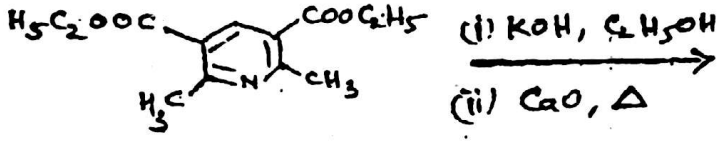
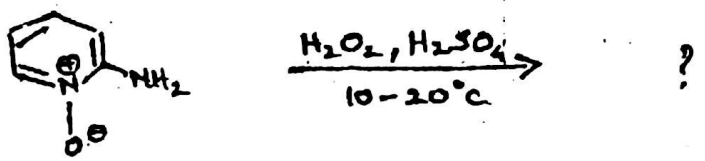
(2½ Hours) [Total Marks : 60

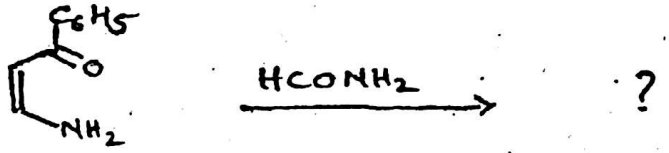
N.B. : (1) **All** questions are **compulsory.**
(2) **Figures** to the **right** indicate **full** marks.

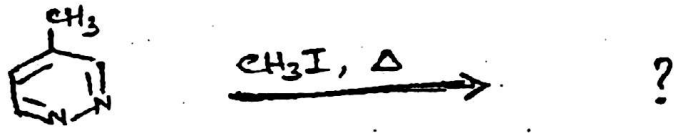
1. (a) Attempt any **two** of the following :— 8

(i) Complete the following reactions :

(I) 

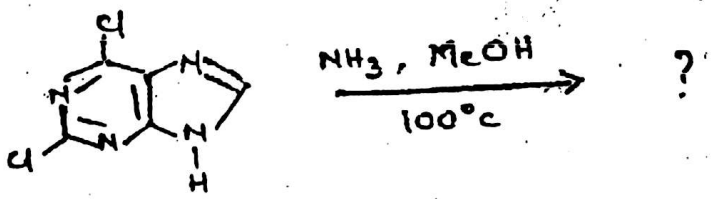
(II) 

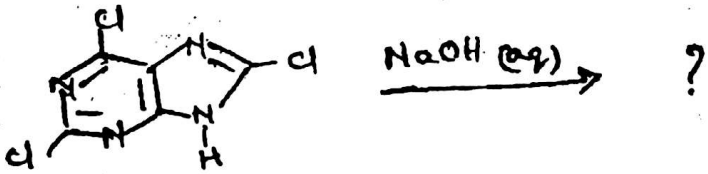
(III) 

(IV) 

(ii) Give the synthesis of pyridine. Explain why electrophilic substitution in pyridine takes place preferentially at positions 3 or 5 ?

(iii) How is purine synthesised ? Complete the following reaction :—

(I) 

(II) 

(iv) Discuss the reactivity of indole. What is the action of Zn/HCl, Li/NH_3 and Pt/CH_3COOH on indole ?

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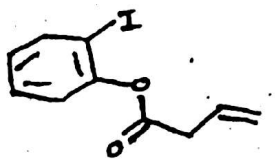
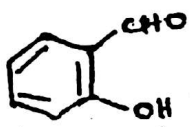
(b) Answer any **one** of the following :—

(i) Give any two methods of synthesis of 1, 3, 5-triazine.

(ii) Complete the following reactions :—

(I) 

(II) 

8

2. (a) Answer any **two** of the following :—

(i) What are corticosteroids ? Explain the stereochemistry of steroids and give the structure of progesterone.

(ii) How is 16-DPA synthesised from cholesterol ?

(iii) Give the synthesis of cinerolone.

(iv) Give synthesis of testosterone from 16-DPA.

4

(b) Answer any **one** of the following :—

(i) Discuss the general structure, classification, occurrence and biological role of bile acids. Give the structure of lithocholic acid.

(ii) Write a note on steroidal alkaloids and give the structure of oestrone.

8

3. (a) Answer any **two** of the following :—

(i) State the biological importance of vitamin B_2 and write its synthesis.

(ii) Give the analytical evidence for the presence of thiazolidine ring in penicillin-G.

(iii) What are natural insecticides ? How are they advantageous over their synthetic analogues ? State the sources of pyrethrums and write the structure of pyrethrin-I.

(iv) Answer the following :—

(I) State the sources and biological importance of vitamin H (β-biotin).

(II) What are antibiotics ? Write the structure of Cephalosporin-C.

4

(b) Answer any **one** of the following :—

(i) State the biological importance of vitamin B_6 and write its synthesis from ethyl ester of N-formyl-DL-alanine.

