

Name/CG: _____

2012 Term 2 Organic Chemistry Revision (Session II)

Deductive Question

1(a) A yellow liquid **A**, $C_7H_7NO_2$, reacts with alkaline potassium manganate (VII) and on acidification gives a yellow solid **B**, $C_7H_5NO_4$.

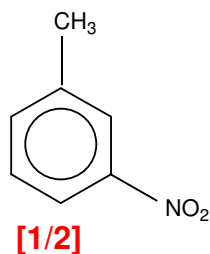
After treating **A** with tin and concentrated hydrochloric acid, the addition of sodium hydroxide releases liquid **C**.

Under suitable conditions for reduction (with hydrogen under pressure at $160^\circ C$ in the presence of nickel) **A** is slowly converted into **D**, $C_7H_{15}N$. **D** reacts with excess of iodomethane to give a quaternary salt, **E**, of formula $C_7H_{13}(CH_3)_xNI$.

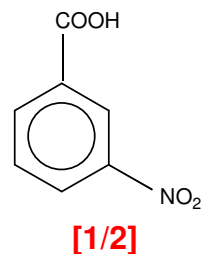
(i) Deduce the possible structures of **A** to **E** giving your reasoning.

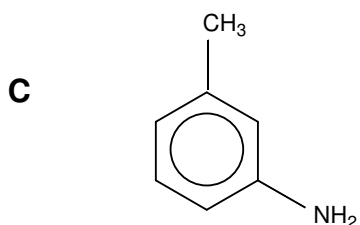
- Number of C and H atoms are comparable and no. of C atoms > 6, hence **A** contains a benzene. [1/2]
- **A** undergoes (side-chain) oxidation [1/2] with alkaline $KMnO_4$ which on acidification gives **B**.
⇒ **A** contains a methyl side chain/methylbenzene [1/2]
⇒ **B** is a carboxylic acid [1/2]
- **A** undergoes reduction [1/2] with tin and concentrated HCl & $NaOH$ to form liquid **C**
⇒ **A** is an nitrobenzene [1/2]
⇒ **C** is a phenylamine [1/2]
- **A** undergoes reduction with H_2 at high temperature and pressure to form **D**, $C_7H_{15}N$
⇒ **D** is a amine [1/2]
- **D** undergoes nucleophilic substitution with excess CH_3I to form quaternary salt, **E**. [1/2]

Hence, **A** is

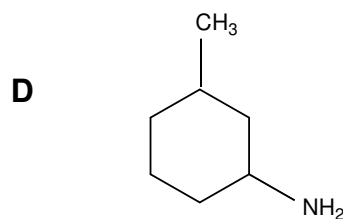


B





[1/2]



[1/2]

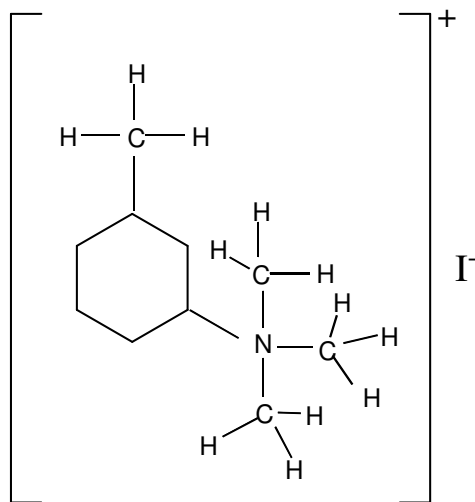
(Total : 5.5 marks)

- (i) State the value of **x** in compound **E** and give its displayed structure. Give a reason to explain why **E** dissolves in water while the rest of the compounds do not.

[8]

Since **E** is a quaternary salt, $x = 3$. [1/2]

Displayed formula of **E** :



[1] (no displayed formula –no mark)

E is soluble in water as it is an ionic compound which can form ion-dipole attraction with water. [1/2]

However, the other compounds contain large hydrophobic benzene and cyclohexane ring which are insoluble in water. [1/2]

(Total : 2.5 marks)

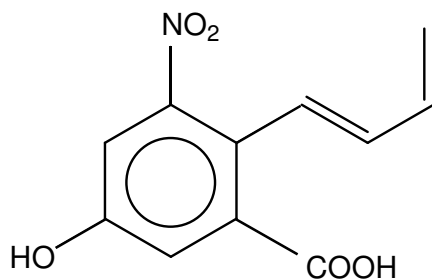
(b) Draw the structural formula of the products formed when compound **Y** is reacted with

(i) cold, alkaline potassium manganate (VII)

(ii) excess of hydrogen gas in the presence of platinum catalyst.

