VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

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JC1 H2 CHEMISTRY
ARENES (AROMATIC HYDROCARBON)

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5 Summary

REFERENCES

1 Modern Organic Chemistry by R.O.C. Norman and D.J.Waddington
2 Principles of Organic Chemistry by Peter R.S. Murray
3 A-Level Chemistry by E.N. Ramsden
4 Chemistry in Context by Hill and Holman

LEARNING OUTCOMES

Candidates should be able to:

(a) 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

(b) 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 Brønsted-Lowry acid catalyst)
  (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)

(c) (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

(d) 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

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

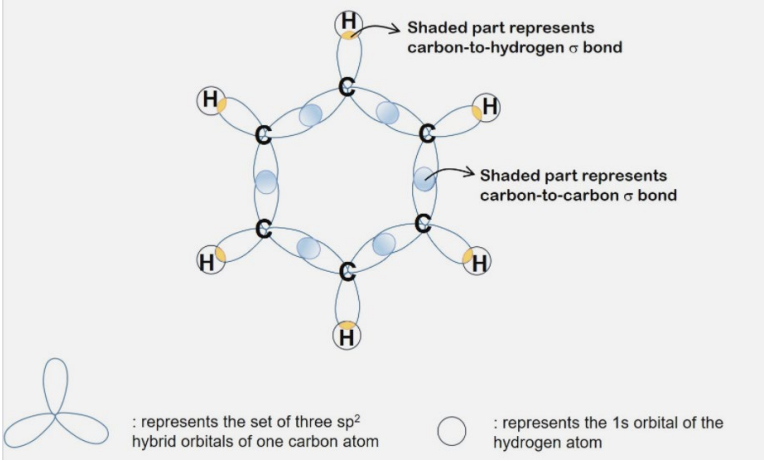
(f) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

1 Introduction

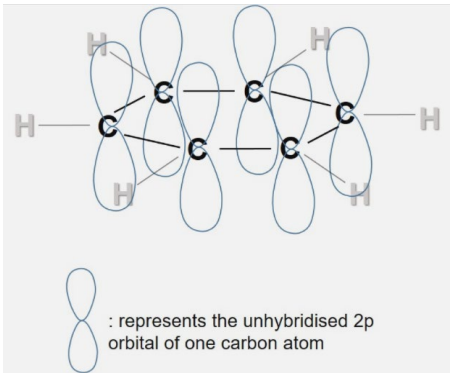
1.1 Structure of Benzene

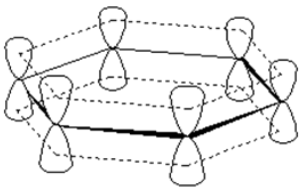
- The molecular formula of benzene is C_6H_6.

- The six carbon atoms of benzene are arranged in a hexagonal ring. Each carbon atom of the benzene molecule is sp^2 hybridised and uses two of the three sp^2 hybrid orbitals to form σ bonds with the sp^2 hybrid orbitals of the adjacent carbon atoms. The remaining sp^2 hybrid orbital overlaps with the 1s orbital of hydrogen atom to form a C–H σ bond.

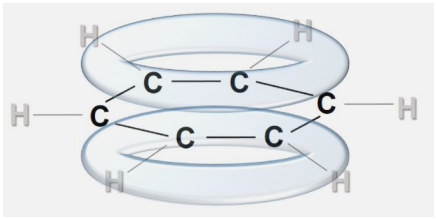


- Each carbon atom in benzene has an unhybridised 2p orbital that is perpendicular to the hexagonal plane of carbon atoms. Since these six 2p orbitals are parallel to one another, each of the 2p orbital can overlap sideways and equally with the adjacent two 2p orbitals to form π bonds. Each of the six 2p unhybridised orbital contains an electron. Hence, the sideways overlap of the 2p orbitals results in a doughnut-shaped delocalised π electron cloud above and below the hexagonal plane of carbon atoms.





pi bond formation



doughnut-shaped delocalised π electron cloud

- Due to delocalisation of the π electrons, benzene molecule exists as a **resonance hybrid** of the resonance structures (I) and (II). Note: resonance structures (I) and (II) do **not** exist. The structural formula of benzene is shown below. The hexagon represents the six carbon atoms arranged in a hexagonal ring and the circle represents the delocalised six π electrons.

(I) (II)
resonance structures of benzene

resonance hybrid of benzene

- The delocalisation of the π electrons conferred **extra stability** to the benzene structure which is said to be **resonance–stabilised**.

- The following evidences show that benzene exists as a resonance hybrid.

  (a) Benzene has the **same** carbon-carbon bond lengths of 0.139 nm which are **intermediate** in length between C–C bond and C=C bond. Hence, carbon–carbon bond in benzene is stronger than C–C bond but weaker than C=C bond.

bond	bond length / nm
C–C	0.154
C=C	0.132

  (b) Heat of hydrogenation (i.e. heat evolved when 1 mol of unsaturated compound is hydrogenated) of benzene has a **lower** magnitude than expected.

  E.g. Compare the heat of hydrogenation of the following molecules.

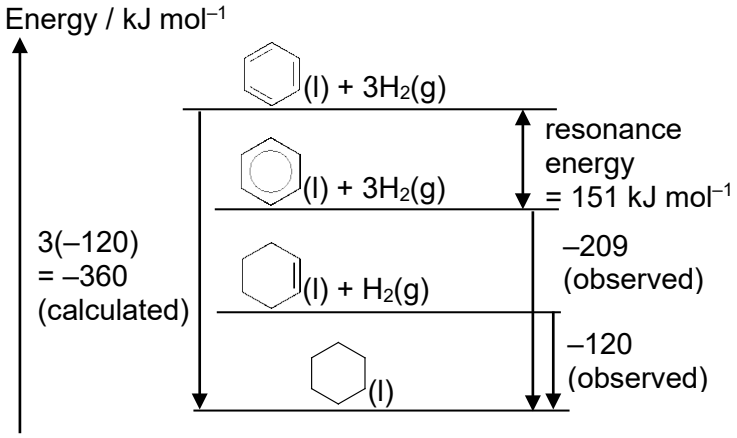

cyclohexene


cyclohexatriene
(non-existent)


benzene

  The product formed after hydrogenation of the above molecules is cyclohexane,  .

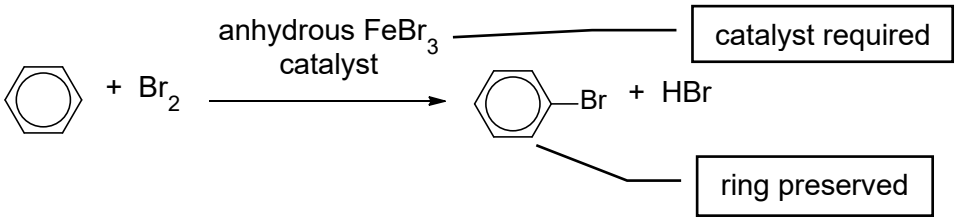
  Energy level diagram:



  Benzene evolves 151 kJ mol^{-1} **less energy** than predicted. Hence, benzene is **more stable** by 151 kJ mol^{-1} than we would have expected cyclohexatriene to be. Thus, benzene is **resonance–stabilised** with resonance energy = 151 kJ mol^{-1}.

