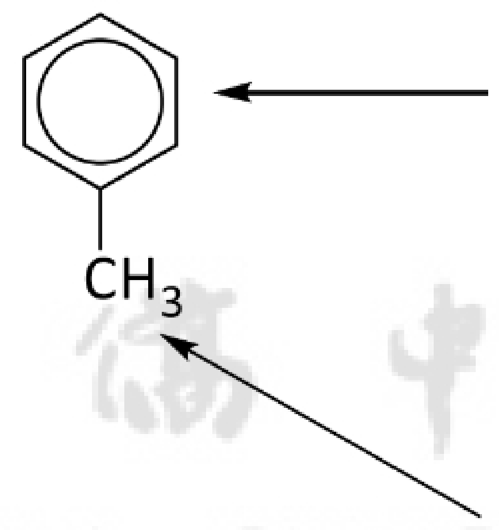
5.1 Structure of methylbenzene

Methylbenzene (commonly known as toluene) is obtained when a methyl group (–CH_3) replaces one of the hydrogen atoms in benzene. It has the molecular formula C_7H_8.

5.2 Physical properties of methylbenzene

Methylbenzene is a colourless liquid which is insoluble in water. It is relatively less toxic than benzene.

For methylbenzene, reactions can occur either at the benzene ring or the methyl group (side chain):

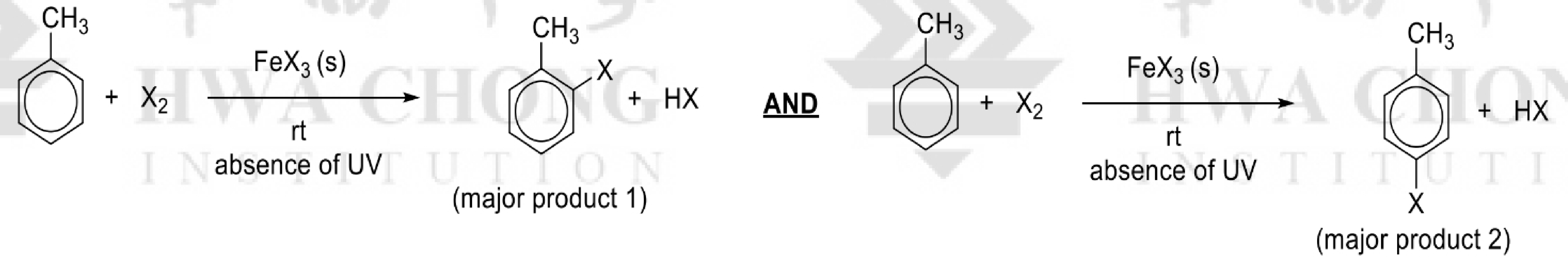


benzene ring can undergo electrophilic substitution like
1. chlorination or bromination
2. nitration
3. Friedel-Crafts alkylation
(view section 5.3)

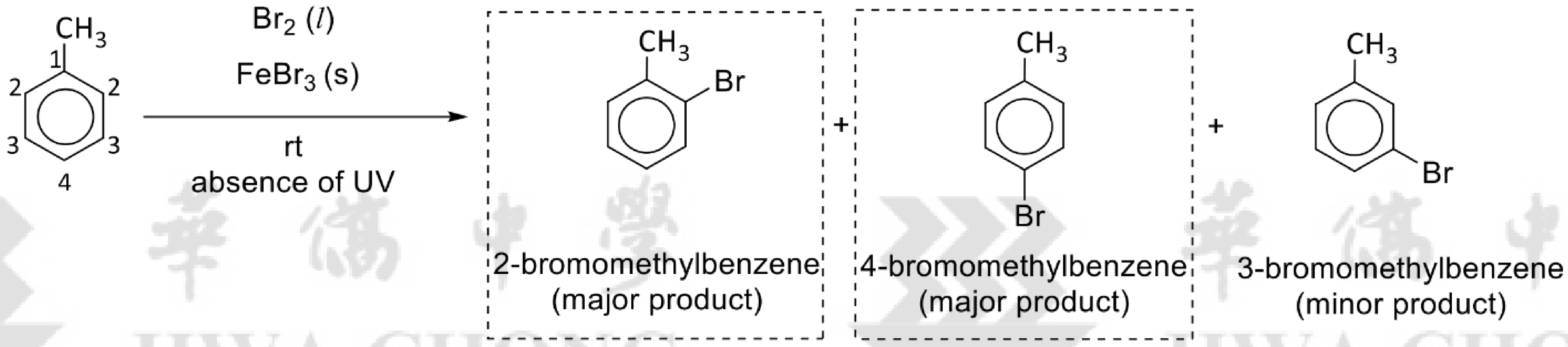
side chain can undergo side-chain reactions like
1. free radical substitution
2. side-chain oxidation
(view section 5.6)

5.3 Electrophilic substitution in methylbenzene

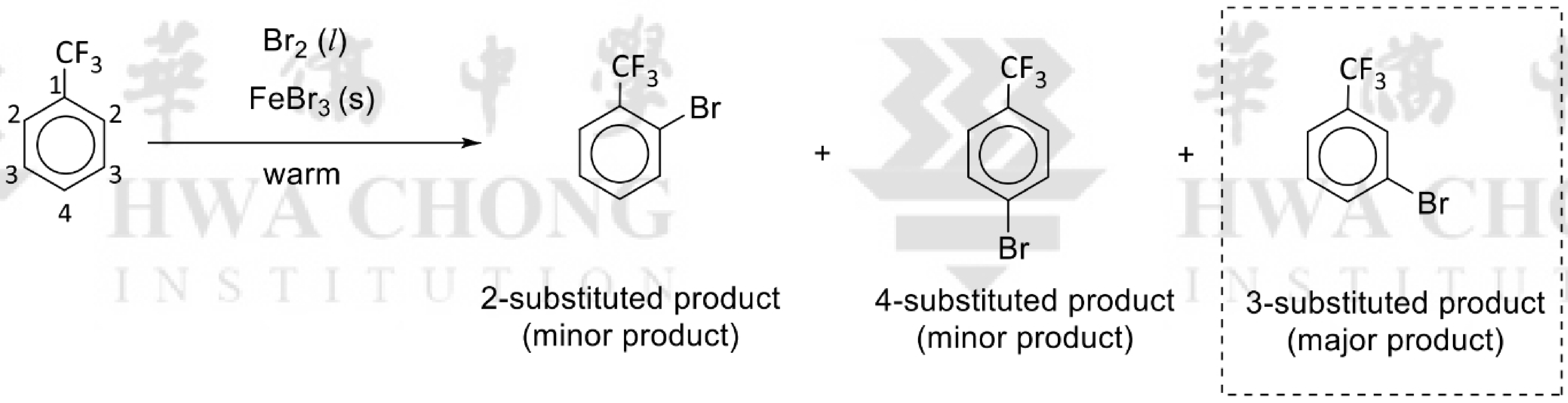
During halogenation of methylbenzene via electrophilic substitution, more than one di-substituted product can be formed:

	
X = Cl	X = Br
Reagents & Conditions: Cl_2 (g), $FeCl_3$(s) as Lewis acid catalyst, rt and absence of UV	**Reagents & Conditions**: $Br_2(l)$, $FeBr_3$(s) as Lewis acid catalyst, rt and absence of UV
Observations: decolourisation of greenish-yellow Cl_2(g) and white fumes of HCl (g)	**Observations**: decolourisation of reddish-brown $Br_2(l)$ and white fumes of HBr (g)
Note: –CH_3 is inductively electron-donating hence activating, therefore milder conditions (i.e. rt) is required as compared to warming required for benzene. (Refer to Section 5.4.3) Absence of UV is to prevent free radical substitution on alkyl side chain. (Refer to Section 5.6.1)	

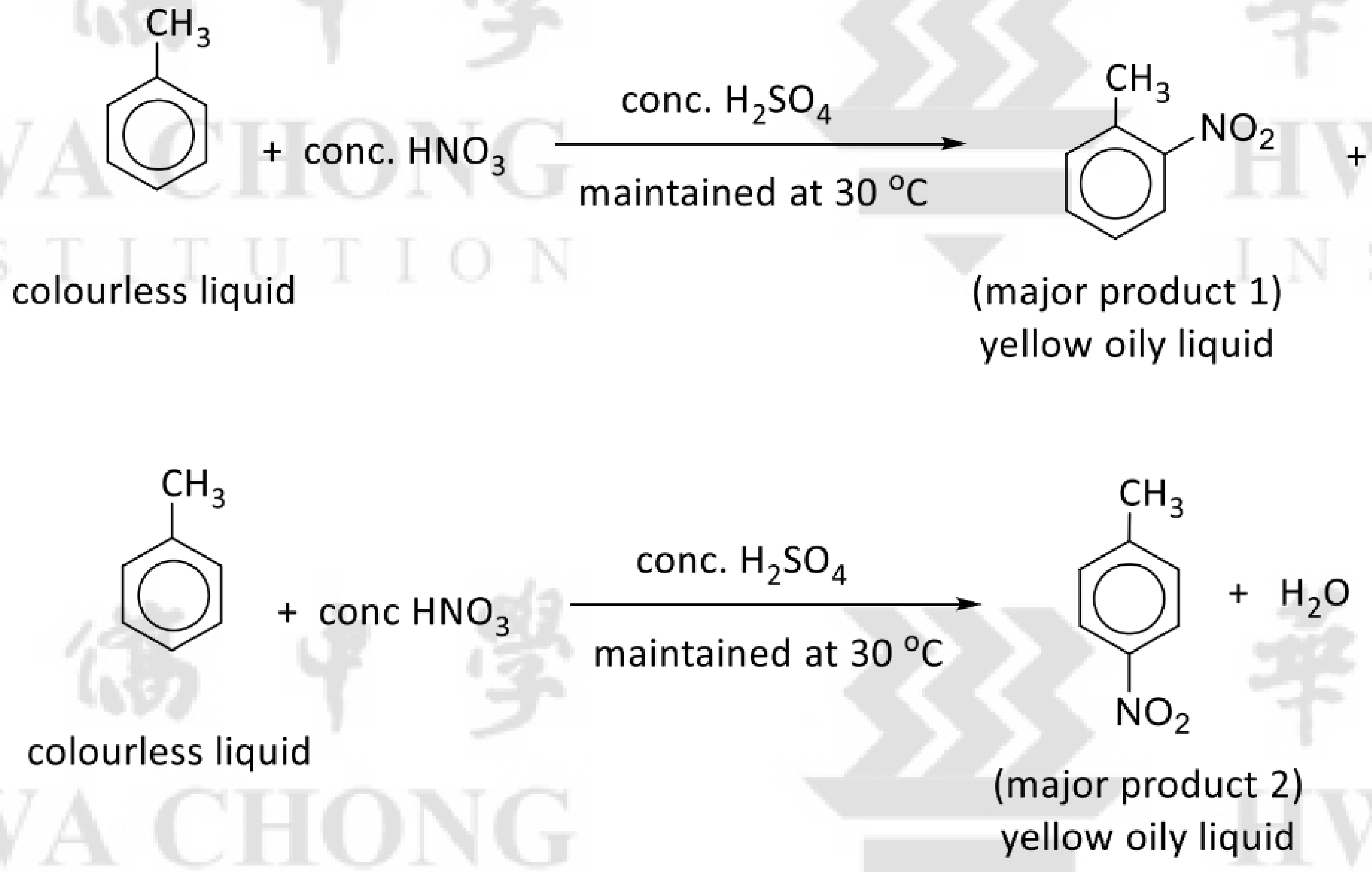
In fact, three di-substituted products (2-bromomethylbenzene, 3-bromomethylbenzene and 4-bromomethylbenzene) are possible from bromination of methylbenzene via electrophilic substitution, but only two are formed as major products. Thus, the **methyl substituent is known as 2,4-directing**. (Refer to Section 5.5)



Bromination of trifluoromethylbenzene via electrophilic substitution, on the other hand, yields almost exclusively the 3-substituted product. The 2- and 4-substituted products are formed in smaller quantities. Thus, the **trifluoromethyl substituent is known as 3-directing** (Refer to Section 5.5). Note: $-CF_3$ is inductively electron-withdrawing hence deactivating.