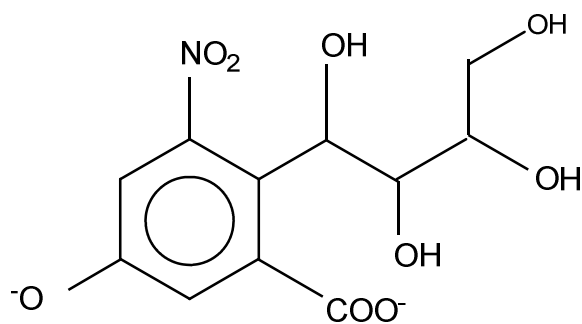
[2]

Name the functional groups present in compound **Y**.



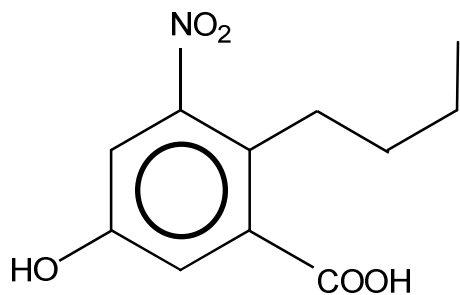
Compound **Y**

(i)



[1]

(ii)



[1]

- 2 Two isomeric organic liquids **A** and **B** contain 80.6% carbon, 7.5% hydrogen and 11.9% oxygen by mass.

When 0.358 g of **A** or **B** was evaporated in a syringe, the volume of the vapour produced, after correction to s.t.p. was 60.0 cm³.

Both **A** and **B** gave an orange precipitate with 2,4-dinitrophenylhydrazine and silver mirror with Tollens' reagent. However, both **A** and **B** do not give a yellow precipitate on warming with aqueous alkaline iodine.

With lithium aluminium hydride in dry ether, **A** was converted to a compound **C** which exists in optically active forms. **B** under the same conditions produced a compound **D** which is isomeric with **C** but cannot exist in optically active forms.

Both **A** and **B** on vigorous oxidation gave compound **E** as an end product, having molecular formula C₇H₆O₂.

Deduce the structural formulae of compounds **A** to **E**, giving your reasoning.

[10]

Empirical formula of **A** and **B**:

	<u>C</u>	<u>H</u>	<u>O</u>
Mass / 100g (g)	80.6	7.5	11.9
No. of mol	6.72	7.5	0.744
Ratio	9	10	1

[1/2]

Empirical formula of **A** and **B**: C₉H₁₀O [1/2]

$$\begin{aligned}\text{No. of mol of vapour} &= \frac{60.0 \times 10^{-3}}{22.4} \\ &= 2.68 \times 10^{-3} \text{ mol [1/2]}\end{aligned}$$

$$\begin{aligned}M_r \text{ of } \mathbf{A} \text{ and } \mathbf{B} &= \frac{0.358}{2.68 \times 10^{-3}} \\ &= 134 \text{ [1/2]}\end{aligned}$$

Molecular formula of **A** and **B**: C₉H₁₀O [1/2]

Number of C and H atoms are comparable and no. of C is greater than 6
⇒ A and B, both contain a benzene ring [1/2]

A and **B** undergo condensation with 2,4-DNPH [1/2]

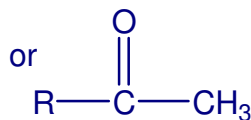
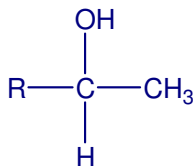
⇒ **A** and **B** are carbonyl compounds [1/2]

A and **B** undergo oxidation with Tollens' reagent [1/2]

⇒ **A** and **B** are aldehydes [1/2]

A and **B** do not undergo oxidation with aqueous alkaline iodine [1/2]

⇒ **A** and **B** do not contain [1/2]



structures

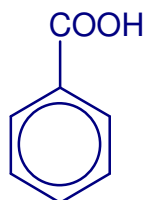
A and **B** undergo reduction with LiAlH_4 to optically active **C** and optically inactive **D** respectively [1/2]

⇒ **C** and **D** are primary alcohols [1/2]

⇒ **C** has a chiral carbon and **D** has no chiral carbon [1/2]

A and **B** undergo vigorous oxidation to form **E**

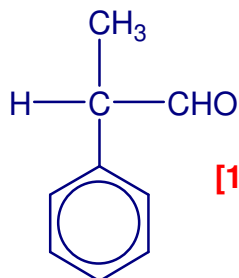
⇒ Compound **E** is



[1/2]

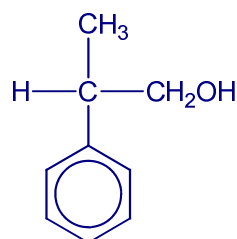
⇒ **A** and **B** are monosubstituted benzenes. [1/2]

