

5 Summary

(a) Mechanism

Similarities and differences between alkene and benzene

Like alkenes, benzene possesses **high π electron density** and is hence attacked by **electrophiles**.

However, benzene differs from alkenes in that:

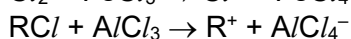
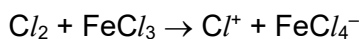
- (1) **delocalisation** of π electrons renders the benzene ring **less nucleophilic** compared to the C=C bond in alkenes. Hence, benzene can only be attacked by **strong electrophiles**.
- (2) benzene undergoes **substitution** instead of addition to **preserve its resonance stabilised ring system**.

Hence, typical reaction of benzene is **electrophilic substitution**.

Step 1:

Halogenation / Friedel-Crafts alkylation

Catalyst acts as a **Lewis acid** by **accepting a lone pair of electrons** from Cl_2 / RCI , thereby generating a **strong electrophile**, Cl^+ / R^+ .

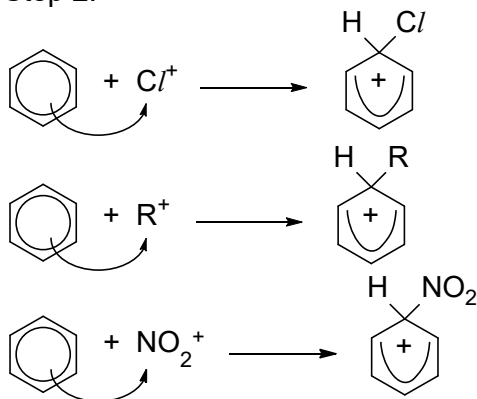


Nitration

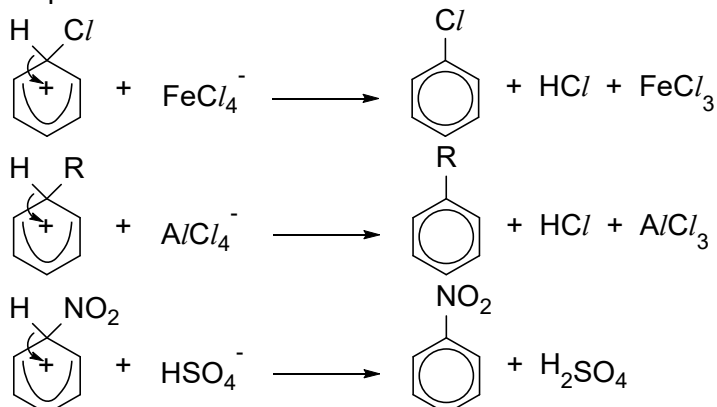
H_2SO_4 catalyst acts as a **Brønsted-Lowry acid** by **donating a proton** which leads to generation of the **strong electrophile**, NO_2^+ .



Step 2:



Step 3:

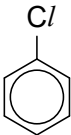


(b) Effect of substituents on benzene ring reactions (given in the *Data Booklet*)

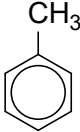
2, 4–directing		3–directing
activating	deactivating	deactivating
–R (alkyl group)	–Cl	–CHO, –COR
–OH or –OR (highly activating)	–Br	–CO ₂ H, –CO ₂ R
–NH ₂ , –NHR or –NR ₂ (highly activating)	–I	–NH ₃ ⁺
–NHCOR		–NO ₂ , –CN

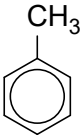
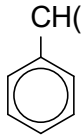
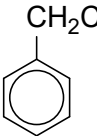
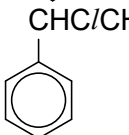
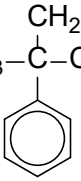
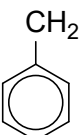
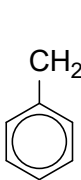
(c) Complete the following tables.