Similarly to halogenation, during nitration of methylbenzene via electrophilic substitution, more than one di-substituted product can be formed:



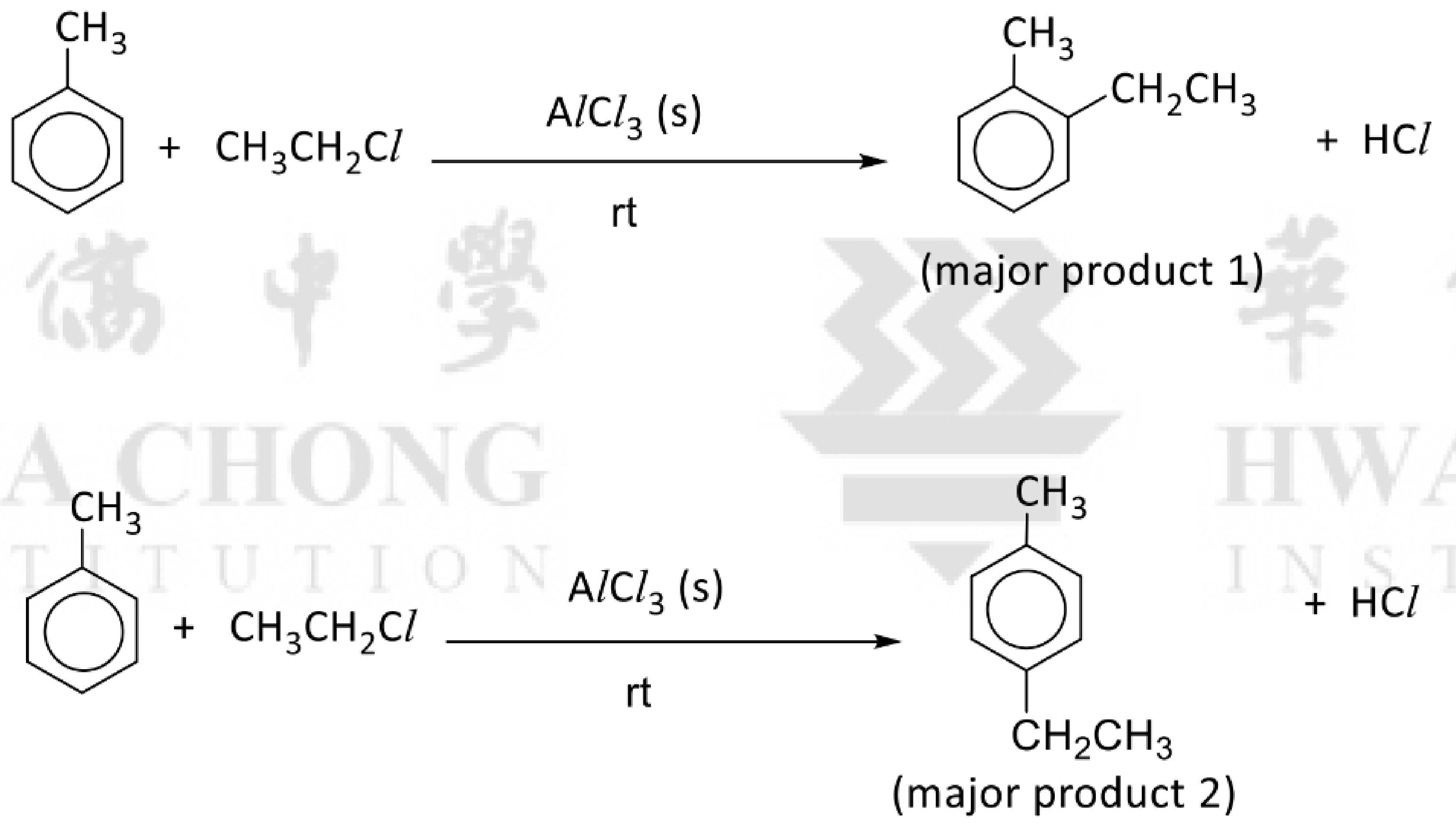
Reagent: Concentrated HNO_3

Conditions: Concentrated H_2SO_4 as Bronsted-Lowry acid catalyst, maintained at 30 °C

Observation: Yellow oily liquid formed

Note: $-CH_3$ is activating, therefore milder conditions (i.e. 30 °C) is required as compared to 55 °C required for benzene. (Refer to Section 5.4.3)

During Friedel-Crafts alkylation of methylbenzene via electrophilic substitution, more than one di-substituted product can be formed:



Reagent: chloroalkane

Conditions: $AlCl_3$ (s) as Lewis acid catalyst, rt

Observation: white fumes of HC*l* (g)

Note: $-CH_3$ is activating, therefore milder conditions (i.e. rt) is required as compared to warming required for benzene. (Refer to Section 5.4.3)

These reactivity and directing trends can be explained by considering **resonance and inductive effects** of substituent on the benzene ring (view the following sections 5.4 and 5.5).

5.4 Substituent effect on the reactivity of the benzene ring

Electron-donating substituents increase the electron density of the benzene ring, thereby increasing the reactivity of the benzene ring. Such substituents are called **activating groups**.

On the other hand, **electron-withdrawing** substituents decrease the electron density of the benzene ring, thereby decreasing the reactivity of the benzene ring, and are called **deactivating groups**.

Recall from Topic 8 Introduction, there are 2 ways in which electrons can be donated into or withdrawn from the benzene ring:

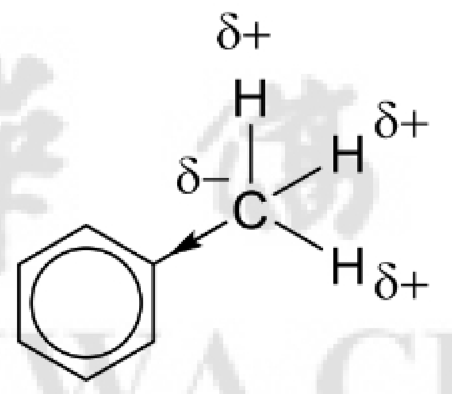
(i) through the sigma bond via **Inductive effect**

(ii) through the pi bond via **Resonance effect**

5.4.1 Inductive effect

Inductive effect is present when there is a **difference in electronegativity** between two covalently-bonded atoms.

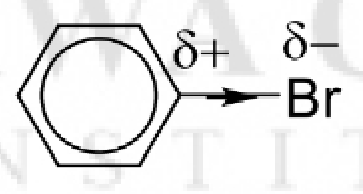
Substituents like alkyl groups (e.g. $-CH_3$, $-CH_2CH_3$) can **inductively donate** electron density **into the benzene ring** through the sigma bond. (The actual reason deals with hyperconjugation which will not be discussed.)



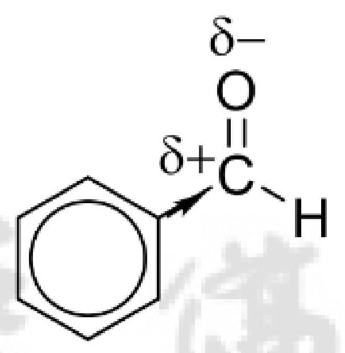
C is slighty more electronegative than H
electrons inductively donate from H to C in CH_3
and overall electrons inductively donate from CH_3 into benzene ring

(Note: the arrow shows the inductive effect, it is not a dative bond)

Substituents like $-OH$, $-OCH_3$, $-NH_2$, $-NHCH_3$, –C*l*, –Br, –I –CHO, $-COCH_3$, $-CO_2H$, $-CO_2CH_3$, $-NO_2$, and –CN can **inductively withdraw** electron density **from the benzene ring** through the sigma bond.



Br is more electronegative than C
electrons inductively withdrawn from C to Br
and overall electrons inductively withdrawn from benzene ring to Br



O is more electronegative than C
electrons inductively withdrawn from C in CHO to O
and overall electrons inductively withdrawn from benzene ring to CHO

(Note: the arrows show the inductive effect, they are not dative bonds)

5.4.2 Resonance effect

Resonance effect is present when there is **overlapping of p orbitals**: in this case between the carbon atom of benzene and the substituent that it is bonded to.

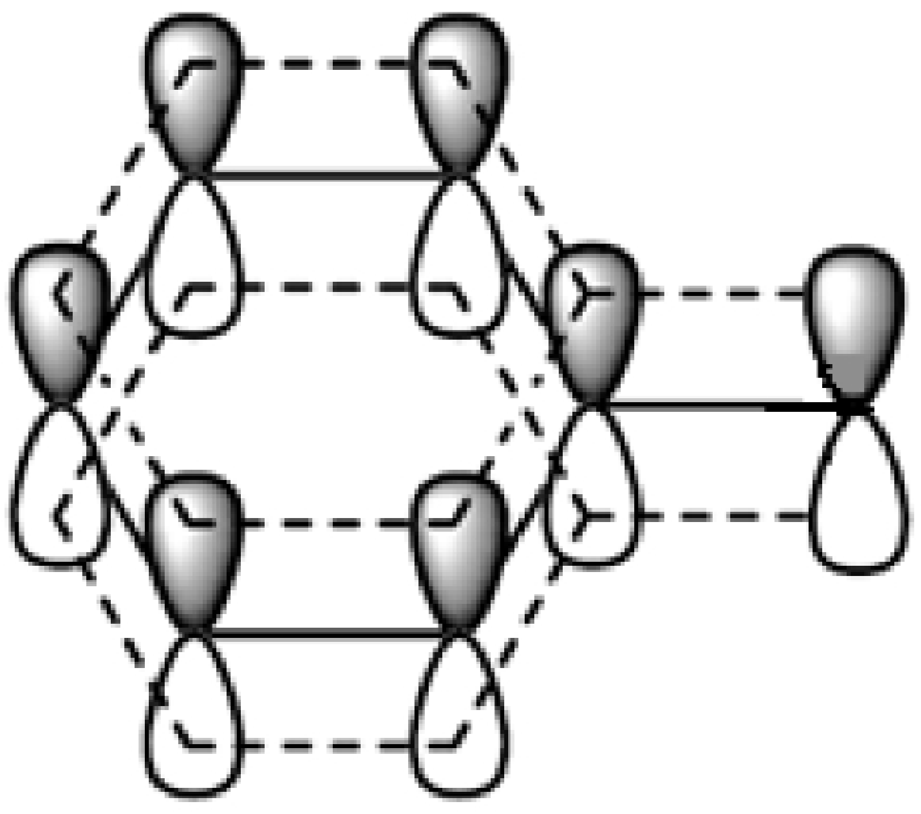
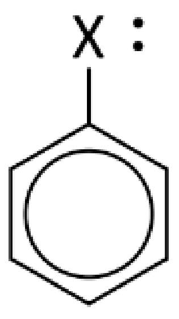


Figure 8. Illustration of resonance effect through p orbitals overlap between carbon atom of benzene and substituent.

Substituents with general structure X, where X has at least one lone pair residing in the *p* orbital, can **donate a lone pair of electrons into the benzene ring via resonance** through the π bond. For example, –OH, –OCH_3, –NH_2, –$NHCH_3$, –C*l*, –Br, and –I.