  (c) Unlike alkenes, benzene undergoes substitution reactions readily rather than addition reactions. This is to preserve its resonance–stabilised ring structure as addition reactions would destroy it.

  E.g. Unlike alkenes, benzene does not decolourise orange-red liquid bromine. Instead, it undergoes substitution reaction with bromine in the presence of anhydrous $FeBr_3$ catalyst.



Exercise
Which of the following could be a result of the delocalised π electron cloud in the benzene molecule? (You may choose more than one correct answer.)

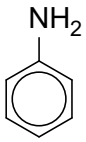
1 Benzene is a good conductor of electricity.
2 Benzene prefers to undergo substitution rather than addition reaction.
3 All the carbon-to-carbon bonds are equal in length.

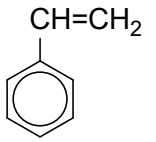
1.2 Nomenclature

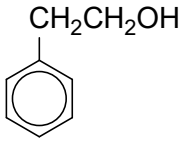
- Phenyl group, C_6H_5–, is where a hydrogen atom is removed from benzene.

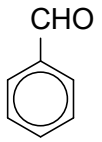
- For monosubstituted benzene,

  (a) if benzene is regarded as a substituent, the name of the compound will have the prefix "phenyl".



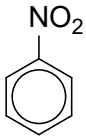


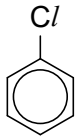


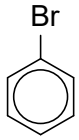


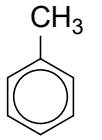
E.g. phenylamine phenylethene 2-phenylethanol phenylmethanal

  (b) if the compound is regarded as a derivative of benzene, the name of the substituent appears as the prefix of "benzene".



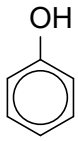


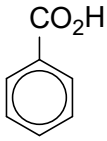


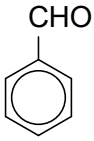


E.g. nitrobenzene chlorobenzene bromobenzene methylbenzene

  (c) there are some special names such as phenol, benzoic acid and benzaldehyde.

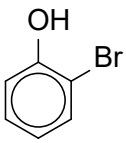


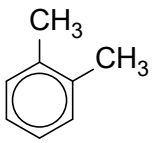


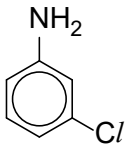


phenol benzoic acid benzaldehyde (= phenylmethanal)

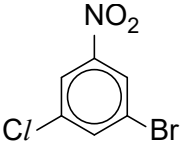
- For two or more substituents attached to the benzene ring, the carbon atoms in the ring are numbered from 1 to 6, beginning with the carbon atom that is bonded to the first substituent and continuing in such a direction as to lead to the **lowest** numbers for the rest of the substituents.

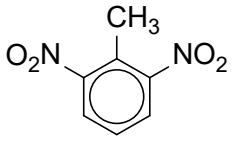






E.g. 2-bromophenol 1,2-dimethylbenzene 3-chlorophenylamine





1-bromo-3-chloro-5-nitrobenzene 2-methyl-1,3-dinitrobenzene

Exercise
Draw the structural formula for each of the following compounds.
(a) 4-hydroxybenzoic acid (b) 2-phenyloctane

You are now ready to attempt Tutorial Questions 1 and 2.

2 Physical Properties of Arenes

- Arenes are liquids or low melting point solids with characteristic 'aromatic' odours. Their vapours are toxic and should avoid inhaling them.

  Note: Benzene is a colourless liquid (boiling point 80 °C, melting point 5.5 °C) and continued inhalation of its vapour can induce anaemia and even leukaemia. Methylbenzene is also a colourless liquid (with a higher boiling point 111 °C).

- Arenes are **soluble** in organic solvents such as CCl_4.

  Note: Both benzene and methylbenzene are useful solvents themselves. Since the fumes of methylbenzene are considerably less toxic than those of benzene, it is preferable, whenever possible, to use it instead of benzene.

- Arenes are **insoluble** in polar solvents such as water and are less dense than water.

- Boiling points of arenes **increase** with increase in relative molecular mass due to **increase in number of electrons** leading to **stronger instantaneous dipole-induced dipole interactions** that require **more energy** to overcome.

  However, their melting point trend is irregular as it depends on molecular symmetry.

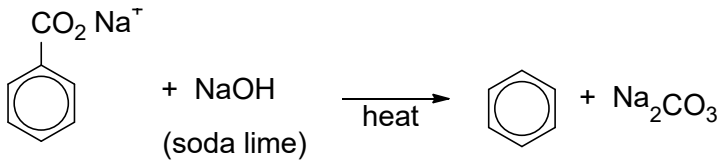
- Arenes are **non-conductors** of electricity.

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

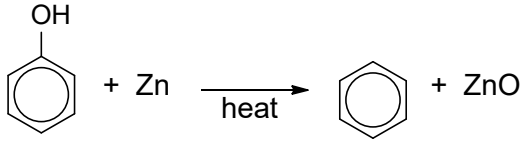
3 Benzene

3.1 Preparation (For information only)

- Fusion of sodium salt of benzoic acid with soda lime (decarboxylation).



- Passing phenol vapour over heated zinc powder (reduction).



3.2 Electrophilic Substitution Reactions

Candidates should be able to:
(a) 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

- Like alkenes, benzene possesses **high π electron density** and serves as a source of electrons. Hence, it is attacked by **electrophiles**.

- Resonance stabilisation of benzene structure due to the **delocalisation of π electrons** makes the benzene ring **less reactive towards electrophiles** compared to the C=C bond in alkenes.

- Hence, benzene can only be attacked by **strong electrophiles**, e.g. Br^+.

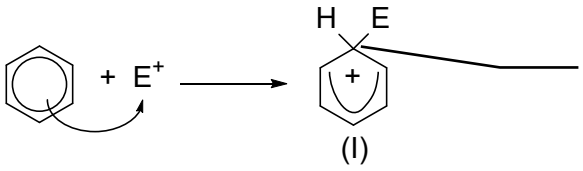
- Benzene undergoes **substitution** reactions rather than addition reactions to **preserve its resonance–stabilised ring system**. Undergoing addition results in a change in hybridisation of C atom from sp^2 to sp^3. Thus, the p orbitals are no longer overlapping throughout the ring and benzene would lose its resonance stability. Hence, the typical reaction of benzene is **electrophilic substitution**.

- *Mechanism*:

  Step 1: Generation of strong electrophile with the use of Lewis acid catalyst (also a halogen carrier).

