

## Chemical Sciences

### Paper II

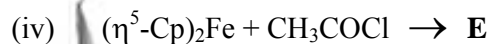
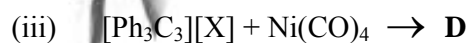
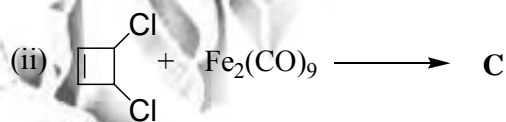
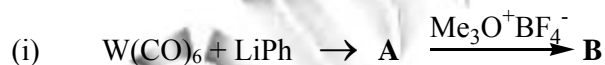
1. (a) What is Zeise's salt? Show its structure and describe the bonding. (5)
- (b) Use Coulomb's law to deduce the dimension of charge. (5)
- (c) Explain which of the following is primarily responsible for the difference in chemical properties of nanomaterials from the bulk. (2)
- lattice defects
  - surface to volume ratio
  - London forces

- (d) Suggest a synthetic method (may need more than one step) for the following transformation. (5)



- (e) Match the following: (3)
- | Compounds       | Type                  |
|-----------------|-----------------------|
| 1. progesterone | i. antiulcer compound |
| 2. amoxicillin  | ii. antiallergic      |
| 3. morphine     | iii. antibacterial    |
|                 | iv. hallucinogen      |
|                 | v. hormone            |

2. (a) Identify the products **A** to **E** in the following reactions. (9)

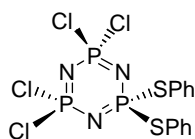


- (b) Draw the structures of  $Co_4(CO)_{12}$  and  $Ir_4(CO)_{12}$ . (6)

3. (a) Write appropriate equations for the synthesis of (i)  $N_3P_3Cl_6$  and (ii)  $N_3P_3F_6$ . (4)

- (b) Sketch the  $^{31}\text{P}$  NMR spectral pattern for the following compound [consider only  $^2J(\text{PP})$ ].

(5)



- (c) Sketch all isomers of  $\text{PF}_3(\text{CH}_3)_2$  assuming a trigonal bipyramidal geometry in each case.

(6)

4. (a) What is the origin of the blue colour in Prussian Blue? Comment on the effect of (i) oxidant and (ii) reductant on its colour.

(7)

- (b) Give an example of a diamagnetic transition metal hydride complex. How is the presence of metal bound hydride detected by spectroscopic methods.

(6)

- (c)  $\text{Rh}(\text{PPh}_3)_3\text{Cl} \xrightarrow{\text{THF, H}_2} \text{A}$

Draw the structure of A above, showing the stereochemistry.

(2)

5. (a) The complex ion  $[\text{Co}(\text{tren})\text{NH}_3\text{Cl}]^{2+}$  (tren =  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ ) exists as red and purple isomers. Draw the structures of these two forms.

(4)

- (b) Red isomer undergoes hydrolysis much more rapidly compared to the purple one. Explain.

(3)

- (c) Match the items in Column I with those in Column II.

Column I	Column II
A. Siderophores	1. Co
B. Chlorophyll	2. Fe
C. Superoxide dismutase	3. Mg
D. Vitamin B <sub>12</sub>	4. Cu-Zn

(8)

6. (a) Sketch the structure of the bis(dimethylglyoximate)nickel(II) complex used in the gravimetric estimation of nickel(II). Why is a large excess of dimethylglyoxime solution avoided in this estimation?

(7)

- (b) Two isomers of  $[\text{PtCl}_2(\text{PEt}_3)_2]$  have  $^1J(^{195}\text{Pt}-\text{P})$  values of 3500 Hz and 2400 Hz respectively. Assign the coupling constants to the isomers, giving reason.

(4)

(c)  ${}^{23}_{11}\text{Na}$  is a stable nucleus. Predict which of the following unstable nuclei decay by  $\beta^-$  or  $\beta^+$  emission.

(i)  ${}^{23}_{10}\text{Ne}$  (ii)  ${}^{23}_{12}\text{Mg}$  (iii)  ${}^{22}_{11}\text{Na}$  (iv)  ${}^{24}_{11}\text{Na}$

(4)

7. (a) Write equations for reduction of oxygen at dropping mercury electrode, when the medium is alkaline.

(4)

(b) Sketch the curve for amperometric titration of  $0.01\text{M Pb}(\text{NO}_3)_2$  with  $0.05\text{ M K}_2\text{Cr}_2\text{O}_7$  at  $-1.0\text{V}$  (vs SCE), the potential at which both the species are electroactive.

