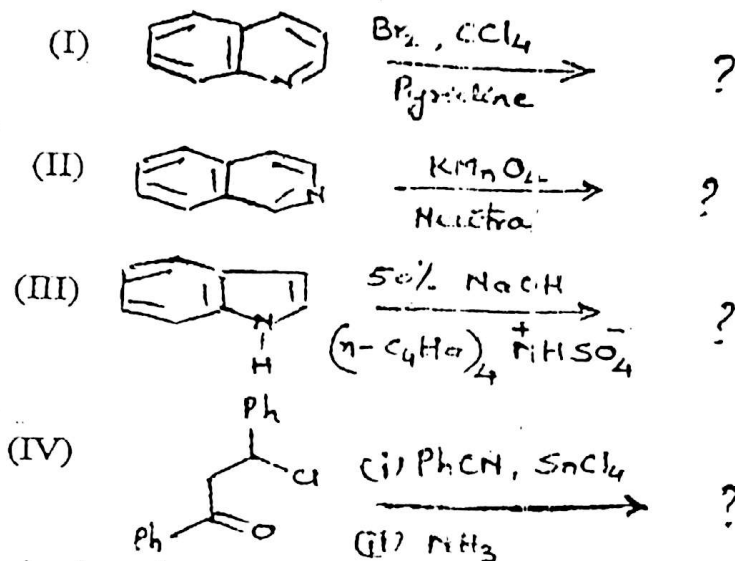


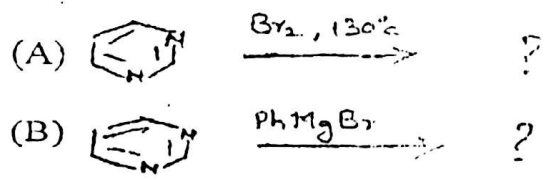
- Q.3. : (1) All questions are compulsory.  
 (2) Figures to the right indicate full marks.

(a) Attempt any two of the following :—

(i) Complete the following reactions :

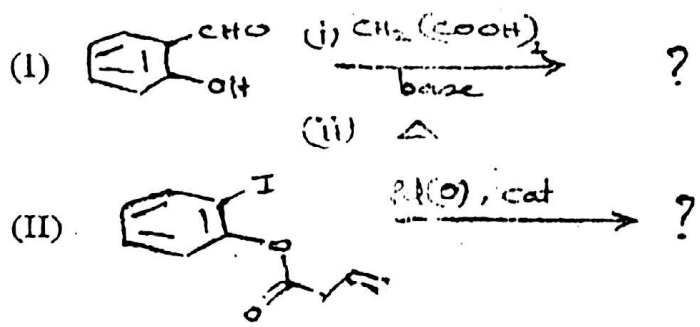


- (ii) "Pyridazine is resistant to electrophilic substitution and oxidation reactions". Explain with illustration.
- (iii) Give the synthesis of pyrazine from :  
 (A) 1, 2-diketones (B) α-aminocarbonyl compounds.
- (iv) (I) Explain why isoquinoline undergoes electrophilic substitution reaction at positions 5 and 8.  
 (II) Complete the following :—



(b) Answer any one of the following :—

- (i) Give any two methods of synthesis of s-triazine.  
 (ii) Complete the following reactions —



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

- (i) What are bile acids? Give important functions of bile acids. Write structure of lithocholic acid.
- (ii) Give the synthesis of 16-DPA from cholesterol.
- (iii) Write the synthesis of allothrolone.
- (iv) How is 16-DPA converted to progesterone?

(b) Answer any one of the following :—

- (i) What are sterols? Discuss the biological role and the stereochemical features of cholesterol.
- (ii) Write a note on steroidal alkaloids and give the structure of androsterone.

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

- (i) Explain the biological importance of vitamin B<sub>6</sub>. How will you convert ethyl ester of N-formyl-DL-alanine to vitamin B<sub>6</sub>?
- (ii) Write the synthesis of D-penicillamine.
- (iii) What are natural insecticides? State the source and biological properties of rotenoids. Write the structure of rotenone.
- (iv) Answer the following :—

- (I) State the sources and biological importance of vitamin K<sub>2</sub>.
- (II) Give an account of acid hydrolysis of Cephalosporin-C.

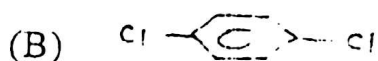
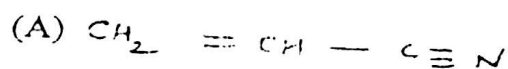
(b) Answer any one of the following :—

- (i) Write the synthesis of phenoxymethyl penicillin from D-penicillamine.
- (ii) State the sources and biological importance of vitamin C and vitamin D.