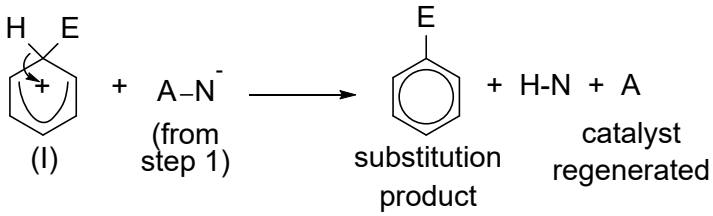
  $$\underset{\text{weak electrophile}}{E\text{–}N} + \underset{\text{Lewis acid catalyst}}{A} \rightarrow \underset{\text{strong electrophile}}{E^+} + A\text{–}N^-$$

  Step 2: Electrophilic attack on benzene to form resonance-stabilised carbocation.

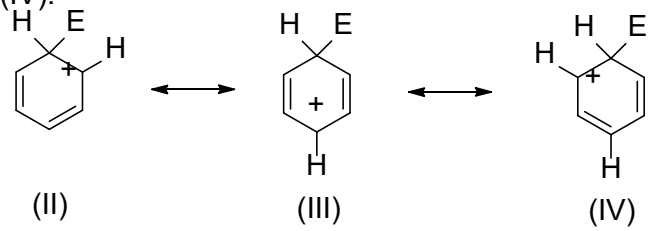


This C atom is sp^3 hybridised. The other five C atoms remain sp^2 hybridised.

  Step 3: Loss of proton from intermediate (I) to form the substitution product and regeneration of the Lewis acid catalyst, A.



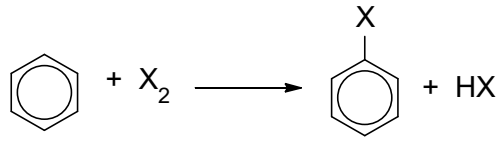
Note: Benzene loses a proton in the process. In (I), the organic intermediate, only five p orbitals are overlapping and the positive charge is delocalised over five carbon atoms ('horseshoe' representation). (I) is a resonance–stabilised carbocation and is a resonance hybrid of (II), (III) and (IV).



Examples of electrophilic substitution reactions:
(a) Halogenation
(b) Nitration
(c) Friedel-Crafts alkylation

3.2.1 Halogenation

Candidates should be able to:
(b) 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)



- Reagents and conditions:
  X_2 (Cl_2 or Br_2), **anhydrous** $AlCl_3$ or $AlBr_3$ or $FeCl_3$ or $FeBr_3$ as Lewis acid catalyst

  Observations:
  When Cl_2 is used, yellowish-green Cl_2 is decoloursed and white fumes of HCl are formed.
  When Br_2 is used, orange-red Br_2 is decoloursed and white fumes of HBr are formed.

  Fe can also be used instead as it is converted to iron(III) halide *in situ* by reaction with the halogen reagent, i.e. $2Fe + 3X_2 \rightarrow 2FeX_3$.

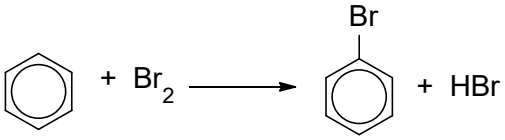
  The Lewis acid catalyst, $AlCl_3$ or $AlBr_3$ or $FeCl_3$ or $FeBr_3$, must be **dry** (i.e. **anhydrous**) to prevent hydrolysis (refer to Periodic Table notes) from taking place such that it will not be able to act as a Lewis acid to generate the strong electrophile.

  The Al atom in $AlCl_3$ or $AlBr_3$ is **electron deficient** as there are only six valence electrons around it. Al in $AlCl_3$ or $AlBr_3$ and Fe in $FeCl_3$ or $FeBr_3$ have energetically accessible vacant orbitals to accept a lone pair of electrons. Thus, they are able to act as Lewis acids.

  Note:
  Under prolonged conditions and in the presence of a higher proportion of the halogen, the 1,2-dihalide and 1,4-dihalide are formed.

Candidates should be able to:
(c) (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

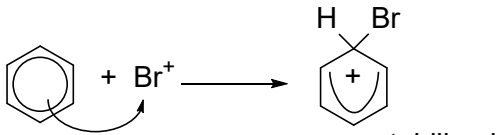
- *Mechanism*:



Step 1: $AlBr_3$ catalyst acts as a **Lewis acid** by **accepting a lone pair of electrons** from the halogen, thereby inducing polarity in the halogen and eventually generating a **strong electrophile, Br^+** (which carries a full positive charge).

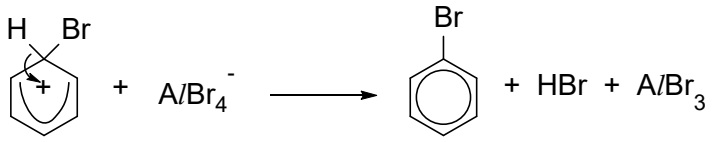
$$Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$$

Step 2: Strong electrophile, Br^+, attacks benzene to form resonance-stabilised carbocation.



resonance stabilised carbocation

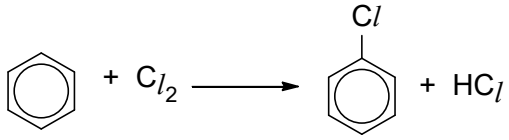
Step 3: Loss of proton, formation of substitution product and regeneration of $AlBr_3$ catalyst at the end of the reaction.



bromobenzene

Exercise

The following questions are related to the electrophilic substitution reaction of benzene with Cl_2 in the presence of anhydrous $FeCl_3$.



Using what you have learnt earlier about the bromination of benzene in the presence of $AlBr_3$, decide which of these statements are true of the intermediate of the above reaction.

Type either 'True' or 'False' in the blanks provided to indicate your response to each statement.

1 The intermediate is a planar ion. Answer: _____

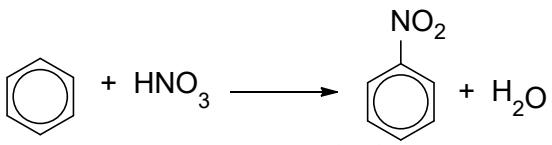
2 The intermediate has five π electrons. Answer: _____

3 The intermediate has the formula of $[C_6H_6Cl]^+$. Answer: _____

You are now ready to attempt Tutorial Question 3.