In general

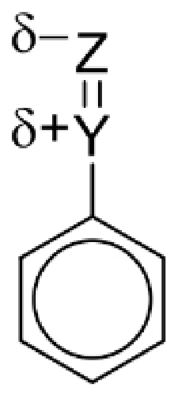


where X
has a lone pair

Figure 9. General structure of a substituent that is electron-donating by resonance effect

Substituents with a general structure –Y=Z, where Z is more electronegative than Y, can **withdraw electrons from the benzene ring via resonance** through the π bond. For example, –CHO, –$COCH_3$, –CO_2H, –CO_2CH_3, –NO_2, –CN.

In general



where Z is more
electronegative
than Y

Figure 10. General structure of a substituent that is electron-withdrawing by resonance effect

5.4.3 Overall effect

Substituent on benzene	**Inductive effect**	**Resonance effect**	**Overall effect**	**Overall effect on reactivity of benzene ring towards electrophilic attack**
–alkyl e.g. $–CH_3$, $–CH_2CH_3$	Electron-donating	NIL	Electron-donating	Activating
–OH, $–OCH_3$, $–NH_2$, $–NHCH_3$	Electron-withdrawing	Electron-donating	Strongly electron-donating	Strongly activating
–C*l*, –Br, –I	Electron-withdrawing	Electron-donating	Electron-withdrawing	Deactivating
–CHO, $–COCH_3$, $–CO_2H$, $–CO_2CH_3$, $–NO_2$, –CN	Electron withdrawing	Electron-withdrawing	Strongly electron-withdrawing	Strongly deactivating

Note: The electron-donating resonance effect of –C*l* substituent is not as effective as –OH or $–NH_2$ substituents. This is because the 3*p* orbital of C*l* atom overlaps less effectively with the 2*p* orbital of the carbon atom (due to different sized *p* orbitals), compared to the more effective 2*p*–2*p* overlap between the orbitals on O or N atoms of the –OH or $–NH_2$ substituents and the carbon atom.

Self-Practice 5.1
Identify the type of inductive effect, resonance effect and the overall effect of $–CH_2OH$ substituent on the reactivity of benzene ring towards electrophilic attack.

The overall effect of substituents on the reactivity of benzene ring towards electrophilic attack is also illustrated in the reagents and conditions required for benzene with different substituents to undergo electrophilic substitution. For example, in the presence of activating group like $–CH_3$ in methylbenzene, milder conditions (i.e. rt) would be required for the monobromination of methylbenzene as compared to warming required for benzene.

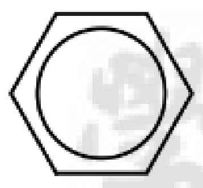
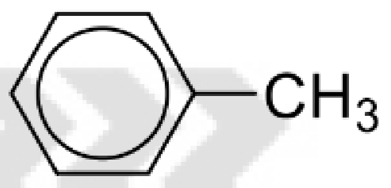
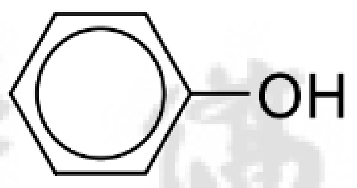
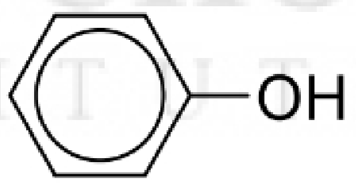
Electrophilic substitution	**Benzene** 	**Methylbenzene** 	**Phenol** 
Monobromination	$Br_2(l)$ $FeBr_3(s)$ Warm	$Br_2(l)$ $FeBr_3(s)$ rt absence of *UV*	$Br_2(l)$ rt
Mononitration	Conc. HNO_3 Conc. H_2SO_4 Maintained at 55 °C	Conc. HNO_3 Conc. H_2SO_4 Maintained at 30 °C	Dilute HNO_3 rt
Monoalkylation	Chloroalkane $AlCl_3(s)$ Warm	Chloroalkane $AlCl_3(s)$ rt	▨

Table 2. Reagents and conditions for various types of electrophilic substitution for benzene, methylbenzene and phenol.

Lecture Exercise 5.1

Explain why phenol,  is more susceptible to electrophilic attack as compared to methylbenzene.

Self-Practice 5.2

a) Explain why nitration of benzene requires 55 °C whereas nitration of methylbenzene requires only 30 °C.

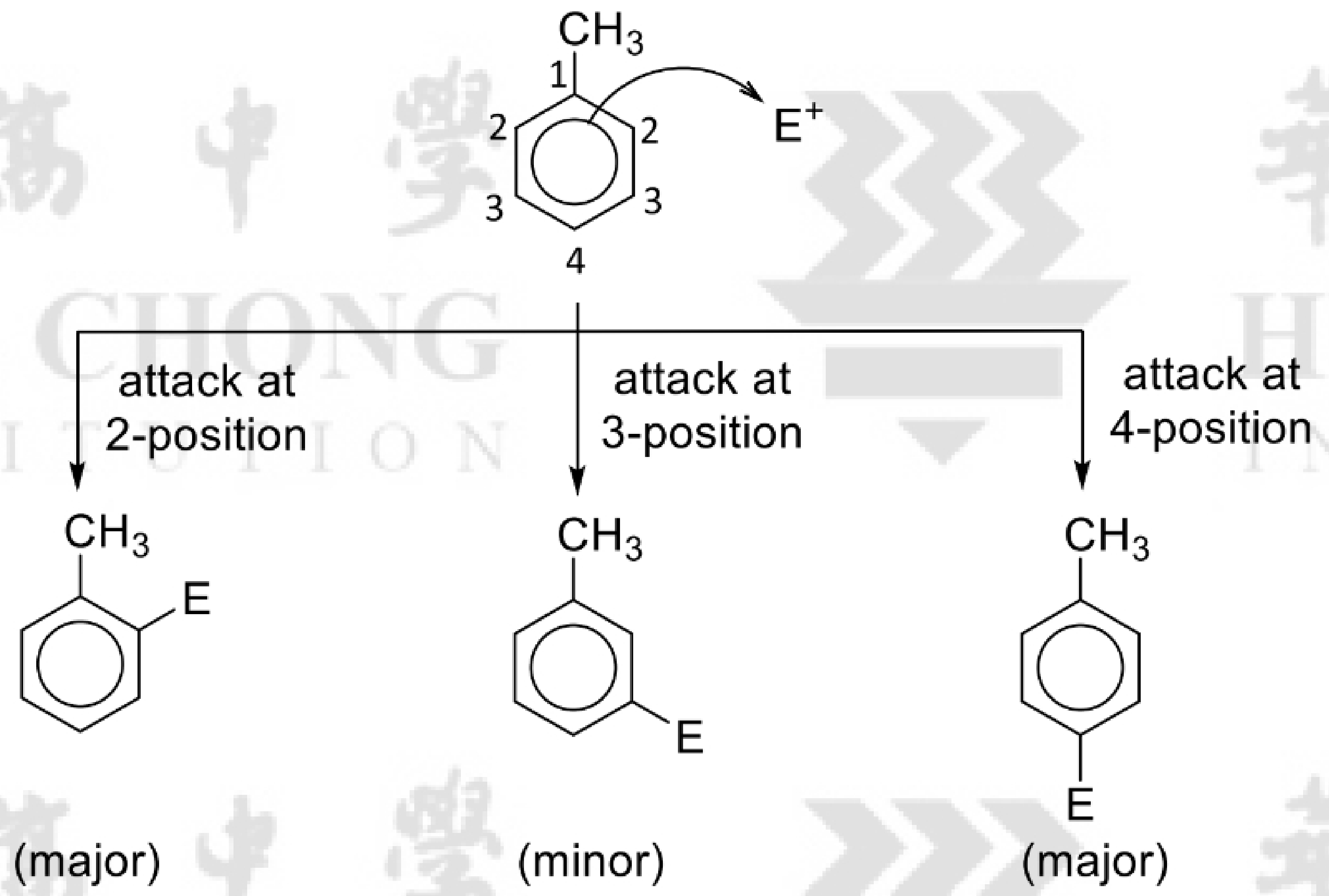
b) What would happen if a temperature higher than 30 °C were used for the nitration of methylbenzene?

5.5 Substituent effect on the position of the incoming electrophile

A substituent which causes the new incoming electrophile to be located predominantly on the 3rd position (relative to the substituent already present) is said to be **3-directing**. Nitro substituent in nitrobenzene is an example of a 3-directing substituent.

A substituent which causes the new incoming electrophile to be located predominantly on the 2nd or 4th positions (relative to the substituent already present) is said to be **2,4-directing**. Methyl substituent in methylbenzene is an example of a 2,4-directing substituent.

For methylbenzene, the incoming electrophile can occupy 3 different positions as shown below. However, the products with the electrophile being added to 2-position or 4-position are the major products, whereas the product with the electrophile being added to 3-position is the minor product.



You can refer to the Appendix to learn the reasons why activating groups and halogens are 2,4-directing, and deactivating groups (with the exception of halogens) are 3-directing.

Summary of substituent effects:

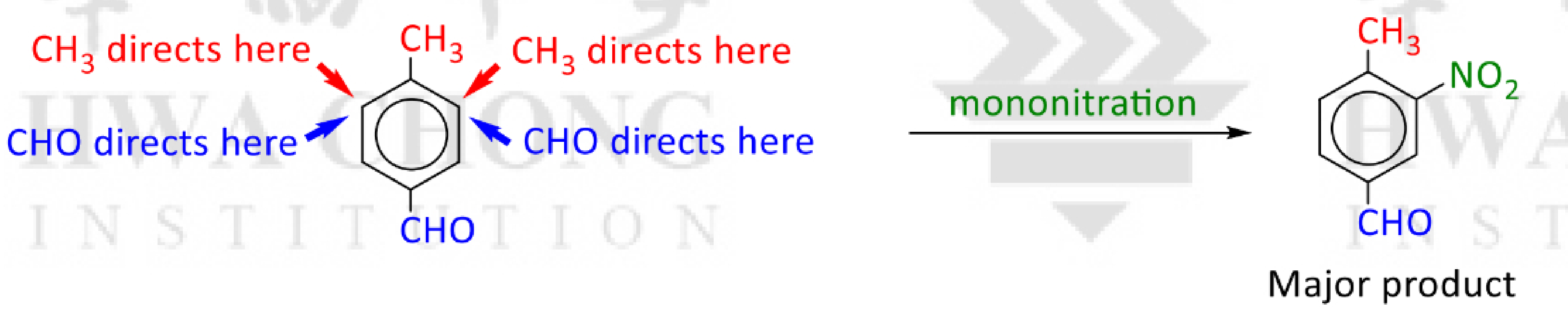
Substituent	**Effect on the reactivity of benzene ring towards electrophilic attack**	**Effect on position of incoming electrophile attack**
–R, –NHCOR where R = alkyl	Activating	2,4-directing
–OH, –OR, $–NH_2$, –NHR, $–NR_2$ where R = alkyl	Strongly activating	2,4-directing
–C*l*, –Br, –I	Deactivating	2,4-directing
–CHO, –COR, $–CO_2H$, $–CO_2R$, $–NH_3^+$, $–NO_2$, –CN where R = alkyl	Strongly deactivating	3-directing

Note: A similar table is provided in your *Data Booklet*.

