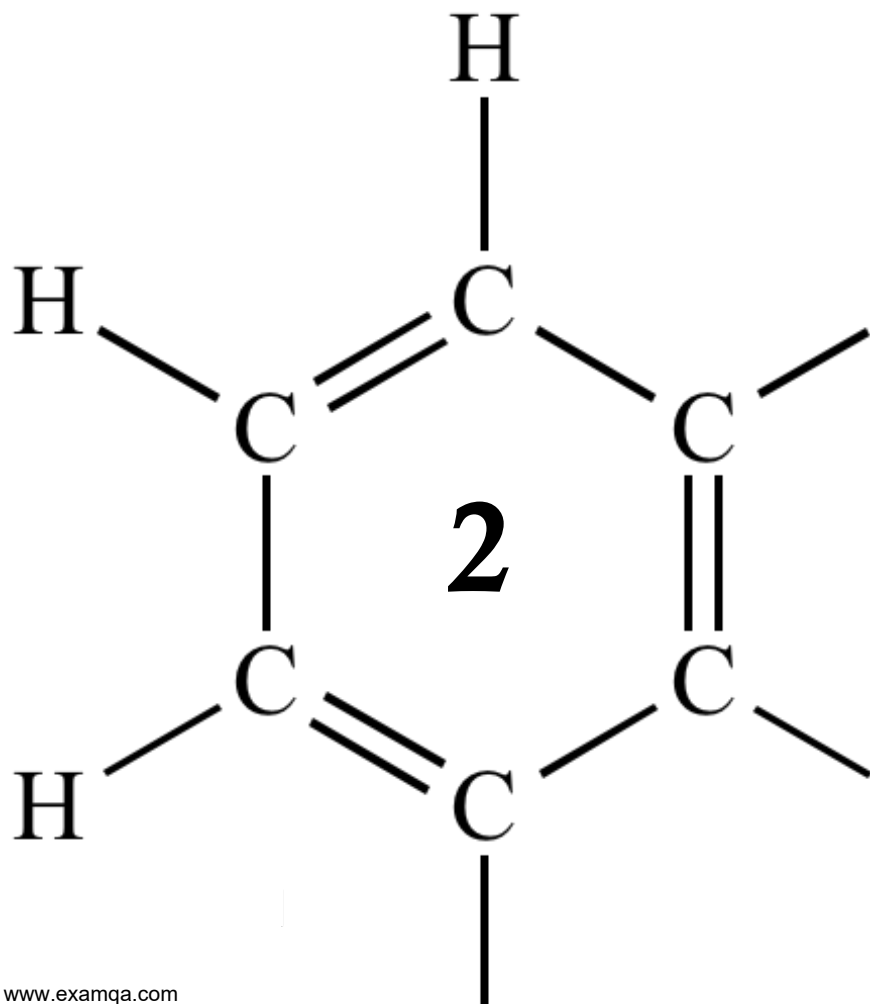


AQA A2 CHEMISTRY  
**AROMATIC ~ AMINES**

AROMATIC



1

Benzene reacts with ethanoyl chloride in a substitution reaction to form  $C_6H_5COCH_3$ . This reaction is catalysed by aluminium chloride.

(a) Write equations to show the role of aluminium chloride as a catalyst in this reaction.

Outline a mechanism for the reaction of benzene.

Name the product,  $C_6H_5COCH_3$ .

.....  
.....  
.....

(6)

(b) The product of the substitution reaction ( $C_6H_5COCH_3$ ) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with  $m/z = 105$ . Draw the structure of this fragment ion.

(1)

- (c) When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene. Suggest why the reaction of methylbenzene is faster.

.....

.....

.....

.....

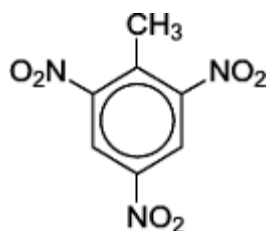
.....

.....

(2)  
(Total 9 marks)

2

Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



- (a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.
- (i) Give the reagents used to produce the electrophile for this reaction. Write an equation or equations to show the formation of this electrophile.

Reagents .....

.....

Equation .....

.....

(3)

- (ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3)

- (b) Deduce the number of peaks in the  $^{13}\text{C}$  n.m.r. spectrum of TNT.

.....

(1)

- (c) Deduce the number of peaks in the  $^1\text{H}$  n.m.r. spectrum of TNT.

.....

(1)

- (d) Using the molecular formula ( $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ ), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

.....

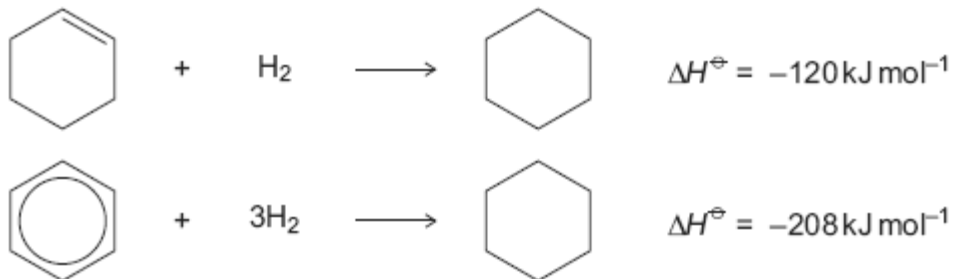
(1)

(Total 9 marks)

3

The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

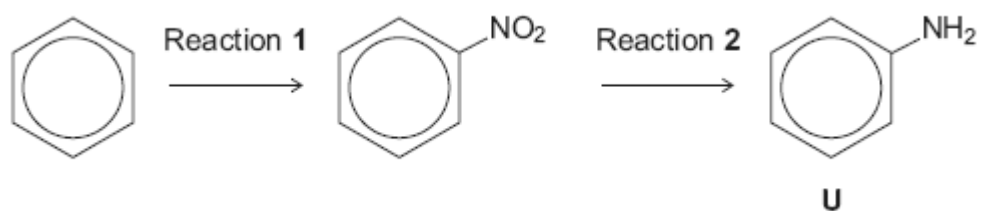
- (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
*(Extra space)* .....  
.....  
.....  
.....

