NOT IN H1 SYLLABUS

2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC – ORGANIC CHEMISTRY
Topic 3: HYDROCARBONS – ARENES (BENZENE AND METHYLBENZENE)

Name: ____ Civics Group: _________

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

(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; see also Section 4)
- (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst; see also Section 4)
- (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts; see also Section 4)

(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

(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 benzoic acid

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

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

References

1 **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes 540 CAN

2 **Cambridge International AS and A Level Chemistry Revision Guide** by Judith Potter and Peter Cann

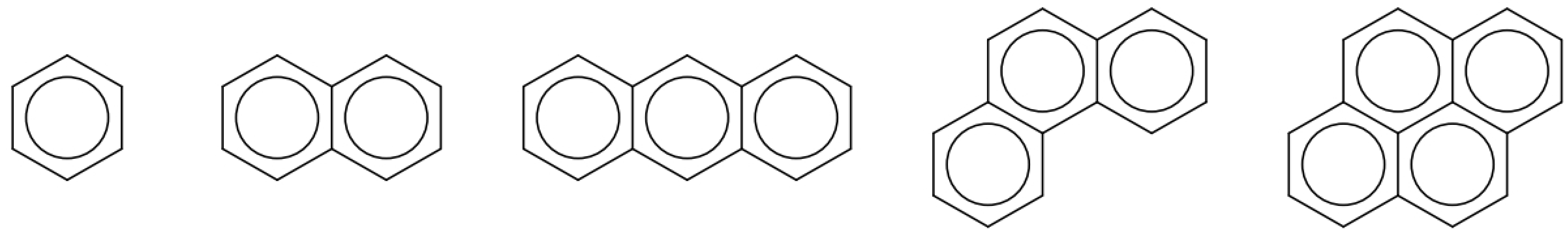
3 **Organic Chemistry (Eleventh Edition)** by Graham Solomons, Craig Fryhle & Scott Snyder

4 **Keynotes in Organic Chemistry (Second Edition)** by Andrew F. Parsons

LECTURE CONTENT

1 Introduction

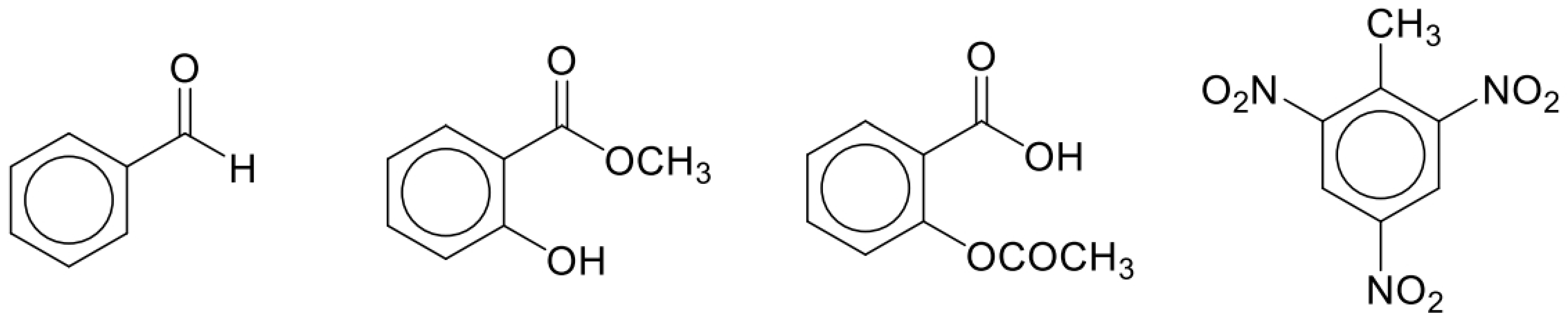
- Arenes are monocyclic and polycyclic ***aromatic*** hydrocarbons.



benzene napthalene anthracene phenanthrene pyrene

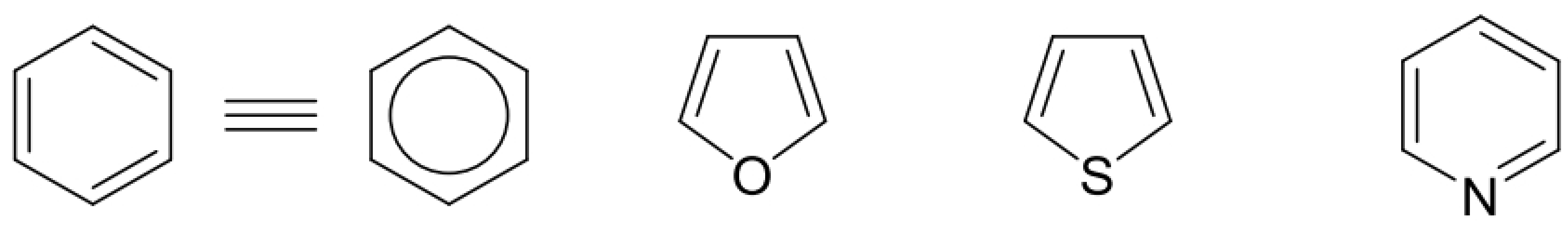
- The first known use of the word "aromatic" as a chemical term occurs in an article by August Wilhelm Hofmann in 1855.
  - Many of the earliest-known examples of aromatic compounds, such as benzene and methylbenzene, have distinctive pleasant smells, presumably leading to the term "aromatic" for this class of compounds.
- Aromatic:
  - In the traditional sense, 'having a chemistry typified by ***benzene***'.
  - A cyclically conjugated molecular entity with a stability (due to delocalisation) significantly greater than that of a hypothetical localised structure is said to possess *aromatic character*.

Examples of aromatic compounds:



benzaldehyde (in oil of almonds) | methyl salicylate (in oil of wintergreen) | acetylsalicylic acid (in aspirin) | 1,3,5-trinitrotoluene (in TNT)

- The benzene ring is not the only aromatic ring system. However, it is by far the most commonly encountered aromatic structure.



benzene furan thiophene pyridine

Checkpoint for §1

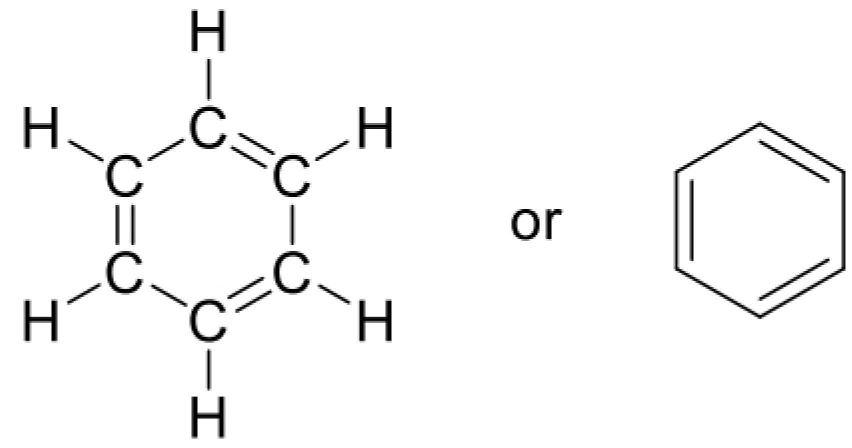
At the end of this section, you must be able to:

– understand that arenes are aromatic hydrocarbons, typically containing the benzene ring

2 Structure of Benzene

- In 1825, Michael Faraday isolated a pure compound of boiling point 80 ºC from the oily mixture that condensed from illuminating gas, the fuel burned in gaslights.
  - Elemental analysis showed an unusually small hydrogen-to-carbon ratio of 1:1, corresponding to an empirical formula of CH.
  - Vapour-density measurement suggested a molecular weight of about 78, for a molecular formula of **C_6H_6**.

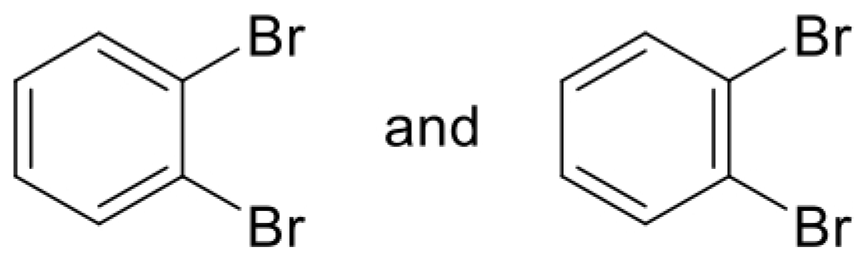
- In 1866, Friedrich August Kekulé proposed a cyclic structure for benzene with three double bonds (*i.e.* cyclohexa-1,3,5-triene). Considering that multiple bonds had been proposed only recently (1859), the cyclic structure with alternating single and double bonds was considered somewhat bizarre.



2.1 The Experimental Evidence

2.1.1 Number of isomers

- The Kekulé structure predicts that there should be two different 1,2-dibromobenzenes, but only one has ever been found. Kekulé suggested (incorrectly) that a fast equilibrium interconverts the two isomers of 1,2-dibromobenzene.

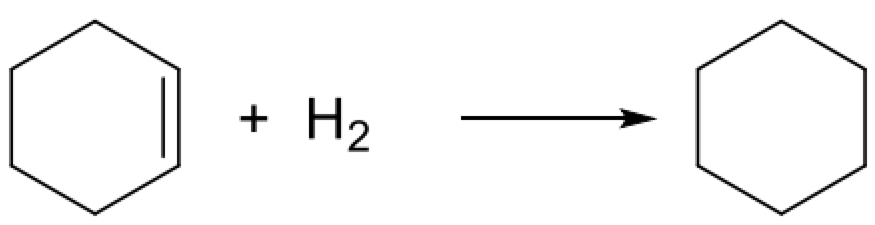


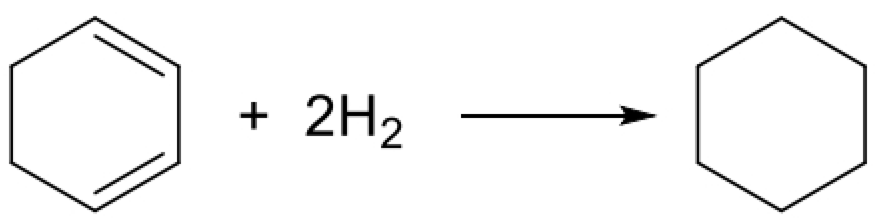
2.1.2 Carbon–carbon bond length in benzene

- X-ray diffraction studies have shown that **all the carbon–carbon bond length in benzene are exactly the same**, 0.140 nm, *i.e.* benzene is a regular hexagon with bond lengths somewhere in between the normal values of a single (0.154 nm) and a double (0.133 nm) bond. This indicates that the carbon–carbon bond in benzene have partial double bond character.

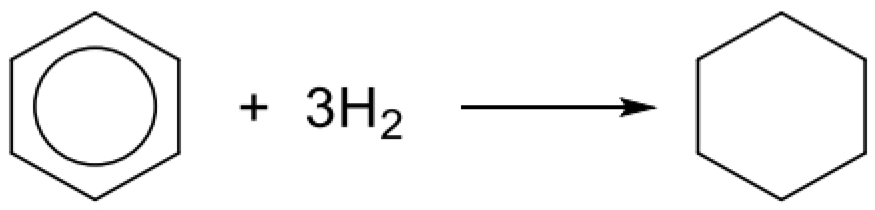
2.1.3 Enthalpy change of hydrogenation of benzene

- Cyclohexene and cyclohexa-1,3-diene can be hydrogenated to give cyclohexane:

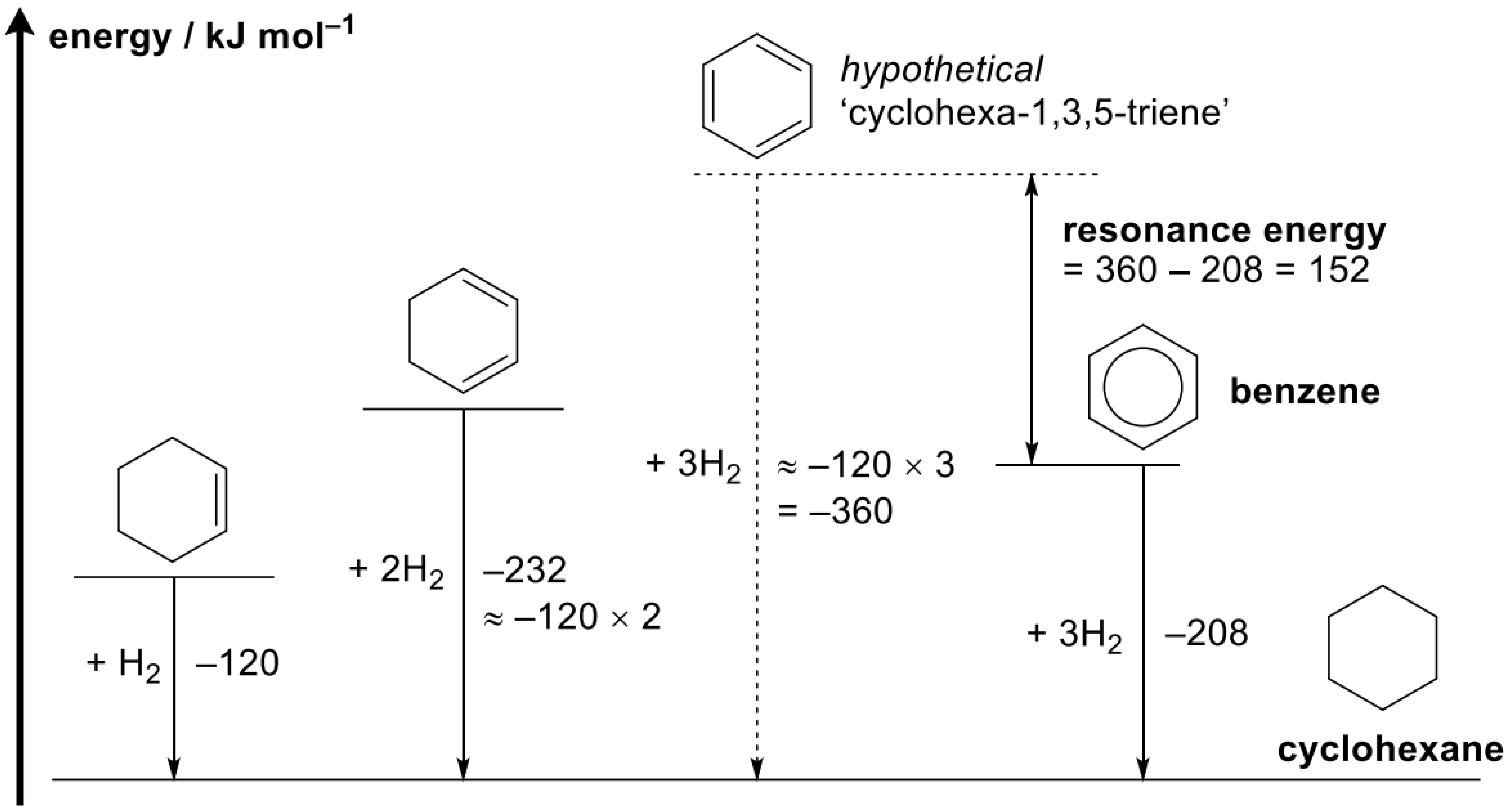
cyclohexene  $\Delta H = -120$ kJ mol^{-1}

cyclohexa-1,3-diene  $\Delta H = -232$ kJ mol^{-1}

- Benzene can also be hydrogenated to give the same final product:

benzene  $\Delta H = -208$ kJ mol^{-1}

- However, the *'real'* benzene is thermodynamically more stable than the *hypothetical* 'cyclohexa-1,3,5-triene' (Kekulé structure) by about 152 kJ mol^{-1} (known as the **resonance energy**); this compares with only approximately 8 kJ mol^{-1} by which the conjugated cyclohexa-1,3-diene is stabilised, with respect to cyclohexene.



2.1.4 Benzene does not react like alkenes

- If benzene were the Kekulé structure, it would be highly unsaturated, and would be expected to undergo addition reactions like an *alkene*:
  - Decolourise bromine through *addition*
  - Decolourise acidified $KMnO_4$ by being *oxidised*
  - *Add hydrogen* rapidly in the presence of a metal catalyst
  - *Add water* in the presence of strong acids

  However, benzene does **none** of these! (Benzene does add H_2 in the presence of finely divided Ni, but only at high temperatures and under high pressures)

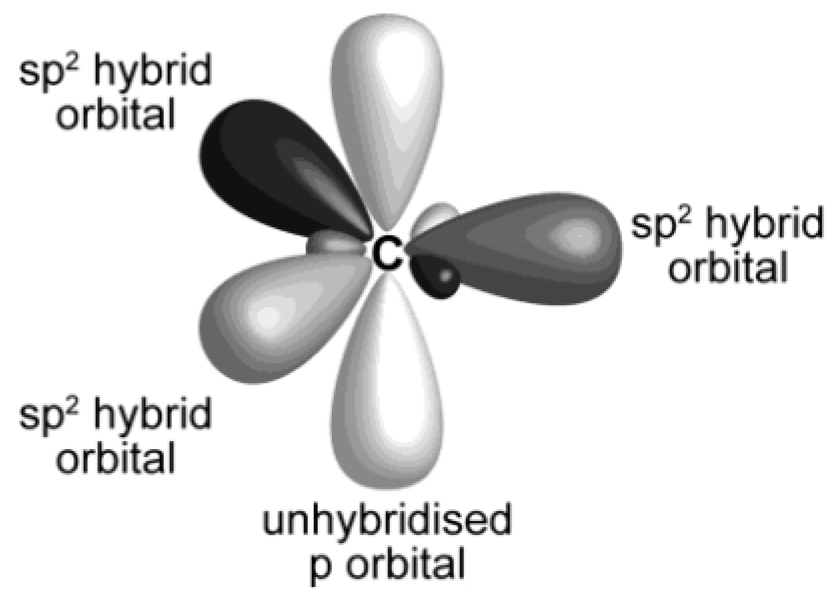
- Benzene does react with bromine but only in the presence of a Lewis acid catalyst such as $FeBr_3$. Most surprisingly, however, it reacts not by addition but by *substitution*:

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$ Substitution observed

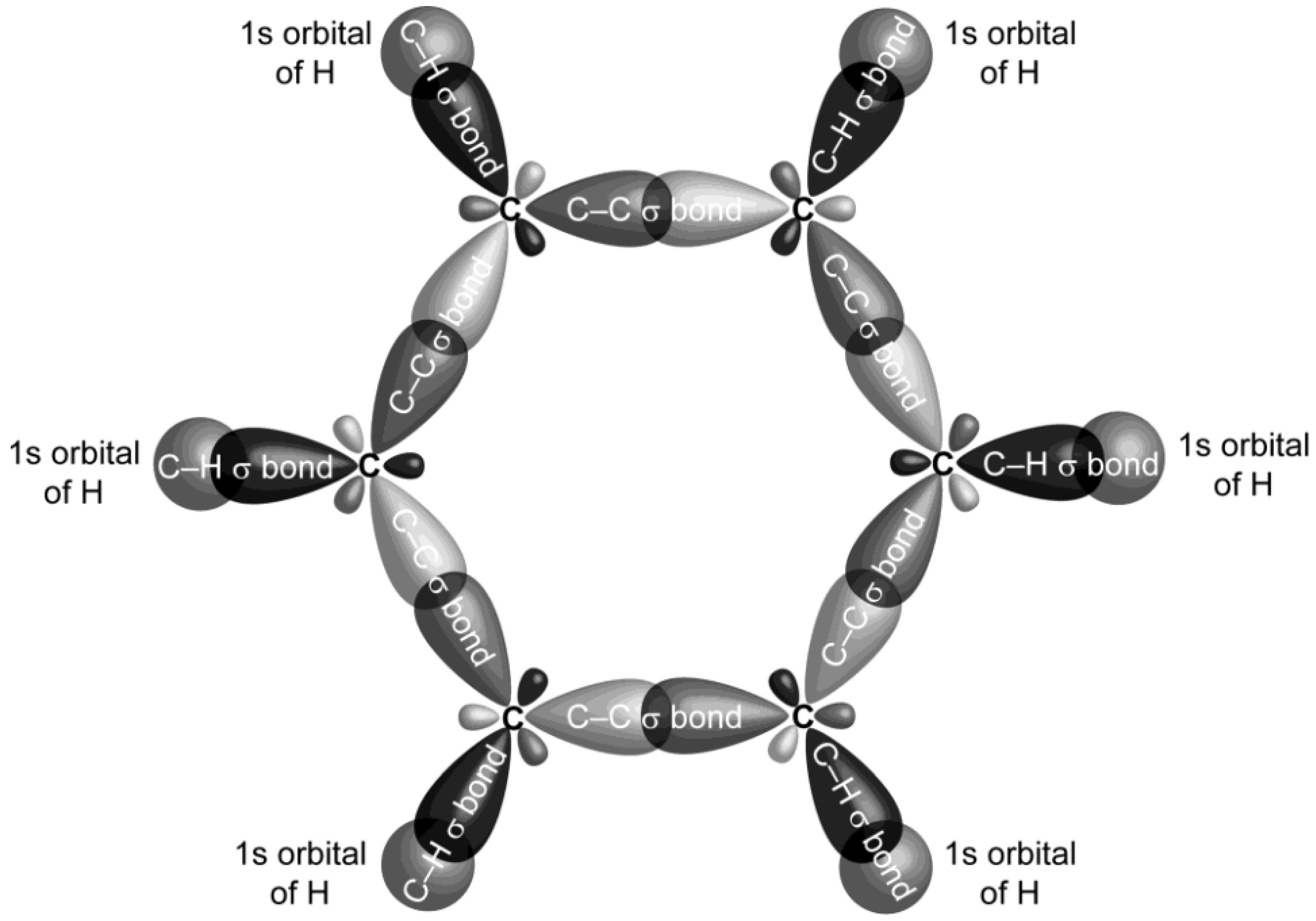
$$C_6H_6 + Br_2 \not\rightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6$$ Addition **not** observed