(4)

(c) Match items in column I with those of II.

(7)

I	II
A. Supporting electrolyte	1. Derivative Thermogravimetry
B. Ilkovic equation	2. Differential Scanning Calorimetry
C. $\frac{dm}{dt}$	3. Quantum yield
D. $\frac{dH}{dt}$	4. Migration current
E. Spectrofluorimetry	5. Diffusion current
F. Atomic Absorption Spectrophotometry	6. Mercury
G. Cold vapour technique	7. Graphite furnace

8. (a) Write equations for the preparation of:

- (i)  $\text{S}_4\text{N}_4$  from  $\text{SCl}_2(\text{liq.})$   
 (ii)  $\text{P}_4\text{S}_{10}$  from white phosphorus

(4)

(b) Sketch the structures of  $\text{S}_4\text{N}_4$  and  $\text{P}_4\text{S}_{10}$

(4)

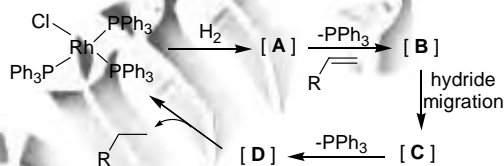
(c) A one-electron paramagnetic copper complex can have two charge distributions:-



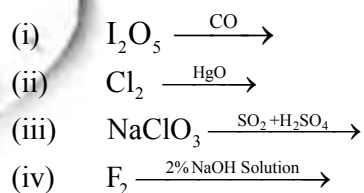
How they can be distinguished by ESR spectroscopy?

(7)

9. (a) Draw generally accepted structure of active site of the enzyme involved in nitrogen fixation. Indicate the site on which nitrogen first binds. (6)
- (b) Bent metallocenes have general formulation  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ML}_x]$ . Write two examples choosing appropriate 'M', having different values of 'x'. (6)
- (c) Examples of carbonylate anions are many more than those of metal carbonyl cations. Explain. (3)
10. (a)  $\text{KMnO}_4$  shows an intense pink colour, while  $\text{KReO}_4$  is colourless. Explain. (5)
- (b) Copper(I) iodide is a stable species, while copper(II) iodide does not exist. Explain. (6)
- (c)  $\text{H}^+$  is a hard acid while  $\text{H}^-$  is a soft base. Explain. (4)
11. (a) Identify **A – D** in the following catalytic cycle with their structures (8)



- (b) Draw the molecular structures of the following compounds in solid state (7)
- (i)  $\text{Ti}(\eta^1\text{-Cp})_2(\eta^5\text{-Cp})_2$  (ii)  $\text{U}(\eta^5\text{-Cp})_4$  (iii)  $\text{Sm}(\eta^5\text{-Cp}^*)_3$
12. (a) What property/properties of lanthanide  $\beta$ -diketonate complex make(s) them useful as shift reagents in NMR spectroscopy? (3)
- (b) Write the products in the following reactions.

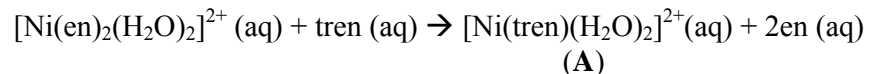


(8)

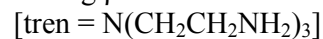
- (c)  $^{10}\text{B}$  used in nuclear reactors participates in two reactions. One reaction yields  $^7\text{Li}$  and another product X. The other reaction yields  $^3\text{T}$  and X. Identify X and write two balanced nuclear reactions.

(4)

13. (a) For the complexation reaction



the  $\log \beta$  value is 1.88. Explain this value giving structure of A.



(5)

- (b) What change in the position of iron in hemoglobin occurs upon binding to oxygen and why?

(4)

- (c) Identify isolobal pairs from the following  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ ,  $\text{Cr}(\text{CO})_4$ ,  $\text{Mn}(\text{CO})_5$ , and  $\text{Co}(\text{CO})_3$

(6)

14. a) The spacing between the first and second lines in the rotational spectrum of a diatomic molecule with an equilibrium bond length of  $1 \text{ \AA}$  is  $40 \text{ cm}^{-1}$ . The spacing between the 9th and 10th lines is  $36 \text{ cm}^{-1}$ . Calculate the extension of the bond due to the centrifugal distortion.

(7)

- b) Calculate the vibrational quantum number at the dissociation limit for a diatomic molecule (given the anharmonicity constant as 0.05).