A :



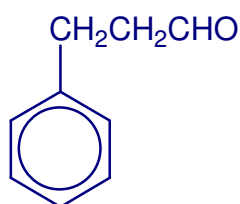
[1/2]

C:



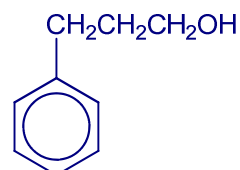
[1/2]

B:



[1/2]

D:



[1/2]

3 The isomers **A**, **B**, **C** and **D** of the formula $C_5H_{12}O$ can react with hot acidified $K_2Cr_2O_7$ to give products **E**, **F**, **G** and **H** respectively.

Out of **E**, **F**, **G** and **H**, only **E** gives a yellow precipitate upon reaction with alkaline aqueous iodine, whilst **F** and **H** does not give an orange precipitate with 2,4-dinitrophenylhydrazine.

H can react with **D** under certain conditions to give a compound that has a formula $CH_3CH_2CH_2CH_2CO_2CH_2CH_2CH_2CH_2CH_3$.

On reacting **D** with hot concentrated sulfuric acid, the resulting product can react with steam under certain conditions to form **A**.

When treated with limited chlorine in the presence of uv light **B** forms ~~three~~ **two** monochloro-substituted products (structural isomers) with one chlorine atom while **C** forms ~~two~~ **three** monochloro-substituted products (structural isomers).

Suggest possible structures for the compounds **A** to **H**, explaining your reasons.

[10]

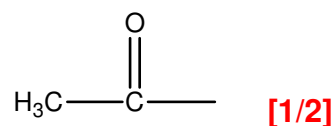
A, **B**, **C** and **D** undergo oxidation [1/2] with acidified $K_2Cr_2O_7$ to form **E**, **F**, **G** and **H** respectively

⇒ **A**, **B**, **C** and **D** are 1° or 2° alcohols [1/2]

⇒ **E**, **F**, **G** and **H** are ketone or carboxylic acid [1/2]

E undergoes oxidation with alkaline aq I_2 [1/2]

⇒ **E** has the structure:



⇒ **A** has $CH_3CH(OH)$ structure [1/2]

F and **H** do not undergo condensation with 2,4-DNPH [1/2]

⇒ **F** and **H** are not carbonyl compounds [1/2]

⇒ **F** and **H** are carboxylic acids [1/2]

⇒ **B** and **D** are 1° alcohols. [1/2]

H, a carboxylic acid reacts with **D**, an alcohol to give ester that has a formula $CH_3CH_2CH_2CH_2CO_2CH_2CH_2CH_2CH_2CH_3$ [1/2]

From the structure of ester,

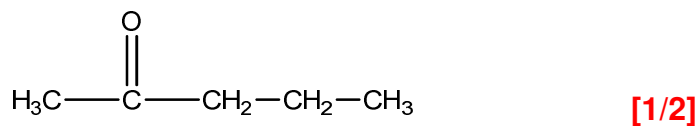
H is likely to be $CH_3CH_2CH_2CH_2CO_2H$. [1/2]

and **D** is likely to be $CH_3CH_2CH_2CH_2CH_2OH$. [1/2]

D undergoes elimination with hot conc. sulfuric acid to form alkene which undergoes electrophilic addition with steam to form **A**, [1/2]

A is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ [1/2]

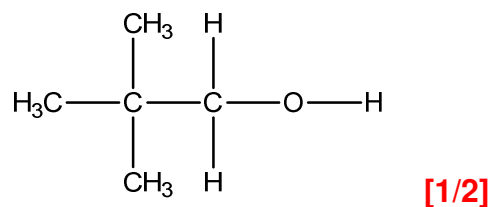
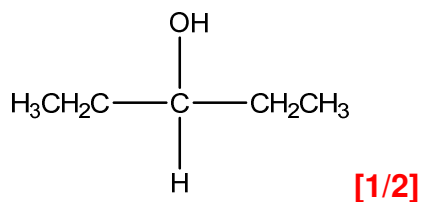
Thus **E** is



B and **C** undergo free radical substitution with chlorine and uv light [1/2] and **B** forms two monochloro-substituted products while **C** forms three monochloro-substituted products.