2.2 Resonance Hybrid Structure of Benzene

- Each of the six carbon atom in benzene is **<u>sp²</u>** hybridised:
  - three sp^2 hybrid orbitals, arranged in a **trigonal planar** manner
  - one unhybridised p orbital, **perpendicular** to the molecular plane

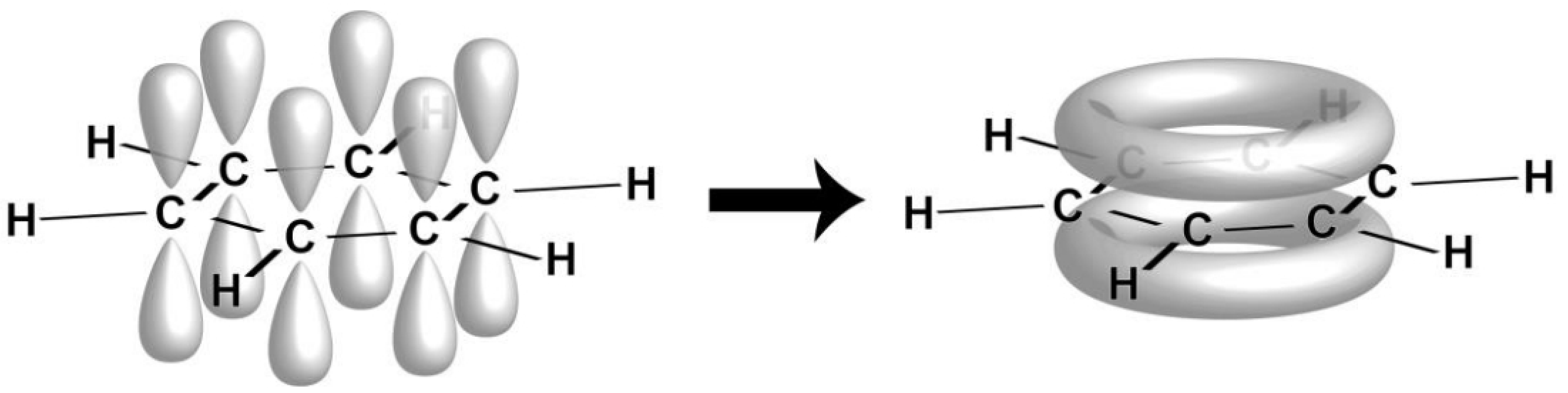


- <u>sp^2 Hybrid orbitals</u>:



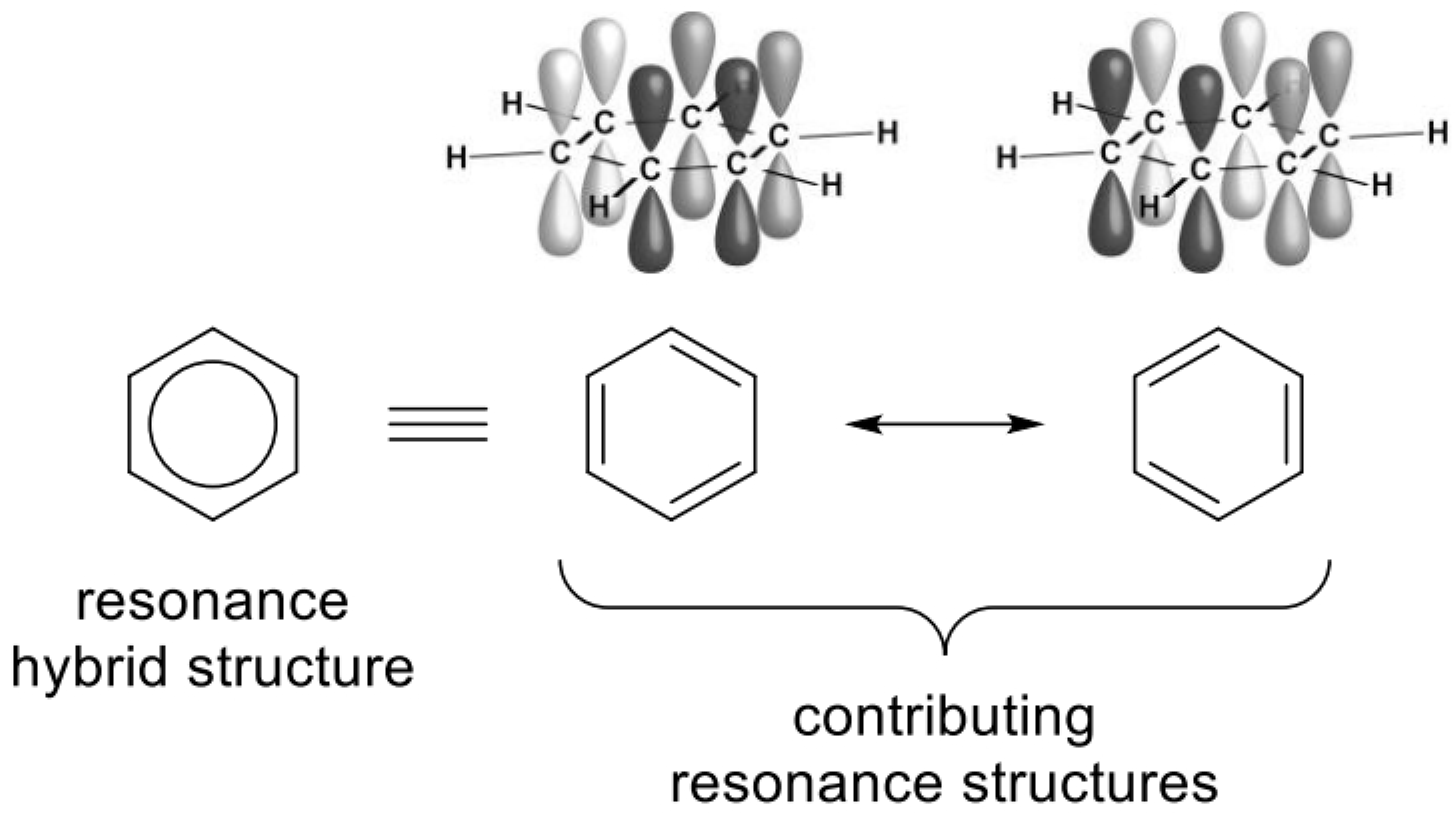
  - Two of the three sp^2 hybrid orbitals of the carbon atom **overlap head-on** with the sp^2 hybrid orbitals of two adjacent carbons to form two **C–C** sigma (σ) bonds.
  - One of the three sp^2 hybrid orbitals of the carbon atom **overlap head-on** with the 1s orbital of the hydrogen atom to form the **C–H** sigma (σ) bond.
  - The benzene molecule is planar with all bond angles in the molecule being 120°.

- <u>Unhybridised p orbital</u>:



  - The unhybridised 2p orbital, which is singly occupied, and is perpendicular to the plane of carbon atoms, overlaps side-on with the 2p orbital of the neighbouring carbon atoms in the ring.
  - The continuous overlap of the unhybridised 2p orbitals results in a **<u>cyclic delocalised π electron cloud</u>** that lies above and below the plane of the ring.

- The delocalised bonding in benzene cannot be satisfactorily expressed by a *single* Lewis structure. Instead, the electronic structure of benzene is best represented in terms of **resonance** between several contributing **resonance structures**:



  - Note the use of a double-headed arrow (⟷) and *not* the equilibrium arrow (⇌).
  - An analogy of resonance is that of a **mule**, which is described as a hybrid of a horse and a donkey. It is not a horse one second, then a donkey the next.
  - The circle in the resonance hybrid structure represents the cyclic delocalised π electron cloud.
  - The term resonance is also used to refer to the delocalisation phenomenon itself.

- The **stabilisation** resulting from delocalisation of the 6 π electrons is linked to the quantum mechanical concept of *'resonance energy'* (see §2.1.3)

Example 2A

1 Which property does benzene have as a consequence of the delocalisation of electrons in the benzene molecule?

A Benzene is a good conductor of electricity.

B The carbon-carbon bond lengths are between those of C–C bonds and C=C bonds.

C Addition reactions of benzene takes place more easily than substitution.

D Substitution in benzene takes place at one particular carbon atom.

[J01/III/21]

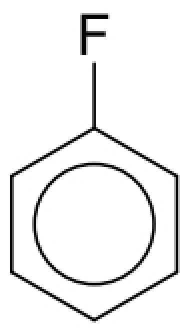
Checkpoint for §2

At the end of this section, you must be able to:
- describe sp^2 hybridisation, and explain the shapes of, and bond angles in, the benzene ring, in relation to σ and π carbon-carbon bonds
- understand the structure of benzene in terms of resonance between several contributing resonance structures
- relate the stability of benzene to its resonance hybrid structure involving delocalisation of its 6 π electrons

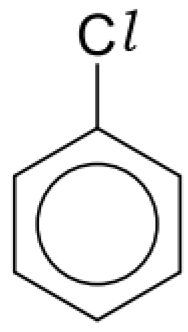
3 Nomenclature of Benzene Derivatives

3.1 Monosubstituted benzene derivatives

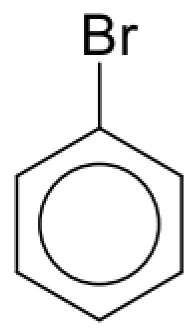
- In many simple compounds, *benzene* is the parent name and the substituent is simply indicated by a prefix added to the word *-benzene*. *E.g.*



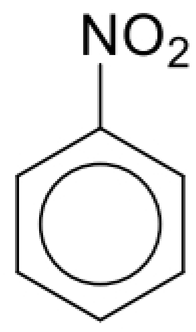
fluorobenzene



chlorobenzene

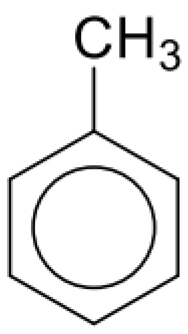


bromobenzene

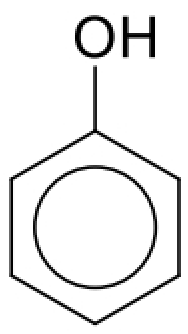


nitrobenzene

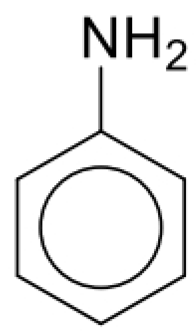
- For other simple and common compounds, the substituent and the benzene ring taken together may form a commonly accepted parent name. *E.g.*



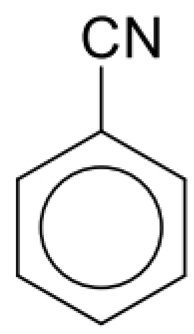
toluene
(methylbenzene*)



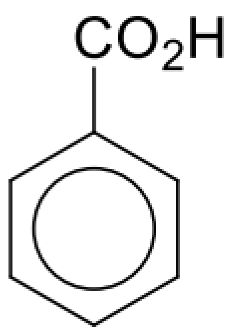
phenol*
(hydroxybenzene)



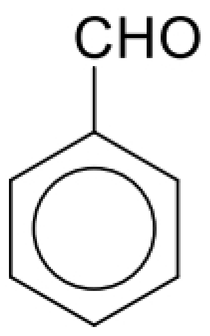
aniline
(aminobenzene)



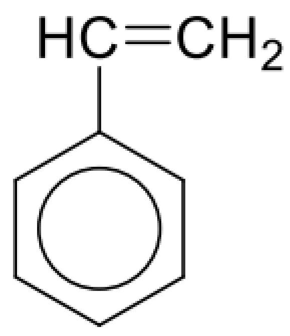
benzonitrile
(cyanobenzene)



benzoic acid*
(benzenecarboxylic acid)



benzaldehyde*
(benzenecarbaldehyde)

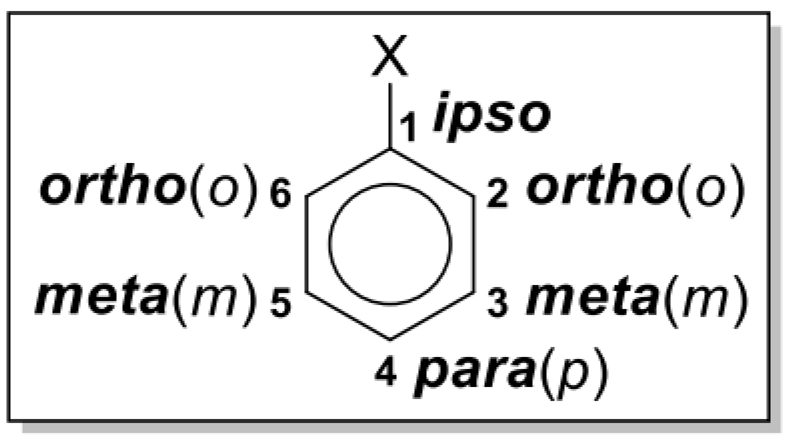


styrene
(ethenylbenzene)

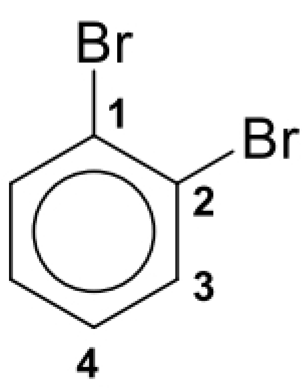
(* names commonly used in GCE A-level papers)

3.2 Polysubstituted benzene derivatives

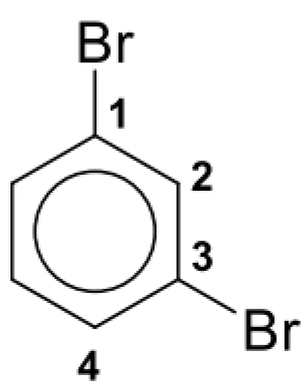
- When two substituents are present, their relative positions are indicated by the use of **numbers** (IUPAC) or historically, by the prefixes ***ortho-***, ***meta-***, and ***para-*** (abbreviated ***o-***, ***m-***, and ***p-***).



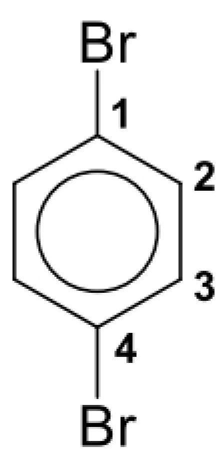
- For the dibromobenzenes we have



1,2-dibromobenzene
(*o*-dibromobenzene)

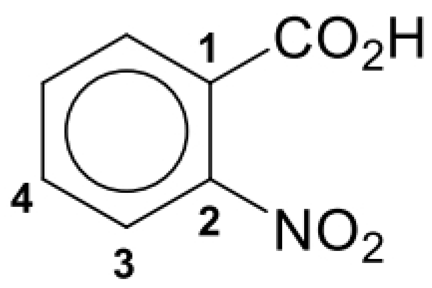


1,3-dibromobenzene
(*m*-dibromobenzene)

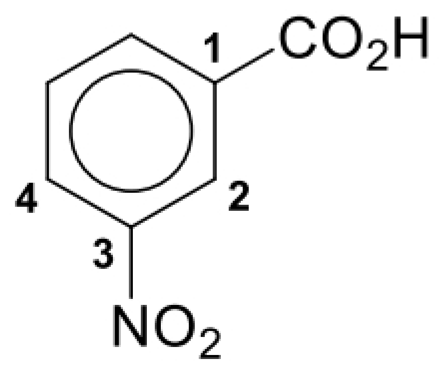


1,4-dibromobenzene
(*p*-dibromobenzene)

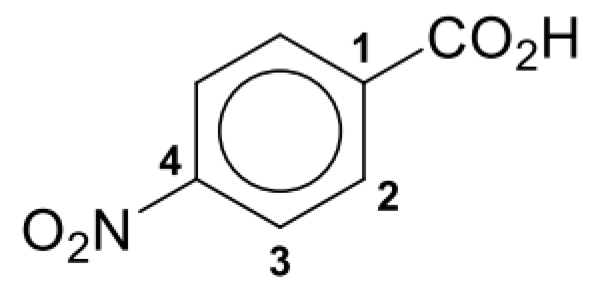
- And for the nitrobenzoic acids



2-nitrobenzoic acid
(*o*-nitrobenzoic acid)

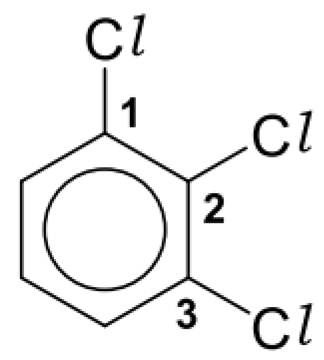


3-nitrobenzoic acid
(*m*-nitrobenzoic acid)

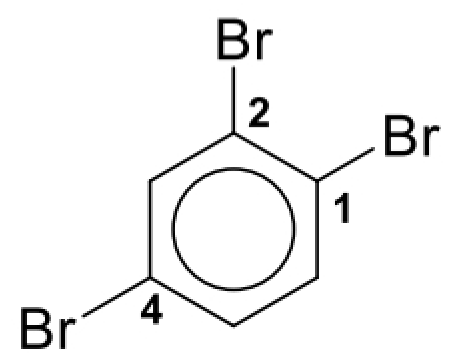


4-nitrobenzoic acid
(*p*-nitrobenzoic acid)

- If more than two groups are present on the benzene ring, their positions must be indicated by the use of *numbers*.

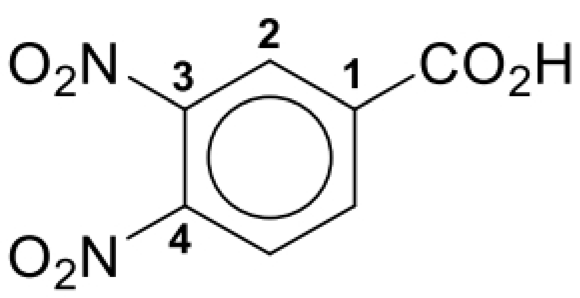


1,2,3-trichlorobenzene

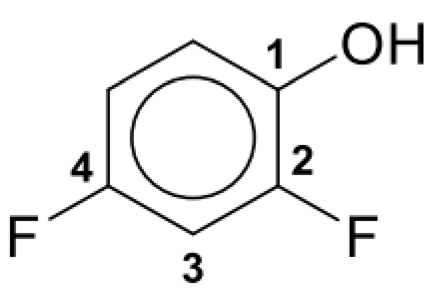


1,2,4-tribromobenzene

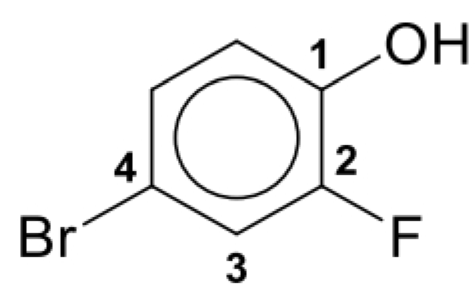
  - The ring is numbered so as to give ***the lowest possible numbers to the substituents***.
  - When more than two substituents are present and the substituents are different, they are listed in alphabetical order.
  - When a substituent is one that together with the benzene ring gives a new base name, that substituent is assumed to be in position 1 and the new parent name is used.



3,4-dinitrobenzoic acid



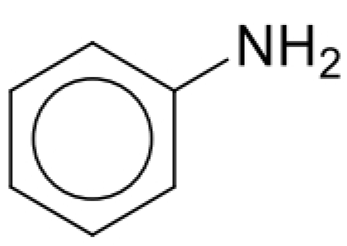
2,4-difluorophenol



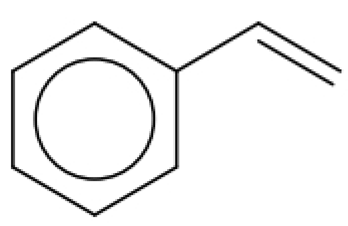
4-bromo-2-fluorophenol

3.3 Phenyl group

- When the C_6H_5— group is named as a substituent, it is called a **phenyl** group. The phenyl group is often abbreviated as C_6H_5— or Ph—.



phenylamine*
(aminobenzene, aniline)


phenylethene
(ethenylbenzene, styrene)

Example 3A

1 Draw the structural formula for each of the following compounds.

(a) 2-iodo-3-nitrophenol

(b) 6-phenylhep-2-ene

Checkpoint for §3

At the end of this section, you must be able to:

– write IUPAC names of simple substituted benzenes given the structural formula and *vice versa*.

4 Physical Properties of Arenes

- Arenes are **liquids or low melting point solids** with characteristic 'aromatic' odours. Their vapours are toxic and one should avoid inhaling them.
  - Benzene is a colourless liquid (boiling point 80 ºC) and continued inhalation of its vapour can induce anaemia and even leukaemia (*carcinogenic*). Methylbenzene is also a colourless liquid (higher boiling point 111 ºC).

- Arenes are **insoluble in polar solvents** such as water, but **soluble in non-polar organic solvents** such as CCl_4.
  - Both benzene and methylbenzene are useful solvents. Since the fumes of methylbenzene are considerably less toxic than those of benzene, it is preferable whenever possible, to use methylbenzene.

- Arenes are **immiscible** and **less dense** than (floats on) water.
  - Generally organic compounds are less dense than water, except for halogenated organic compounds.