3.2.2 Nitration

Candidates should be able to:
(b) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:
(ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst)

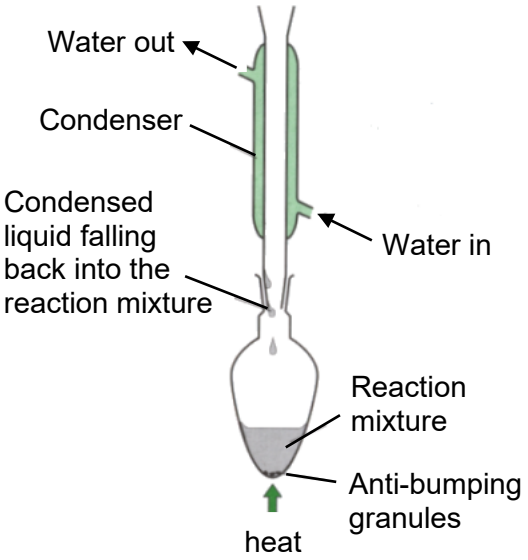


nitrobenzene

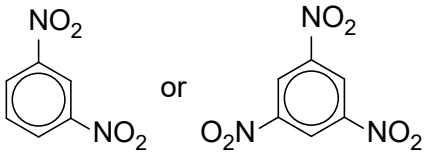
- Reagents and conditions:
  concentrated HNO_3, concentrated H_2SO_4 catalyst, heat at 55–60 °C (under reflux)

Note:
The reflux apparatus is shown.

The purpose of the condenser is to prevent escape of volatile organic compounds through vaporisation, thus increasing the yield of the product obtained.



- Nitrobenzene is a pale yellow liquid with an almond smell.
- Temperature for this reaction needs to be carefully controlled as high temperatures (100 °C or above) will lead to formation of the di-substituted product or tri-substituted product.

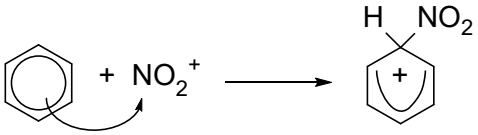


- *Mechanism*:

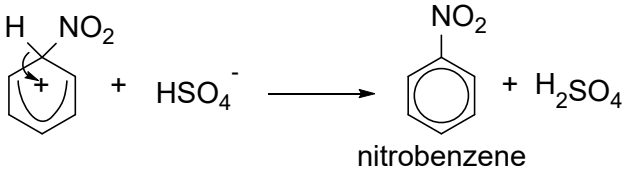
Step 1: H_2SO_4 catalyst acts as a **Brønsted–Lowry acid** by **donating a proton**, which leads to generation of the **strong electrophile, NO_2^+**.

$$2H_2SO_4 + HNO_3 \rightarrow \underset{\text{nitronium ion}}{NO_2^+} + H_3O^+ + 2HSO_4^-$$

Step 2: Strong electrophile, NO_2^+, attacks benzene to form resonance-stabilised carbocation.



Step 3: HSO_4^- abstracts H^+ from carbocation to yield substitution product. H_2SO_4 catalyst is regenerated at the end of the reaction.

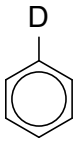


Exercise [N2002/I/21]
Which is a correct statement about the intermediate complex, $[C_6H_6NO_2]^+$, formed during the mononitration of benzene?

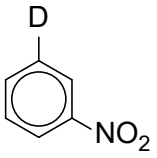
A It is planar.
B It contains a chiral centre.
C It can exist in either a *cis* or a *trans* form.
D It contains only one tetrahedrally-bonded carbon atom.

Exercise [J1997/III/22; N2001/III/23]
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

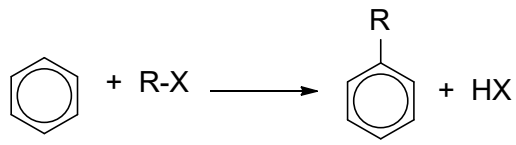


3-nitrodeuteriobenzene

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

3.2.3 Friedel-Crafts Alkylation

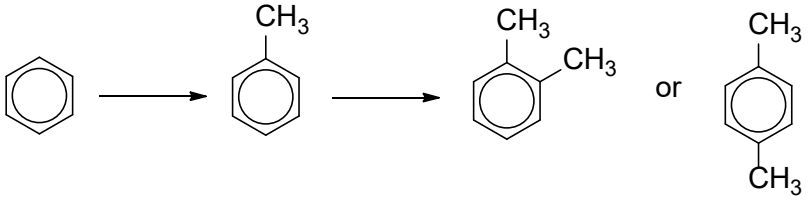
Candidates should be able to:
(b) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:
(iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)



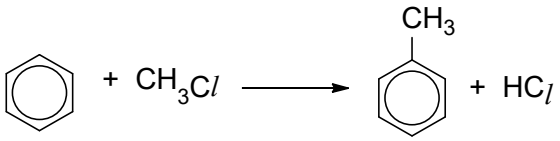
- Reagents and conditions:
  RX (RC*l* or RBr), **anhydrous** A*l*C*l*$_3$ or A*l*Br$_3$ or BF_3 or FeC*l*$_3$ or FeBr$_3$ as Lewis acid catalyst, **excess benzene**

  A*l*C*l*$_3$ or A*l*Br$_3$ or BF_3 or FeC*l*$_3$ or FeBr$_3$ are able to accept electron pairs as they are **electron-deficient** molecules. They must be **anhydrous** to prevent hydrolysis (refer to Periodic Table notes) from taking place.

  Note:
  Further alkylation occurs even more readily. Hence, it is necessary to start with **excess benzene** to prevent further alkylation.



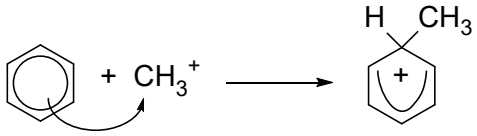
- This reaction is used to synthesise homologues of benzene.
- *Mechanism*:



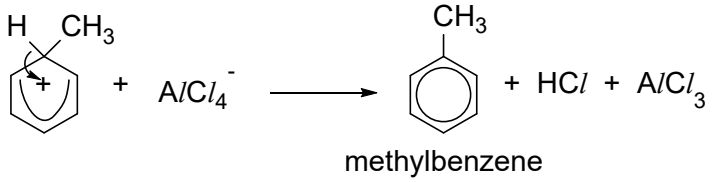
Step 1: A*l*C*l*$_3$ catalyst acts as a **Lewis acid** by **accepting a lone pair of electrons** from C*l* in CH_3Cl, thereby generating a **strong electrophile, CH_3^+**.

$$CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$$

Step 2: Strong electrophile, CH_3^+, attacks benzene to form resonance-stabilised carbocation.



Step 3: Loss of proton, formation of substitution product and regeneration of $AlCl_3$ catalyst at the end of the reaction.

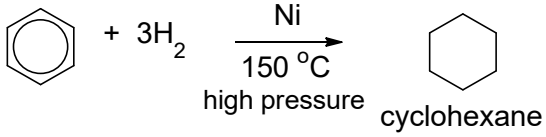


methylbenzene

3.3 Addition of Hydrogen Reaction (Reduction)

- Unlike alkenes, benzene typically does **not** undergo addition reactions as addition results in the destruction of the resonance-stabilised ring system in benzene.