(8)

15. a) The character table of the point group  $D_3$  is given below:

$D_3$	E	$2C_3$	$3C_2$	
$A_1$	1	1	1	
$A_2$	1	1	-1	z
E	2	-1	0	(x,y)

Show that the row  $A_2$  is orthogonal to the row E.

(4)

b) Given the reducible representation,  $\Gamma$ , in  $D_3$

	E	$2C_3$	$3C_2$
$\Gamma$	7	1	1

Determine its irreducible components.

(5)

c) Use the above character table to determine whether the  $A_1 \rightarrow A_2$  transition is allowed when the change in transition moment is (i) along  $z$  – axis and (ii) in the  $x$ - $y$  plane.

(6)

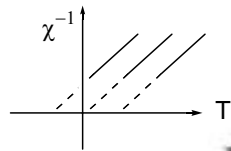
16. a) Show that all Bragg reflections of a primitive cubic crystal have the same intensity.

(7)

b) Plot the Fermi factor  $f(E)$  versus energy,  $E$ , for a free electron metal at  $T = 0$  K and  $T > 0$  K.

(4)

c) The temperature variation of the high-temperature magnetic susceptibility,  $\chi$ , of three solids is shown below. Identify the ferromagnet, paramagnet and antiferromagnet.



(4)

17. a) For a particle in a one-dimensional ( $x$ ) box of length  $a$ , where the potential is given by

$$\begin{aligned} V(x) &= \infty & x < 0, x > a \\ V(x) &= 0 & 0 \leq x \leq a \end{aligned}$$

write the wavefunctions (without derivation) for all states for the full region of  $x$ . State if the wavefunctions are even or odd (*i.e.* have parity symmetry). State the boundary conditions involved in the derivation.

(4+1+3)

b) Discuss the parity of the wavefunctions if, in the above problem, the origin is shifted to the centre of the box, *i.e.* the potential  $V(x)$  is

$$\begin{aligned} V(x) &= \infty & x < -a/2, x > a/2 \\ V(x) &= 0 & -a/2 \leq x \leq a/2 \end{aligned}$$

Write the wavefunctions in this case.

(7)

18. a) Find the inverse of the matrix  $\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$  (8)

b) How do the states  $\psi$ ,  $\psi^*$ ,  $-i\psi$ , and  $e^{i\alpha}\psi$  differ with respect to observable properties and why? (7)

19. a) Show that  $\langle x \rangle = 0$  for systems that respect parity as a constant of motion. (6)

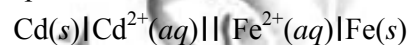
b) Evaluate the commutator  $[L_x^2, L_z]$ . (9)

20. a) Two variables  $x_i$  and  $y_i$  are related by  $y_i = 3 - 2x_i$ . Show that the covariance of  $x$  and  $y$ , defined by  $c(x, y) = \langle xy \rangle - \langle x \rangle \langle y \rangle$ , is equal to  $-2\Delta x^2$ , where  $\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2$ . (10)

b) For a polydisperse polymer solution, use basic definitions to show that  $\langle M_w \rangle = \langle M_n^2 \rangle / \langle M_n \rangle$ . (5)

21. a) Calculate the mean ionic activity coefficient of  $0.01 \text{ mol L}^{-1}$  NaCl aqueous solution at 298 K ( $A = 0.509$  for an aqueous solution at 298 K). (8)

b) Write the cell reactions and predict whether it is spontaneous or non-spontaneous in a cell at 298 K.



Given:  $E^0(\text{Cd}^{2+}/\text{Cd}) = -0.403 \text{ V}$  and  $E^0(\text{Fe}^{2+}/\text{Fe}) = -0.447 \text{ V}$  (7)

22. a) For a second order reaction  $2A \rightarrow P$ , show that  $t_{1/2} \propto 1/[A]_0$  where  $t_{1/2}$  is the half-life and  $[A]_0$  is the initial concentration. (10)

b) The equilibrium constant (K) for the elementary reaction at 1000 K  $\text{C}_2\text{H}_6(g) \rightleftharpoons 2 \text{CH}_3(g)$  is  $1.30 \times 10^{-13} \text{ mol L}^{-1}$  and the rate constant for the forward reaction ( $k_1$ ) is  $1.57 \times 10^{-3} \text{ s}^{-1}$ . Write the rate law and calculate the rate constant for the reverse reaction ( $k_{-1}$ ) (5)