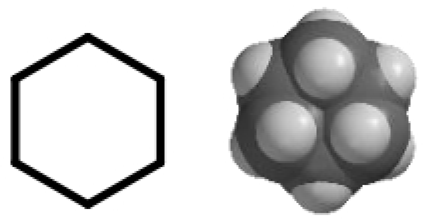
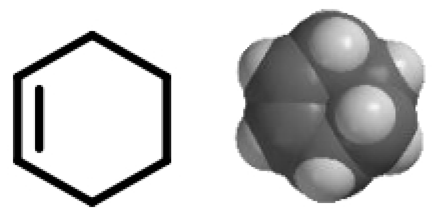
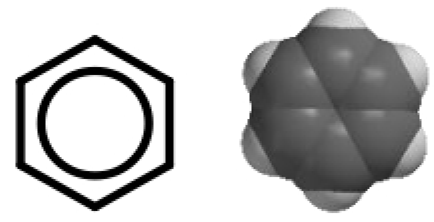
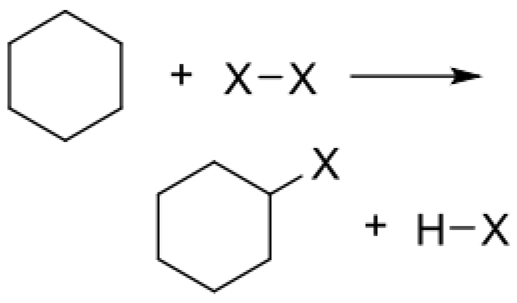
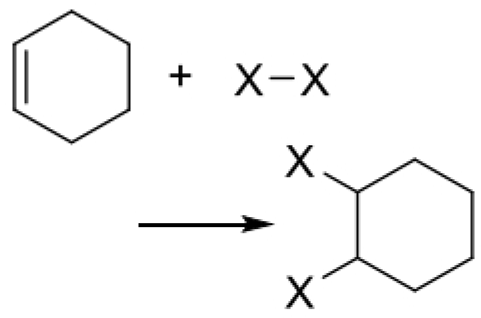
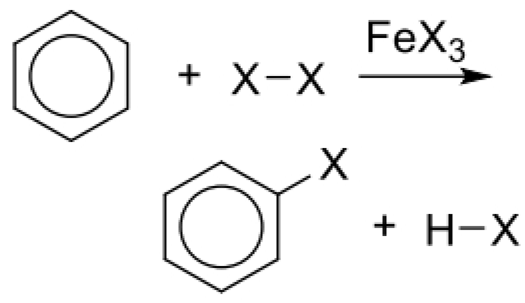
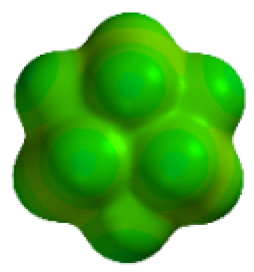
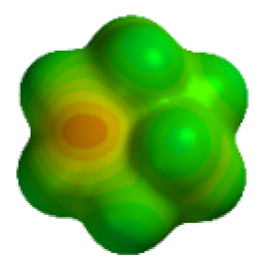
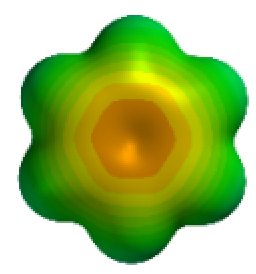
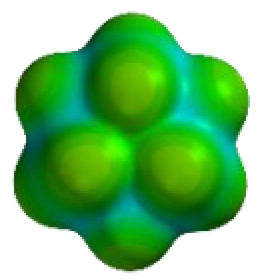
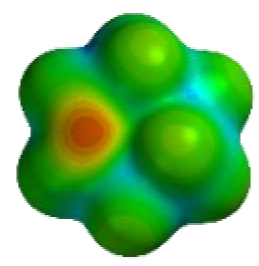
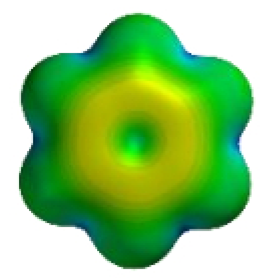
- Boiling points of arenes increase with increase in relative molecular mass due to increase in number of electrons and hence the polarizability of the electron cloud, thereby possessing stronger **instantaneous dipole-induced dipole forces of attraction** between molecules. (However, their melting point trend is *irregular* as it depends on molecular *symmetry*, which affects the packing of the molecules in the lattice.)

- Arenes burn with a **smoky** and **luminous orange flame**, owing to their relatively high carbon content (*i.e.* high C:H ratio).

5 Reactions of Benzene

LO **(h)** explain, in terms of delocalisation of π electrons, the difference between benzene and alkene:
(i) reactivity toward electrophiles
(ii) preference of benzene to undergo substitution rather than addition reaction

5.1 Reactivity of the Hydrocarbons with Halogens

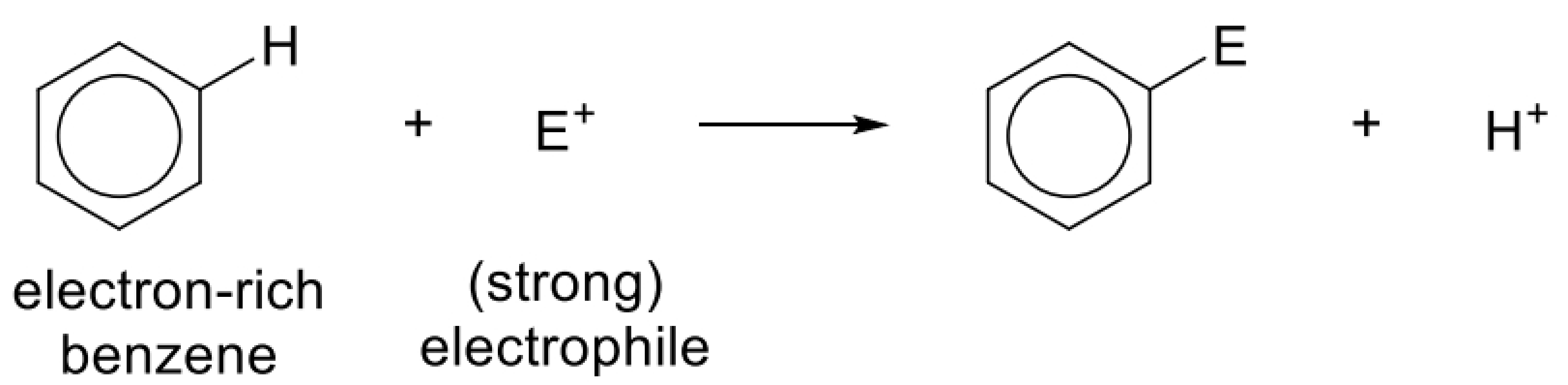
	Cyclohexane	**Cyclohexene**	**Benzene**
			
Reaction with Cl_2 and Br_2			
Electrostatic Potential Map (reflects regions of electron excess and electron deficiency)			
Electronic Property	Non-polar	C=C π bond is region of high electron density ⇒ Nucleophilic	π electron cloud is region of high electron density ⇒ Nucleophilic
Type of Reagent			
Local Ionisation Potential Map (reflects relative ease of electron removal)			
Site of Attack	**Non-selective** attack of radicals	C=C is ***highly*** susceptible to electrophilic attack	π electron cloud is susceptible to electrophilic attack
Reactivity	Strong non-polar C–H bonds require highly reactive radicals to react	Resonance stabilisation of benzene due to delocalisation of π electrons renders benzene less reactive (less nucleophilic) toward electrophiles than alkenes	
Reactive Intermediate	X• radical from homolytic fission of X–X bond	$\overset{\delta+}{X}$ from induced polarisation of X–X bond	Strong X^+ electrophile from reaction of X_2 with Lewis acid
Type of Reaction			
Reason	Saturated; Strong C–X and H–X bonds from weak X–X bond	Two strong C–X bonds from one weak C–C π bond	To preserve resonance-stabilised benzene ring

LO **(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; see also Section 4)
(ii) nitration with concentrated nitric acid
(recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst; see also Section 4)
(iii) Friedel-Crafts alkylation with halogenoalkanes
(recognise the use of Lewis acid as catalysts; see also Section 4)
(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

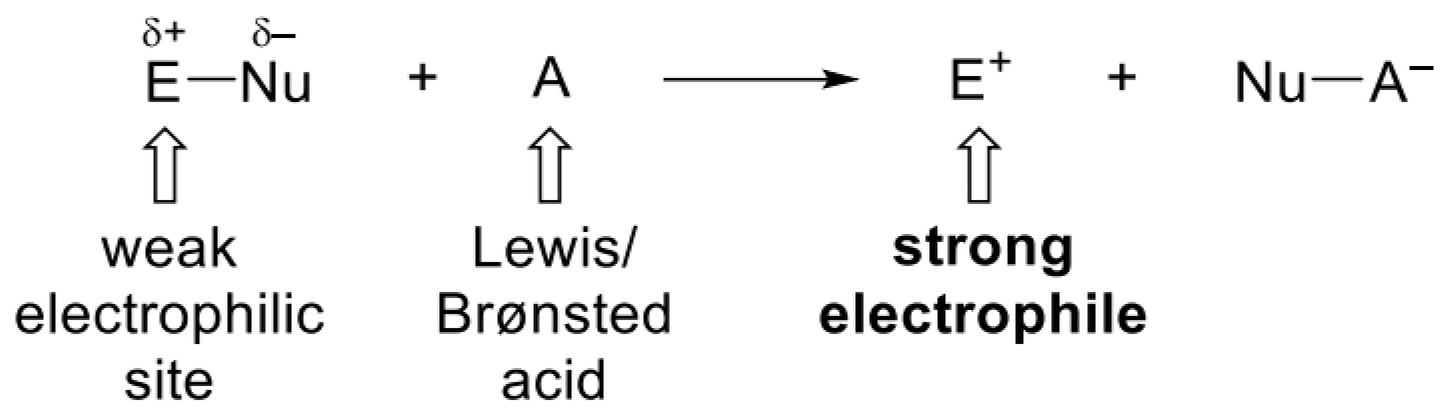
5.2 Electrophilic (Aromatic) Substitution

- The presence of the six π electrons means that benzene is electron-rich. It is thus susceptible to attacks by **electrophiles** (electron-deficient or electron-seeking species).
  - In contrast to alkenes which undergo electrophilic addition reactions, benzenes undergo **electrophilic substitution** reactions to retain the resonance-stabilised benzene ring.

- For benzene to react, **strong electrophiles** (a fully positive species) are needed for reactions and they need to be generated.

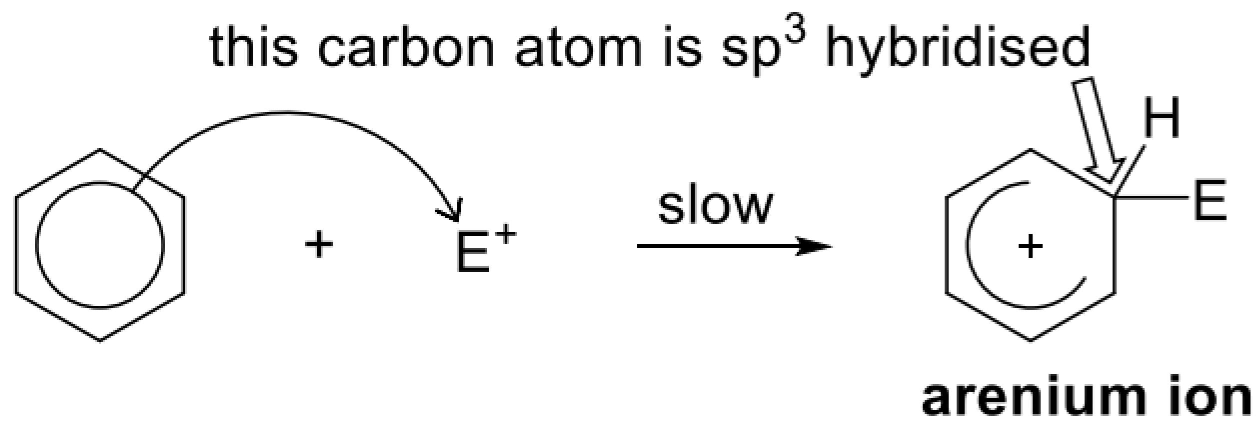


- The electrophilic substitution reaction of benzene follows the general mechanism shown.
  - **Step 1:** <u>Generation</u> of **strong electrophile**:



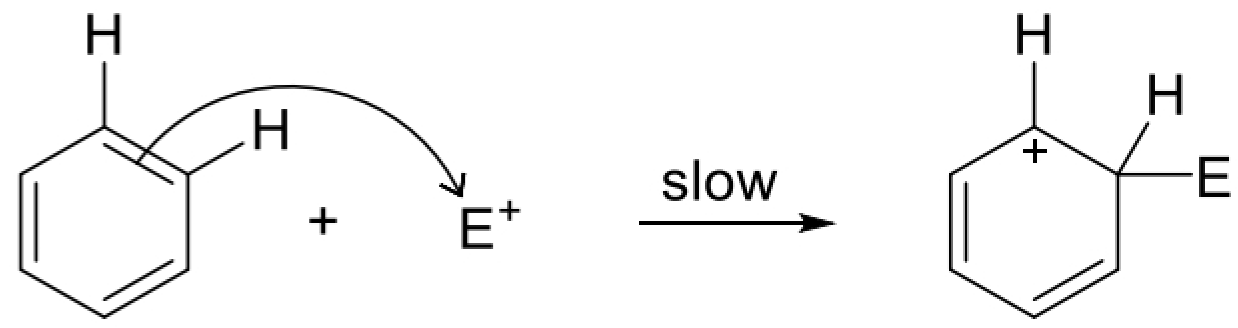
    - E^+ is a much stronger electrophile compared to the $E^{\delta+}$ in $\overset{\delta+}{E}—\overset{\delta-}{Nu}$.
    - A strong electrophile is needed as benzene is resonance-stabilised, hence the π electrons are less susceptible to electrophilic attack than those in C=C.

  - **Step 2:** <u>Electrophilic attack</u> of E^+ on benzene ring to form a resonance-stabilised **arenium ion**:

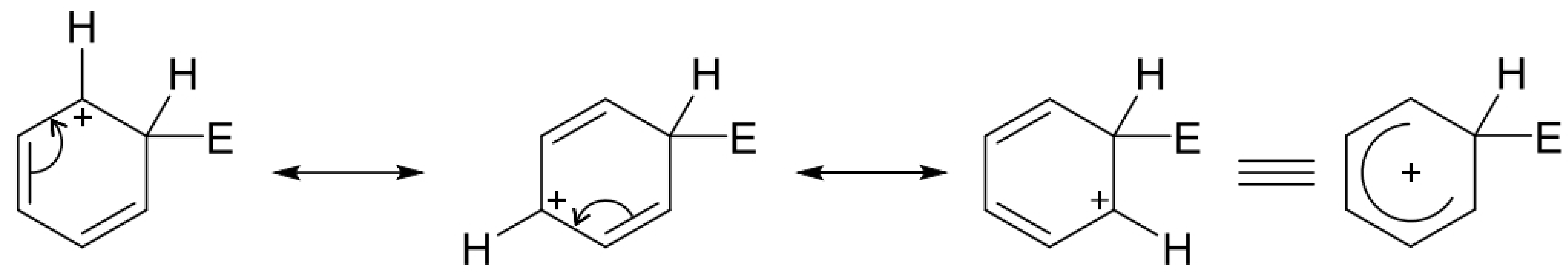


    - This is the **rate-determining step** because it involves destruction of the aromaticity of the benzene ring.

- The electrophile attacks the electron rich benzene ring and uses two of the six π electrons in the delocalised π electron cloud to form a σ bond to one carbon atom of the benzene ring.
- This leads to a *change in hybridisation* of the carbon undergoing substitution, from sp^2 in the benzene ring to sp^3 in the arenium ion intermediate.
- If the benzene is represented using the Kekulé structure, this step is similar to the electrophilic attack on a C=C in alkene:

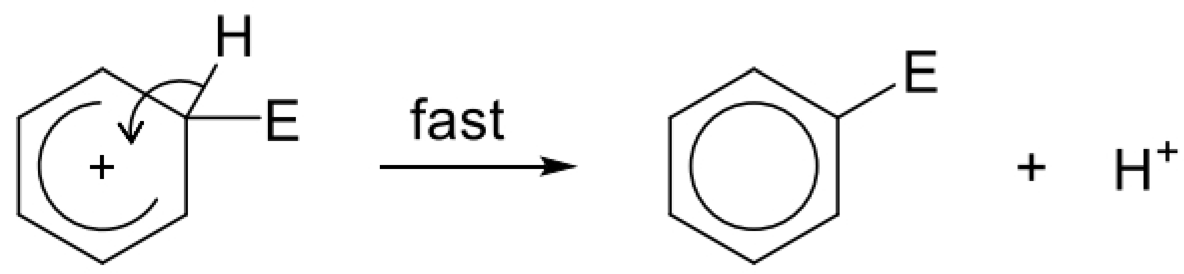


- However, due to presence of the two double bonds, the positive charge is delocalised over all five carbon atoms, represented by the arenium ion:



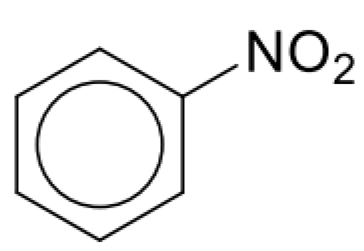
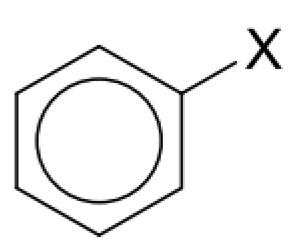
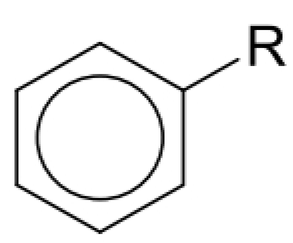
- The arenium ion is resonance-stabilised, but not aromatic (no cyclic π electron cloud).

Step 3: <u>Deprotonation</u> and **regeneration of benzene ring**

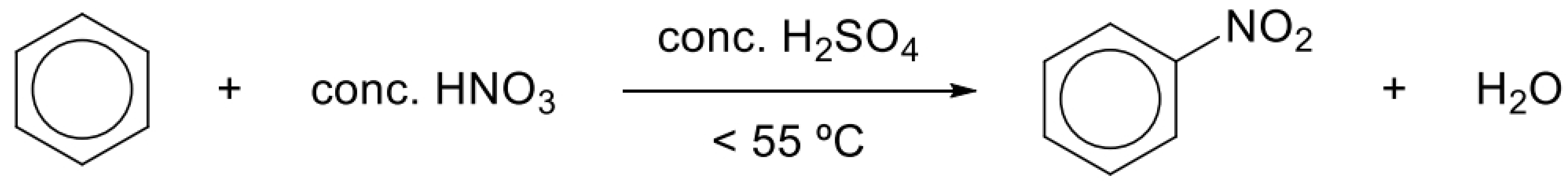


- This step is a fast step, involving abstraction of a proton from the arenium ion.
- The two electrons that bonds the proton to the carbon bearing the electrophile becomes part of the delocalised π electron cloud, restoring the aromaticity of the benzene ring.

The following table summarises the electrophilic substitution reactions of benzene.

reaction	reagent	catalyst	conditions	electrophile	organic product
nitration	conc. HNO_3	conc. H_2SO_4	< 55 ºC (for mononitration)	NO_2^+	
halogenation	X_2 (X = C*l*, Br)	A*l*X_3 or FeX_3	room temperature	X^+	
Friedel-Crafts alkylation	R–X (X = C*l*, Br)	A*l*X_3 or FeX_3	room temperature	R^+	

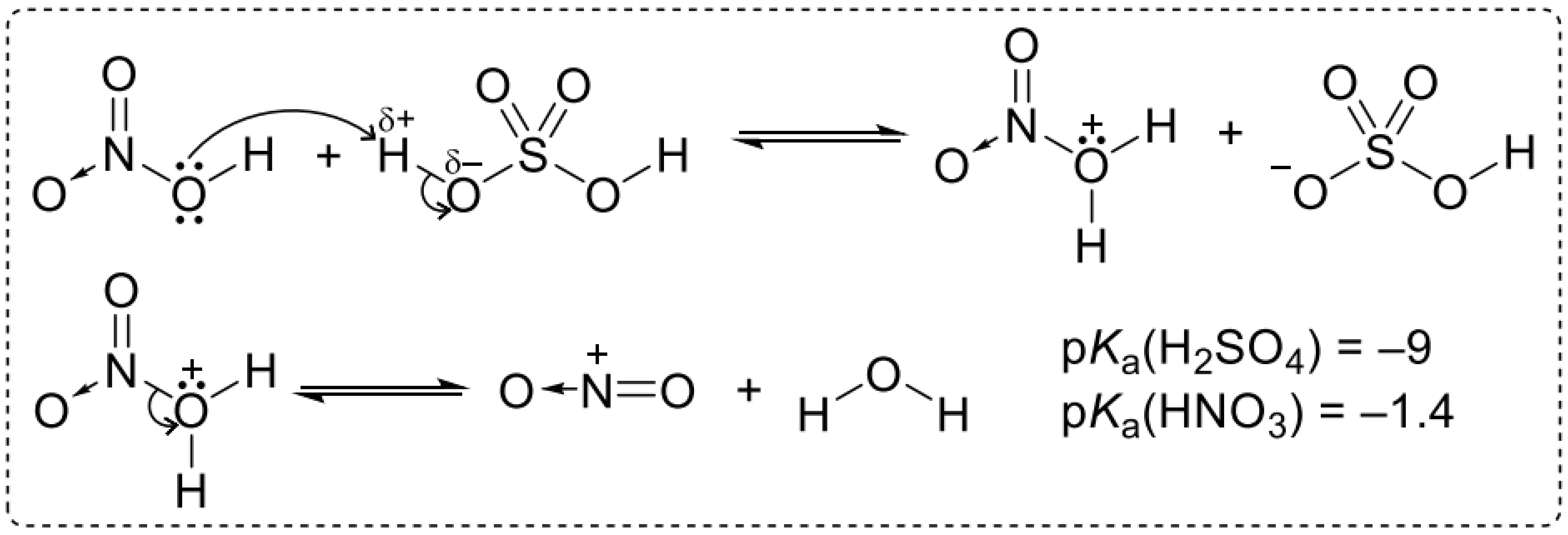
5.2.1 Nitration



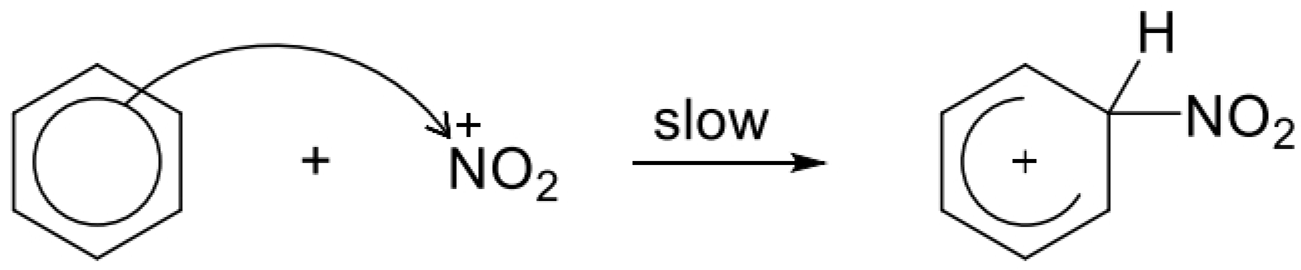
Reagents and conditions: concentrated HNO_3 and concentrated H_2SO_4 catalyst, temperature maintained below 55 ºC

- Name of mechanism: **Electrophilic Substitution**
  - **Step 1:** Generation of electrophile, NO_2^+ (nitronium ion)
    - In the nitrating mixture, HNO_3 acts as a Brønsted-Lowry base to accept a proton from the Brønsted-Lowry acid H_2SO_4.