  Exception: Addition of hydrogen (reduction)

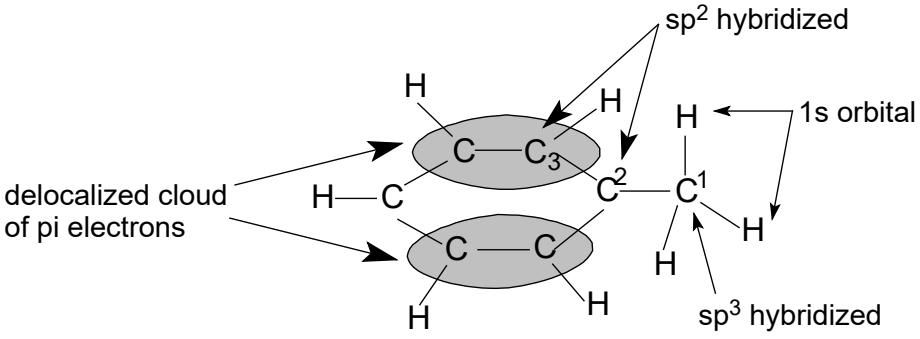


cyclohexane

4 Methylbenzene

4.1 Structure of Methylbenzene

- Methylbenzene, as its name suggests, consists of one methyl group bonded to the benzene ring. The structural formula of methylbenzene is $C_6H_5CH_3$, and it is commonly known as toluene.



- <u>Formation of σ bonds in methylbenzene</u>
  C_1–C_2 σ bond: **head-on** overlap of sp^2 hybrid orbital of C_2 with sp^3 hybrid orbital of C_1
  C_2–C_3 σ bond: **head-on** overlap of sp^2 hybrid orbital of C_2 with sp^2 hybrid orbital of C_3
  C_1–H σ bond: **head-on** overlap of sp^3 hybrid orbital of C_1 with 1s orbital of H
  C_3–H σ bond: **head-on** overlap of sp^2 hybrid orbital of C_3 with 1s orbital of H

- <u>Formation of π electron cloud</u>
  Similar to benzene, the π electron cloud is formed from the **sideways** overlap of the six p orbitals of benzene C atoms.

- Methylbenzene is **planar** with respect to the **carbon atoms only** (as C_1 is sp^3 hybridised and hence has a tetrahedral shape). The hydrogen atoms on C_1 are not planar.

4.2 Preparation

- Refer to Friedel–Crafts alkylation of benzene (see section 3.2.3).

4.3 Reactions

4.3.1 Effect of Substituent Groups

- Any substituent group attached to the benzene ring will affect the **reactivity** of the benzene ring and determine the **orientation** (i.e. position) of the substitution.

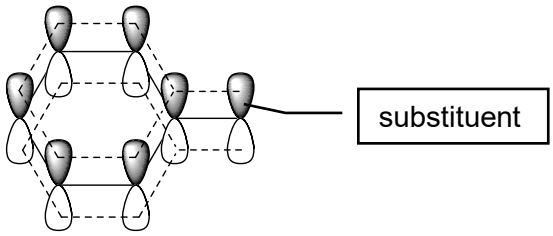
- *Reactivity*

(a) An **electron-donating** substituent group, such as $–NH_2$, –OH, –R (R = alkyl group) increases the electron density in the benzene ring. Hence, the monosubstituted benzene is **more reactive** towards electrophilic substitution, i.e. the benzene ring is **activated** towards electrophilic substitution. Thus, the reaction conditions used for electrophilic substitution are **milder**.

(b) An **electron-withdrawing** substituent group, such as –C*l*, –CHO, $–CO_2H$, decreases the electron density in the benzene ring. Hence, the monosubstituted benzene is **less reactive** towards electrophilic substitution, i.e. the benzene ring is **deactivated** towards electrophilic substitution. Thus, the reaction conditions used for electrophilic substitution are **harsher**.

(c) There are two ways in which electrons can be donated into or withdrawn from the benzene ring, namely **resonance** effect and **inductive** effect.

The **resonance effect** is the donation or withdrawal of electrons through the overlap of p orbital on the substituent with a p orbital on the C atom of benzene ring.



The **inductive effect** is the donation or withdrawal of electrons through a sigma bond due to electronegativity difference between the atoms.

(d) Substituents with an **electron-donating resonance effect** include –OH, $–OCH_3$, $–NH_2$, where the O and N atoms have a **lone pair of electrons** (usually in a p orbital) available for donation to the benzene ring.

Substituents with an **electron-withdrawing resonance effect** include –CN, $–NO_2$ (**doubly or triply bonded**), where the more electronegative N and O atoms respectively are able to withdraw electrons from the benzene ring.

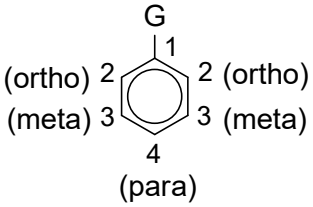
(e) Substituents with an **electron-donating inductive effect** include –R, where they inductively donate electrons through the sigma bond linking the substituents to a benzene ring.

Substituents with an **electron-withdrawing inductive effect** include –C*l*, –Br, –I, where they inductively withdraw electrons through the sigma bond linking the substituents to a benzene ring.

- *Orientation of substitution*

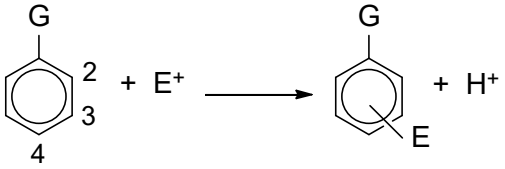
(a) The substituent group on the benzene ring determines the position of the incoming electrophile after the reaction.

Note: Taking the carbon attached to the substituent, G, as 1, positions 2, 3 and 4 will correspond to the next three positions adjacent to G. Alternatively, the terms "ortho", "meta" and "para" can also be used to designate the positions.



(b) G is either **2,4-directing** and directs the electrophile onto positions 2 and 4 or is **3-directing** and directs the electrophile onto position 3.

(c) The position of the incoming group, E, is determined by the nature of the group, G, already bonded to the ring, and **not** by the nature of the incoming group E (given in the *Data Booklet*).



G	–R } electron-donating inductive effect –OH, –OR, –NH_2, –NHR, –NR_2 } electron-donating resonance effect (highly activating) –NHCOR } electron-donating resonance effect	–C*l*, –Br, –I: electron-withdrawing inductive effect	–CHO, –COR, –CO_2H, –CO_2R, –NH_3^+, –NO_2, –CN } electron-withdrawing resonance effect
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

If multiple substituents are present, the **more** activating group will dominate the orientation of substitution.

(d) Recall the nitration of benzene forms nitrobenzene (see section 3.2.2). Nitrobenzene undergoes further substitution to form 1,3-dinitrobenzene and 1,3,5-trinitrobenzene at **higher** temperatures.

Reason: $–NO_2$ group is 3–directing and **deactivating**.