- Reactions common to both benzene and methylbenzene

Type of reaction	Reagents and conditions	Products for	
		benzene	methylbenzene
			
	CH ₃ CH ₂ Br, anhydrous AlBr ₃ catalyst, excess benzene / methylbenzene (for monosubstitution)		
	Concentrated HNO ₃ , concentrated H ₂ SO ₄ catalyst, 55 °C for benzene / 30 °C for methylbenzene		

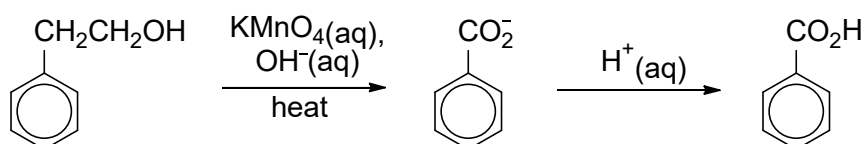
- Reactions for alkylbenzene only (side-chain reactions)

Type of reaction	Reagents and conditions	Reactant	Products
	Br ₂ , uv light or heat / high temperature (excess organic compound for monosubstitution)		

Type of reaction	Reagents and conditions	Reactant	Products
	$\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat Note: $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat cannot affect this reaction		
		Side chain with benzylic H but not alkene:   	
		Side chain with no benzylic H: 	
		Side chain with alkene: 	
		Side chain with alkene: 	

N.B. For side chain with C=C bond, consider oxidative cleavage of alkene followed by oxidation to benzoic acid due to presence of benzylic hydrogen.

Note: **Alkaline** KMnO_4 gives the **salt** of carboxylic acid which must be first **acidified** before solid benzoic acid can be obtained.



Arenes (Aromatic Hydrocarbon) Tutorial

Nomenclature

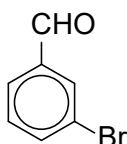
1 Write the structural formulae for the following benzene derivatives.

(a) 2,4,6-trinitrophenylamine

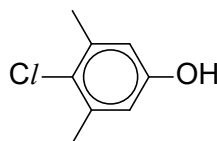
(b) 2-hydroxybenzoic acid

2 Name the following compounds.

(a)



(b)



Electrophilic Substitution

3 (a) Nitrobenzene is prepared by reacting benzene with a mixture of concentrated sulfuric acid and concentrated nitric acid. The electrophile in this reaction is the NO_2^+ cation.

(i) Explain the meaning of the term *electrophile*.

(ii) Write an equation to show how NO_2^+ is formed from the reagents used in the reaction.

(iii) Describe the mechanism for the formation of nitrobenzene from benzene.

(iv) Explain why benzene undergoes substitution reactions rather than addition reactions.

(b) (i) Iodine monochloride, ICl , can be prepared by passing chlorine gas over iodine crystals and it is collected as a dark brown liquid.

Draw the structure of the likely organic product of the reaction of ICl with benzene in the presence of a Lewis acid catalyst. Explain your answer.

(ii) Explain why benzene reacts with ICl in the presence of a Lewis acid catalyst unlike an alkene which reacts with ICl in the absence of a catalyst.

4 Which statement is true regarding the formation of chlorobenzene from benzene and chlorine?

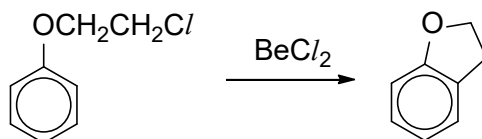
A A catalyst is not required for the reaction to take place.

B The six carbon atoms in benzene remain sp^2 hybridised throughout the reaction.

C The relative molecular mass of the organic product is 35.5 greater than that of benzene.

D The reaction involves an intermediate which contains four delocalised electrons.

- 5 Consider the following electrophilic substitution reaction, in which a compound of beryllium, BeCl_2 , is involved.