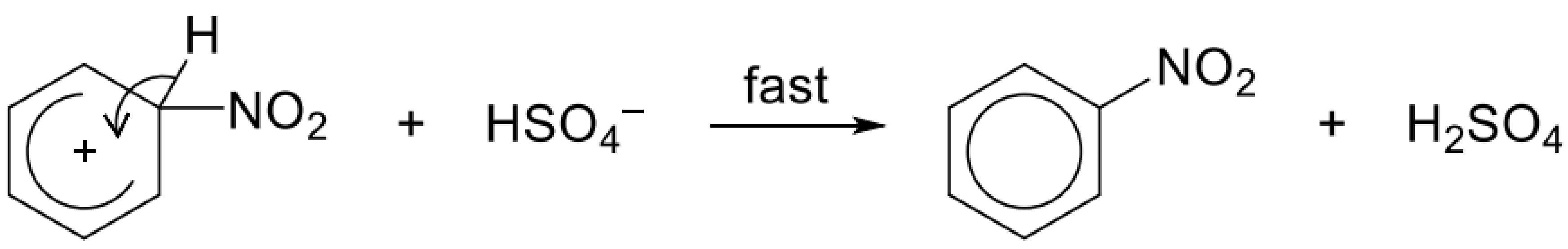
$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$



  - **Step 2:** Electrophilic attack of NO_2^+ on benzene ring to form resonance-stabilised arenium ion

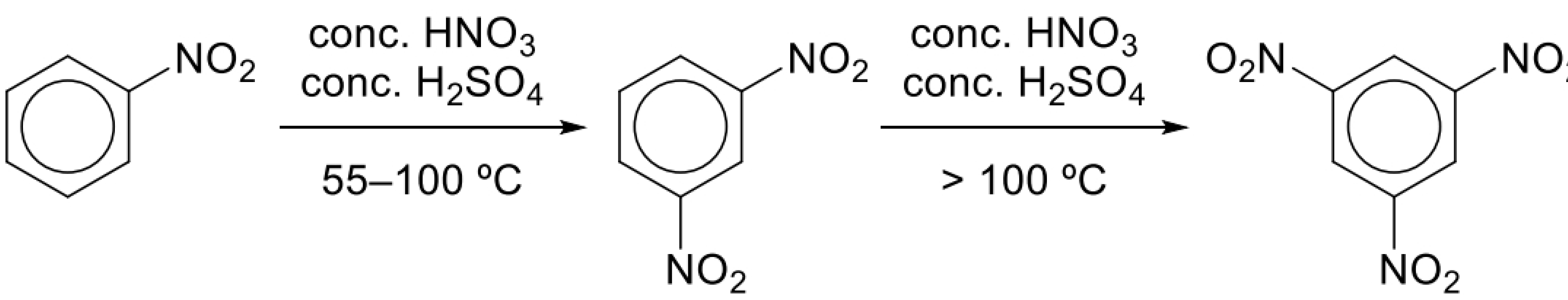


  - **Step 3:** HSO_4^- abstracts H^+ from arenium ion to give nitrobenzene



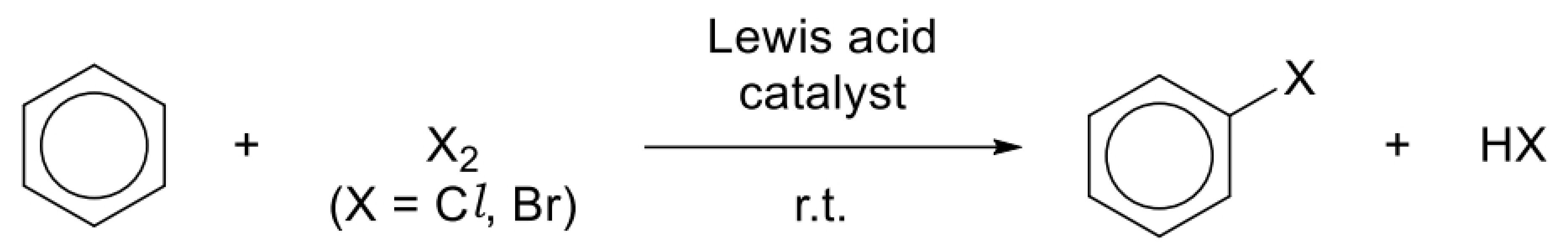
    - H_2SO_4 acts as a catalyst as it is regenerated at the end of the reaction.
    - Nitrobenzene is a pale yellow liquid (boiling point: 210 ºC) with an almond smell.

- The reaction is exothermic and must be cooled to maintain the temperature below 55 ºC.
  - Nitrobenzene undergoes further substitution to form **1,3**-dinitrobenzene and **1,3,5**-trinitrobenzene at higher temperatures:



Reason: –NO_2 group is deactivating and 3-directing (See §6)

5.2.2 Halogenation



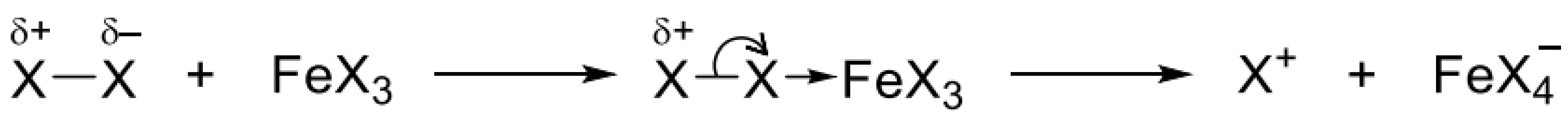
Reagents and conditions: X_2 (X = Cl or Br), Lewis acid catalyst (*e.g.* AlX_3 or FeX_3), room temperature

- The reaction requires a Lewis acid which acts as a **halogen carrier**, *e.g.* anhydrous $AlCl_3$/$AlBr_3$, anhydrous $FeCl_3$/$FeBr_3$ or Fe.
  - Water must be excluded from the reaction as otherwise, anhydrous AlX_3 and FeX_3 will undergo hydrolysis, incapacitating the catalyst.

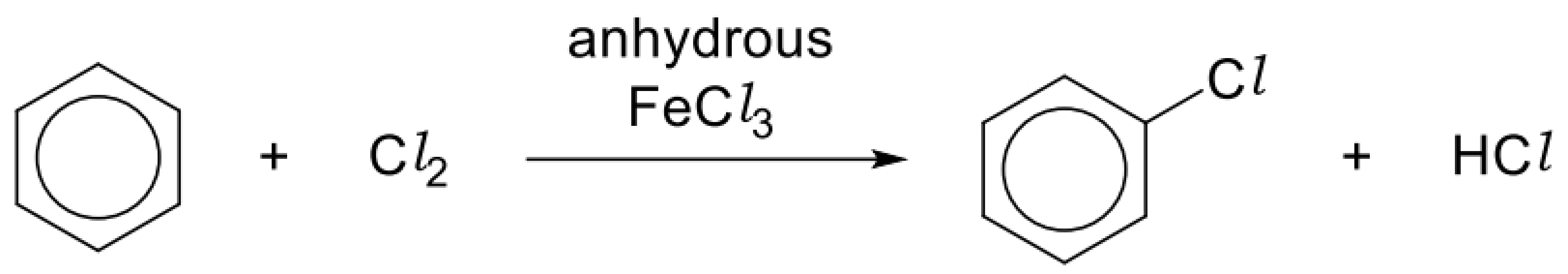
- If finely divided Fe is used, it is converted to iron(III) halide ***in situ*** by reacting with the halogen reagent:

$$2Fe + 3X_2 \rightarrow 2FeX_3$$

- The Lewis acid induces a high degree of polarity in the halogen molecule by accepting a lone pair of electrons from it, thereby generating a strong electrophile, X^+ required to disrupt the π-electron cloud during electrophilic substitution. *E.g.*



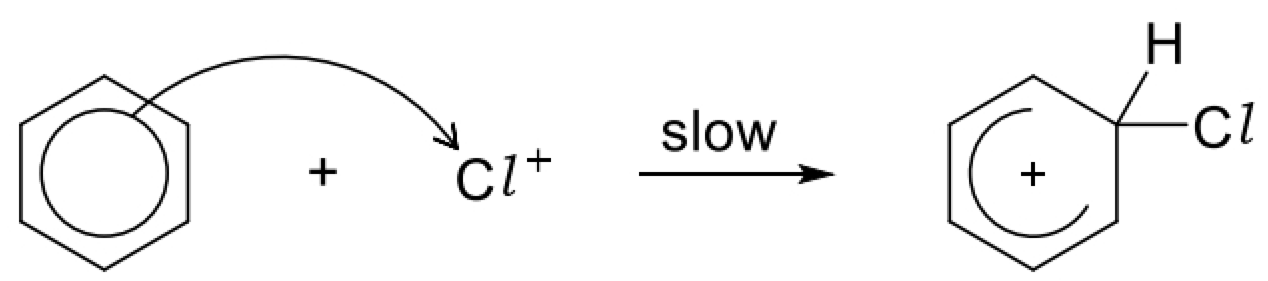
For the reaction:



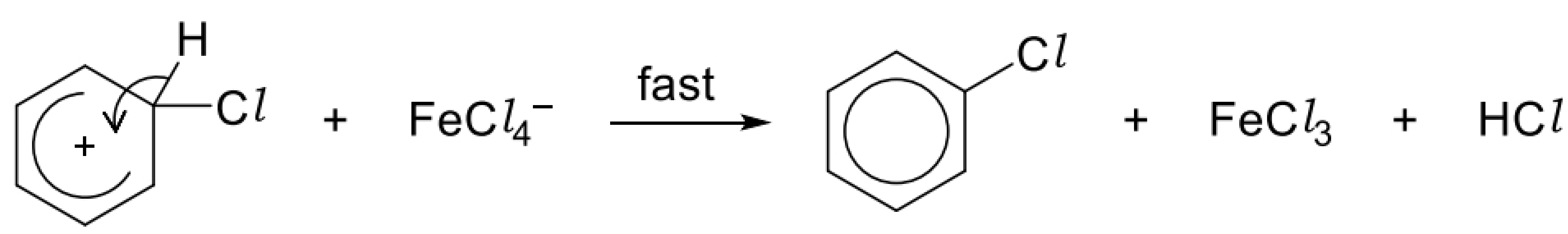
- Name of mechanism: **Electrophilic Substitution**
  - **Step 1:** Generation of electrophile, Cl^+ (chlorine cation)

$$Cl{-}Cl + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

  - **Step 2:** Electrophilic attack of Cl^+ on benzene ring to form resonance-stabilised arenium ion

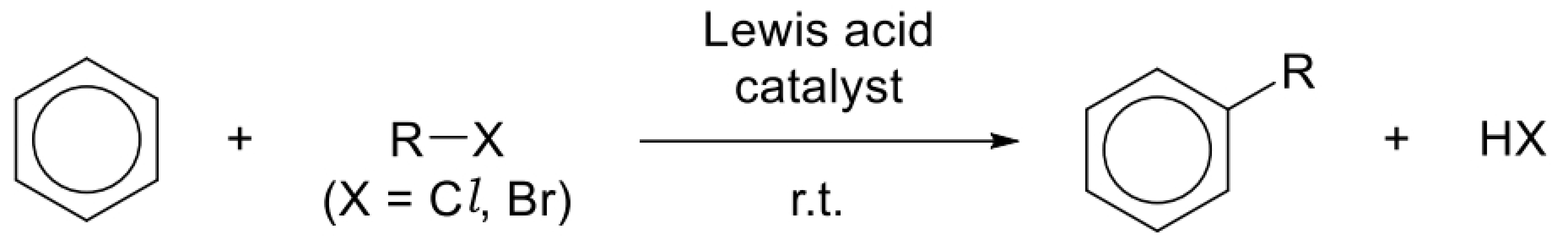


  - **Step 3:** $FeCl_4^-$ abstracts H^+ from arenium ion to give chlorobenzene



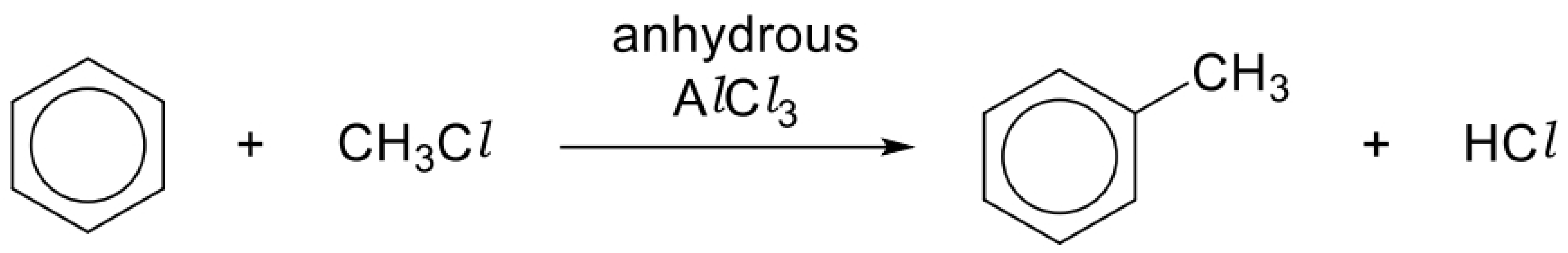
    - $FeCl_3$ acts as a catalyst as it is regenerated at the end of the reaction.

5.2.3 Friedel-Crafts Alkylation



Reagents and conditions: RX (X = C*l* or Br) and excess benzene, Lewis acid catalyst (*e.g.* A*l*X_3 or FeX_3), room temperature

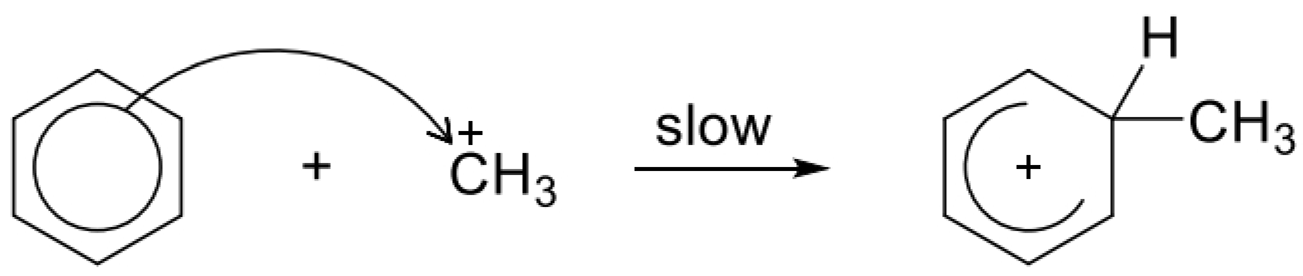
For the reaction:



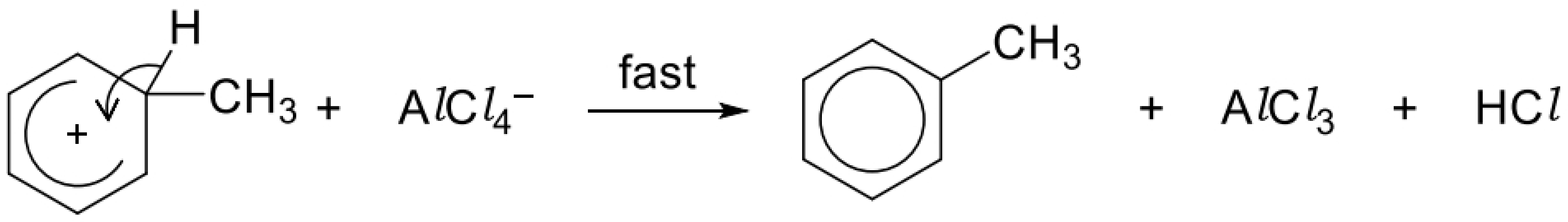
- Name of mechanism: **Electrophilic Substitution**
  - **Step 1:** Generation of electrophile, CH_3^+ (methyl carbocation)

$$CH_3-Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$$

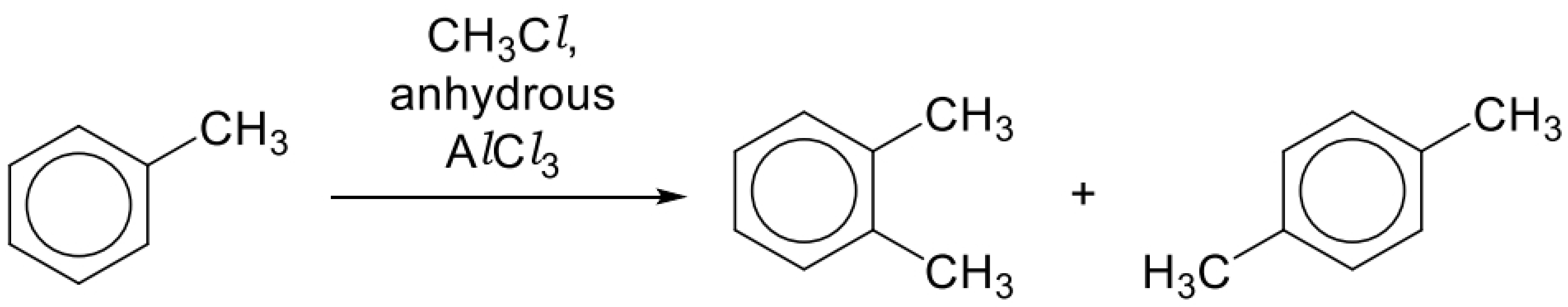
  - **Step 2:** Electrophilic attack of CH_3^+ on benzene ring to form resonance-stabilised arenium ion



  - **Step 3:** A*l*Cl_4^- abstracts H^+ from arenium ion to give methylbenzene

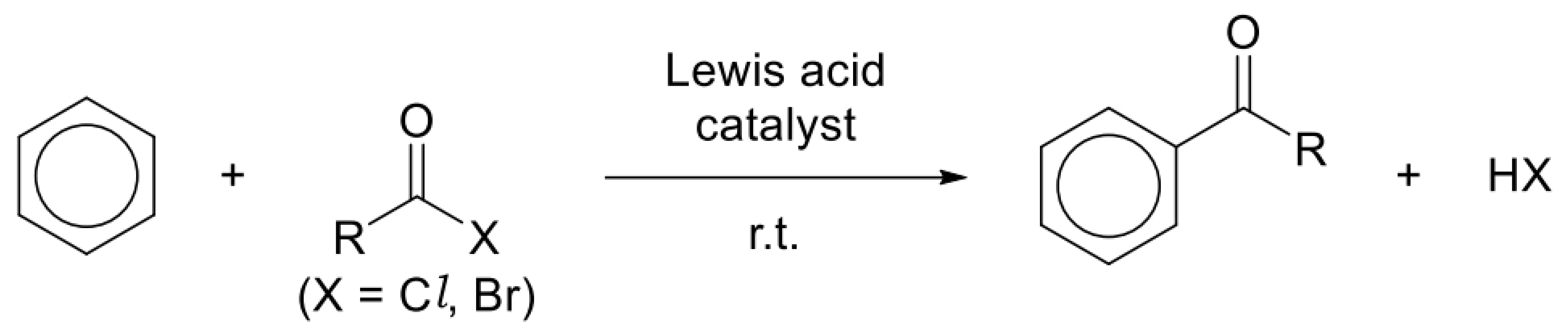


    - A*l*Cl_3 acts as a catalyst as it is regenerated at the end of the reaction.
    - Further alkylation (polyalkylation) of methylbenzene occurs readily to give **1,2**-dimethylbenzene and **1,4**-dimethylbenzene:



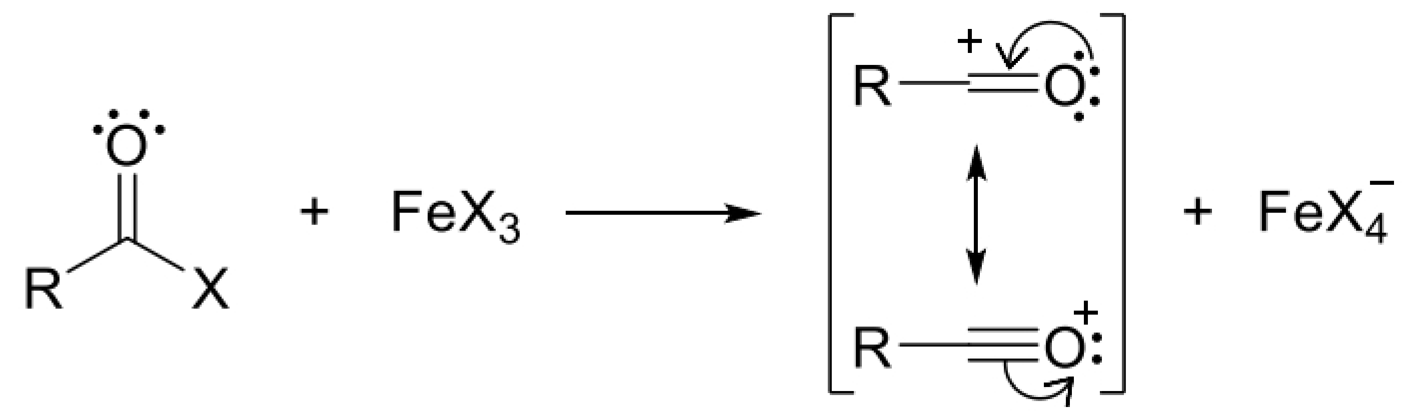
Reason: –CH_3 (an alkyl) group is activating and 2-/4-directing (See §6)
Hence, to ensure a good yield of the monoalkylated product, it is necessary to employ an *excess* of benzene.