23. a) 3.64 g of compound A (molar mass 150) is dissolved in 180 g of benzene and the vapour pressure of this solution is 756 torr at the boiling point of benzene. Calculate the molar mass of A in benzene and explain the discrepancy, if any [assume dilute solution]. (8)

b) First two quantum states of an atom A ( $^3P_0$  and  $^3P_1$ ) are separated by  $300 \text{ cm}^{-1}$ . Calculate the electronic partition function at 1000 K for this system ( $h/1000k_b = 4.8 \times 10^{-14} \text{ s}$ ). (7)

24. a) Calculate the entropy of mixing and Gibbs free energy of mixing of 5 moles of component A and 5 moles of component B at  $27^\circ\text{C}$ . (10)

b) Show that, if an engine takes up heat  $Q$  from a sink at a temperature  $T_2$  and gives to a source at a temperature  $T_1$  without any work, the process would violate the principle  $\Delta S(\text{universe}) \geq 0$ . (5)

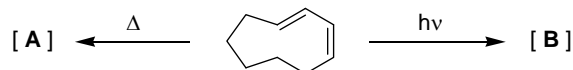
25. a) During an adiabatic reversible expansion ( $a \rightarrow b$ ), 1 mole of a monatomic ideal gas undergoes a decrease of temperature from 400 K to 100 K. If the initial volume is 32.8 L, calculate the final volume.



b) Transformation  $a \rightarrow b$  can also be achieved by undergoing (i) an isothermal reversible expansion ( $a \rightarrow c$ ) and (ii) an isochoric reversible process ( $c \rightarrow b$ ). Calculate the entropy change in each process and the total entropy change in going from  $a \rightarrow b$ . (5+5+1)

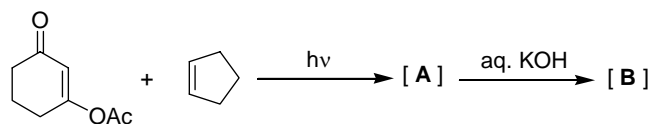
26 (a) Draw a correlation diagram for **disrotatory** opening of a cyclobutene to buta-1,3-diene. Predict the outcome of the reaction in the ground state. (10)

(b) Predict the products **A** and **B** in the following reactions, and suggest mechanism of their formation. (5)

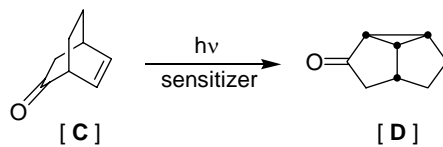


27 (a) Predict the products **A** and **B** (with correct stereochemistry) in the following reaction, and suggest a mechanism of formation of **B**. (6)

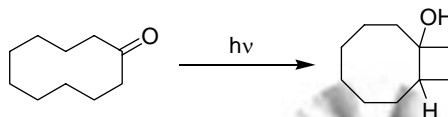




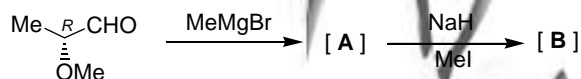
- (b) Triplet sensitized irradiation of compound **C** gives **D**. Suggest a mechanism. (6)



- (c) Suggest a plausible mechanism for the following transformation. (3)



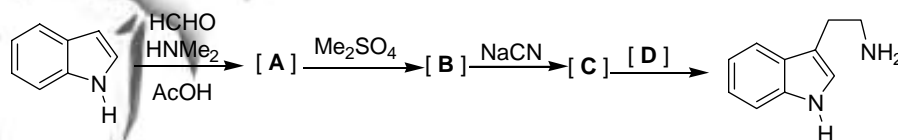
- 28 (a) In the following transformation, predict the structures (with appropriate stereochemistry) of compounds **A** and **B**. (6)



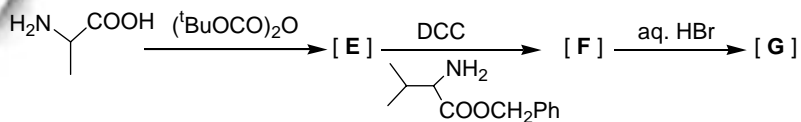
- (b) Explain the origin of stereoselectivity in the formation of **A** with Cram chelate or Felkin-Anh model. (4)

- (c) Predict the absolute configuration of the newly formed stereocentre and state whether the compound **B** will be optically active or not. (5)