(e) Recall the Friedel-Crafts alkylation of benzene forms methylbenzene (see section 3.2.3). Further alkylation of methylbenzene occurs **more readily** to give 1,2-dimethylbenzene and 1,4-dimethylbenzene.

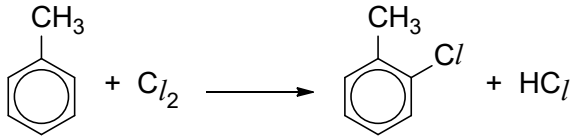
Reason: $–CH_3$ group is 2,4–directing and **activating**.

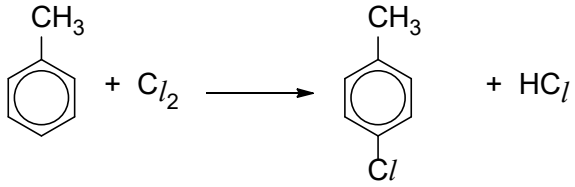
4.3.2 Electrophilic Substitution Reactions (similar to benzene)

- $-CH_3$ is 2,4–directing and activating. Hence, methylbenzene undergoes **electrophilic substitution** reactions like benzene except that they take place **more** readily. Both 2– and 4–isomers are produced as major products.

Candidates should be able to:
(b) 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)

(a) Halogenation



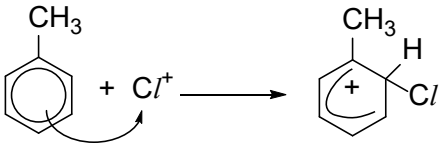


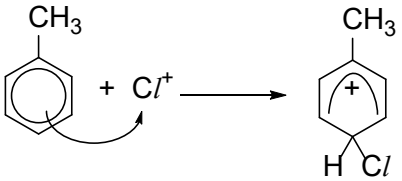
Reagents and conditions: Cl_2, anhydrous $FeCl_3$ or $AlCl_3$ as Lewis acid catalyst
Observations: Similar to benzene

Mechanism:

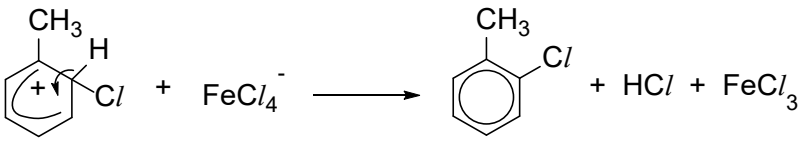
Step 1: $Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$

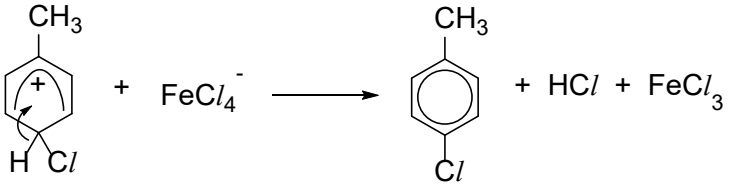
Step 2:



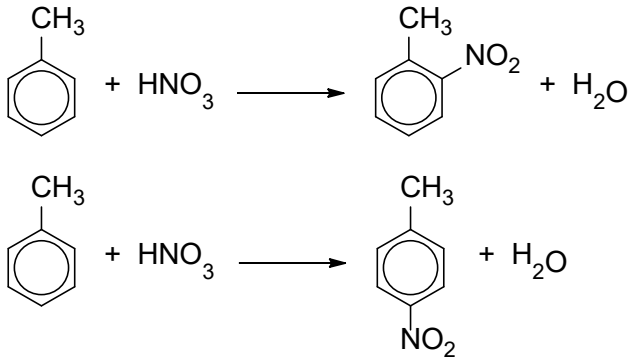


Step 3:



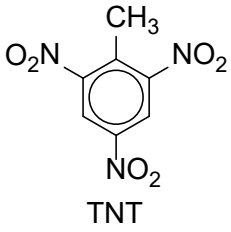


(b) Nitration



Reagents and conditions:
concentrated HNO_3, concentrated H_2SO_4 catalyst, 30 ^oC
The temperature of reaction is lower than that for benzene as $–CH_3$ is activating.

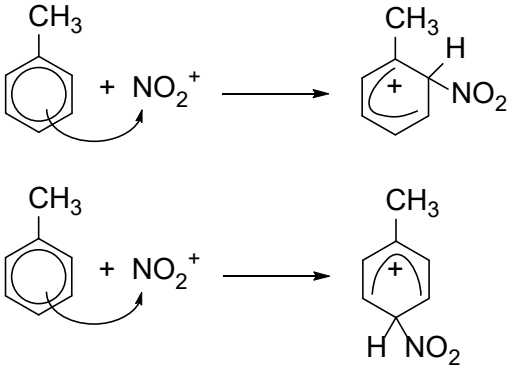
Note: Prolonged nitration at higher temperature leads to formation of the common explosive, trinitrotoluene, TNT (or 2,4,6-trinitromethylbenzene).



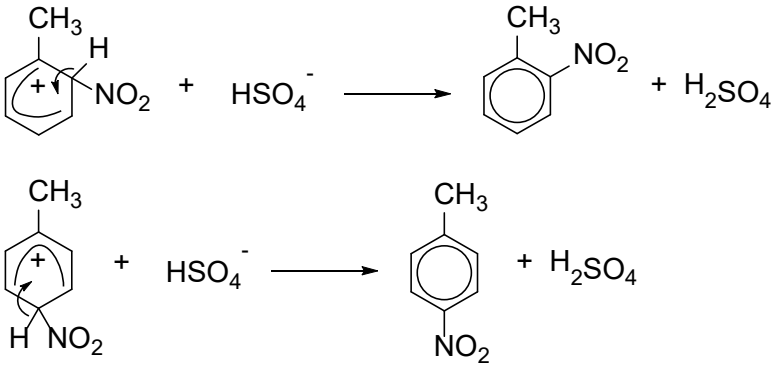
Mechanism:

Step 1: $2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

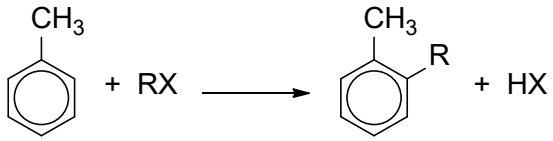
Step 2:

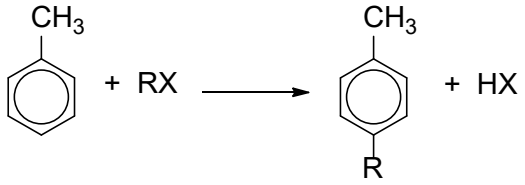


Step 3:



(c) Friedel-Crafts Alkylation



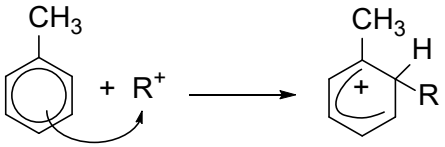


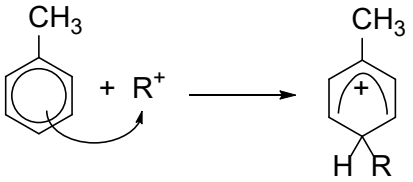
Reagents and conditions:
RC*l*, anhydrous A*l*C*l*$_3$ or FeC*l*$_3$ as Lewis acid catalyst, **excess methylbenzene**

Mechanism:

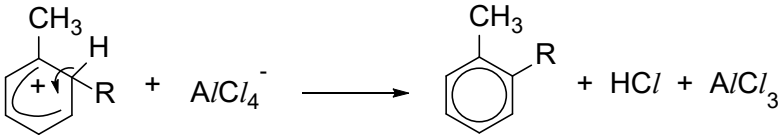
Step 1: RC*l* + A*l*C*l*$_3$ $\rightarrow$ R^+ + A*l*C*l*$_4^-$

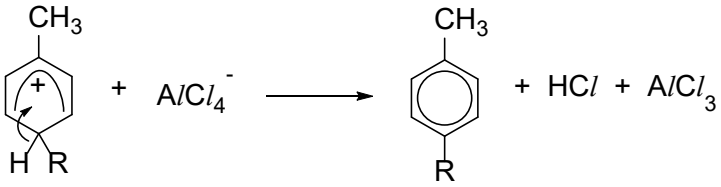
Step 2:





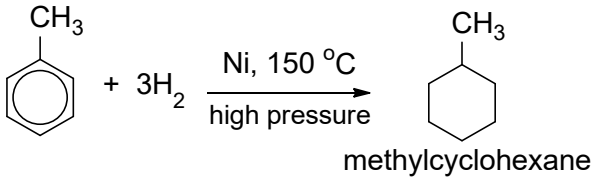
Step 3:





4.3.3 Addition of Hydrogen Reaction (Reduction) (similar to benzene)

- Exception: Addition of hydrogen (reduction)

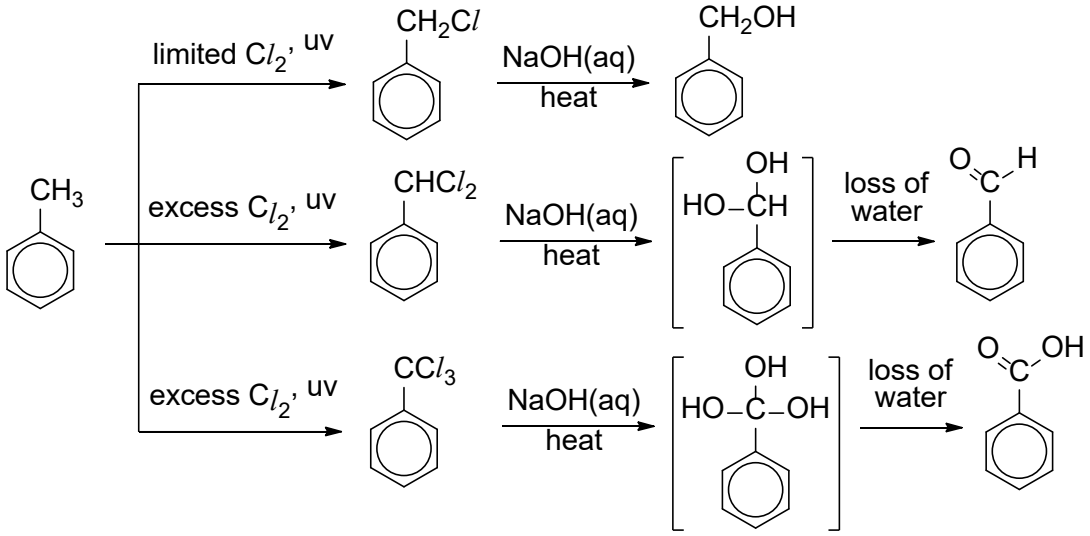


4.3.4 Free Radical Substitution Reaction (side–chain reaction similar to alkanes)

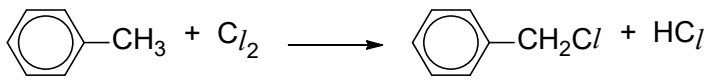
Candidates should be able to:
(d) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
(i) free-radical substitution by chlorine and by bromine

- Reagents and conditions: X_2 (Cl_2 or Br_2), uv light or heat/high temperature

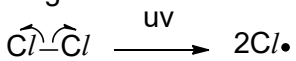
- The reaction proceeds via free radical substitution mechanism. In excess methylbenzene, mono-substituted product is obtained. In excess X_2, di- or tri-substituted products are obtained. All the products formed can be hydrolysed using aqueous NaOH and heat to give alcohols, carbonyl compounds or carboxylic acids.



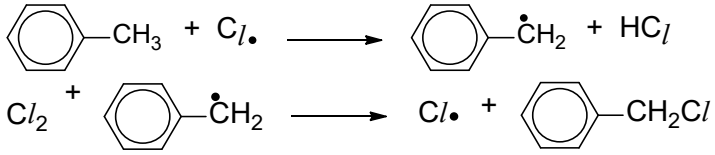
- *Mechanism*:

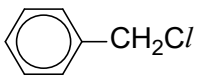
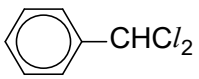
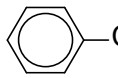


Stage 1: Initiation

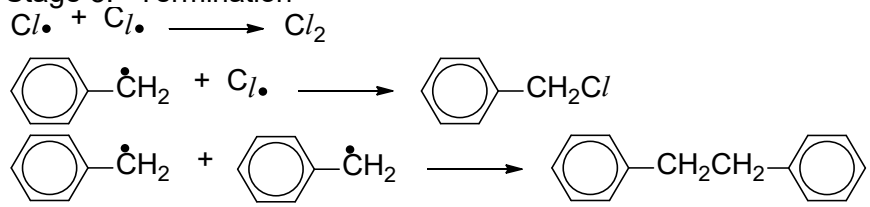


Stage 2: Propagation



Further substitution of  can take place to give  and  .

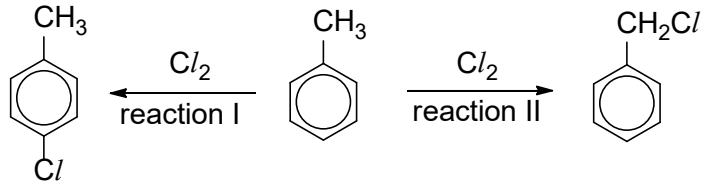
Stage 3: Termination



Candidates should be able to:
(e) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

Exercise

Methylbenzene can react with chlorine in two ways, depending on the conditions of the reaction.