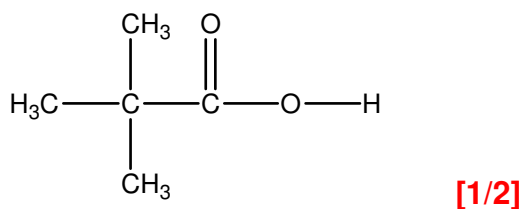
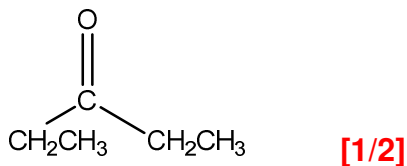
C is

and **B** is



F is

and **F** is

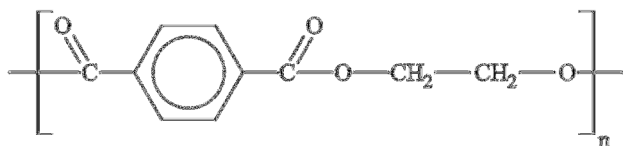


- 4 A solid compound **J** ($C_{15}H_{15}NO$) is insoluble in both hydrochloric acid and dilute sodium hydroxide.

On warming with aqueous sodium hydroxide, **J** forms a liquid **K** (C_7H_9N) on the surface of an alkaline mixture, **X**. Liquid **K** can be separated from the alkaline mixture **X** by steam distillation, and dissolves in dilute hydrochloric acid.

K can also react with excess bromomethane to give a compound **L** which has the formula $C_9H_{14}NBr$.

On the other hand, upon acidification, the alkaline mixture **X** yields a solid **M** ($C_8H_8O_2$) which gives rapid effervescence with aqueous sodium carbonate. Oxidation of **M** yields one of the monomers that is used to make *Terylene*.



Terylene

Deduce the structures of **J**, **K**, **L** and **M**, explaining your reasoning. Give balanced equations where appropriate.

[10]

Number of C and H are comparable and no. of C is greater than 6,

⇒ **J** contains a benzene ring. [1/2]

J is insoluble in both acid and base

⇒ **J** is neutral [1/2]

⇒ **J** is an amide [1/2]

J thus undergoes basic hydrolysis with warm NaOH to give **K** and **M**. [1/2]

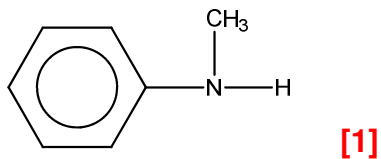
K undergoes neutralization with dilute HCl [1/2]

⇒ **K** is basic [1/2]

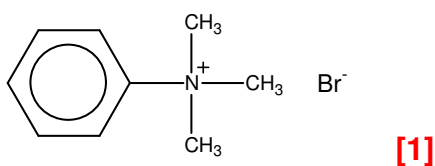
⇒ **K** is an amine [1/2]

Bromoethane undergoes nucleophilic substitution with **K** to form **L**. [1/2]
Since **K** gains 2 $-CH_3$ groups upon reaction with excess bromoethane to form **L**,
K is a secondary amine. [1/2]

K is

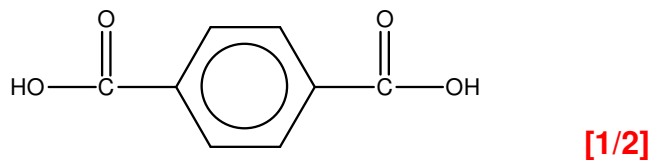


L is

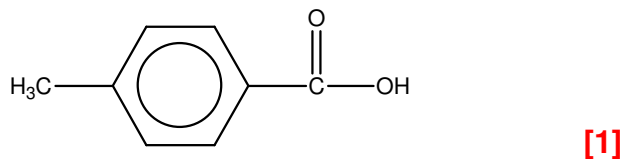


M undergoes neutralisation with sodium carbonate to give CO_2 gas
 \Rightarrow **M** is a carboxylic acid [1/2]

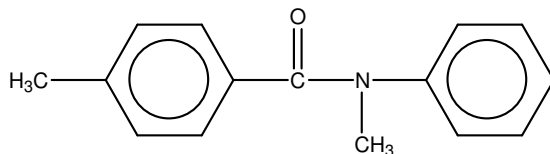
Since oxidation of **M** gives one of the monomers that is used to make Terylene,
the monomer involved is diacid monomer, i.e.