5.5.1 Multi-substituted benzene and their net effect on the position of the incoming electrophile

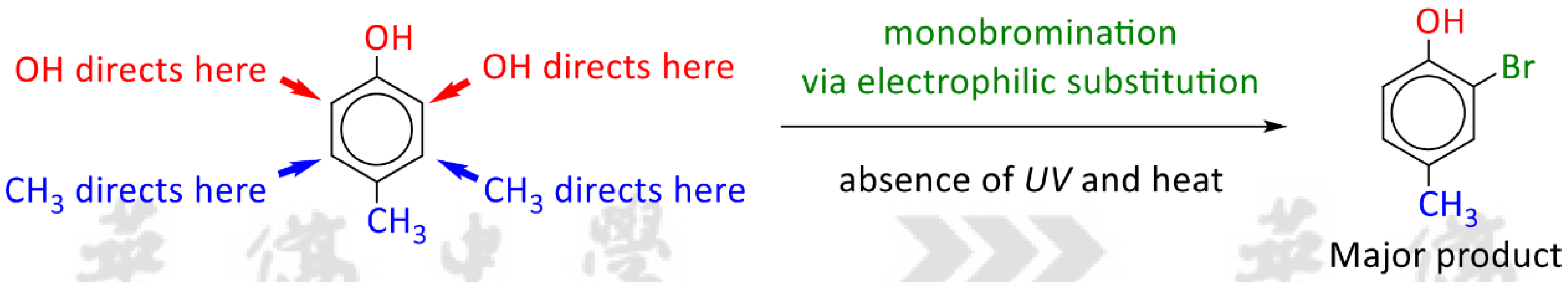
What happens when there are **two** substituents on the benzene ring?

- If the directing effects of both substituents **direct to the same position on the ring**, then that is where electrophilic substitution will predominantly occur.



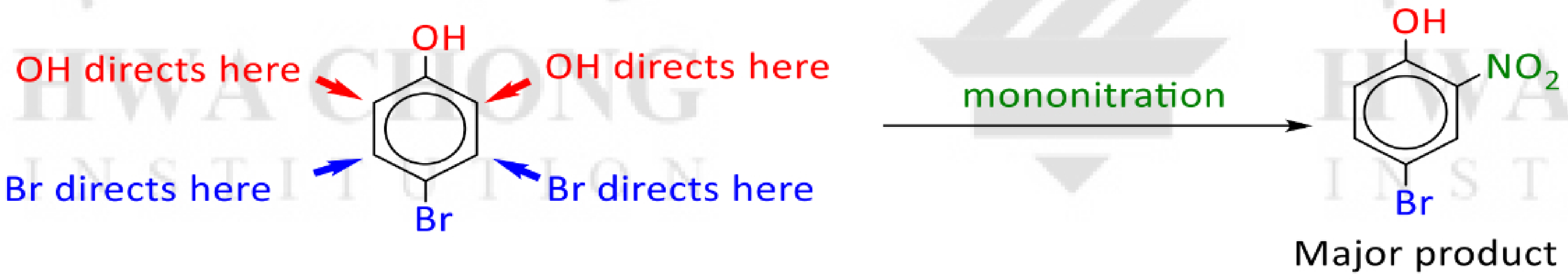
Comments:
CH_3 is 2,4-directing, but 4-position (with reference to CH_3) is occupied, hence CH_3 only direct incoming electrophile to 2-position (with reference to CH_3). CHO is 3-directing, since both substituents directs the incoming electrophile to the same position the major product is a result of substitution at that position.

- If both substituents are activating, and direct to different positions, the **directing effect of the more activating substituent will dominate**.



Comments:
Both OH and CH_3 are 2,4-directing,
but 4-positions (with reference to each substituent) are occupied,
hence they only direct incoming electrophile to 2-positions (with reference to each substituent),
but **OH is more activating than CH_3**,
hence the major product is due to the OH directing the incoming electrophile
to 2-position with reference to OH

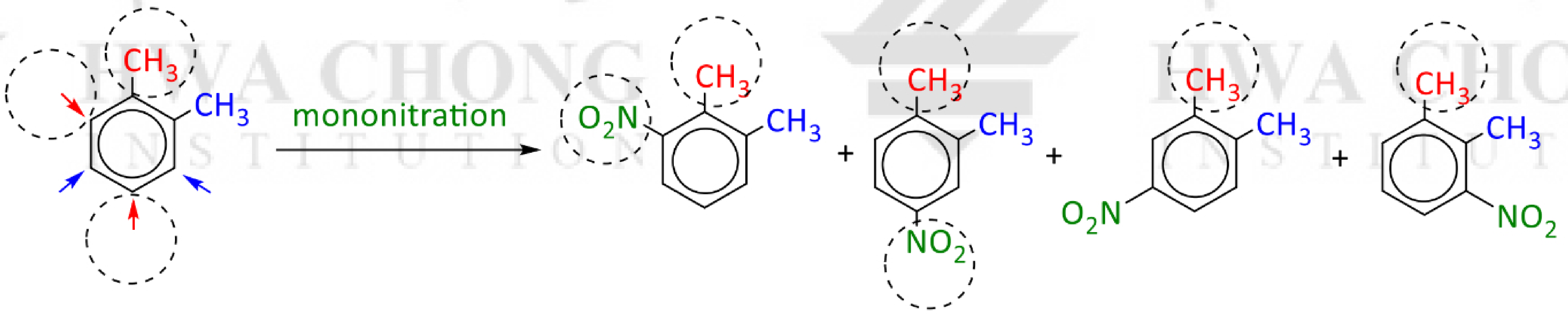
- If the substituents consist of a strongly activating group, and a deactivating group, the **directing effect of the strongly activating substituent will dominate**.



Comments:
Both OH and Br are 2,4-directing,
but 4-positions (with reference to each substituent) are occupied,
hence they only direct incoming electrophile to 2-positions (with reference to each substituent),
but **OH is strongly activating whereas Br is deactivating**,
hence the major product is due to the OH directing the incoming electrophile
to 2-position with reference to OH

- If the substituents consist of
  - other combinations of activating and deactivating groups
  - groups with similar activating effects
  - groups with similar deactivating effects

and each group directs towards different positions, it will result in **a mixture of products**. This situation is not ideal and is avoided if possible as the reaction will give poor yields of the desired product. The following is an example of such situation.



Lecture Exercise 5.2

Draw the structures of the major organic products in each of the following reactions:

1. monochlorination of nitrobenzene

2. mononitration of bromobenzene

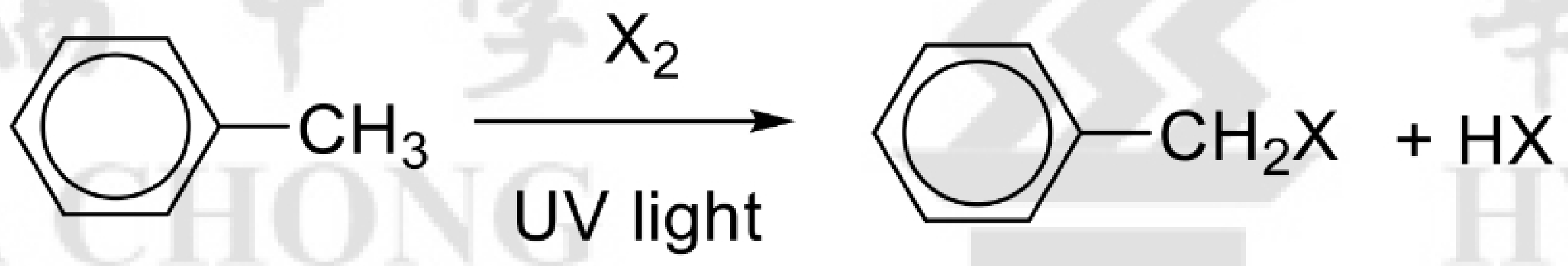
3. monobromination of 4-hydroxylbenzoic acid

4. mononitration of 4-aminomethylbenzene

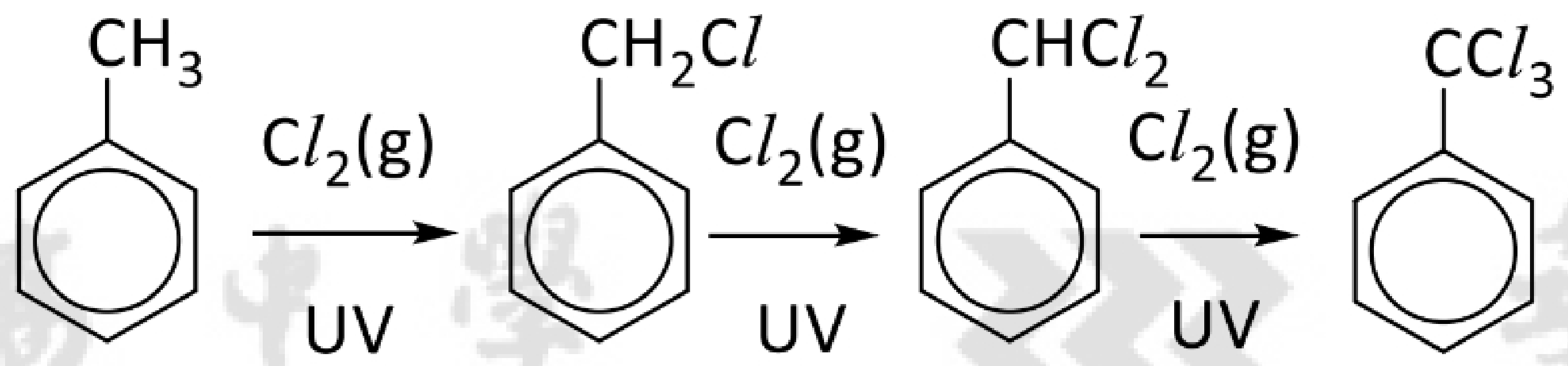
5.6 Side-chain reactions of methylbenzene

5.6.1 Free Radical Substitution

During the side-chain halogenation, methylbenzene and other alkylbenzenes undergo free-radical substitution with chlorine or bromine in the presence of UV light or heat. The alkyl side chain reacts like an alkane (Recall from Topic 10 Alkanes).

	
X = C*l*	X = Br
Reagents and conditions: Cl_2 (g), UV light or heat	**Reagents and conditions:** Br_2 (*l*), UV light or heat
Observation: greenish-yellow Cl_2 (g) decolourises slowly	**Observation:** Reddish brown Br_2 (*l*) decolourises slowly
Note: To preferably obtain product of monohalogenation on the alkyl side chain, limited Cl_2 (g) or excess alkylbenzene is usually employed.	

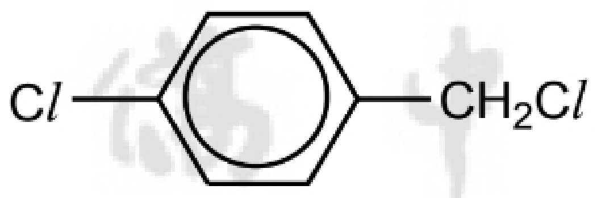
More than one chlorine or bromine atom can be incorporated onto the alkyl side chain if **excess** Cl_2(g) or Br_2(*l*) is used. For example:



Self-practice 5.3

a) Why must the synthesis of 2-bromomethylbenzene from methylbenzene be carried out in the absence of light and without heat?

b) Chlorine was passed into methylbenzene under reflux in the presence of aluminium chloride.