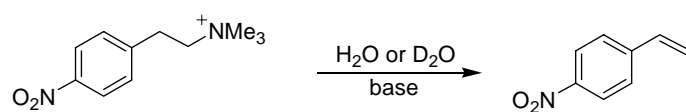
- 29 (a) Write the structures of the compounds **A-C** and the reagent **D** in the reaction sequence given below. (10)



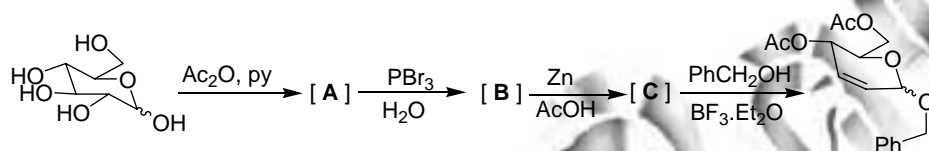
- (b) Write the structures of the products **E-G**, and write the name of the dipeptide **G**. (5)



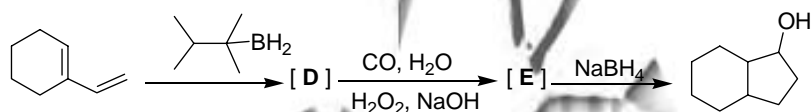
- 30 (a) The  $k_H/k_D$  of base catalysed elimination reaction given below in  $H_2O$  and  $D_2O$  was found to be 0.13. Write suitable mechanism consistent with this observation.



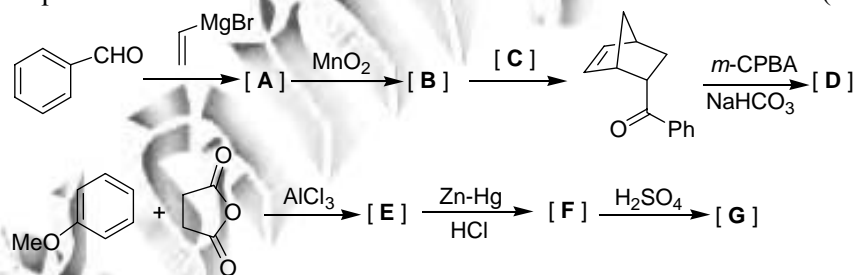
- (b) D-Glucose is converted to unsaturated sugar as given below. Write the structures of **A-C**.



- (c) Write the structures of **D** and **E** in the sequence given below.

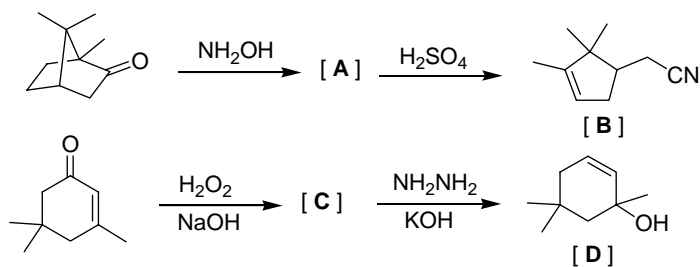


- 31 Identify **A-G** (with appropriate stereochemistry) in the following synthetic sequences. (15)



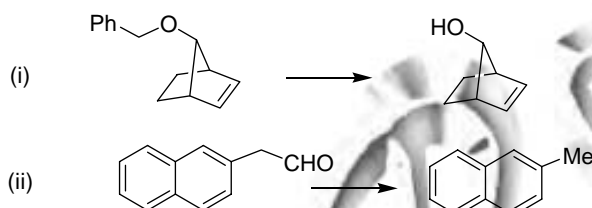
32 (a) Write the structure of the compounds **A** and **C**, and suggest suitable mechanism for their conversion to the products **B** and **D**, respectively.

(10)



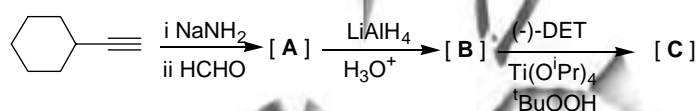
(b) Suggest suitable reagents for the following selective transformations.

(5)



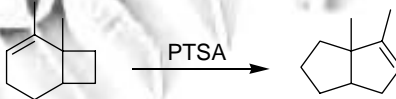
33 (a) Identify the products **A** to **C** in the following reaction sequence.

(6)



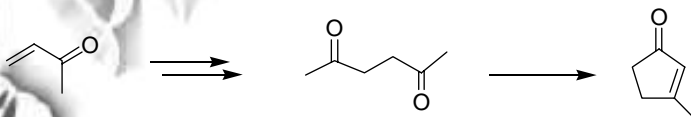
(b) Suggest a mechanism for the following transformation.