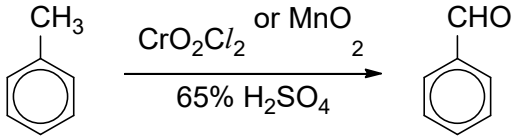
Describe the conditions used to produce **A** and **B** respectively.

Solution

Reaction I: Reaction II:

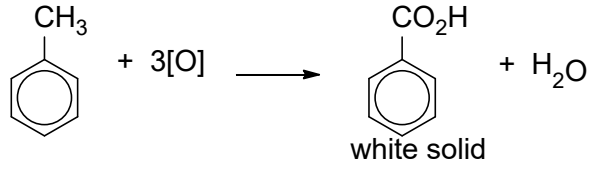
4.3.5 Oxidation Reaction (side–chain reaction)

- Product of oxidation reaction depends on the reagents used.
- Weak oxidising agents



Candidates should be able to:
(d) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene: (ii) complete oxidation to give benzoic acid

- Strong oxidising agent



Reagents and conditions: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat (under reflux)

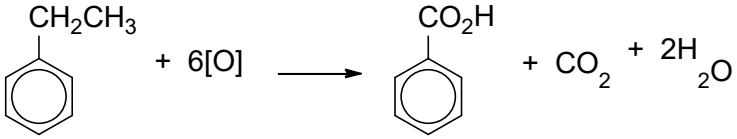
Observations: Decolourisation of purple solution of acidified $KMnO_4(aq)$ with formation of white solid.

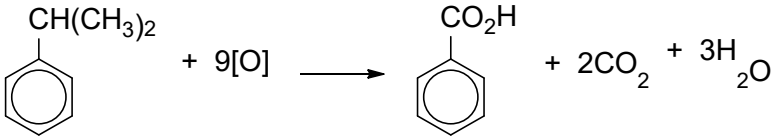
Note:

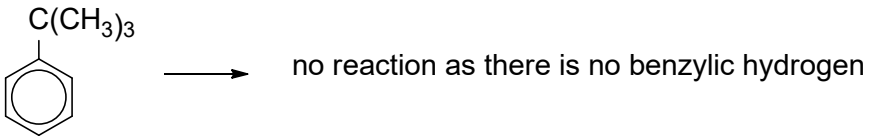
(a) This is a chemical test to distinguish between benzene and methylbenzene.

(b) The strong oxidising agents ($KMnO_4(aq)$, $H_2SO_4(aq)$) are capable of oxidising the longer side chains with a benzylic hydrogen (i.e. at least one H atom bonded to C atom adjacent to the benzene ring) to form benzoic acid (white solid) with effervescence of CO_2. The rest of the side chain is destroyed, forming carbon dioxide and water.

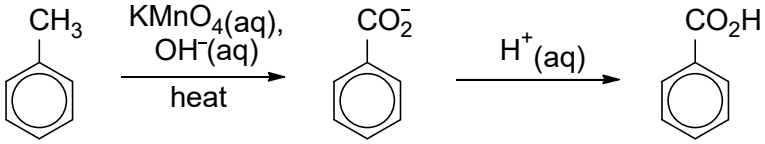
E.g.







(c) **Alkaline** $KMnO_4$ gives the **salt** of carboxylic acid which must be first **acidified** before solid benzoic acid can be obtained.



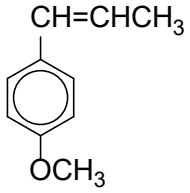
(d) Potassium dichromate(VI), $K_2Cr_2O_7$, is **unable** to oxidise the side chain of benzene.

Exercise

1,4-dimethylbenzene can be oxidised to benzene-1,4-dicarboxylic acid. Using the [O] notation for the oxidation of organic compounds, write a balanced equation for this oxidation.

Solution

Exercise [N2007/II/5(b)(ii)]
The compound below, which is present in cinnamon, appears to be effective as a pesticide.



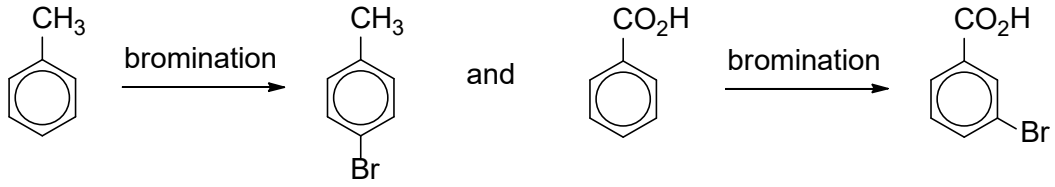
The group $-OCH_3$ can be regarded as inert.

Draw the structural formulae of the organic compounds formed when the above compound is heated under reflux with acidified manganate(VII) ions.

Solution

Candidates should be able to:
(f) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

Exercise [N2002/III/6(b)]
During aromatic substitution, the position of the incoming group, the new substituent, is determined by the nature of the group already present in the ring. For example, the following reactions produce the bromo-compounds shown.

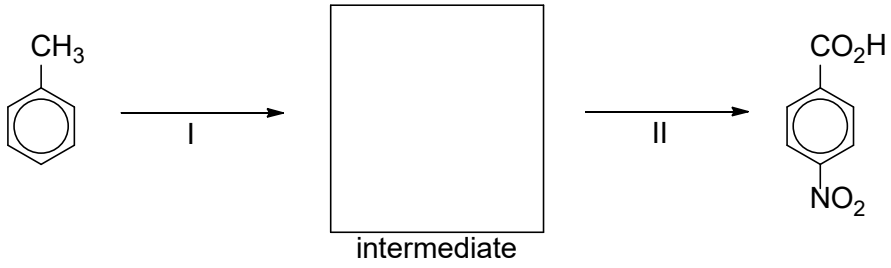


Use this knowledge to devise two-step synthesis, starting with methylbenzene, of

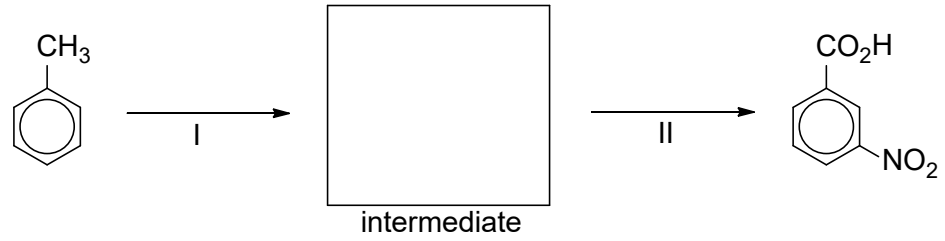
(i) 4-nitrobenzoic acid, (ii) 3-nitrobenzoic acid.

Identify the reagents and conditions at each step, and draw the structural formulae of the intermediates.

Solution
(i)



(ii)



You are now ready to attempt Tutorial Questions 4 to 9 and to complete the table of reactions in the Summary.