5.2.4 Friedel-Crafts Acylation



Reagents and conditions: RCOX (X = Cl or Br) and benzene, Lewis acid catalyst (*e.g.* AlX_3 or FeX_3), room temperature

- Analogous to Friedel-Crafts Alkylation, in which the alkyl halide, RX, replaced by an acyl halide, RCOX.
  - Leads to the substitution of an aromatic H by an acyl group, –COR, resulting in an aromatic carbonyl compound.
  - The first step involves generation of the strong electrophile, in this case, the resonance-stabilised acylium ion:

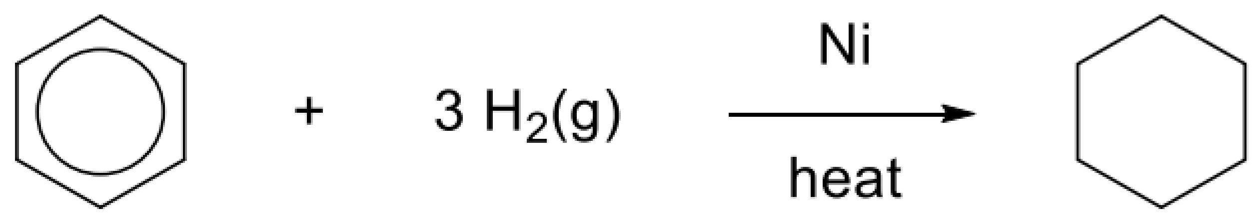


acylium ion

- Unlike Friedel-Crafts Alkylation, polysubstitution is not common in Friedel-Crafts Acylation as the acyl group, –COR, is a deactivating group (see §6.1).

5.3 Catalytic Hydrogenation of Benzene

- Alkenes add on H_2 over a Ni, Pd or Pt catalyst readily at room temperature. Benzene requires an *elevated* temperature as the activation energy for destruction of the aromatic ring upon addition of H_2 is very high.



Reagents and conditions: H_2(g) and Ni *or* Pd *or* Pt catalyst, heat

Example 5A

1 Which is a correct statement about the intermediate complex, $[C_6H_6NO_2]^+$, formed during the mononitration of benzene?

A It is planar.

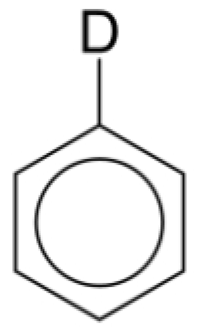
B It contains a chiral centre.

C It can exist in either a *cis* or a *trans* form.

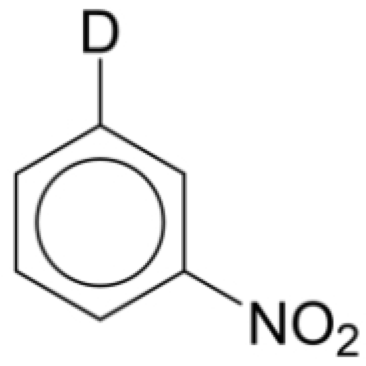
D It contains only one tetrahedrally-bonded carbon atom. **[N02/1/21]**

2 Deuterium, D, is a heavy isotope of hydrogen. Deuteriobenzene is reacted with a mixture of nitric acid and sulfuric acid under controlled conditions, so that only mononitration takes place.

Assuming that the carbon-deuterium bond is broken as easily as a carbon-hydrogen bond, which proportion of the nitrated products will be 3-nitrodeuteriobenzene?



deuteriobenzene



3-nitrodeuteriobenzene

A 16% **B** 20% **C** 33% **D** 45%

[N01/3/23]

Checkpoint for §5

At the end of this section, you must be able to:

– describe the reagents and conditions for electrophilic substitution reactions of benzene:
  - halogenation with Cl_2 and with Br_2, using FeX_3 or AlX_3 catalyst
  - nitration with conc. HNO_3, using conc. H_2SO_4 catalyst
  - Friedel-Crafts alkyation with RX, using FeX_3 or AlX_3 catalyst

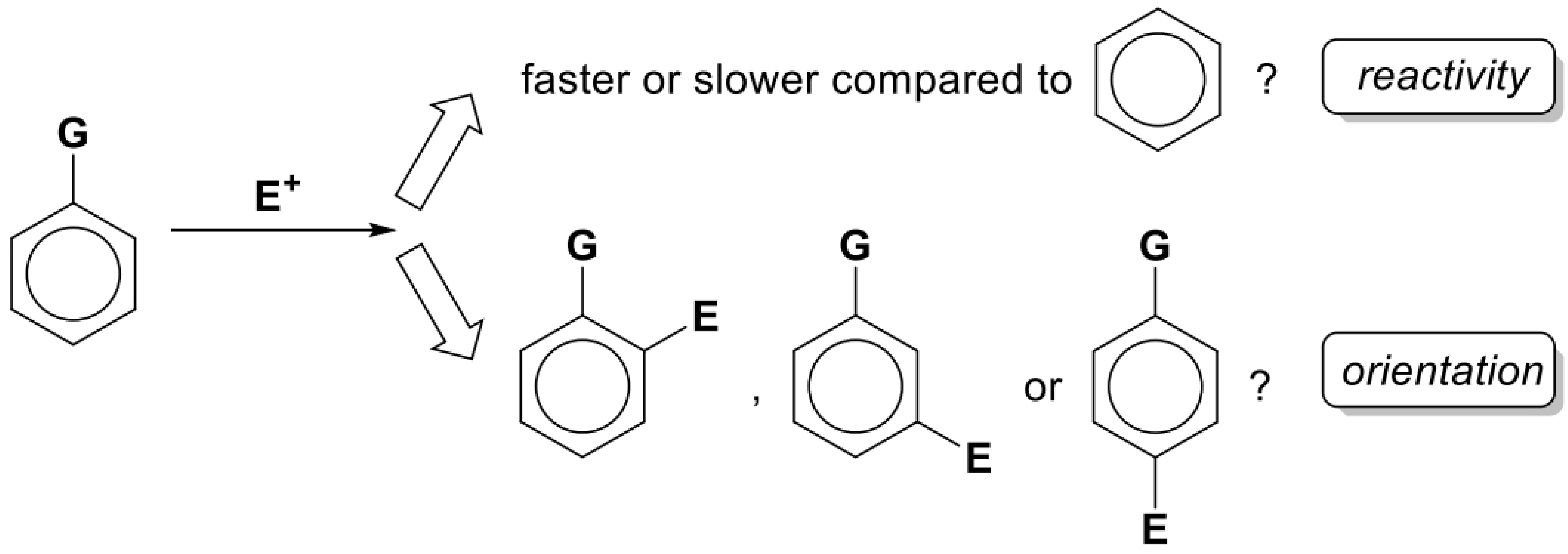
– describe the mechanism of electrophilic substitution in benzene involving:
  - generation of the strong electrophile
  - electrophilic attack on benzene ring giving resonance-stabilised arenium ion intermediate
  - deprotonation and regeneration of aromatic ring

6 Effect of Substituents on Electrophilic Substitution

LO **(m)** apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

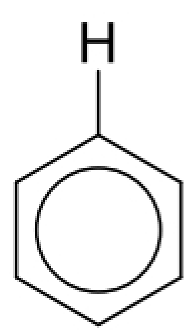
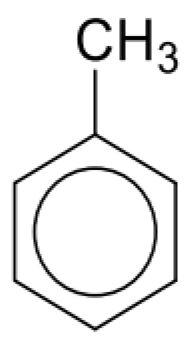
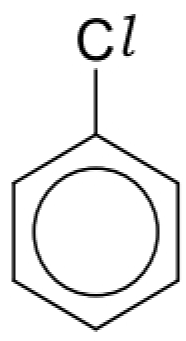
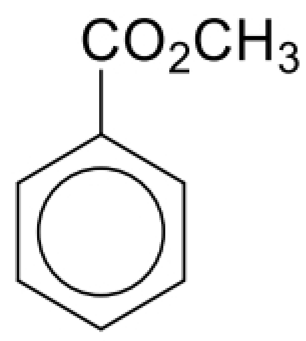
- A substituent, **G**, already present on the benzene ring determines
  - the **reactivity** (*i.e.* **how readily** the ring reacts compare to benzene), and
  - the **orientation** (*i.e.* the **position** in which the new group is introduced, relative to that substituent on the benzene ring)

  toward electrophilic substitution reaction.



6.1 Reactivity of Benzene Rings: Activating and Deactivating Substituents

- Relative rates of nitration of substituted benzene compared to benzene:

compound				
relative rate	1.0	24.5	0.033	0.004

- Substituents that <u>increases the *rate* of electrophilic substitution</u>, relative to a hydrogen atom (*i.e.* compared to benzene), are known as **activating groups**. *E.g.* –CH_3 group.
  - Activating groups **donate** electron density to the benzene ring,
    - increasing the availability of the π electron cloud, and
    - *stabilising* the arenium intermediate by *dispersing* the positive charge,

    hence *lowering the activation energy*, rendering the benzene ring more susceptible toward electrophilic attack.

- Substituents that <u>decreases the *rate* of electrophilic substitution</u>, relative to a hydrogen atom (*i.e.* compared to benzene), are known as **deactivating groups**. *E.g.* –C*l* and –CO_2CH_3.
  - Deactivating groups **withdraw** electron density away from the benzene ring,
    - decreasing the availability of the π electron cloud, and
    - *destabilising* the arenium intermediate by *intensifying* the positive charge

    hence *raising the activation energy*, rendering the benzene ring less susceptible toward electrophilic attack.

Donation and withdrawal of electron density by a substituent can occur *via*

effect	inductive effect (*I*)	mesomeric (resonance) effect (*M*)
origin	due to *polarisation of the σ bonds* in the molecule, arising from an *electronegativity difference*	due to overlap of its p- or π-orbitals with the π-orbitals of the benzene ring, extending *delocalisation*
electron-donating (+) *flow of electronic charge* to ring from the substituent	*e.g.* alkyl groups such as $-CH_3$ • sp^3-hybridised carbon in alkyl groups are less electronegative than the sp^2-hybridised carbon of the benzene ring due to the smaller s-character of the former. • the substituent is thus electron-donating by inductive effect (+*I*).	*e.g.* –OH, $-NH_2$, –C*l*, –Br • the substituent has a lone pair of electrons (in a p-orbital) on the atom directly bonded to the benzene ring, which can be delocalised into the ring. • the substituent is thus electron-donating by mesomeric effect (+*M*).
electron-withdrawing (–) *flow of electronic charge* from ring to the substituent	*e.g.* $-NO_2$, –C=O, –OH, –C*l*, –Br • atoms such as N, O and C*l* are more electronegative than C in benzene. They draw electron density away from C through the σ bonds. • the substituent is thus electron-withdrawing by inductive effect (–*I*).	*e.g.* $-NO_2$, –C=O, –C≡N • the substituent is directly attached to the benzene ring *via* an atom that is bonded to a more electronegative atom by a double or triple bond, where the π electron cloud of the benzene ring can be delocalised onto the substituent. • the substituent is thus electron-withdrawing by mesomeric effect (–*M*).

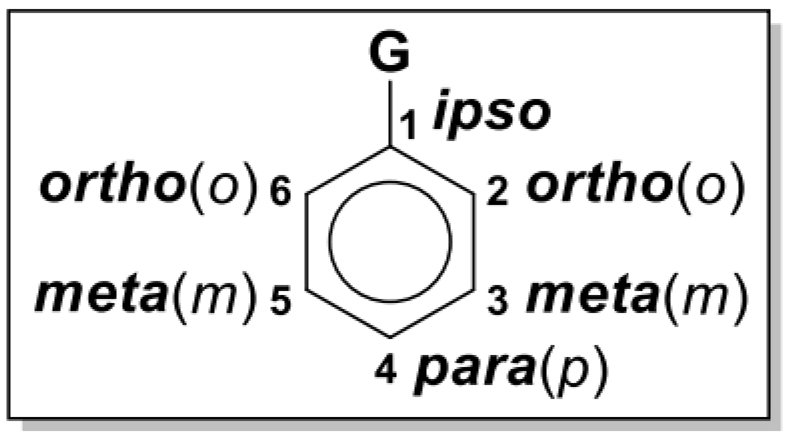
The stronger the $\begin{Bmatrix}+\\-\end{Bmatrix}$ *M* and/or $\begin{Bmatrix}+\\-\end{Bmatrix}$ *I* effect, the more $\begin{Bmatrix}\text{activating}\\\text{deactivating}\end{Bmatrix}$ the substituent and the $\begin{Bmatrix}\text{more}\\\text{less}\end{Bmatrix}$ reactive the benzene ring is to electrophilic attack:

activating groups			deactivating groups		
NHR, NH_2	(+*M*, –*I*)	*most reactive* ↑	C*l*, Br, I	(+*M*, –*I*)	↓ *least reactive*
OR, OH	(+*M*, –*I*)		CHO, COR	(–*M*, –*I*)	
NHCOR	(+*M*, –*I*)		CO_2H, CO_2R	(–*M*, –*I*)	
aryl (Ar)	(+*M*, +*I*)		CN	(–*M*, –*I*)	
alkyl (R)	(+*I*)		NO_2	(–*M*, –*I*)	

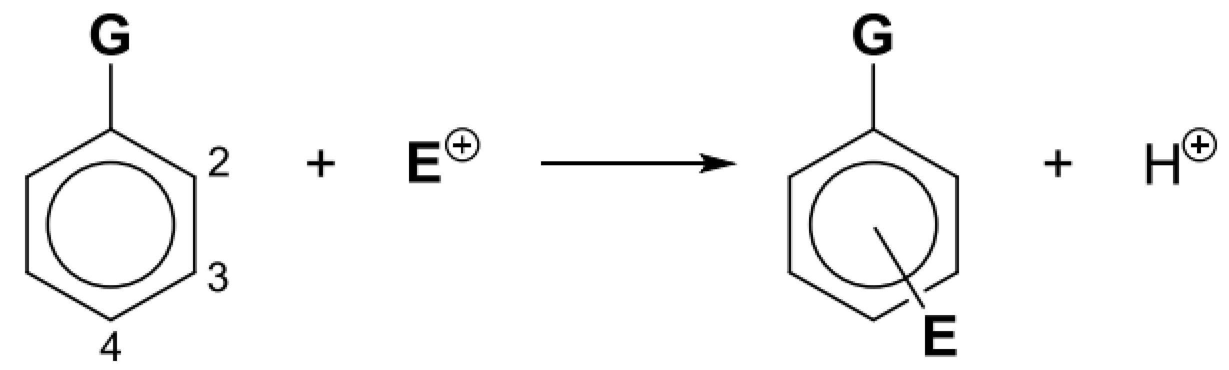
- The +*M* effect due to the lone pair of electrons on N and O is stronger than the –*I* effect due to their electronegativity, rendering the hydroxy/alkoxy and amino groups among the most strongly activating groups.
- On the other hand, the –*I* effect due to the electronegativity of C*l*, Br and I is stronger than the +*M* effect due to the lone pair of electrons (*why is this so?*)

6.2 Orientation of Incoming Electrophile

- Electrophilic substitution can occur at the *ortho*- (2-/6-), *meta*- (3-/5-) or *para*-(4-) positions of the benzene ring.
  - The inductive and/or mesomeric effects of the **existing substituent (G)** determine which position the new substituent (**E**) is introduced on the ring.



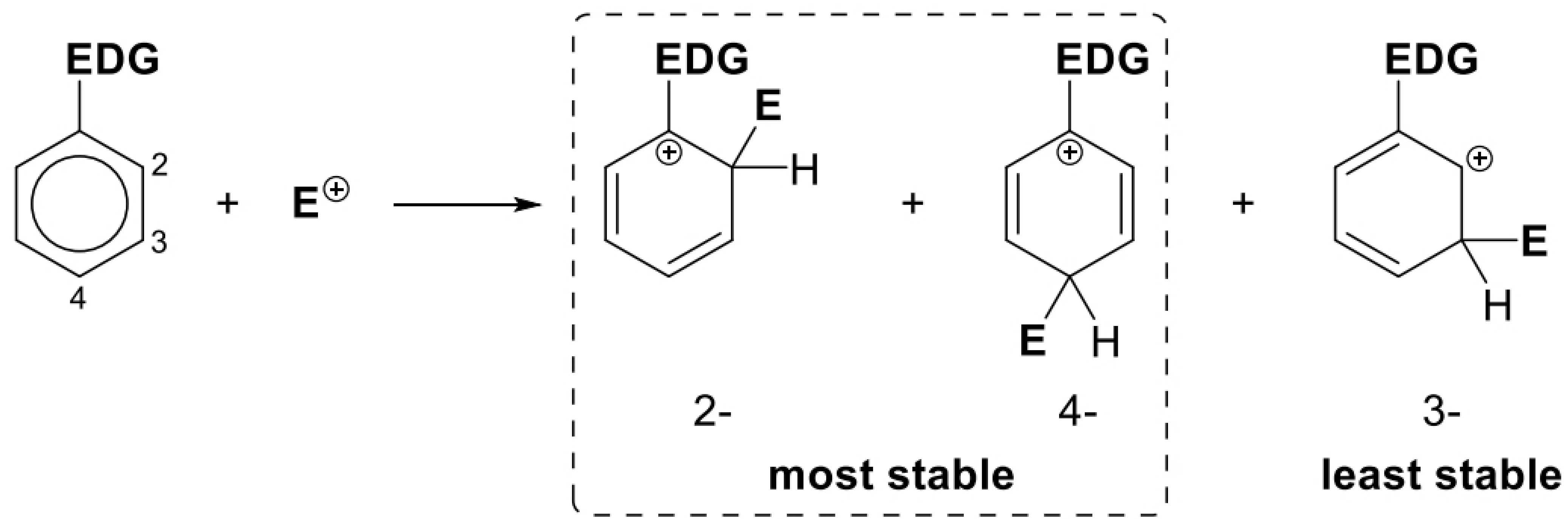
- Substituents are classified as
  (i) 2-/4-directing activators;
  (ii) 2-/4-directing deactivators; or
  (iii) 3-directing deactivators.