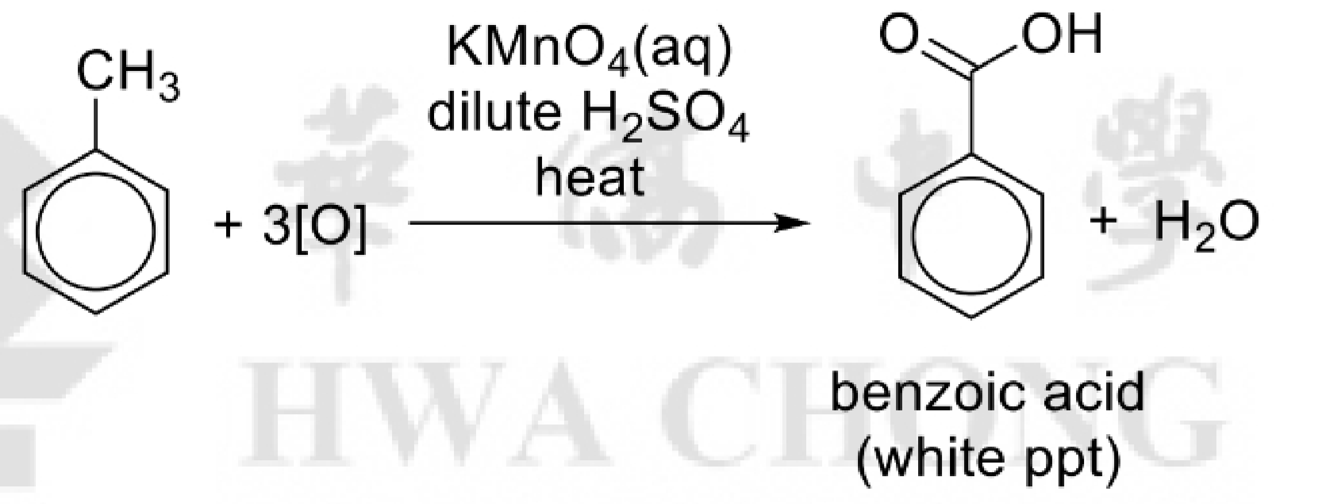
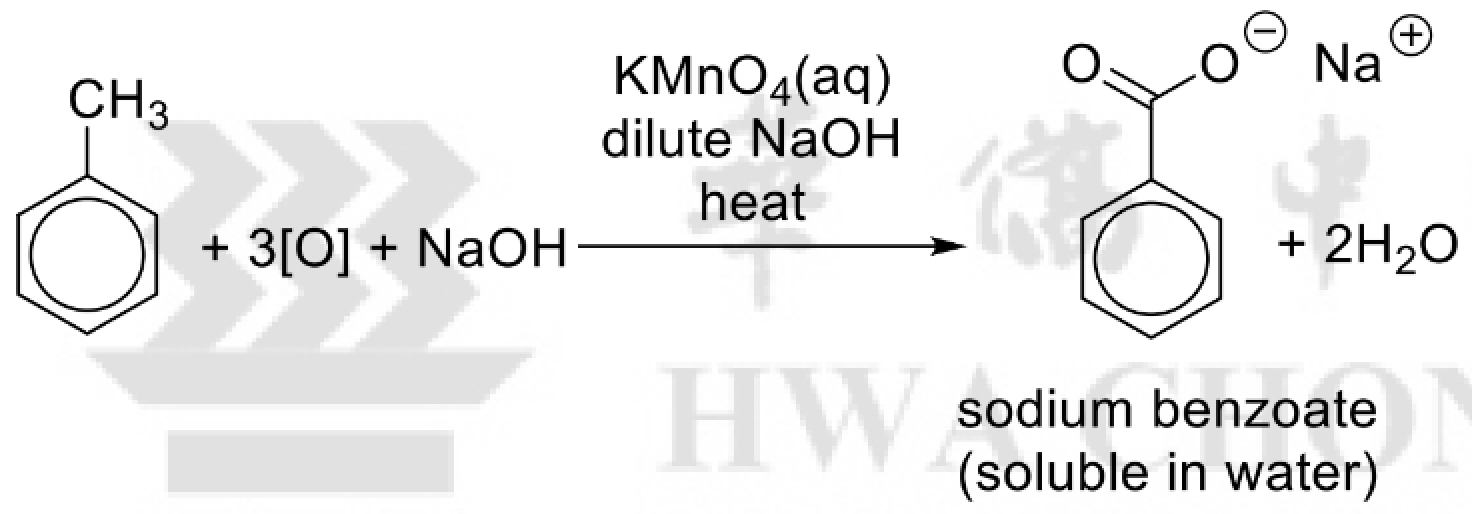
The compound  was found to be present in the product. How is the mechanism for the formation of this product best described?

A electrophilic and free-radical substitution
B electrophilic and nucleophilic substitution
C nucleophilic and free-radical substitution
D nucleophilic substitution only

[N94/4/19]

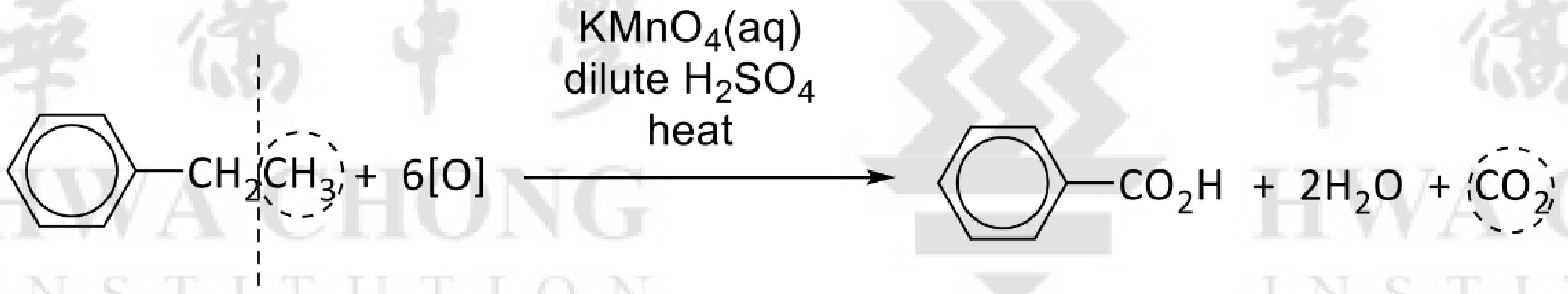
5.6.2 Side-Chain Oxidation

When particular alkylbenzenes are heated with aqueous potassium manganate(VII) in the presence of dilute H_2SO_4 or dilute NaOH, oxidation of the side chain occurs.

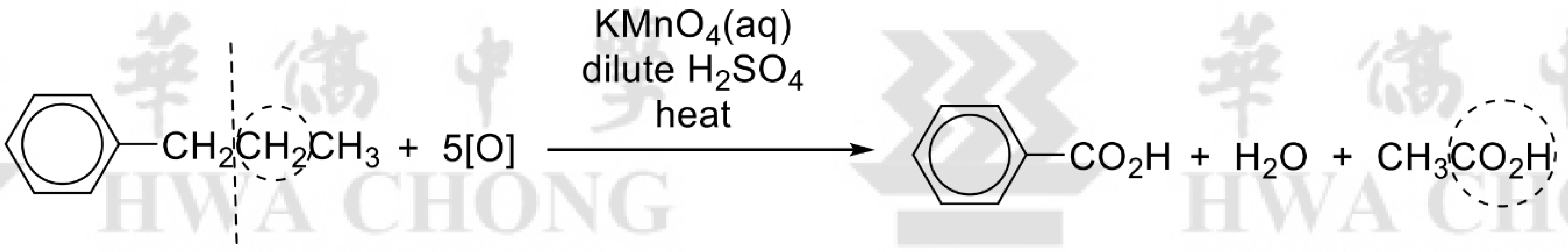
	
Reagents and conditions: $KMnO_4$(aq), dilute H_2SO_4, heat	**Reagents and conditions:** $KMnO_4$(aq), dilute NaOH, heat
Observations: purple $KMnO_4$(aq) decolourises and white precipitate of benzoic acid is formed	**Observations:** purple $KMnO_4$(aq) decolourises and brown precipitate of manganese dioxide, MnO_2(s) is formed

Regardless of the length of the alkyl side chain **(with the exception when there are three alkyl groups attached to the C atom beside the benzene ring)**, the alkyl group will be oxidised to $-CO_2H$ in acidic or alkaline medium.

For example, ethylbenzene will also undergo side chain oxidation in acidic medium producing benzoic acid but the second carbon in the side chain is oxidised to CO_2(g).

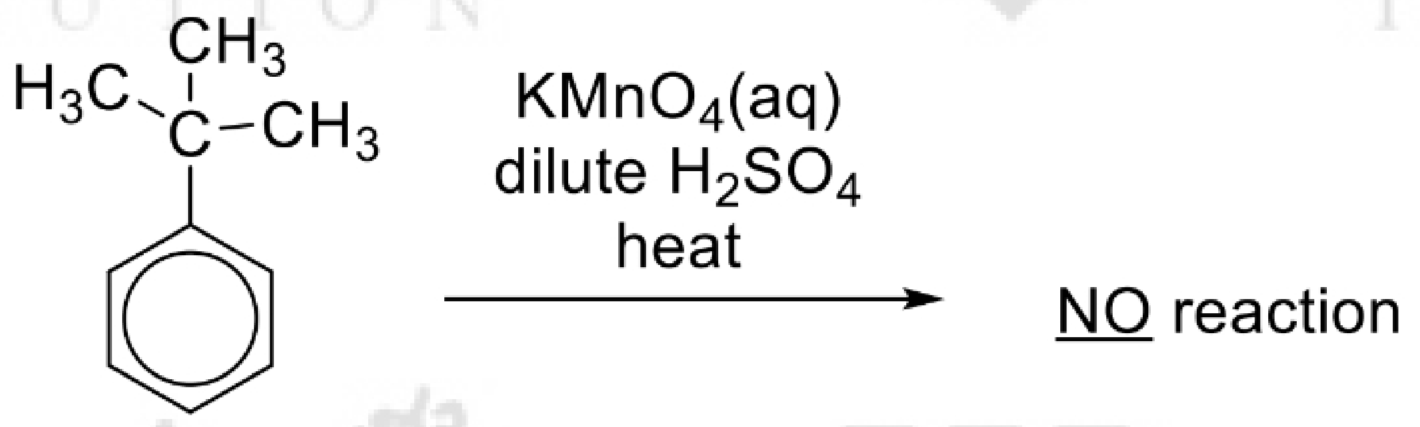


If the side chain consists of a propyl group (or a longer straight chain alkyl group), the products after oxidation in acidic medium will consist of benzoic acid and the rest of the side chain gets oxidised to a carboxylic acid.



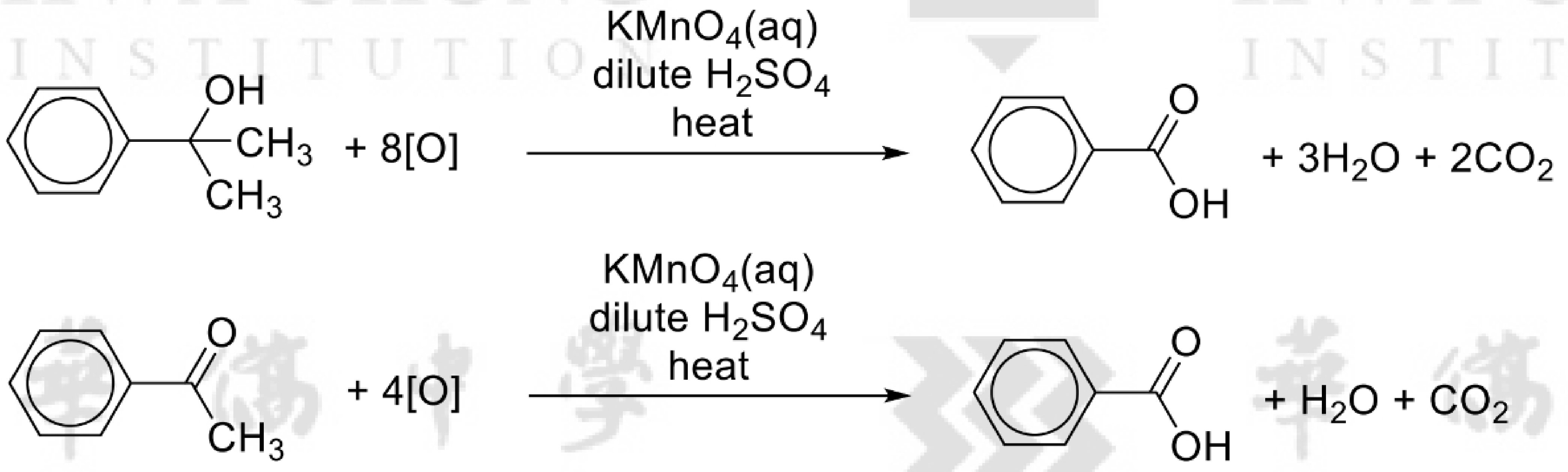
EXCEPTION

When there are three alkyl substituents attached to the C atom beside the benzene ring, the alkylbenzene will <u>not</u> undergo side-chain oxidation.