(ii) Answer the following :—

(I) Write the synthesis of tert-butylphthalimide malonaldehyde.

(II) Write the synthesis of vitamin K_1.

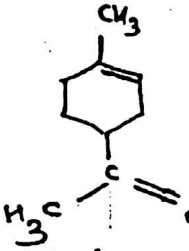
(a) Answer any **two** of the following :— 8

(i) Answer the following :—

(I) Indicate the number of ^{13}C signals in the proton decoupled spectrum and assign the multiplicity for each signal in the off-resonance decoupled spectrum for the following compounds :

(A) 1, 4-dibromobenzene (B) toluene

(II) For the following organic molecule,



state the number of ^{13}C signals (with the phase of the signals) in DEPT-135,
DEPT–90,
DEPT–45,
and in the proton decoupled spectrum.

(ii) The ^1H NMR spectrum of 1-propanol shows the following signals :
δ (ppm) : 3·5 (t), 3·0 (s, D_2O exchangeable), 1·5 (m) and 0·8 (t).
Sketch the COSY spectrum of the above compound using the data given above.

(iii) Answer the following :—

(I) A compound having molecular formula C_2H_2BrCl exhibits 2 doublets (J = 16 Hz) in its ^1H NMR spectrum. Suggest the structure and justify your answer.

(II) A compound having molecular formula C_6H_8 is highly symmetrical and shows 2 singlets in noise decoupled ^{13}C spectrum. The off-resonace decoupled spectrum shows only a triplet and a doublet. Suggest the structure and justify your answer.

(iv) What is ESR spectroscopy ? Discuss its principle and state the applications.

(b) Attempt any **one** of the following :— 4

(i) Answer the following :—

(I) State the number of ^{13}C peaks and assign the multiplicity to each one in ^{13}C proton decoupled spectrum in the following compounds A and B containing ^{19}F and ^{31}P respectively.

[A] $CF_3—CH_2OH$

[B] $CH_3O—\underset{\displaystyle O\,CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{P=O}}}}$

(II) Discuss the applications of NMR spectroscopy in the field of medical science.

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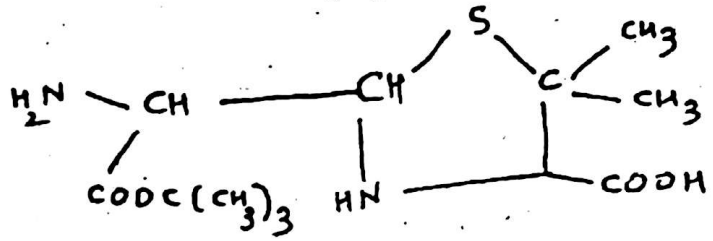
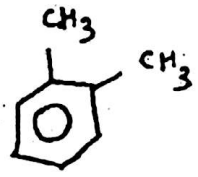
(ii) The ^1H NMR spectrum of 2-nitropropane shows the following signals :—
δ(ppm) : 1·56 (d), 4·66 (septet)
Its ^{13}C NMR spectrum shows peaks at δ (ppm) : 21 and 79.
Draw a sketch of $^1H - ^{13}C$ HETCOR spectrum, showing the positions of cross-peaks you would expect to observe, using the data given above. **12**

3. Attempt any **four** of the following :—
   (a) Give the Doebner-Miller synthesis of 2-methylquinoline.
   (b) Outline the general route of synthesis for pyrazine.
   (c) Give the synthesis of oestriol from 16-DPA.
   (d) Give the synthesis of exaltone.
   (e) Write the reactions involved in the preparation of phenoxymethylpenicillin from :

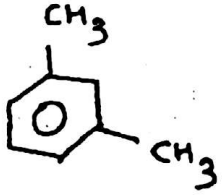


   (f) Write the synthesis of α-tocopherol.
   (g) Two isomeric compounds A and B have molecular formula C_7H_8O and exhibit the following spectral data :—
   Compound A :
   PMR : δ : 2·34 (3H, s), 6·67 (2H, d, J = 8·8 Hz) ; 7·12 (2H, d, J = 8·8 Hz) 7·95(1 H, s, D_2O exchangeable)
   Compound B :
   PMR : δ : 7·92—7·2(5 H, m), 5·5(1 H, s, D_2O-exchangeable), 4·3 (2H, s)
   Assign suitable structures to A and B and justify your answer.
   (h) How will you distinguish between the following three isomers A, B and C using ^{13}C NMR spectroscopy ?

A



B



C

Assign ^{13}C chemical shift to all the aromatic carbon atoms in compound C using the following incremental shift table.

substituent	increments in ppm			
	ipso	o–,	m–	p–
$-CH_3$	+9·3	+0·7	−0·1	-2·9

S