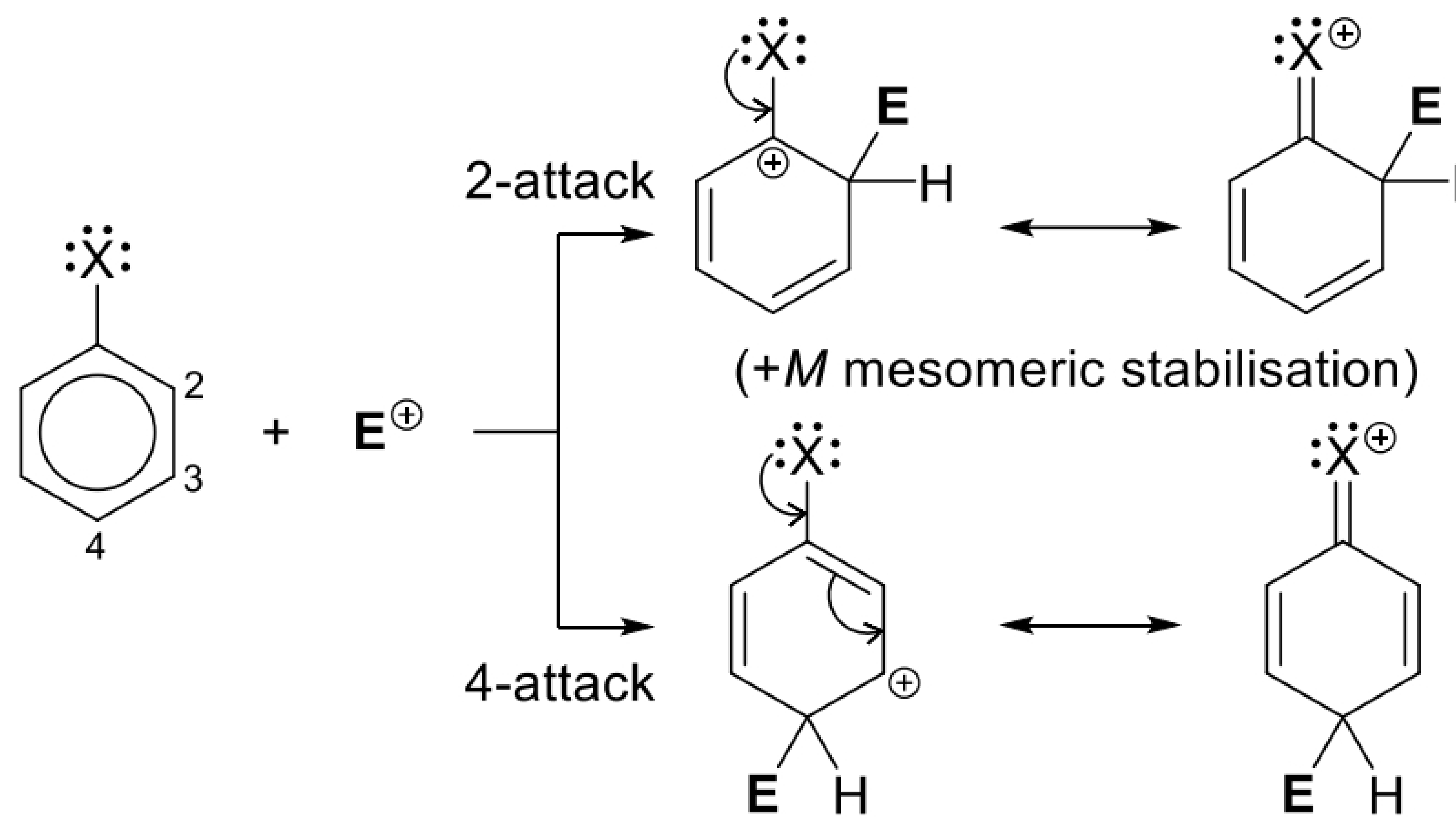
	(i)	(ii)	(iii)
G	–alkyl, –aryl –OH or –OR $–NH_2$, –NHR or $–NR_2$ –NHCOR	–C*l*, –Br, –I	–CHO, –COR $–CO_2H$, $–CO_2R$ $–NH_3^+$ $–NO_2$, –CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4- (*ortho*- and/or para-)	2- and/or 4- (*ortho*- and/or para-)	3- (*meta*-)

(Available in §8, pg 17, of the *Data Booklet*)

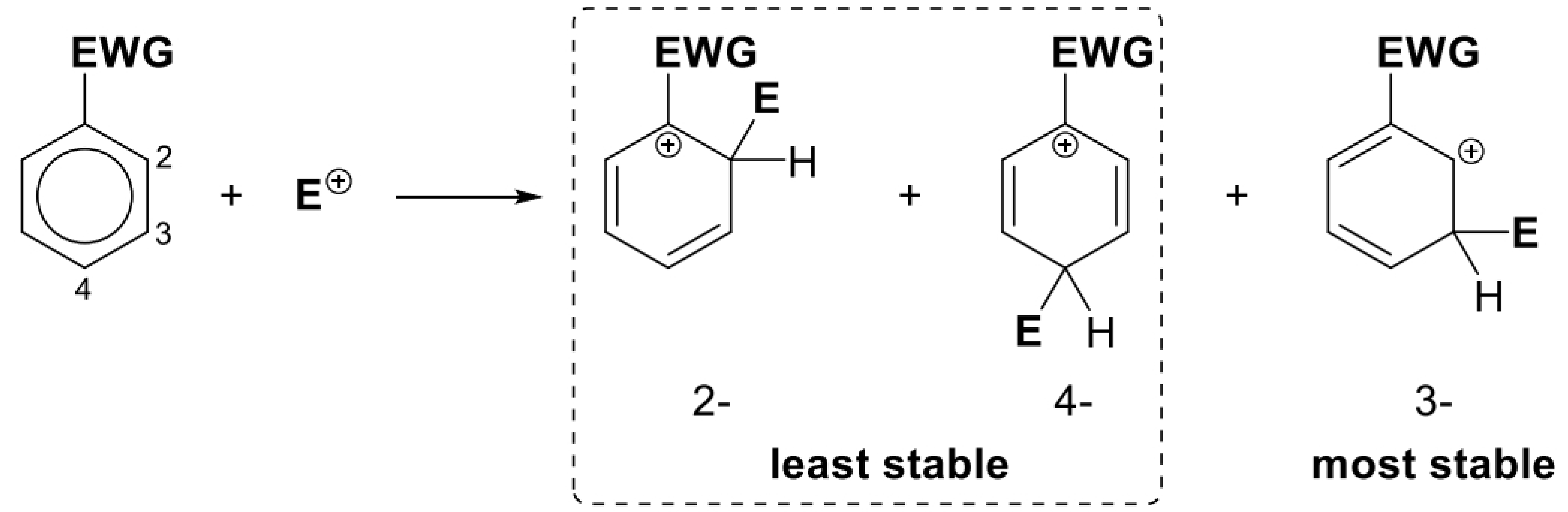
- **Electron-donating** +*I* and/or +*M* groups (**EDG**), which make the ring more nucleophilic than benzene, will stabilise the intermediate arenium ion most effectively when new substituents are introduced at the 2- or 4- positions. For the 3-isomer, the positive charge in the arenium intermediate does not reside adjacent to the EDG in any of the resonance structures.



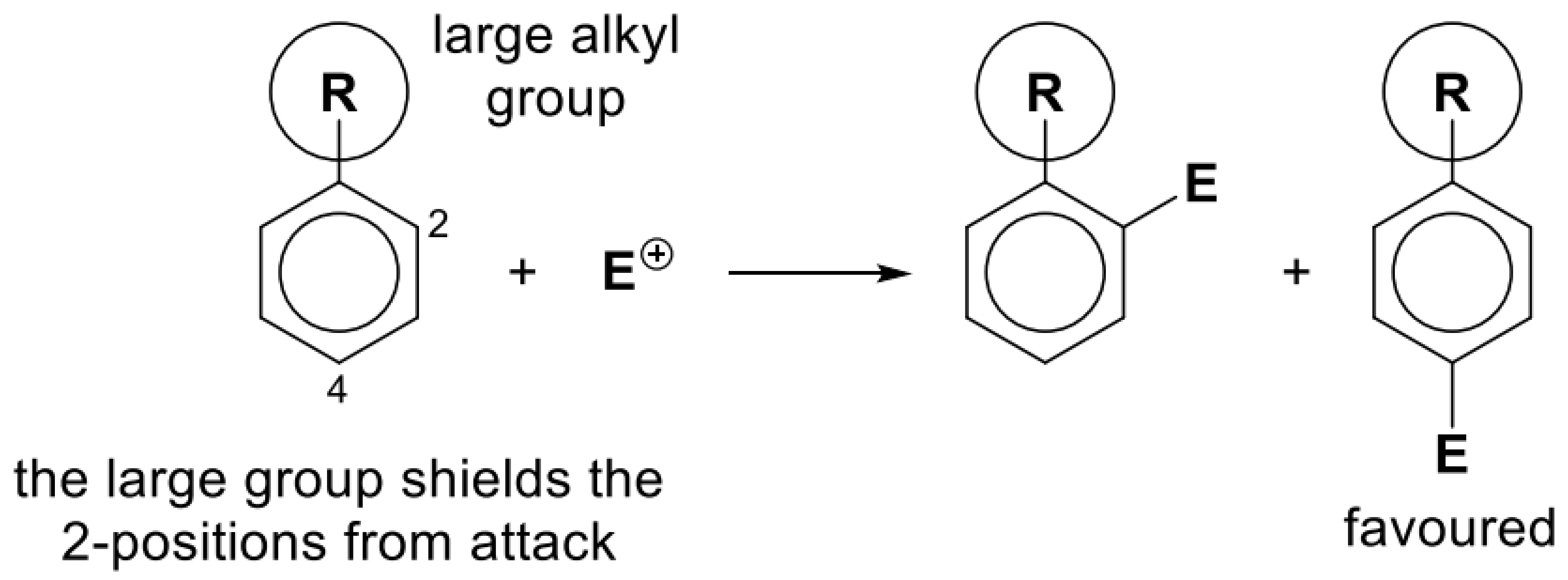
- **Halogen groups** are unique in that they direct 2-/4- and yet they deactivate the benzene ring. The +*M* effect of C*l*, Br and I is weak because these atoms are all larger than carbon, hence the orbital containing the lone pairs do not overlap well with the 2p orbital of carbon. Nonetheless, the weak +*M* effect does ensure that the halogens are 2-/4- directing but the strong –*I* effect (which deactivates the ring) is more significant in terms of the reactivity of halogenoarenes.



- **Electron-withdrawing** –*I*/–*M* groups (**EWG**), which make the ring less nucleophilic than benzene, will deactivate the 3- position less than the 2-/4- positions. The arenium ion produced from attack at the 3- position will be the most stable because this does not reside adjacent to the EWG in any of the resonance structures.



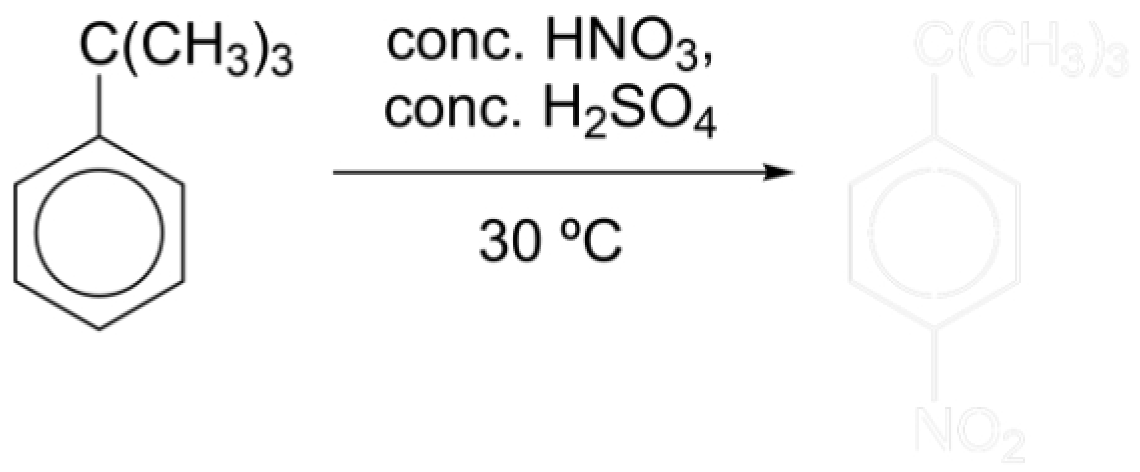
- With activating groups, we would expect the ratio of attack at the 2- and 4- positions to be 2:1 (as there are two 2- positions to one 4- position on the ring). However, attack at the 2-position is often less than this because of **steric hindrance**. The size of the group on the benzene ring strongly influences the substitution at the adjacent 2- position. In general, the larger the size of the group on the ring, the greater the proportion of 4- substitution.



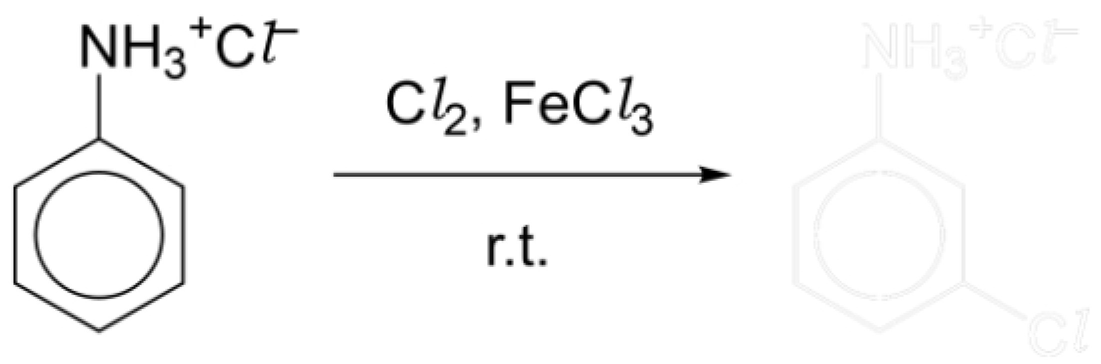
Example 6A

1 Suggest the **major** product for the following electrophilic substitution reactions.

(a)



(b)



2 Suggest syntheses of the following compounds starting from benzene.

(a) 1-chloro-4-ethylbenzene

(b) 3-bromonitrobenzene

Checkpoint for §6

At the end of this section, you must be able to:
– identify, using *Data Booklet*, a substituent on a benzene ring as
  - activating and 2,4-directing : alkyl, –OH, $–NH_2$
  - deactivating and 2,4-directing : –C*l*, –Br
  - deactivating and 3-directing : $–NO_2$, –CN, –C=O, including acid derivatives

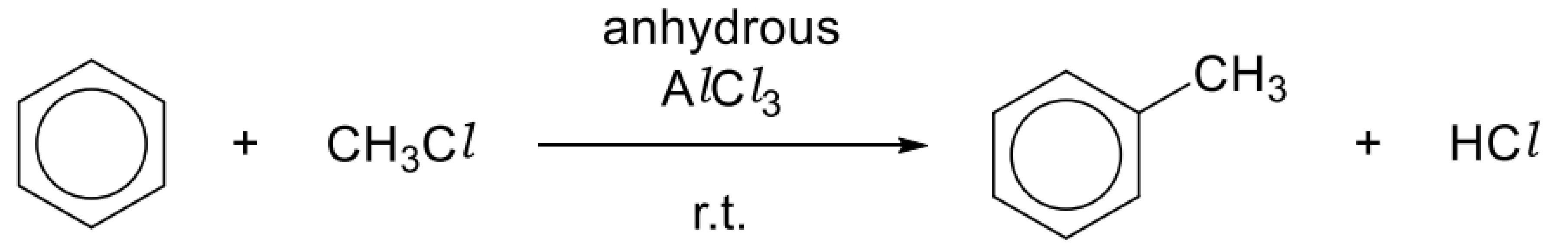
– understand and apply knowledge of the electronic and steric effect of a substituent on mono-substituted benzene ring in terms of
  - reactivity : activating or deactivating
  - orientation : 2,4-directing or 3-directing

7 Reactions of Methylbenzene (Alkylbenzenes)

LO **(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 benzoic acid
(l) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

7.1 Introduction

- Methylbenzene (or other alkylbenzene) can be prepared by Friedel-Crafts Alkylation of benzene.

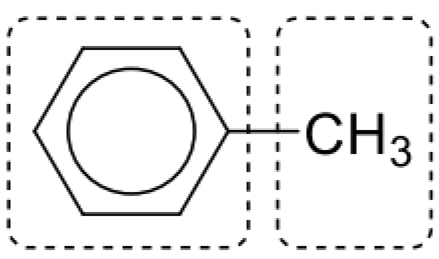


Reagents and conditions: CH_3Cl and excess benzene, anhydrous $AlCl_3$ catalyst, r.t.

- Methylbenzene has two portions:
  - an *aromatic* portion (benzene ring), and
  - an *aliphatic* portion (the alkyl group),

  which gives methylbenzene its chemical properties. The two portions also changes the properties of the other portion.

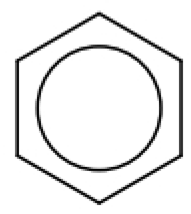
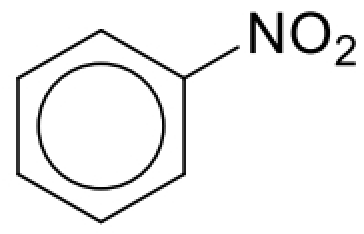
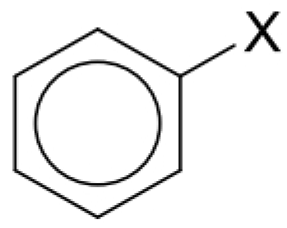
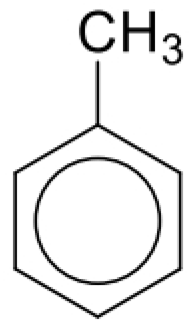
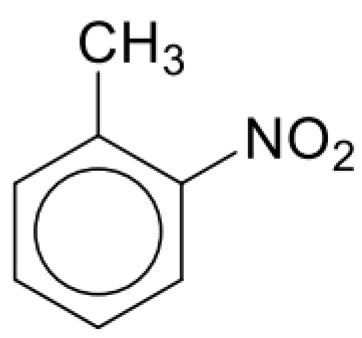
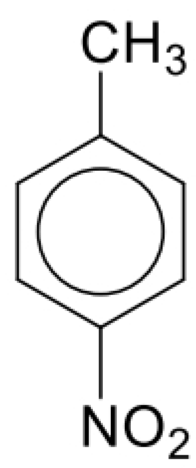
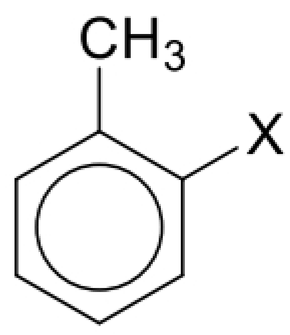
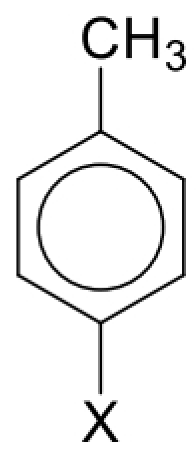
aromatic portion
- undergoes electrophilic substitution reaction



aliphatic portion
- undergoes free radical substitution reaction
- undergoes side-chain oxidation

7.2 Reactions of the Aromatic Nucleus

Consider the nitration and halogenation reactions for benzene and methylbenzene.

	reagents and conditions	organic products
 benzene	<u>nitration</u> conc. HNO_3, conc. H_2SO_4 catalyst, < 55 °C	
	<u>halogenation</u> X_2 (X = C*l* or Br), Lewis acid catalyst (*e.g.* A*l*X_3 or FeX_3), room temperature	
 methylbenzene	<u>nitration</u> conc. HNO_3, conc. H_2SO_4 catalyst, 30 °C	 , 
	<u>halogenation</u> X_2 (X = C*l* or Br), Lewis acid catalyst (*e.g.* A*l*X_3 or FeX_3), room temperature	 , 

Presence of the methyl (–CH_3) group in methylbenzene affects the **reactivity** and **orientation** of incoming substituents for an electrophilic substitution reaction.

effect on **reactivity**	effect on **orientation**
- A lower temperature is used for nitration of methylbenzene compared to benzene. - This shows that methylbenzene is more reactive than benzene toward nitration. - The methyl (–CH_3) group is thus an **activating group** as it increases the susceptibility of methylbenzene to electrophilic attack.	- The major products from nitration and halogenation of methylbenzene include –NO_2/–X at the 2- and 4- positions on benzene relative to –CH_3. - The methyl (–CH_3) group is thus said to be **2,4-directing**.

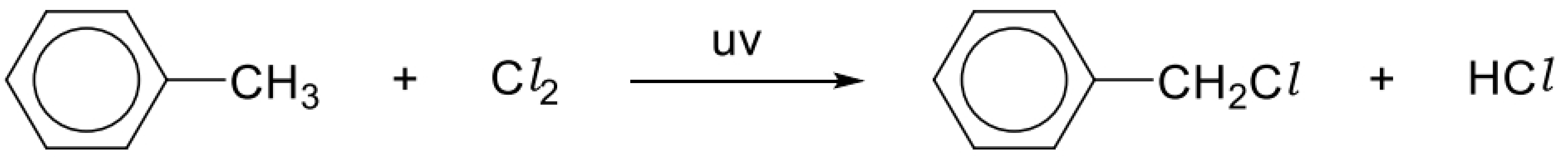
7.3 Reactions of the Aliphatic (Alkyl) Side-Chain

- The alkyl side-chain of alkylbenzenes behaves just like an alkane, undergoing free radical substitution reaction with halogens under suitable conditions. Strong oxidising agents such as $KMnO_4$ can convert an alkyl side-chain into a carboxyl ($–CO_2H$) group.

7.3.1 Side-Chain (Free Radical) Substitution

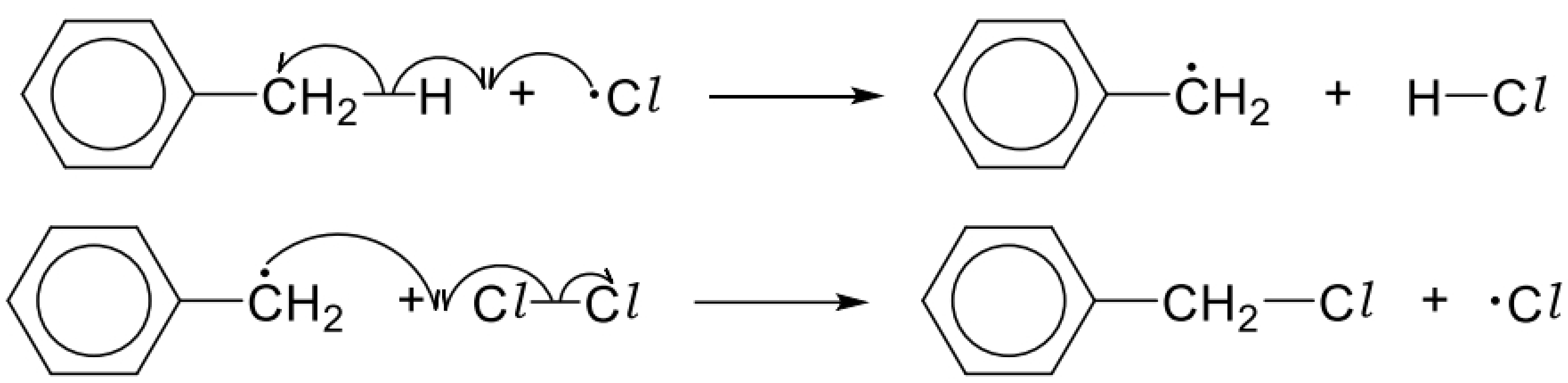
- Side-chain halogenation reaction proceeds *via* free radical substitution mechanism, similar to the halogenation of alkanes. The reaction occurs when the halogen is bubbled into methylbenzene in the presence of uv light. In excess methylbenzene, the mono-substituted product is obtained. In excess X_2, di- and tri-substituted products are obtained.