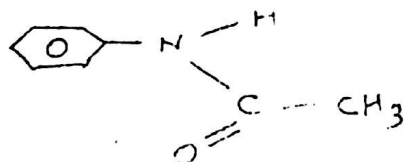
4. (a) Answer any two of the following :—

(i) Answer the following :

- (I) Indicate the number of <sup>13</sup>C signals in the proton decoupled spectrum of the following compounds and assign the multiplicity expected for each signal in the off-resonance decoupled spectrum, for the following compounds :



(II) State true or false and give reasons :



For the above conformation of acetanilide, the signals at  $\delta$  8.8 (1 H, D<sub>2</sub>O-exchangeable) and  $\delta$  2.13 show a cross peak in the NOSEY spectrum.

[TURN OVER

- (ii) A compound with molecular formula  $C_5H_{12}O_2$  shows the following spectral data. Suggest the structure of the compound with reasons :

$^1H$  NMR :  $\delta$  (ppm) : 1.2 (t, 6 H), 3.6 (q, 4 H), 4.7 (s, 2 H).

$^{13}C$ NMR proton decoupled spectrum	DEPT - 135	DEPT - 90
15 ppm	positive	no peak
63 ppm	negative	no peak
95 ppm	negative	no peak

- (iii) A compound having molecular formula  $C_5H_8O_2$  shows the following spectral data :

IR ( $cm^{-1}$ ) : 1735

$^1H$  NMR  $\delta$  (ppm) : 1.08 (2 H), 1.16 (2 H), 2.08 (2 H), 3.71 (2 H)

$^{13}C$  NMR  $\delta$  (ppm) : 19.0, 22.2, 29.9, 68.8, 170.0

Predict the structure and draw a sketch of COSY SPECTRUM for the above molecule showing the expected diagonal and off-diagonal peaks.

- (iv) (I) Discuss the application of NMR spectroscopy in the field of medical science.

(II) Discuss the applications of fluorescence spectroscopy.

- (b) Attempt any one of the following :—

- (i) Solve the following :—

- (I) State the number of  $^1H$  peaks and assign the multiplicity to each signal in the  $^{13}C$  proton decoupled spectrum for the following compounds A and B containing  $^{19}F$  and  $^{31}P$  respectively :



- (II) Assign a suitable structure to the organic compound having molecular formula  $C_8H_{14}O_3$  that shows the following spectral data :

UV :  $\lambda$  max (n-hexane) : 225 nm [ $\epsilon = 50$ ]

IR ( $cm^{-1}$ ) : 3000, 2875, 1820, 1760, 1456

$^1H$  NMR  $\delta$  (ppm) : 2.7 (2 H, septet,  $J = 6.7$  Hz),  
1.2 (12 H, d,  $J = 6.7$  Hz)

(ii) Answer the following :—

- (I) Discuss the applications of ESR spectroscopy.  
 (II) A compound having molecular formula  $C_6H_{12}O$  shows in its  $^{13}C$  proton decoupled NMR spectrum, signals at 22.8, 25.0, 30.4, 37.9 and 207.3 ppm.  
 The mass spectrum of the compound shows a base peak at  $m/z$  : 43 and another intense peak at  $m/z$  : 58. Predict the structure of the compound.

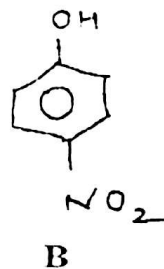
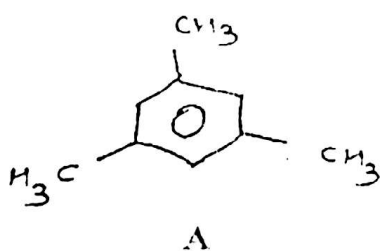
5. Attempt any four of the following :—

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- (a) Explain the following with reactions :  
 (I) Nitration of pyridine-N-oxide.  
 (II) Electrophilic substitution *via* lithiated intermediate of pyridine.  
 (b) Give Fischer synthesis of indole.  
 (c) Outline the synthesis of oestradiol from 16-DPA.  
 (d) Give the synthesis of cinerolone.  
 (e) Write the synthesis of  $\alpha$ -tocopherol.  
 (f) Give the classification of antibiotics on the basis of activity.  
 (g) The PMR spectrum of 2-methyl-1-propanol shows the following signals :  
 $\delta$  : 3.28 (2 H, d), 2.93 (1 H,  $D_2O$ -exchangeable), 1.68 (1 H, m) and 0.83 (6 H, d)

Give a schematic diagram of the  $^{13}C$  -  $^1H$  correlation (HETCOR) spectrum showing the positions of cross peaks using the data given above.

- (h) Assign  $^{13}C$  chemical shifts to all the aromatic carbons using the chemical shift correlation table given below, for the following compounds A and B :



Substituent	increments in ppm			
	ipso	o -	m -	p -
-OH	+ 28.8	- 12.7	+ 1.6	- 7.3
-NO <sub>2</sub>	+ 19.6	- 4.9	+ 0.9	+ 6.0
-CH <sub>3</sub>	+ 9.3	+ 0.7	- 0.1	- 2.9