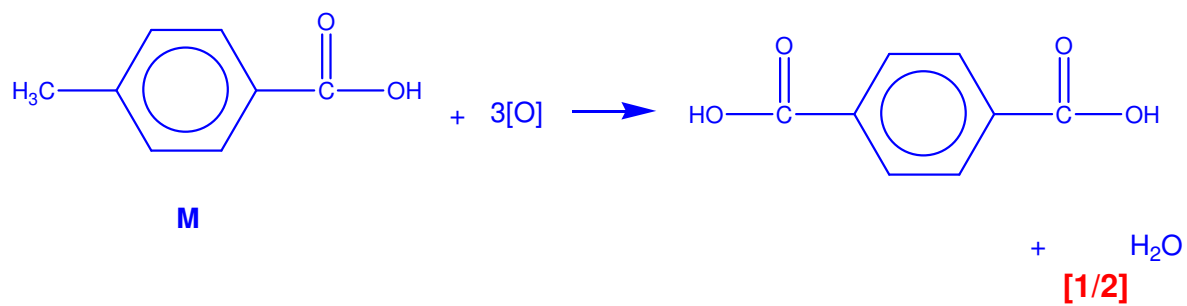
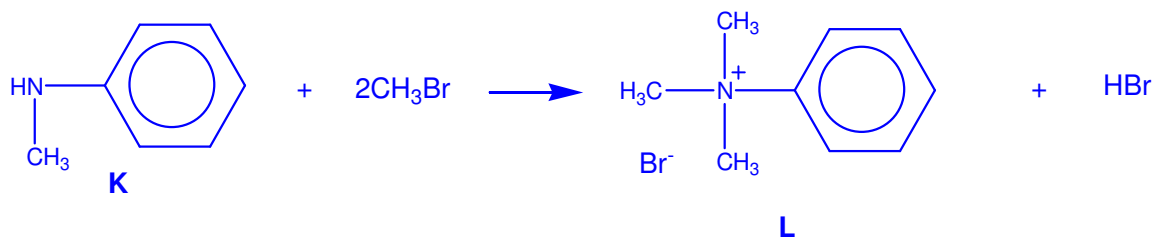
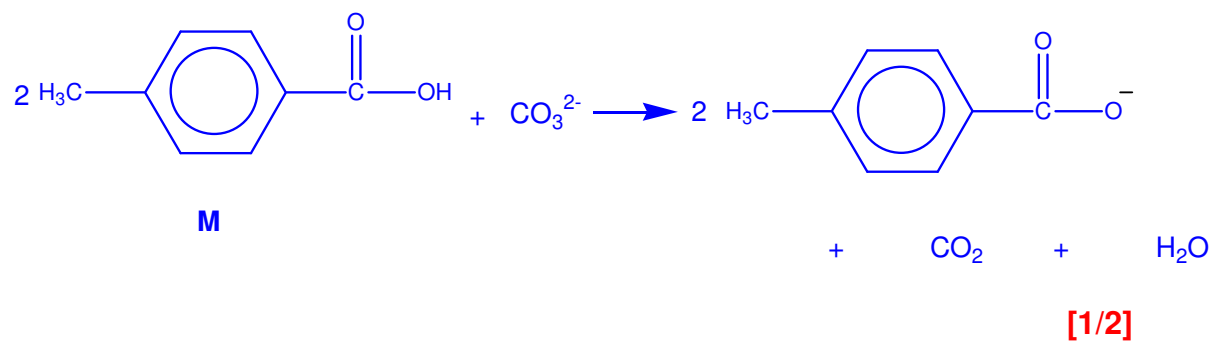
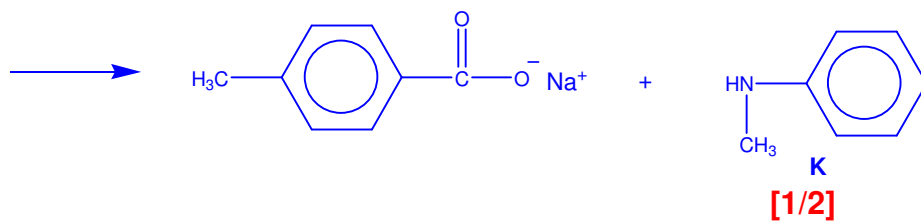
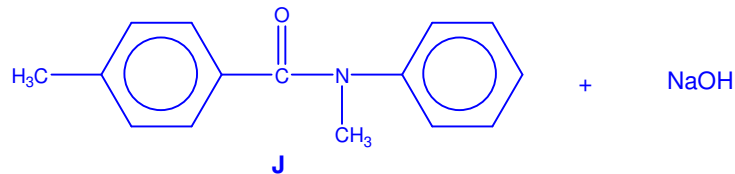
M is



J is



The relevant equations are :



Max 10m

- 5 A neutral compound **T** contains 46.2% carbon, 7.7% hydrogen and 46.1% oxygen by mass. When heated with aqueous sodium hydroxide, **T** gives compound **U**, $C_2H_6O_2$, and sodium ethanoate.

When one mole of **U** reacts with only one mole of hydrogen chloride, compound **V**, C_2H_5OCl , is formed. Compound **V** gives compound **W**, C_3H_5ON , on heating with ethanolic potassium cyanide.