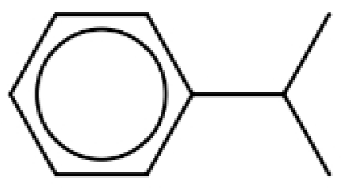
tert-butylbenzene

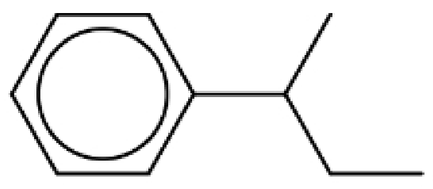
OTHER CASES OF SIDE-CHAIN OXIDATION

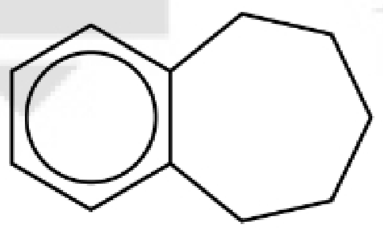


[2009/P2/4c and 2003/P3/7]

Lecture Exercise 5.3

1. Write a balanced equation for the side-chain oxidation of  in acidic medium.

2. Write a balanced equation for the side-chain oxidation of  in acidic medium.

3. Write a balanced equation for the side-chain oxidation of  using dilute NaOH.

6 DISTINGUISHING TESTS

Bromine in tetrachloromethane can be used as a **distinguishing test to differentiate between alkenes and arenes**. For example: 1-methylcyclohexene and benzene.

Procedure for distinguishing test between 1-methylcyclohexene and benzene as example

1. Add bromine in tetrachloromethane **dropwise with shaking** to 1 cm^3 of each compound in separate test tubes.

Observations

Benzene: Reddish-brown Br_2 in CCl_4 not decolourised

1-methylcyclohexene: Reddish-brown Br_2 in CCl_4 decolourises

Note

- Bromine in tetrachloromethane is usually employed instead of liquid bromine because it is easier to handle than liquid bromine which is a volatile liquid at rtp that constantly gives rise to toxic bromine gas.
- In the presence of light, both electrophilic addition and free radical substitution occur to 1-methylcyclohexene. However, free radical substitution is **not** usually used as a distinguishing test.

Aqueous bromine can be used as a **distinguishing test to differentiate between alkenes and arenes**. For example: 1-methylcyclohexene and benzene.

Procedure for distinguishing test between 1-methylcyclohexene and benzene as example

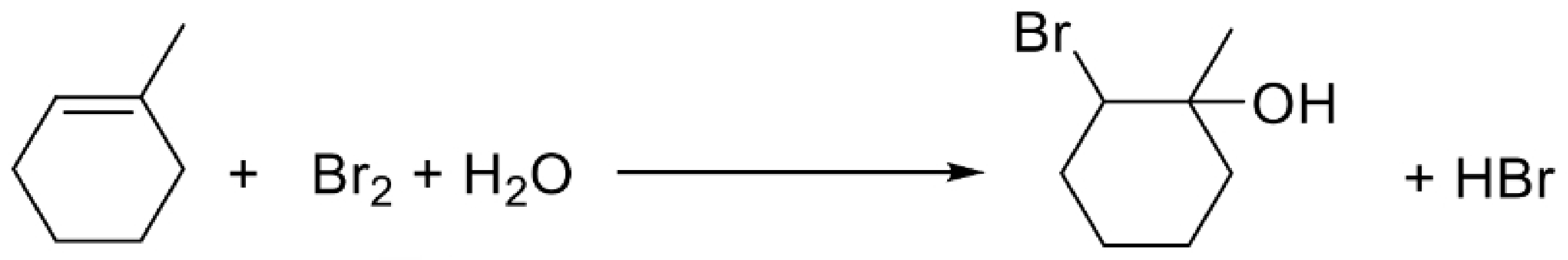
1. Add aqueous bromine **dropwise with shaking** to 1 cm^3 of each compound in separate test tubes.

Observations

Benzene: Yellow-orange $Br_2(aq)$ not decolourised

1-methylcyclohexene: Yellow-orange $Br_2(aq)$ decolourises

Equation:

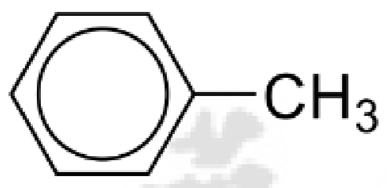
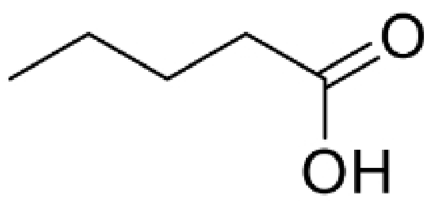
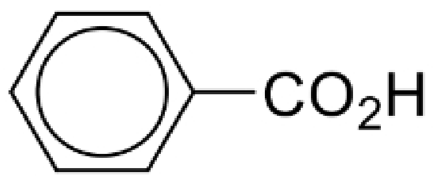


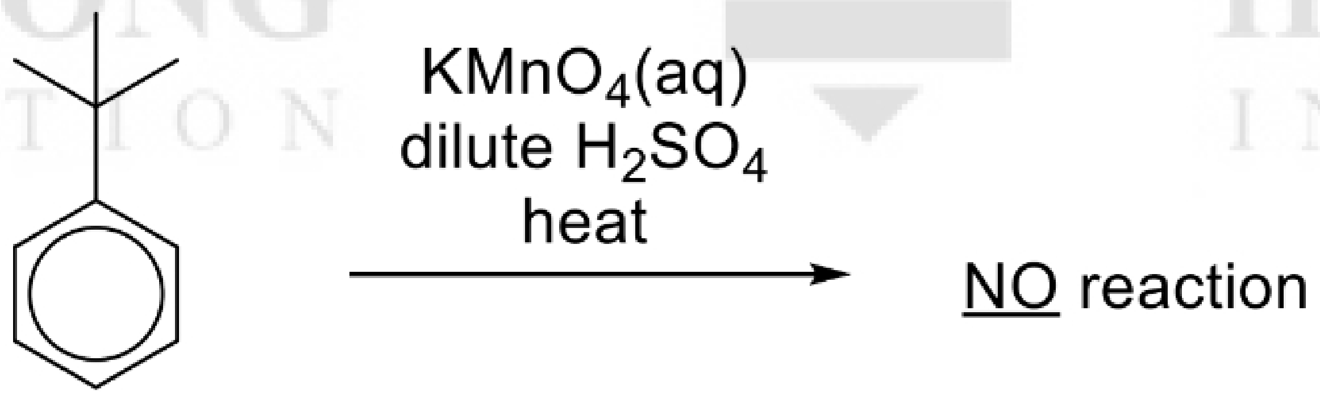
(major product)

Note:

The difference between aqueous bromine and bromine in tetrachloromethane is that in the presence of light, free radical substitution does not occur with the use of aqueous bromine.

Heating with aqueous potassium manganate(VII) and dilute H_2SO_4 can be used as a **distinguishing test to differentiate between certain alkenes and certain alkylbenzenes, and between certain alkylbenzenes**. For examples: hexene and methylbenzene, and methylbenzene and *tert*-butylbenzene.

	Hexene	Methylbenzene
Structure		
Physical appearance at rtp	Colourless liquid	Colourless liquid
Reagents and conditions	$KMnO_4$(aq) Dilute H_2SO_4 Heat	$KMnO_4$(aq) Dilute H_2SO_4 Heat
Type of reaction	Oxidative cleavage	Side chain oxidation
Organic product		
Observations	Effervescence of CO_2(g) and purple $KMnO_4$(aq) decolourises No white ppt	Purple $KMnO_4$(aq) decolourises, and white ppt of benzoic acid No effervescence



tert-butylbenzene
(colourless liquid at rtp)

Procedure for distinguishing test between methylbenzene and *tert*-butylbenzene as example

1. Add 5 drops of $KMnO_4$(aq) to 1 cm^3 of dilute H_2SO_4 in a test tube.
2. To 1 cm^3 of each compound in separate test tubes, add 2–3 drops of the $KMnO_4$(aq)/H_2SO_4(aq) mixture **dropwise with shaking**. Warm this test tube in a water bath for a few minutes.

Observations

Methylbenzene: Purple $KMnO_4$(aq) decolourises, and white ppt of benzoic acid forms

tert-butylbenzene: Purple $KMnO_4$(aq) not decolourised. No white ppt.

Self-Practice 6.1

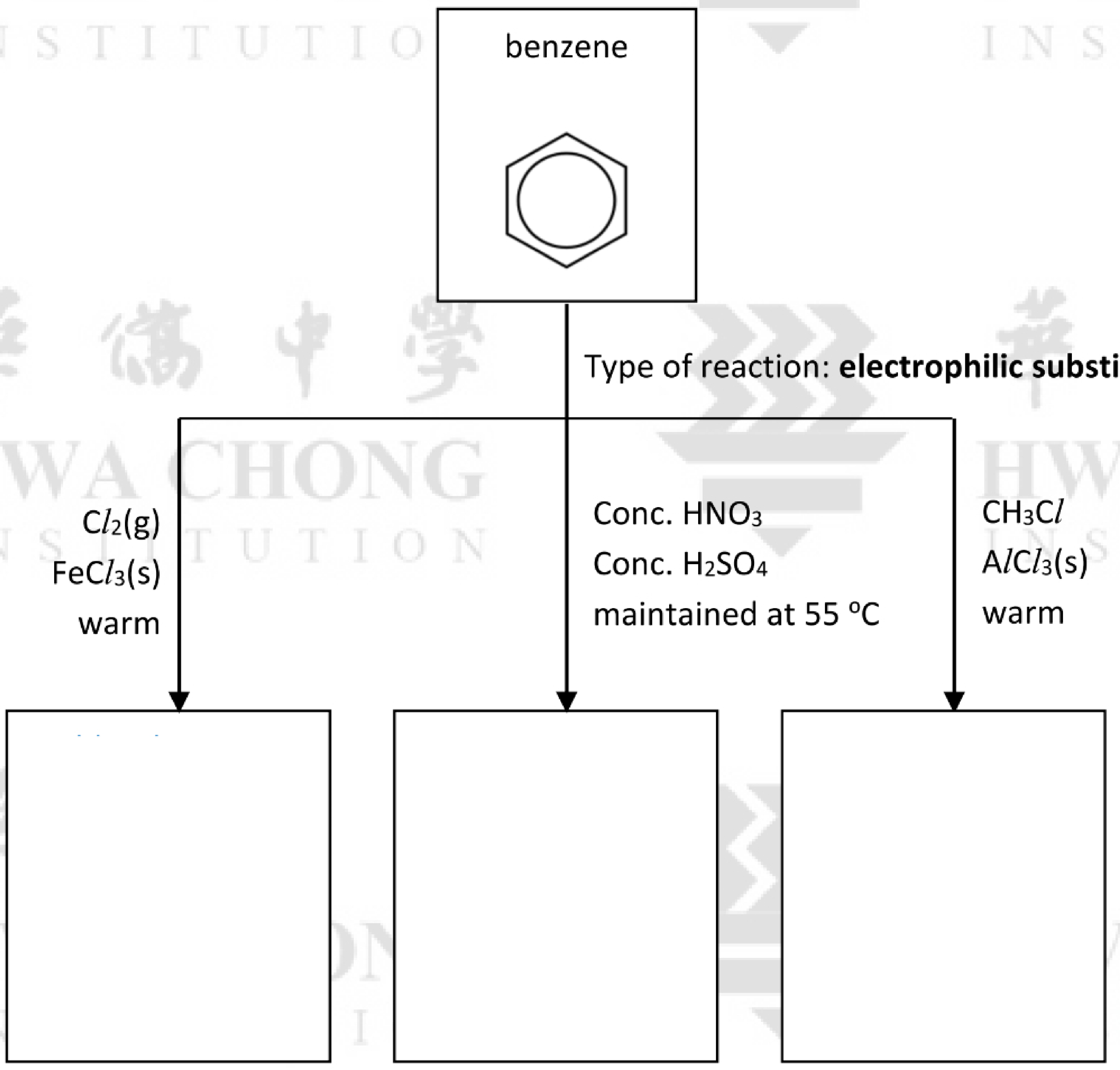
Suggest a simple chemical test to distinguish between each of the following pairs of compounds. State the reagents and conditions required, and expected observations for each compound.