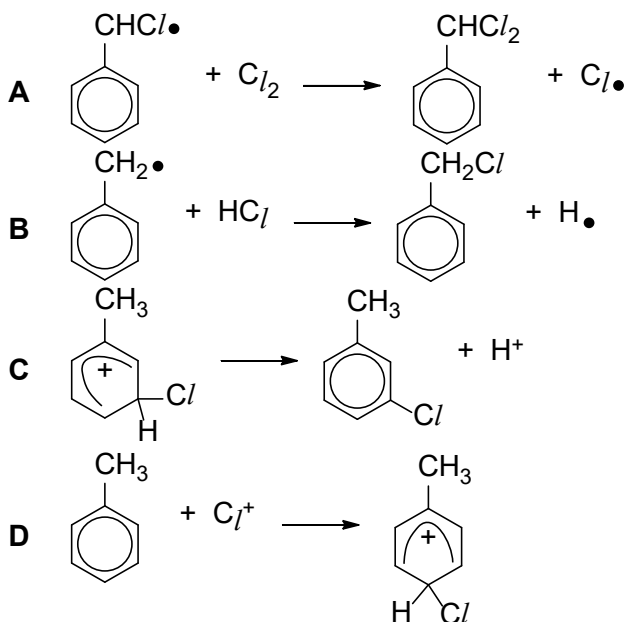


- (a) BeCl_2 has two roles during this reaction. State and describe the roles of BeCl_2 during the reaction.
- (b) Describe the mechanism of the reaction. You should include curly arrows indicating the movement of electrons, and all charges in your answer.

Integrated Questions

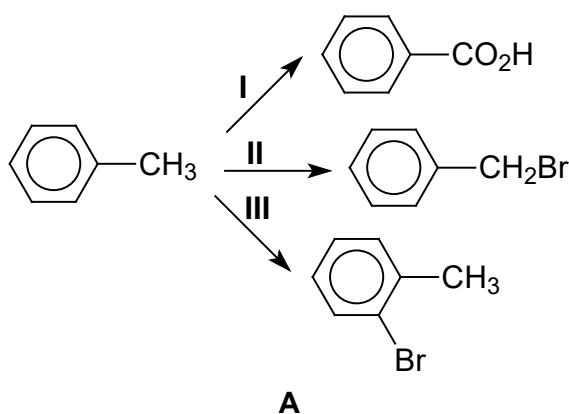
6 N1992/IV/22 (modified)

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?



7 N1997/II/6

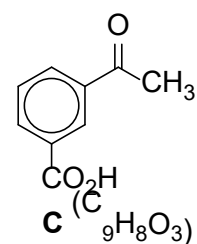
Methylbenzene can be used as an additive in unleaded petrol. Some chemical transformations of methylbenzene are given below.



- (a) Suggest reagents and conditions for each of the reactions I, II and III, and describe as fully as you can the type of reaction undergone in each case.
- (b) There are two other positional isomers of **A**. Draw their structural formulae, and suggest which one is more likely to be formed along with **A** in reaction III.

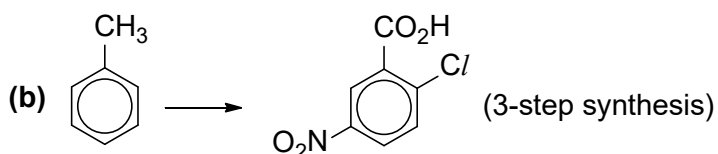
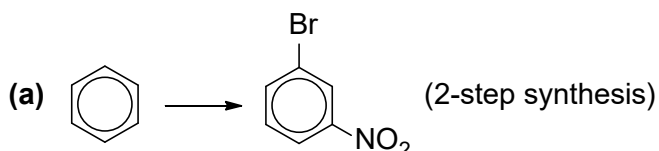
- 8 Compound **A** has the molecular formula $C_{10}H_{12}$. When **A** was treated with bromine in CCl_4 in the absence of light, compound **B** with the molecular formula $C_{10}H_{12}Br_2$ was formed. **A** can also be heated under reflux with acidified $KMnO_4$ to produce compound **C** as shown below.

Deduce possible structures for compounds **A** and **B**. Explain the types of reaction involved and the functional groups present.



Effect of Substituent Groups

- 9 Devise syntheses of the following compounds from the given starting material. Your proposed syntheses should allow as high a yield of the products as possible. Identify the reagents and conditions at each step, and draw the structural formulae of the intermediates.

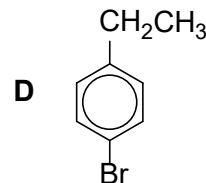
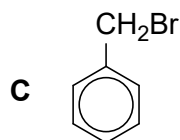
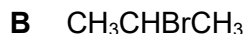
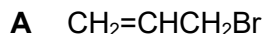


Victoria Junior College
Arenes (Aromatic Hydrocarbon) Supplementary Questions

Electrophilic Substitution

1 N1998/III/22

Which compound can be obtained by reacting a hydrocarbon with bromine in the presence of a halogen carrier?