When **W** is heated with dilute sulfuric acid, an optically inactive liquid **X**, $C_3H_6O_3$, is obtained. On heating **X** alone, a sweet smelling liquid **Y**, $C_3H_4O_2$, is formed. Oxidation of **X** gives a solid **Z**, $C_3H_4O_4$, which is soluble in water.

Deduce the structural formula of compound **T** to **Z** giving your reasoning.

[10]

Element	C	H	O
% Mass	46.2	7.7	46.1
mole	$\frac{46.2}{12}$ = 3.85	$\frac{7.7}{1}$ = 7.7	$\frac{46.2}{16}$ = 2.89
Divide by smallest mole	$\frac{3.85}{2.89} = 1.33$	$\frac{7.7}{2.89} = 2.66$	$\frac{2.89}{2.89} = 1$
Ratio	4	8	3

[1/2]

Empirical formula of **T** is $C_4H_8O_3$ [1/2]

T undergoes basic hydrolysis with hot $NaOH(aq)$ to form **U** and CH_3COONa [1/2]

⇒ **T** is an ester [1/2]

⇒ **U** is an alcohol [1/2] with two carbons

One mole of U undergoes nucleophilic substitution with one mole of HCl to form **V** [1/2]

⇒ **V** is a halogenoalkane [1/2]

V undergoes nucleophilic substitution with ethanolic KCN^- to form **W** [1/2]

⇒ **W** is a nitrile compound (contains a CN group) [1/2]

W undergoes acidic hydrolysis with hot dilute H_2SO_4 to form *optically inactive X* [1/2]

⇒ **X** is a carboxylic acid [1/2]

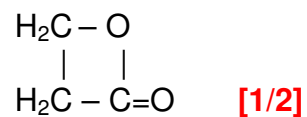
⇒ **X** does not have a chiral carbon [1/2]

On heating **X**, a sweet smelling **Y** is formed.

⇒ **Y** is cyclic ester **[1/2]**

X is **CH₂(OH)CH₂COOH** **[1/2]**

Y is



X undergoes oxidation to form **Z**

⇒ **Z** is HOOCCH₂COOH **[1/2]**

Hence,

W is **CH₂(OH)CH₂CN** **[1/2]**

U is CH₂(OH)CH₂(OH) **[1/2]**

V is CH₂(OH)CH₂Cl **[1/2]**

T is CH₂(OH)CH₂OOCCH₃ **[1/2]**

- 6 An organic compound **A**, $C_9H_{11}Br$, on treatment with hot aqueous potassium hydroxide gave a compound **B**, $C_9H_{12}O$. **B** responded to oxidation in three different ways. With acidified potassium dichromate it yielded **C**, $C_9H_{10}O$. With sodium hydroxide and iodine it yielded **D**, $C_8H_7O_2Na$ and a yellow precipitate. With hot, acidic potassium manganate (VII) it yielded **E**, $C_7H_6O_2$.

Identify compound **A** to **E** and explain the above reactions.

[7]

Number of C and H is comparable in **A** and number of C atoms is greater than 6,
 \Rightarrow **A** contains benzene [1/2]

A undergoes nucleophilic substitution with hot KOH to form **B** [1/2]

\Rightarrow **A** is a halogenoalkane [1/2]

\Rightarrow **B** is an alcohol [1/2]

B undergoes oxidation with acidified $K_2Cr_2O_7$ to form **C**, $C_9H_{10}O$

\Rightarrow **C** is a ketone [1/2]

\Rightarrow **B** is a secondary alcohol [1/2]

B undergoes oxidation with sodium hydroxide and iodine to form **D**, $C_8H_7O_2Na$ and a yellow ppt

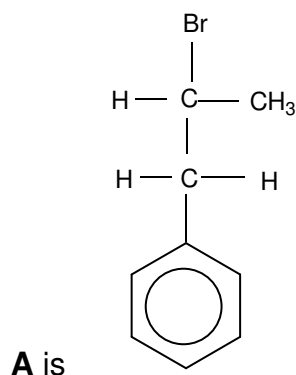
\Rightarrow yellow ppt is CHI_3 [1/2]

\Rightarrow **B** contains $CH_3CH(OH)$ structure [1/2]

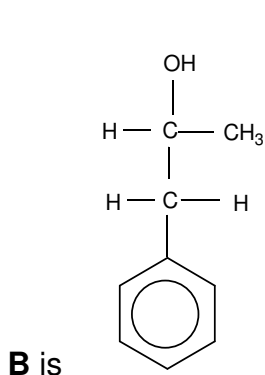
B undergoes (side-chain) oxidation with acidified $KMnO_4$ to form **E**, $C_7H_6O_2$.