a) 1-methylcyclohexene and methylbenzene, both appears as colourless liquid

b) Benzene and methylbenzene, both appears as colourless liquid

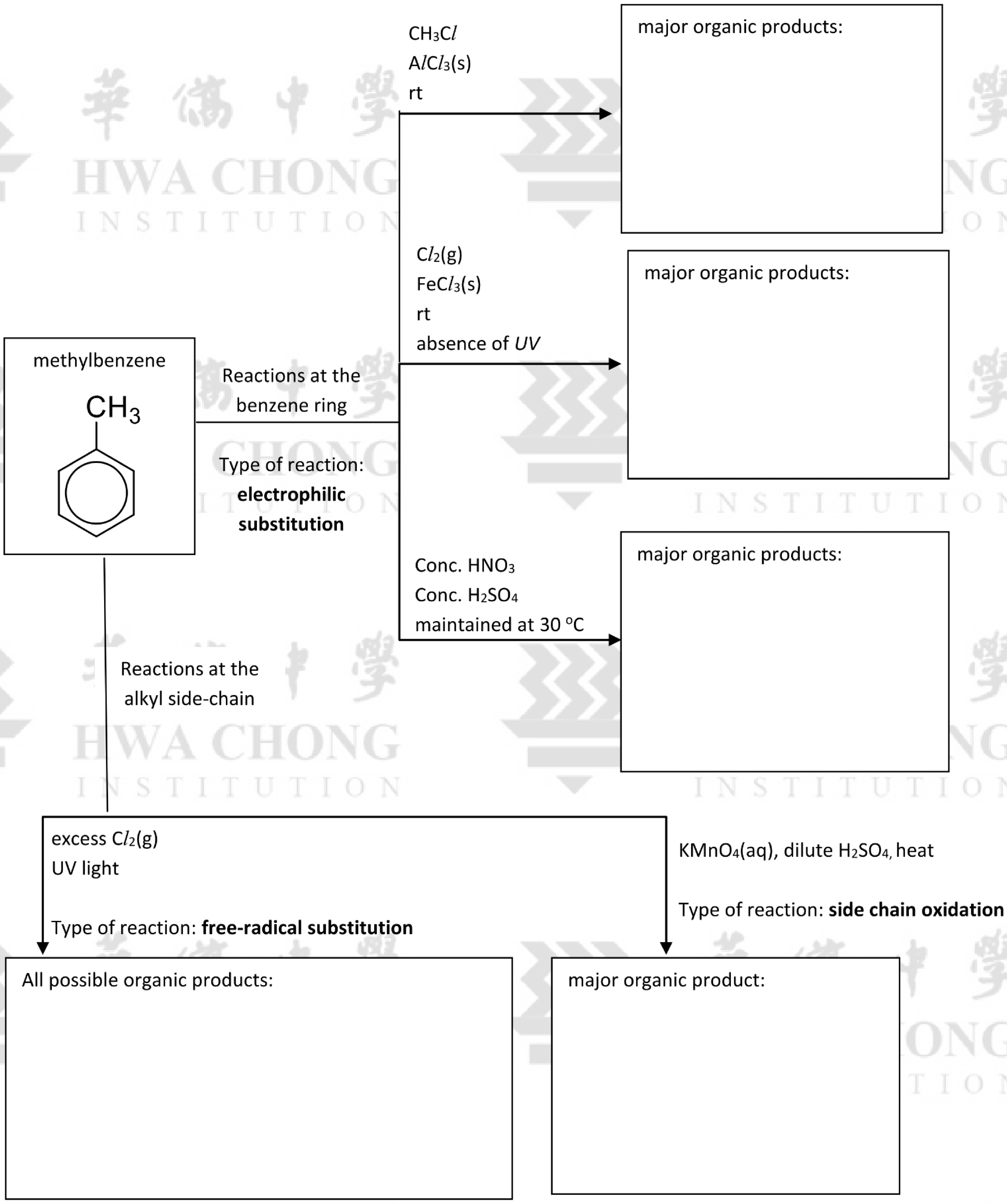
Summary of reactions of benzene

Fill in the boxes with the correct compounds.



Summary of reactions of methylbenzene

Fill in the boxes with the correct compounds.



APPENDIX

Effect on the position of the incoming electrophile

2,4-directing groups

Activating groups and halogens are 2,4-directing. The reason can be explained by the stability of the carbocation intermediates. The fundamental principle is that **"A more stable carbocation is formed faster than a less stable one"**.

Consider the nitration of methylbenzene in the following example. NO_2^+ can be added to methylbenzene at 2-, 3- or 4-position to give three carbocation intermediates as shown in the following figure. The carbocation intermediates formed from 2- and 4-substitution are stabilised more than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have a resonance structure where the positive charge is on the methyl-substituted carbon. These carbocation intermediates are stable tertiary carbocations that are stabilised by the electron-donating methyl substituent by inductive effect (see the box). The carbocation intermediates formed from 2- and 4-substitution are therefore more stable and form faster, giving rise to higher product yields of 2-nitromethylbenzene and 4-nitromethylbenzene than 3-nitromethylbenzene.

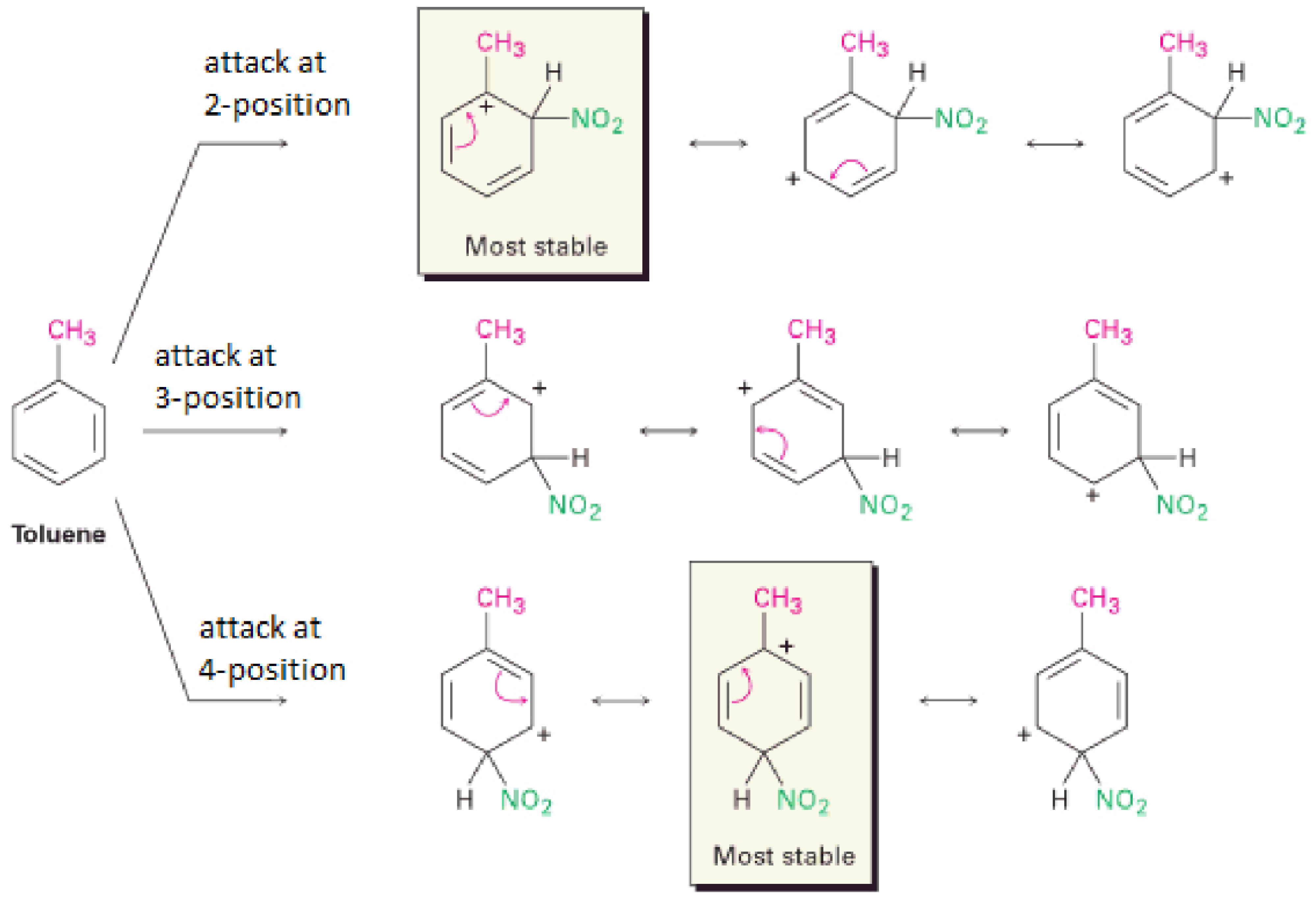


Figure 11. Carbocation intermediates in the nitration of methylbenzene. Note: It is more convenient to use one of the resonance structures of toluene for illustration.

Consider the nitration of phenol in the following example. The carbocation intermediates formed from 2- and 4-substitution are more stable than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have a resonance structure where the positive charge is stabilised by the electron-donating OH substituent by resonance effect i.e. donation of lone pair from O.