2 N1999/III/23 (modified)

What is the correct set of conditions for the conversion of benzene into nitrobenzene?

	acid	temperature
A	dilute HNO_3	100 °C
B	concentrated HNO_3	50 °C
C	concentrated HNO_3 and concentrated H_2SO_4	50 °C
D	concentrated HNO_3 and concentrated H_2SO_4	120 °C

3 During the nitration of benzene, a nitro group substitutes at a carbon atom.

What is the arrangement of the bonds at this carbon atom during the reaction?

	at the start of the reaction	in the intermediate complex	at the end of the reaction
A	planar	planar	planar
B	planar	tetrahedral	planar
C	planar	tetrahedral	tetrahedral
D	tetrahedral	tetrahedral	tetrahedral

4 N2015/II/5

(a) Compound **Y** has a molecular formula of $\text{C}_6\text{H}_5\text{Cl}$.

Suggest **three** possible structures for **Y**. State the name of each structure you have drawn.

(b) Mononitration of compound **Y** produces just one compound rather than a mixture of isomers.

Use this additional information to identify which structure in (a) is that of **Y**, and write an equation for the mononitration of **Y** with a suitable reagent.

Integrated Questions

5 Which of the following about methylbenzene and its derivatives are correct?

- There are four aromatic isomers of molecular formula $\text{C}_7\text{H}_7\text{Cl}$.
- Methylbenzene reacts with warm acidified potassium dichromate (VI) solution.
- Methylbenzene is a planar molecule.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

6 N1998/II/5

(a) On complete combustion, 0.00754 mol of a hydrocarbon **E** gave 2.654 g of CO_2 and 0.543 g of H_2O .

(i) Determine the molecular formula of **E**.

(ii) Construct an equation for the complete combustion of **E**.

(b) **E** burns with a smoky flame. 1 mol of **E** reacts with 1 mol of bromine molecules.

(i) Draw the displayed formula of **E**.

(ii) Draw the displayed formula of the product formed between **E** and bromine.

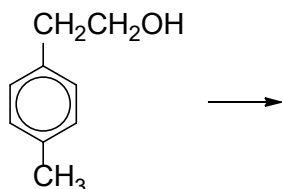
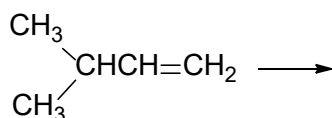
(c) (i) What organic product would you expect if **E** is heated under reflux with concentrated alkaline potassium manganate (VII)?

(ii) Suggest what colour change might be observed.

7 N2008/II/3(a)

Potassium manganate(VII), KMnO_4 , in acidic or alkaline solution, is widely used as an oxidising agent in organic and inorganic chemistry.

Draw the structures of the organic compounds formed when the following compounds are heated under reflux with concentrated alkaline KMnO_4 , followed by acidification.



8 Describe how you would distinguish between the following pairs of compounds. Include clearly in your answers the reagents, conditions and observations for each compound.

(a) benzene and cyclohexene

(b) benzene and methylbenzene

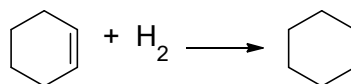
9 Methylbenzene is manufactured by passing heptane, C_7H_{16} , vapour over a catalyst. In the process, there is one gaseous by-product.

(a) Construct an equation for this process, showing the structural formulae of the organic molecules.

(b) The reaction is endothermic. Explain what conditions of temperature would favour a high equilibrium yield.

(c) Use the equation in (a) to explain what conditions of pressure would favour a high equilibrium yield.

- 10 (a)** By using relevant data from the *Data Booklet*, calculate the enthalpy change for the hydrogenation of cyclohexene.



- (b)** In 1865, Friedrich Kekule described benzene as a ring of alternating single and double bonds:



From experimental determination, the enthalpy change of hydrogenation of benzene was found to be -205 kJ mol^{-1} .

Explain, in terms of the structure of benzene, why this value is not three times your answer in **(a)**. Use an energy level diagram to illustrate your answer.

Answers for Supplementary Questions

1 D

2 C

3 B

5 D

10(a) -124 kJ mol^{-1}