(4)

(b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



The mechanism of Reaction 1 involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction 1.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

*(Extra space)* .....

.....

.....

.....

.....

.....

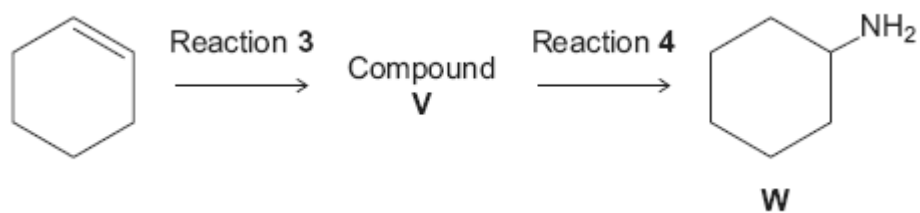
.....

.....

.....

**(6)**

(c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

(6)

(d) Explain why amine **U** is a weaker base than amine **W**.

.....  
.....  
.....  
.....  
.....

(Extra space) .....  
.....  
.....

(3)  
(Total 19 marks)

**4**

Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

(a) Consider the reaction of benzene with  $\text{CH}_3\text{CH}_2\text{COCl}$

- (i) Write an equation for this reaction and name the organic product.  
Identify the catalyst required in this reaction.  
Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....

(5)



(ii) Name and outline a mechanism for the reaction of benzene with this reactive intermediate.

.....

.....

.....

.....

.....

.....

.....

.....

.....

**(4)**

(b) Consider the reaction of propanal with HCN

(i) Write an equation for the reaction of propanal with HCN and name the product.

.....

.....

.....

**(2)**

(ii) Name and outline a mechanism for the reaction of propanal with HCN

.....

.....

.....

.....

.....

.....

.....

.....

.....

**(5)**

- (iii) The rate-determining step in the mechanism in part (b) (ii) involves attack by the nucleophile.  
Suggest how the rate of reaction of propanone with HCN would compare with the rate of reaction of propanal with HCN  
Explain your answer.

.....

.....

.....

.....

.....

.....

.....

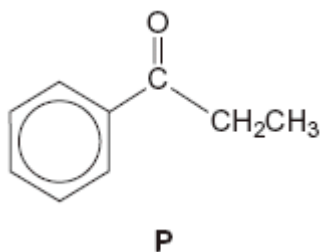
.....

.....

(2)  
(Total 18 marks)

5

Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.



- (a) Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

.....

.....

.....

.....

.....

.....

(3)

(b) Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

(3)

(c) Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

.....

.....

.....

.....

.....

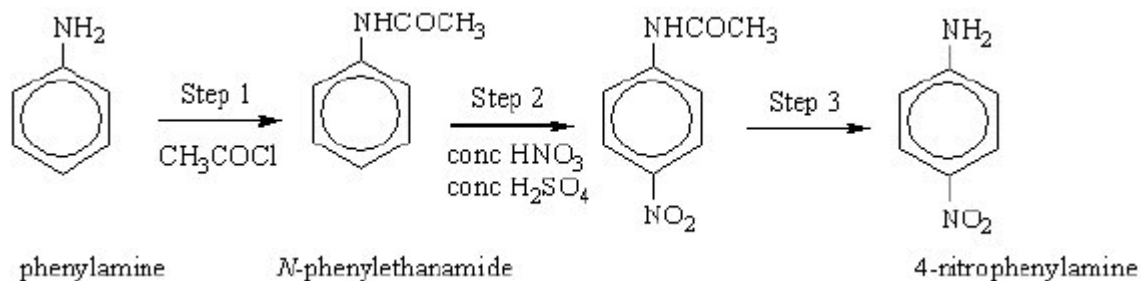
.....

(2)  
(Total 8 marks)

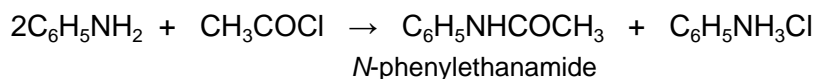
**6**

Synthetic dyes can be manufactured starting from compounds such as 4-nitrophenylamine.

A synthesis of 4-nitrophenylamine starting from phenylamine is shown below.



- (a) An equation for formation of *N*-phenylethanamide in Step 1 of the synthesis is shown below.



- (i) Calculate the % atom economy for the production of *N*-phenylethanamide ( $M_r = 135.0$ ).
- (ii) In a process where 10.0 kg of phenylamine are used, the yield of *N*-phenylethanamide obtained is 5.38 kg.

Calculate the percentage yield of *N*-phenylethanamide.

- (iii) Comment on your answers to parts (i) and (ii) with reference to the commercial viability of the process.

**(7)**

- (b) Name and outline a mechanism for the reaction in Step 1.

**(5)**

- (c) The mechanism of Step 2 involves attack by an electrophile. Write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

**(4)****(Total 16 marks)**