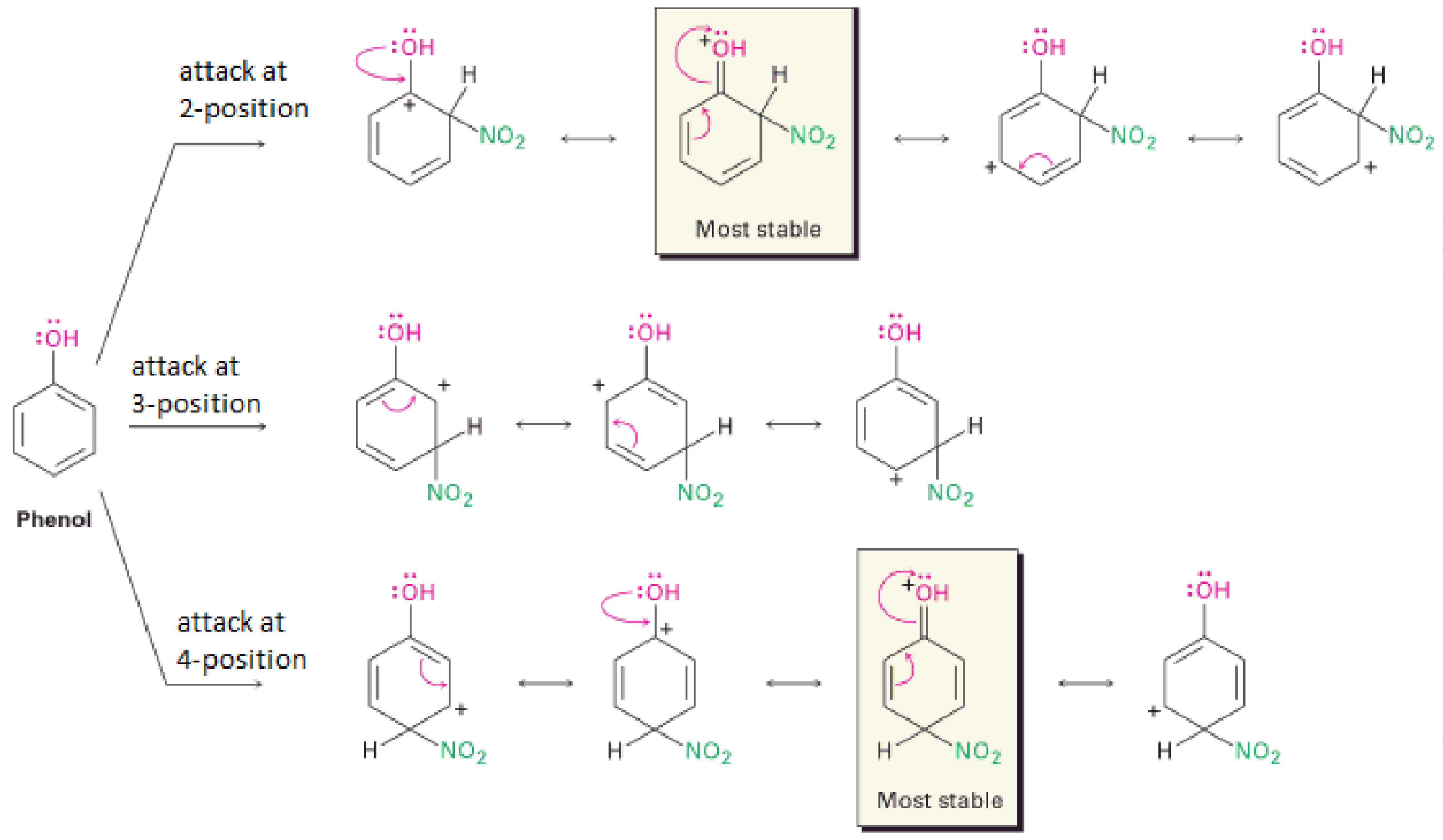


Figure 12. Carbocation intermediates in the nitration of phenol. Note: It is more convenient to use one of the resonance structures of phenol for illustration.

Consider the nitration of chlorobenzene in the following example. The carbocation intermediates formed from 2- and 4-substitution are more stabilised than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have a resonance structure where the positive charge is stabilised by the electron-donating C*l* substituent by resonance effect i.e. donation of lone pair from C*l*.

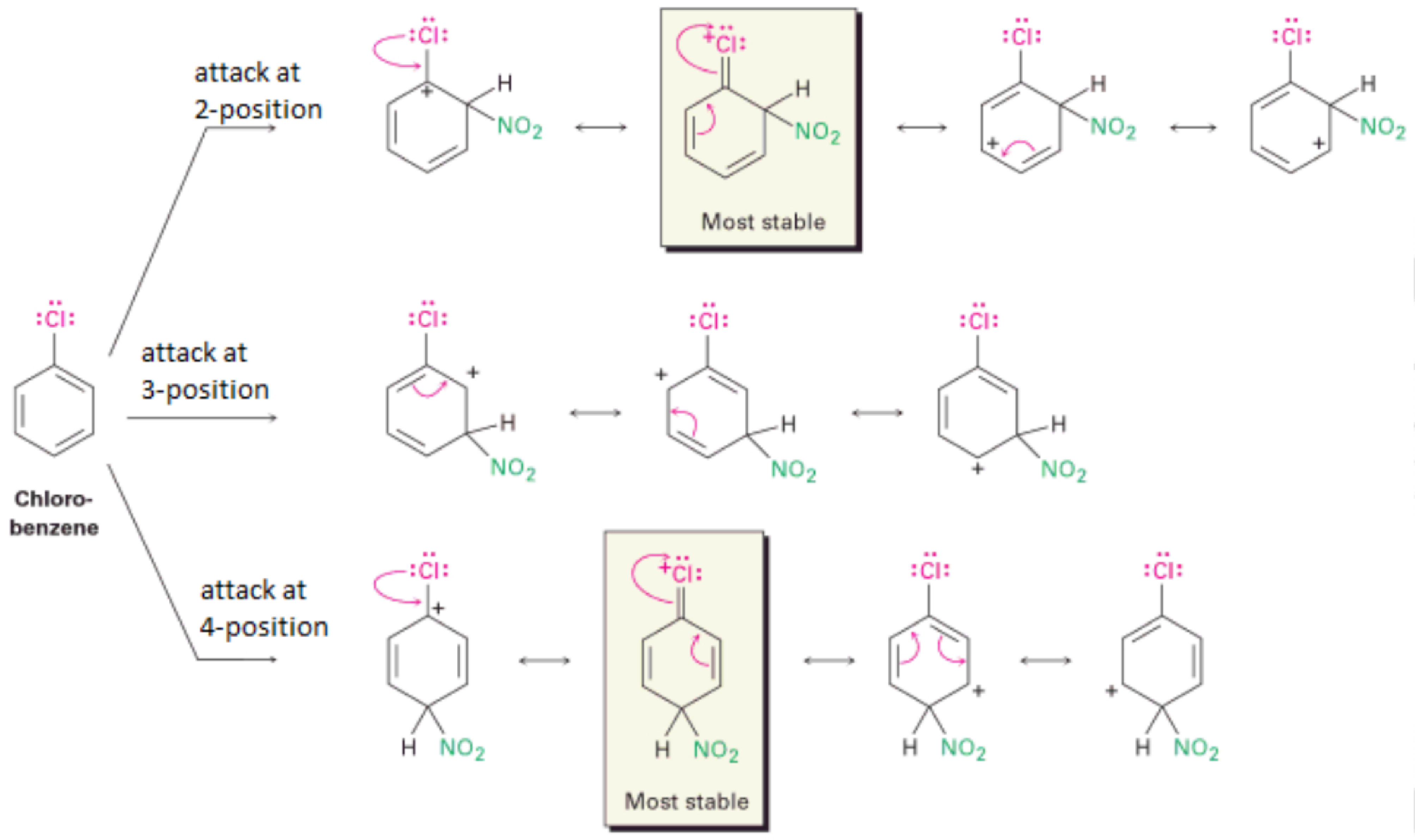


Figure 13. Carbocation intermediates in the nitration of chlorobenzene. Note: It is more convenient to use one of the resonance structures of chlorobenzene for illustration.

3-directing groups

Deactivating groups (with the exception of halogens) are 3-directing. Consider the nitration of benzaldehyde in the following example. The carbocation intermediates formed from 3-substitution is more stable than the intermediate formed from 2- and 4-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have a resonance structure where the positive charge is on the carbon bearing the deactivating group. These carbocation intermediates will be destabilised by the electron-withdrawing deactivators by both inductive and resonance effects. (See the box)

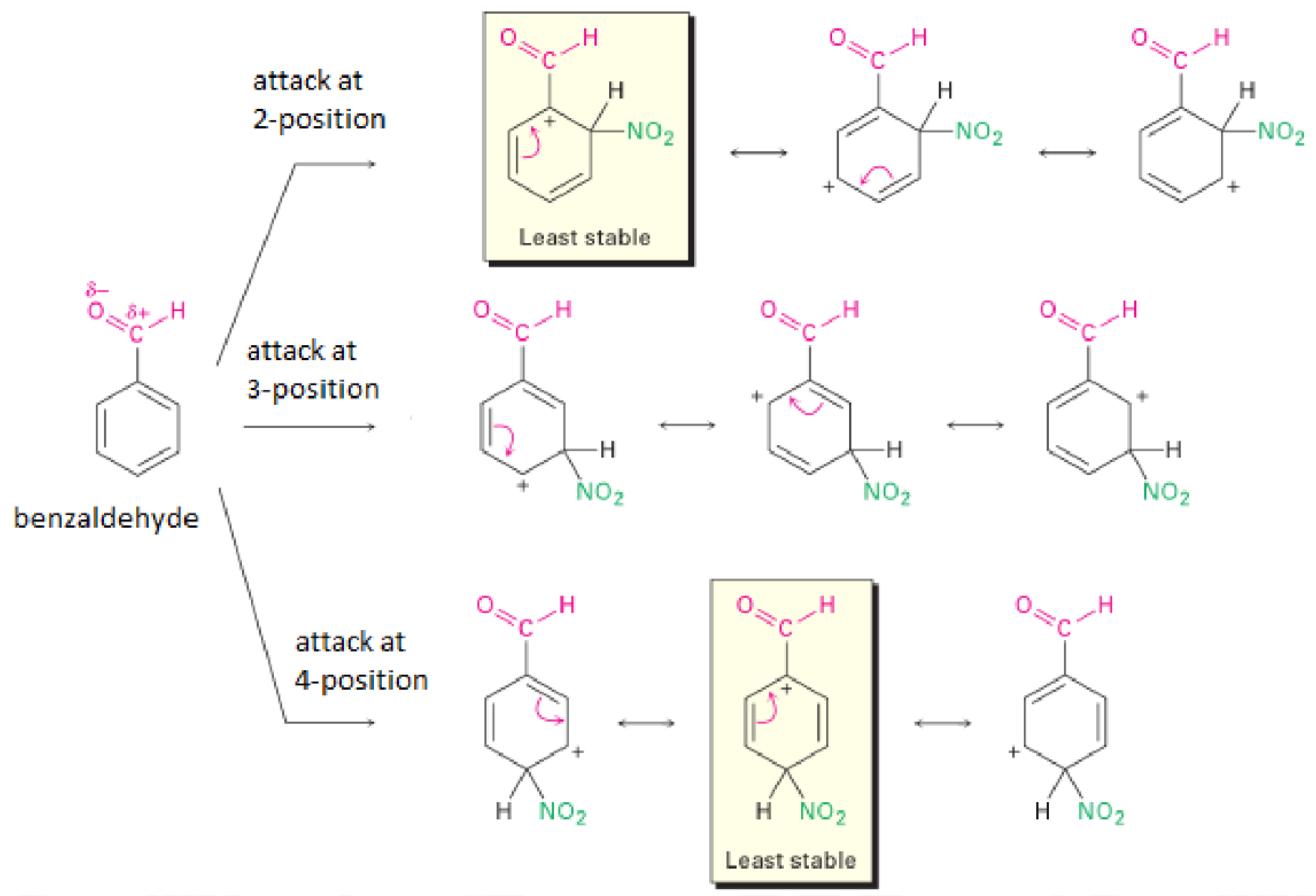


Figure 14. Carbocation intermediates in the nitration of benzaldehyde. Note: It is more convenient to use one of the resonance structures of benzaldehyde for illustration.