\Rightarrow **E**, benzoic acid, C_6H_5COOH [1/2]

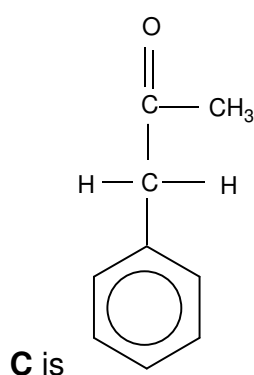
\Rightarrow **B** is monosubstituted benzene. [1/2]



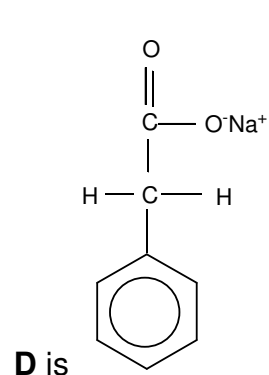
[1/2]



[1/2]



[1/2]



[1/2]

7 A substance **A**, $C_4H_9NO_2$ is an optically active solid with a high melting point. It dissolves in water to give a nearly neutral solution.

B which is formed from **A** has the formula, $C_4H_8O_3$. On warming **B** with ethanol and excess concentrated sulfuric acid, a liquid ester **C**, $C_6H_{10}O_2$, is formed. On exposure to light, **C** slowly forms a glassy solid which is an addition polymer.

B reacts with PCl_5 to give **D**, which rapidly reacts with water to give **E**, $C_4H_7ClO_2$.

Treatment of **E** with hot aqueous sodium hydroxide followed by acidification will reform **B**. Compound **B** undergoes dehydration in the presence of concentrated sulfuric acid to form compound **F**, $C_4H_6O_2$.

Deduce the structures of the compounds of **A**, **B**, **C**, **D**, **E** and **F**. Explain the chemistry of the reactions involved.

[10]

A, $C_4H_9NO_2$ is an optically active solid with a high melting point

⇒ **A** could be an amino acid [1/2]

⇒ **A** contains a chiral C [1/2]

B which is formed from **A** has the formula, $C_4H_8O_3$.

⇒ **B** contains a chiral C

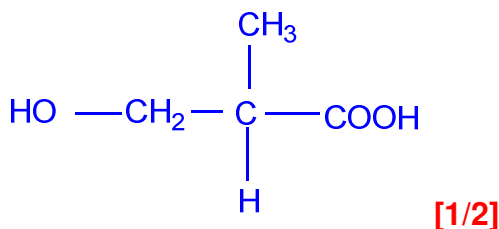
B undergoes esterification with ethanol to form liquid ester **C** [1/2]

⇒ **B** is carboxylic acid. [1/2]

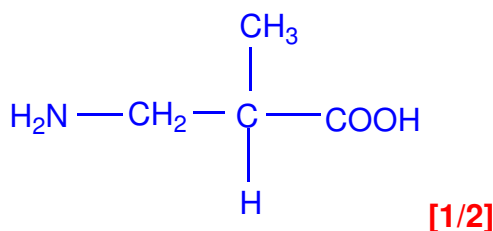
B also undergoes elimination with excess conc. H_2SO_4 , [1/2]

⇒ **B** is alcohol [1/2]

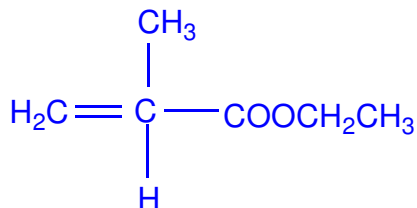
B is



Hence **A** is



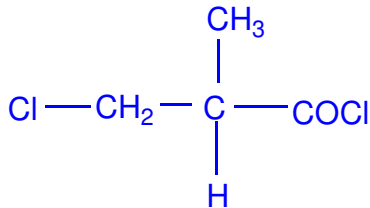
C undergoes **addition polymerisation** to form **D**,
⇒ **C** contains **C=C bonds**. [1/2]



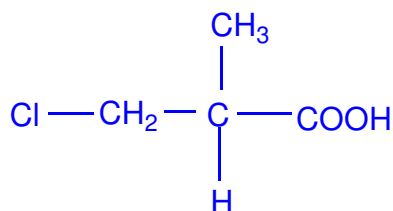
C is [1/2]

B undergoes **nucleophilic substitution** with PCl_5 to give **D** [1/2] and **D** undergoes **nucleophilic substitution** with water to form **E** [1/2]

E undergoes **nucleophilic substitution** with hot NaOH(aq) to reform **B** [1/2]
⇒ **E** contains **-Cl (halogenoalkane)** [1/2] and **-COCl (acyl chloride)** groups. [1/2]