(4)



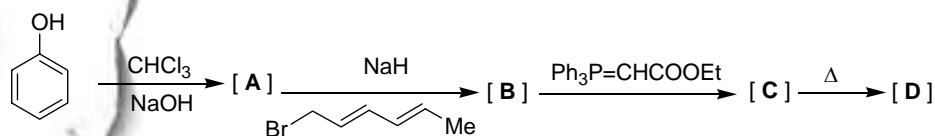
(c) Suggest a suitable synthetic sequence for the following transformation.

(5)

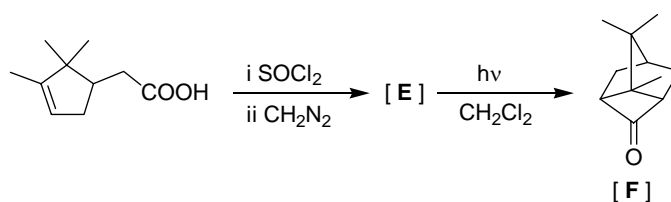


34 (a) Identify the products **A** to **D** in the following reaction sequence

(10)



- (b) Identify the compound **E** and suggest a suitable mechanism for its conversion to compound **F**. (5)

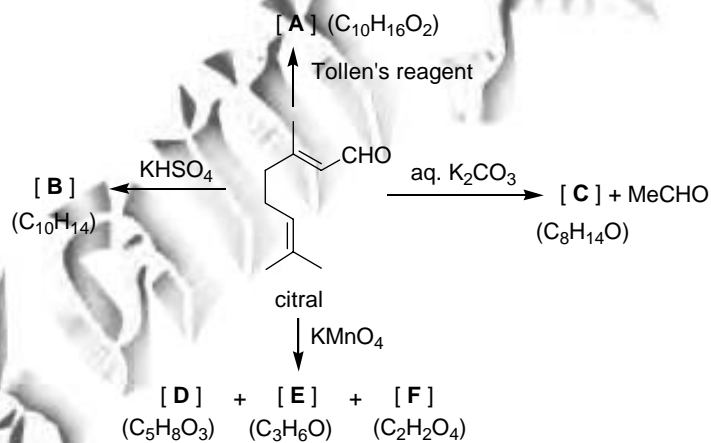


- 35 (a) Write the structures of the two possible products **A** and **B** in the reaction given below, and give suitable mechanism of their formation. Suggest how  $^1\text{H}$  NMR spectrum can be used to differentiate **A** and **B**. (10)

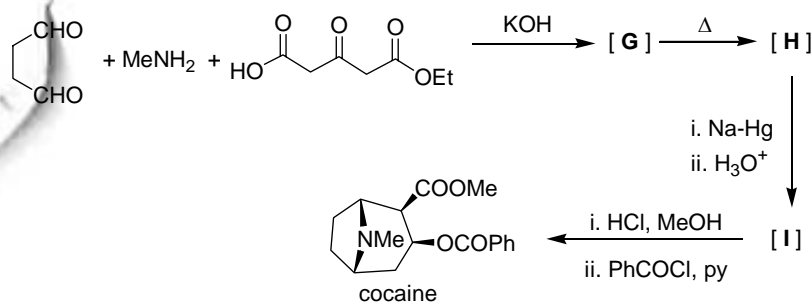


- (b) How would you distinguish 2-methylbutanal and 3-methylbutanal using mass spectrometry. (5)

- 36 (a) The monoterpene citral undergoes reactions given below. Write the structures of the products **A-F**. (9)



- (b) Identify the products **G** to **I** in the synthesis of cocaine (6)



37 Deduce the structure of the organic compound having the following analytical and spectral data.

Analysis C, 74.98; H, 6.86

Mass 176, 131 (base peak), 103, 77.

IR  $\nu_{\max}$  1714, 1639  $\text{cm}^{-1}$

$^1\text{H}$  NMR  $\delta$  1.31 (t, 3 H,  $J=7.1$  Hz), 4.2 (q, 2 H,  $J=7.1$  Hz), 6.43 (d, 1 H,  $J=15.8$  Hz), 7.24-7.57 (m, 5 H), 7.67 (d, 1 H,  $J=15.8$  Hz).

$^{13}\text{C}$  NMR  $\delta$  14.3, 60.4, 118.4, 128.1, 128.9, 130.2, 134.5, 144.5, 166.8.

(15)