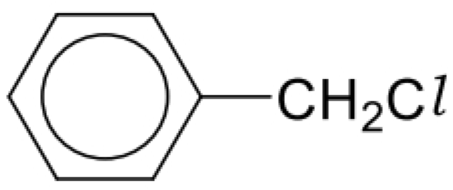
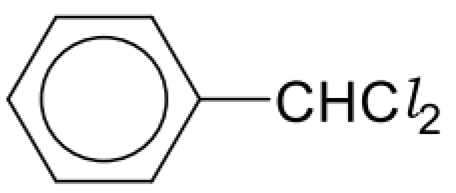
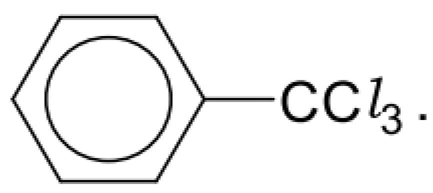
For the reaction:



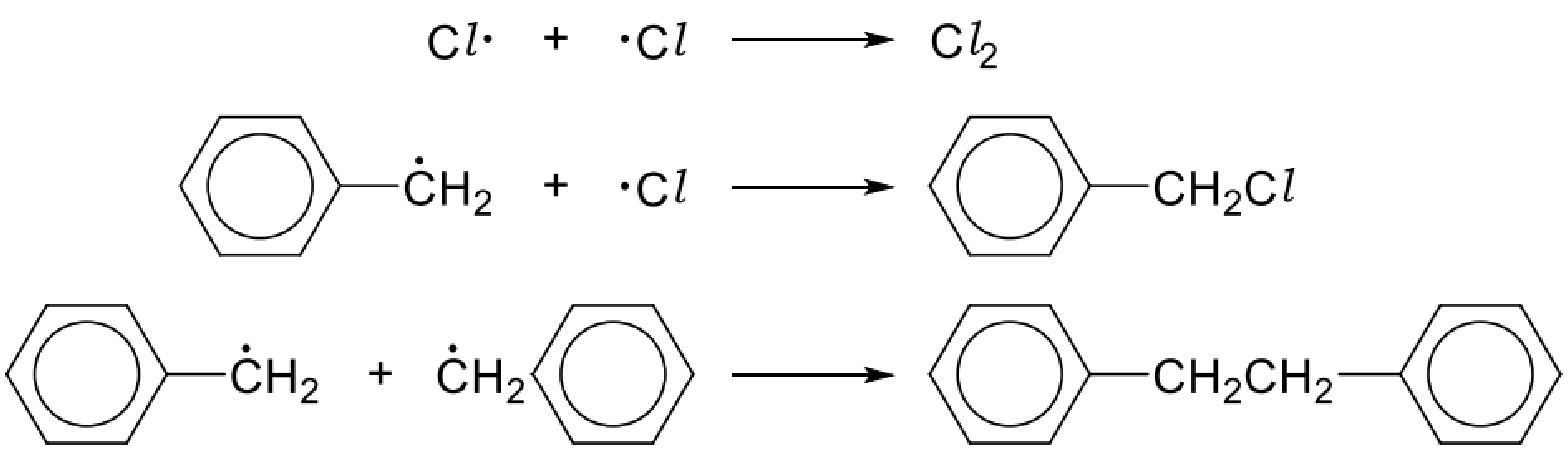
- Name of mechanism: **Free Radical Substitution**
  - **Step 1:** Initiation

  - **Step 2:** Propagation



Further substitution of  can take place to give  and .

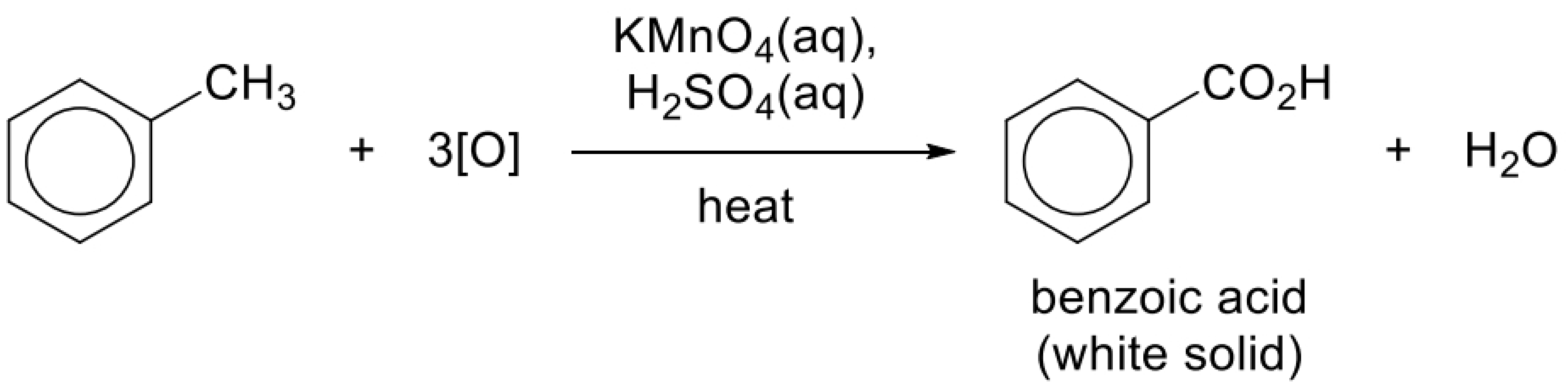
  - **Step 3:** Termination



7.3.2 Side-Chain Oxidation

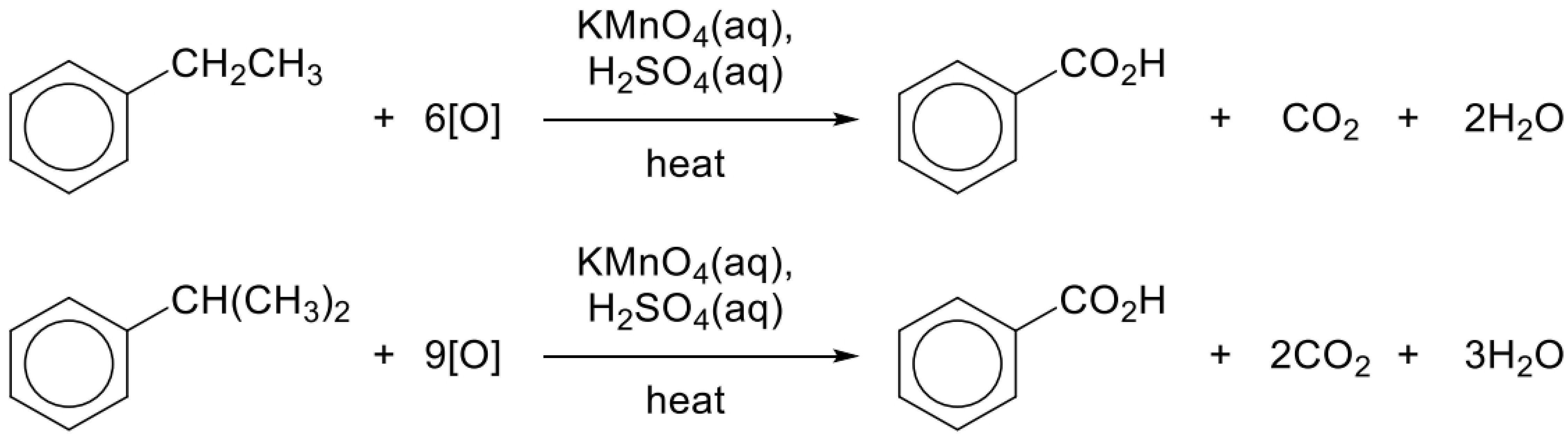
- While both alkanes and benzene themselves do not react with oxidising agents such as $KMnO_4$, the alkyl chain on a benzene ring is susceptible to oxidation.

- Side-chain oxidation of methylbenzene produces benzoic acid (a white solid).

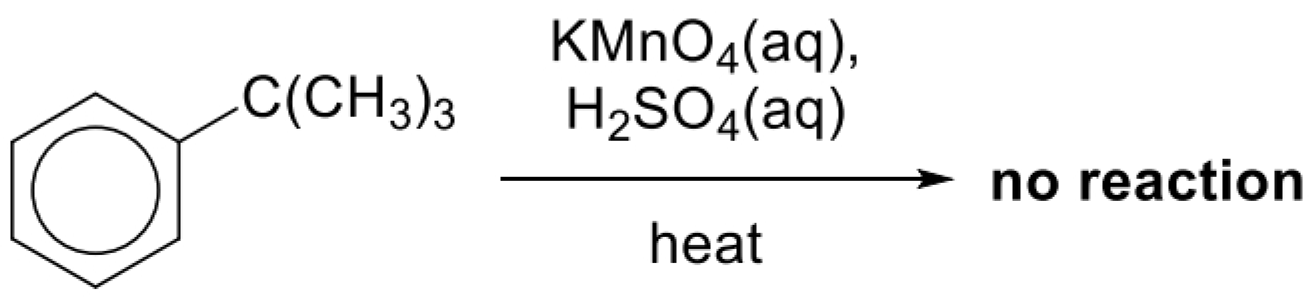


Reagents and conditions: $KMnO_4$ in dilute H_2SO_4, heat
Observations: Purple $KMnO_4$ solution is decolourised, with formation of a white precipitate upon cooling (benzoic acid is soluble in hot water)

- Longer side-chain of alkylbenzenes are also oxidised to form benzoic acid, *e.g.*

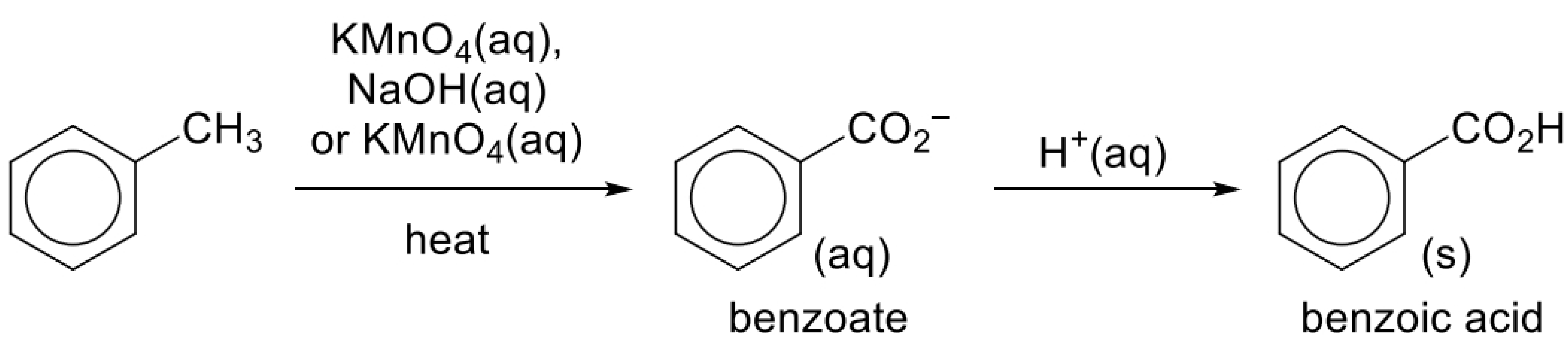


  - There must be at least one hydrogen atom on the carbon that is bonded directly to the benzene ring for the oxidation to proceed.

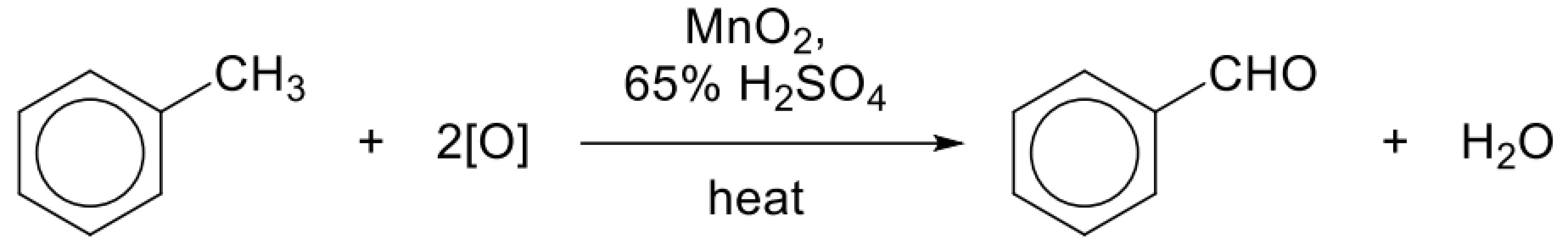


  - Only a carboxylic acid group will remain to indicate the original position of the side chain. The remaining atoms from the alkyl side chain forms carbon dioxide and water.

- With aqueous $KMnO_4$ or alkaline $KMnO_4$, the salt of benzoic acid is formed which must be acidified before solid benzoic acid can be obtained.



- With weaker oxidising agent, *e.g.* MnO_2 with 65% H_2SO_4, methylbenzene is oxidised to benzaldehyde.

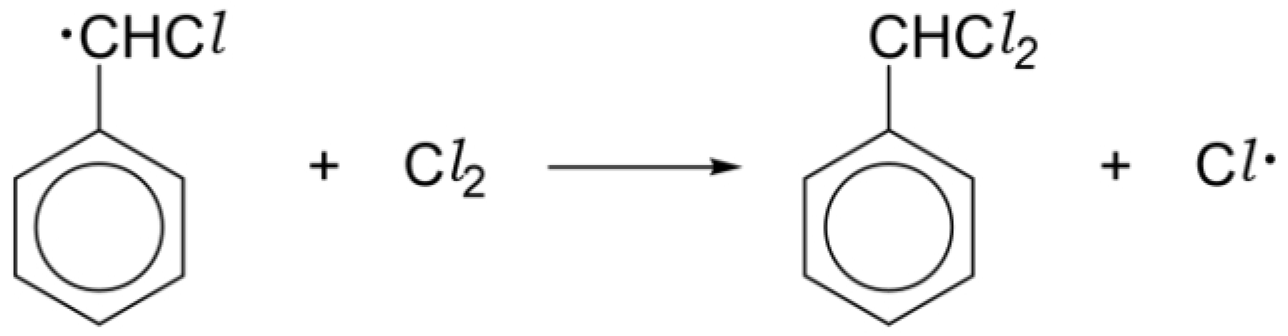


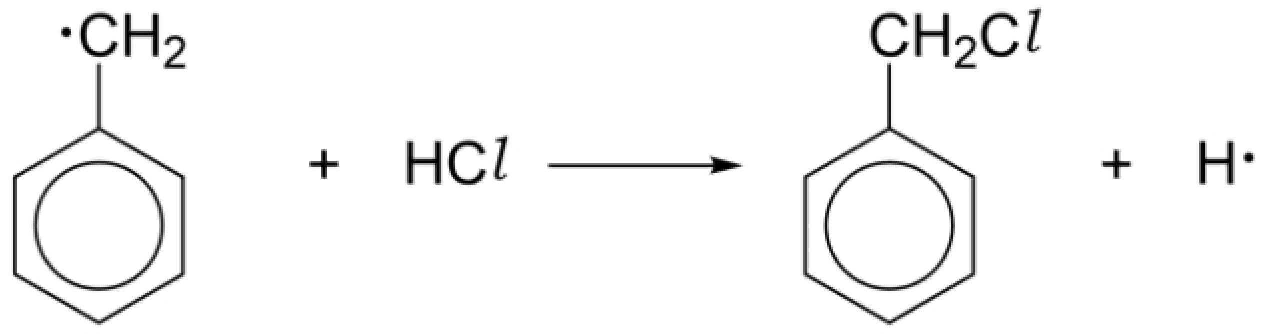
Note: $K_2Cr_2O_7$ is not strong enough as an oxidising agent for side-chain oxidation.

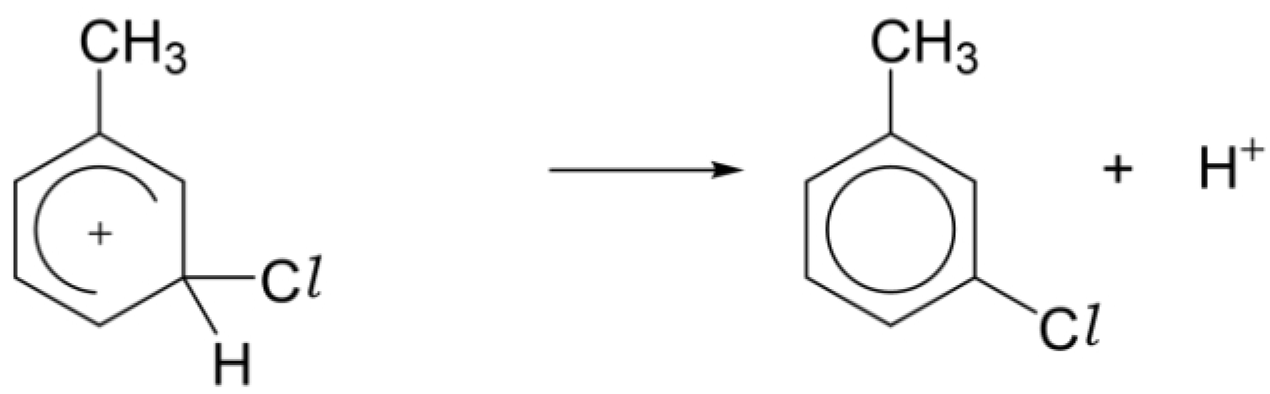
Example 7A

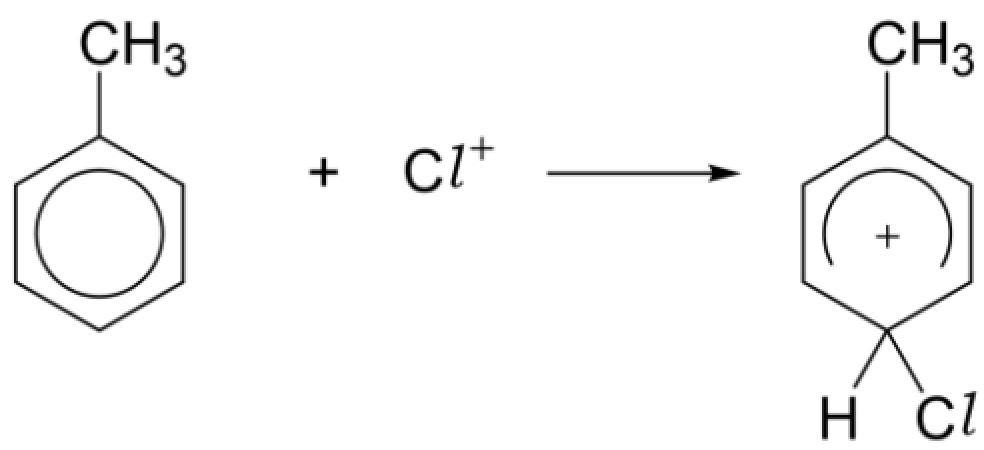
1 The reaction between boiling methylbenzene and chlorine takes place in a number of steps to give several products.

Which of the following could be one of the steps?