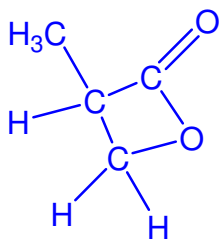


E is [1/2]



D is [1/2]

B undergoes **self-esterification** with conc. sulphuric acid to form an **F** [1/2]
F is a **cyclic ester**. [1/2]



F could be [1/2]

[Total = 10]

8 This question is about compound **F**, $C_9H_{13}NO$.

The following information is given about **F**:

- Compound **F** is insoluble in water but it dissolves readily in aqueous HCl.
- When **F** is treated with PBr_3 , **F** forms compound **G**, $C_9H_{12}NBr$.
- When **F** is treated with acidified $KMnO_4$, no decolourisation of purple $KMnO_4$ is observed.
- **F** can be formed when compound **E** reacts with tin metal and concentrated hydrochloric acid.

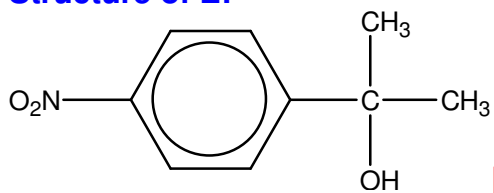
G forms **H**, $C_9H_{11}N$, when heated with alcoholic KOH and **H** in turn gives compound **I**, $C_9H_{10}NOBr_3$, when reacted with aqueous Br_2 in the dark.

Deduce the structures of the compounds **E**, **F**, **G**, **H** and **I**. Explain the chemistry of the reactions described..

[10]

- Number of C atoms and H atoms are comparable and no. of C is more than 6, **F** contains a benzene ring. [1/2]
- **F** undergoes neutralisation with aqueous HCl [1/2]
 - ⇒ **F** is basic [1/2]
 - ⇒ **F** is an amine [1/2]
- **F** undergoes nucleophilic substitution with PBr_3 to form **G** [1/2]
 - ⇒ **F** is alcohol [1/2]
 - ⇒ **G** is halogenoalkane [1/2]
- **F** does not undergo oxidation with acidified $KMnO_4$ [1/2]
 - ⇒ **F** is 3° alcohol [1/2]
- **E** undergoes reduction with Sn and conc. HCl to form **F** [1/2]
 - ⇒ **E** is nitrobenzene [1/2]
 - ⇒ **F** is phenylamine [1/2]
- **G** undergoes elimination with alcoholic KOH to form **H**. [1/2]
 - ⇒ **H** contains an alkene group. [1/2]
- **H** undergoes electrophilic substitution with aq Br_2 [1/2] and electrophilic addition with aq Br_2 [1/2] to form **I**, $C_9H_{10}NOBr_3$
 - ⇒ **H** contains phenylamine and alkene functional groups [1/2]
 - ⇒ **H** is either 2- or 4- substituted phenylamine [1/2]

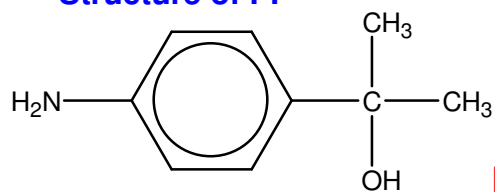
- **Structure of E:**



[1/2]

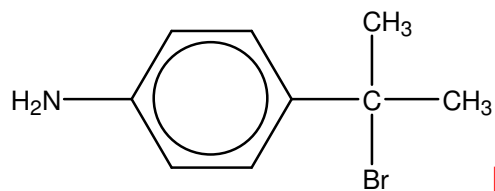
accept 1,2-position

- **Structure of F:**



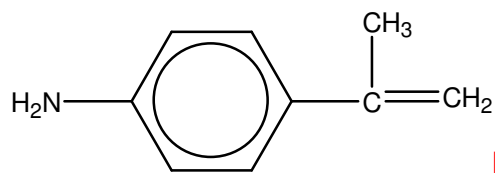
[1/2]

- **Structure of G:**



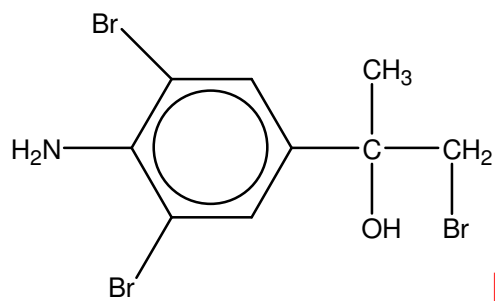
[1/2]

- **Structure of H:**



[1/2]

- **Structure of I**



[1/2]

[max: 10]