A


B


C


D


[modified N92/4/22]

2 With which of the following reagents do benzene and methylbenzene behave differently?

1 warming with aqueous alkaline potassium manganate(VII)

2 warming with bromine in the presence of an iron catalyst

3 warming with a mixture of concentrated nitric acid and concentrated sulfuric acid

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

[N91/1/39]

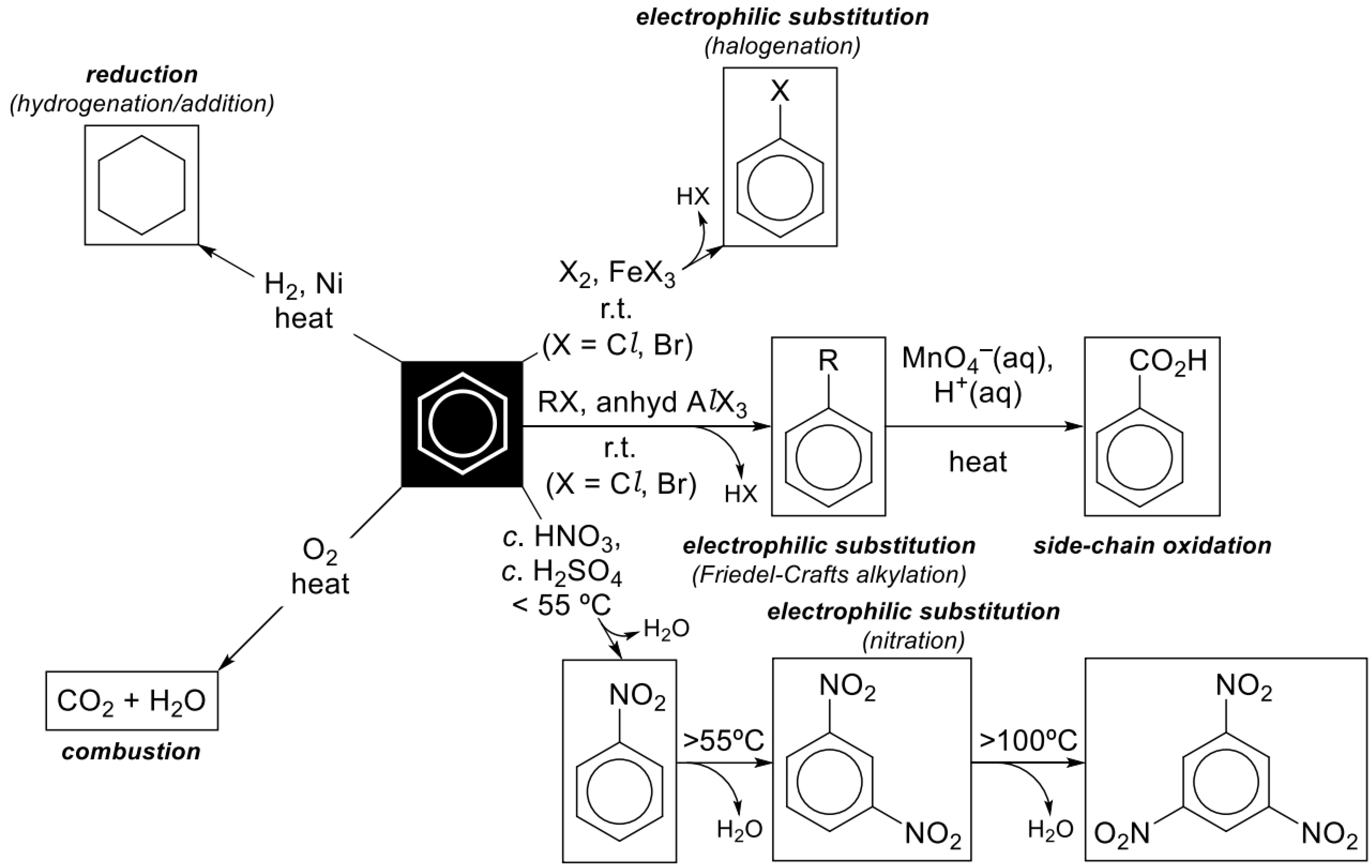
Checkpoint for §7

At the end of this section, you must be able to:

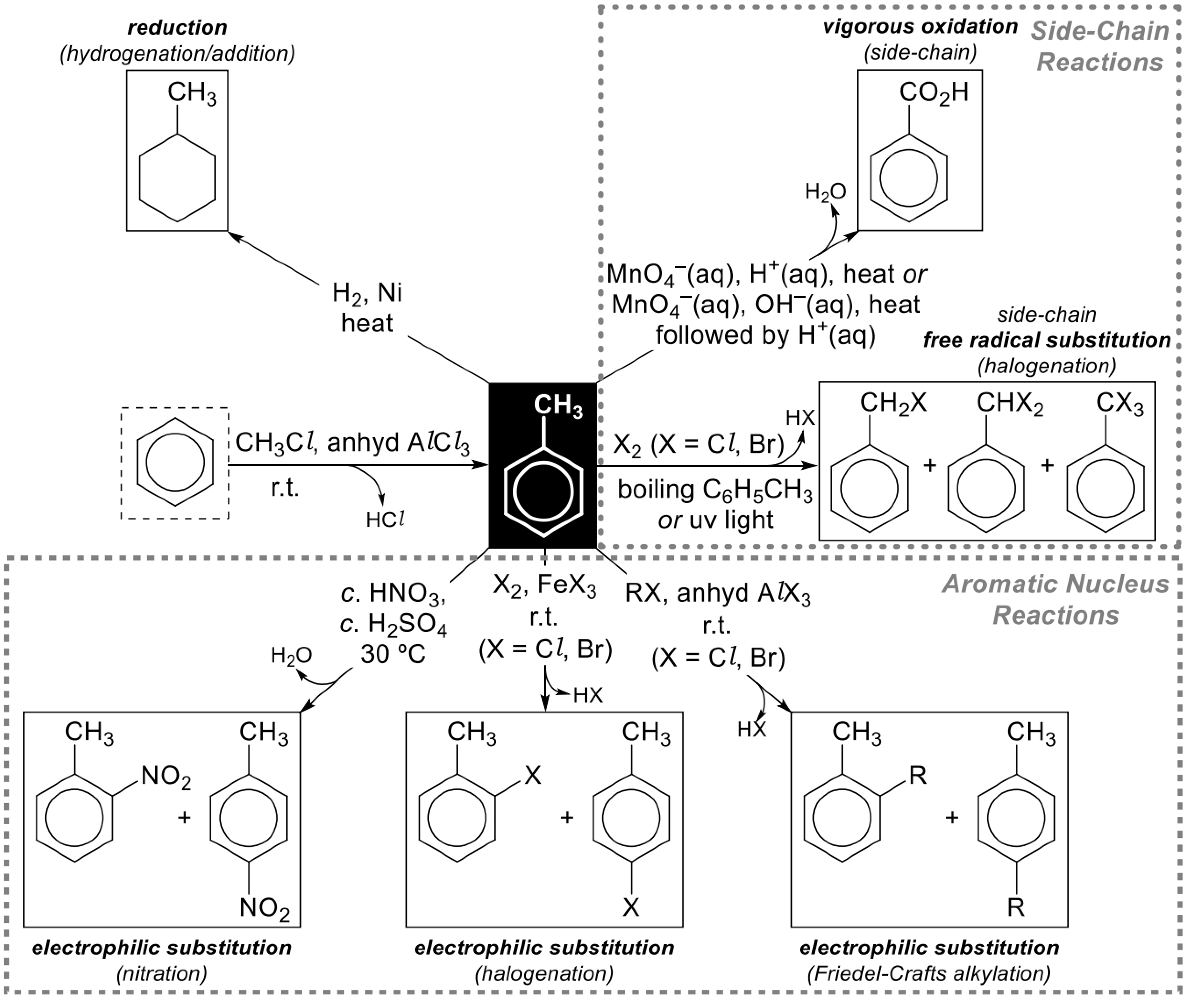
– describe the reagents and conditions for the reactions of methylbenzene:
  - electrophilic substitution with Cl_2 and with Br_2, using FeX_3 or AlX_3 catalyst
  - electrophilic substitution with conc. HNO_3, using conc. H_2SO_4 catalyst
  - electrophilic substitution with RX, using FeX_3 or AlX_3 catalyst
  - free-radical substitution with with Cl_2 and with Br_2, using uv light
  - side-chain oxidation with $KMnO_4$

– predict whether halogenation (substitution) occurs in the
  - side-chain : free-radical – uv light or heat
  - aromatic nucleus : electrophilic – Lewis acid catalyst

8 Summary



electrophilic substitution
(halogenation)
reduction
(hydrogenation/addition)
HX
X
X2, FeX3
r.t.
(X = Cl, Br)
H2, Ni
heat
RX, anhyd AlX3
r.t.
(X = Cl, Br)
HX
R
MnO4−(aq), H+(aq)
heat
CO2H
electrophilic substitution
(Friedel-Crafts alkylation)
side-chain oxidation
O2
heat
c. HNO3,
c. H2SO4
< 55 ºC
H2O
electrophilic substitution
(nitration)
CO2 + H2O
combustion
NO2
>55ºC
H2O
>100ºC
H2O
O2N



reduction
(hydrogenation/addition)
CH3
vigorous oxidation
(side-chain)
Side-Chain
Reactions
CO2H
H2O
MnO4−(aq), H+(aq), heat or
MnO4−(aq), OH−(aq), heat
followed by H+(aq)
H2, Ni
heat
side-chain
free radical substitution
(halogenation)
CH3Cl, anhyd AlCl3
r.t.
HCl
X2 (X = Cl, Br)
boiling C6H5CH3
or uv light
HX
CH2X
CHX2
CX3
c. HNO3,
c. H2SO4
30 ºC
H2O
X2, FeX3
r.t.
(X = Cl, Br)
HX
RX, anhyd AlX3
r.t.
(X = Cl, Br)
Aromatic Nucleus
Reactions
NO2
X
R
electrophilic substitution
(nitration)
electrophilic substitution
(halogenation)
electrophilic substitution
(Friedel-Crafts alkylation)

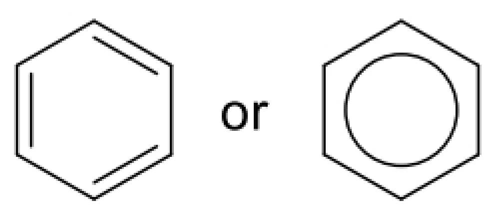
9 Appendix

A Little Bit of History … …

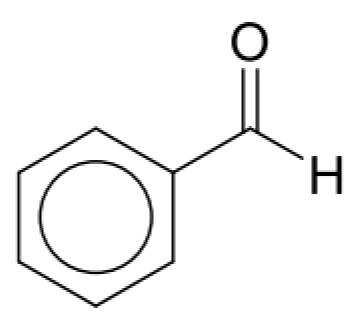
In ordinary conversation, the word "aromatic" conjures pleasant associations—the odour of freshly prepared coffee, a warm cinnamon bun, a freshly cut pine tree. Similar associations occurred in the early history of organic chemistry when pleasantly aromatic compounds were isolated from natural oils produced by plants. Once the structures of these materials were elucidated, many were found to possess a unique, highly unsaturated, six-carbon structural unit also found in benzene.

This special ring became known as the benzene ring. Aromatic compounds that contain a benzene ring are now part of a much larger family of compounds classified as aromatic, not because of their smell (since many of the molecules that contain them have no odour – for example, aspirin), but because they have special electronic features.

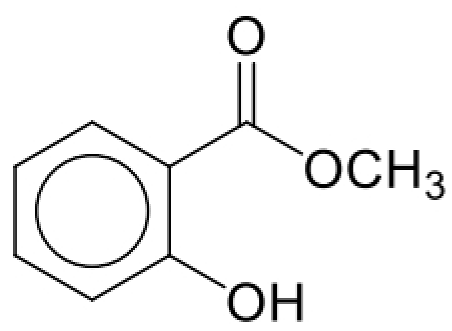
The following are a few examples of aromatic compounds, including benzene itself.



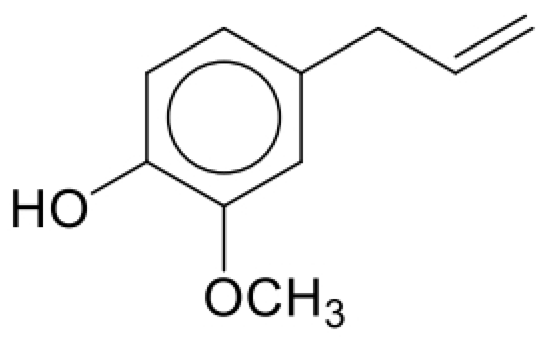
benzene



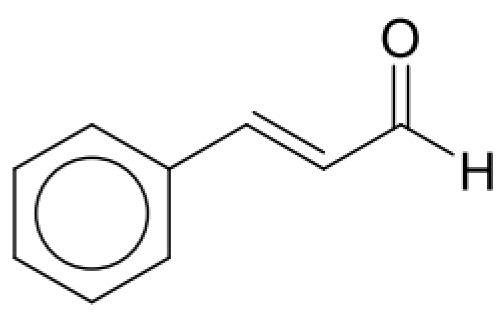
benzaldehyde
(in oil of almonds)



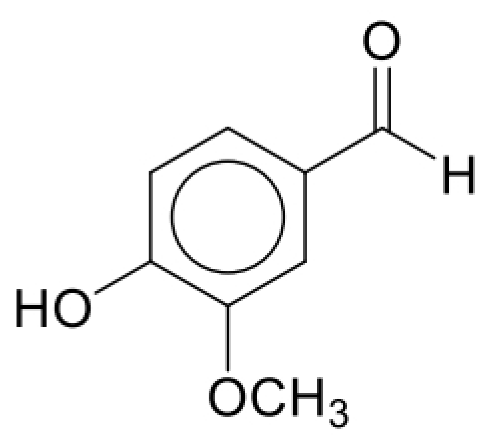
methyl salicylate
(in oil of wintergreen)



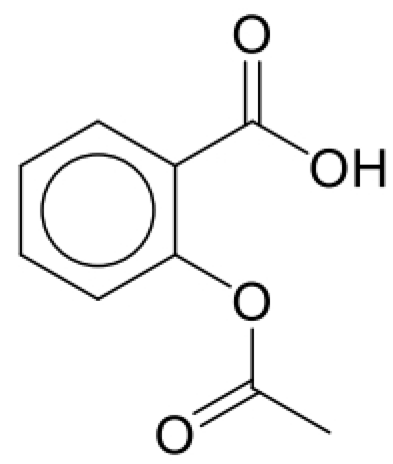
eugenol
(in oil of cloves)



cinnamaldehyde
(in oil of cinnamon)



vanillin
(in oil of vanilla)



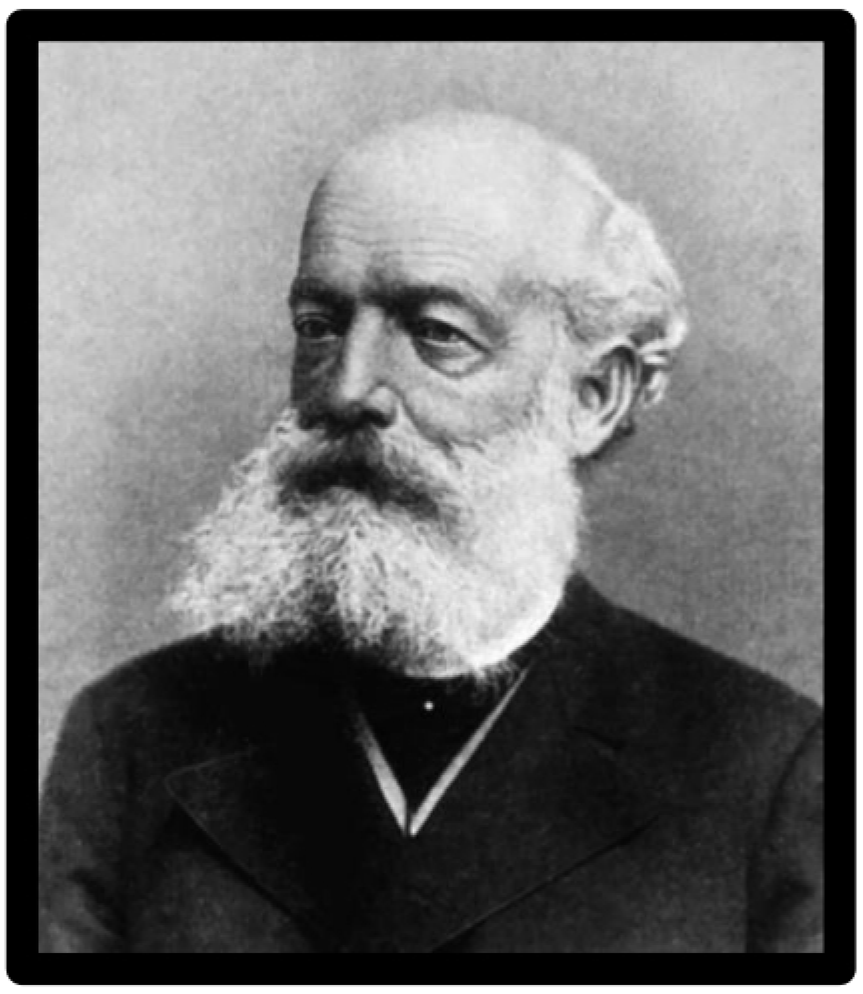
acetylsalicylic acid
(aspirin)

The study of the class of compounds that organic chemists call aromatic compounds began with the discovery in 1825 of a new hydrocarbon by the English chemist Michael Faraday (Royal Institution). Faraday called this new hydrocarbon "bicarburet of hydrogen"; we now call it benzene. Faraday isolated benzene from a compressed illuminating gas that had been made by pyrolysing whale oil. In 1834 the German chemist Eilhardt Mitscherlich (University of Berlin) synthesised benzene by heating benzoic acid with calcium oxide. Using vapour density measurements, Mitscherlich further showed that benzene has the molecular formula C_6H_6.

$$\underset{\text{benzoic acid}}{C_6H_5CO_2H} + CaO \xrightarrow{\text{heat}} \underset{\text{benzene}}{C_6H_6} + CaCO_3$$

The molecular formula itself was surprising. Benzene has only as many hydrogen atoms as it has carbon atoms. Most compounds that were known then had a far greater proportion of hydrogen atoms, usually twice as many. Benzene, having the formula of C_6H_6, should be a highly unsaturated compound because it has a degree of unsaturation equal to 4. Eventually, chemists began to recognise that benzene was a member of a new class of organic compounds with unusual and interesting properties as it does not show the behaviour expected of a highly unsaturated compound.

During the latter part of the nineteenth century the Kekulé–Couper–Butlerov theory of valence was systematically applied to all known organic compounds. One result of this effort was the placing of organic compounds in either of two broad categories; compounds were classified as being either **aliphatic** or **aromatic**. To be classified as aliphatic meant then that the chemical behaviour of a compound was "fatlike." (Now it means that the compound reacts like an alkane, an alkene, an alkyne, or one of their derivatives.) To be classified as aromatic meant then that the compound had a low hydrogen-to-carbon ratio and that it was "fragrant." Most of the early aromatic compounds were obtained from balsams, resins, or essential oils.



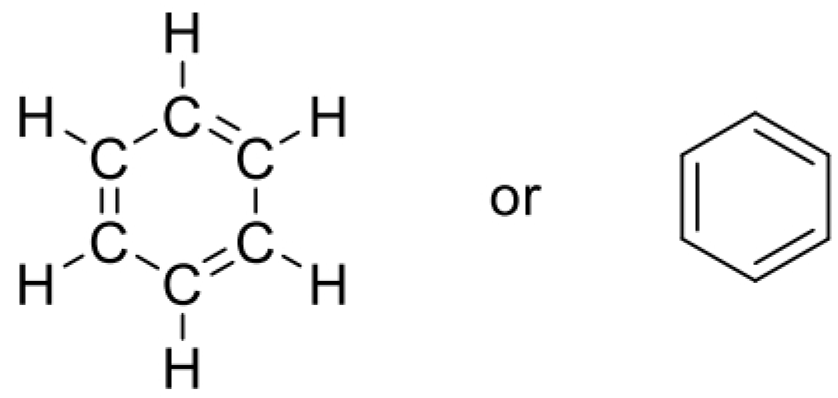
Friedrich August Kekulé, a German chemist, was the first to recognise that these early aromatic compounds all contain a six-carbon unit and that they retain this six-carbon unit through most chemical transformations and degradations. Benzene was eventually recognised as being the parent compound of this new series. It was not until the development of quantum mechanics in the 1920s, however, that a reasonably clear understanding of its structure emerged.

In 1890, at the 25th anniversary of the benzene structure discovery, Kekulé reminisced about his major accomplishments and told of two dreams that he had at key moments of his work. In his first dream, in 1865, he saw atoms dance around and link to one another. He awakened and immediately began to sketch what he saw in his dream.

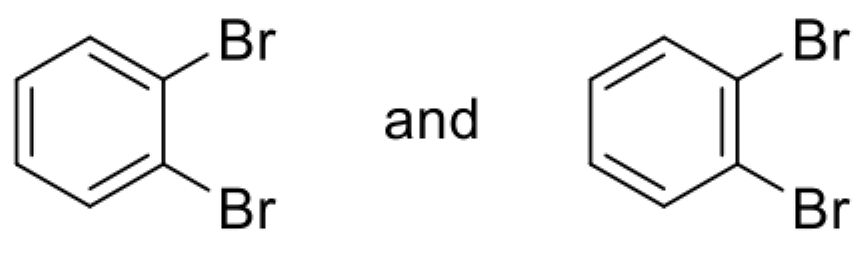
Later, Kekulé had another dream, in which he saw atoms dance around, then form themselves into strings, moving about in a snake-like fashion. This vision continued until the snake of atoms formed itself into an image of a snake eating its own tail. This dream gave Kekulé the idea of the cyclic structure of benzene.

<u>Kekulé Structure</u>

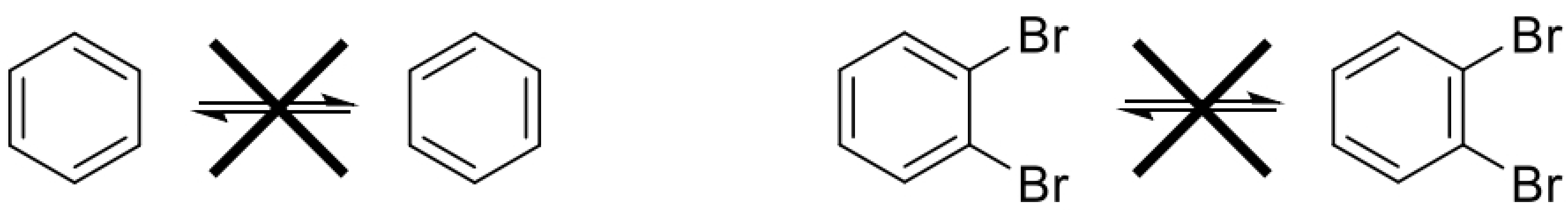
- In 1865, Friedrich August Kelulé proposed the first definite structure for benzene, a structure that is still used today (although it's given a meaning different from the meaning Kekulé gave it).



- A problem soon arose with the Kekulé structure, however. The Kekulé structure predicts that there should be two different 1,2-dibromobenzenes, but only one has ever been found.



- Kekulé proposed that the two forms of benzene (and of benzene derivatives) are in a state of rapid equilibrium that prevents isolation of the separate compounds:



We now know that this proposal was **incorrect** and that *no such equilibrium exists*!!

(Adapted from **Organic Chemistry (Eleventh Edition)** by Graham Solomons, Craig Fryhle & Scott Snyder, pp. 626–628; https://web.chemdoodle.com/kekules-dream/)