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End Semester Examination of Semester–III, 2015
Subject : CHEMISTRY (PG)
Paper : CEM–303 (Org. Spl) (Th)
Full Marks : 40
Time : 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

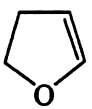
Illustrate the answers wherever necessary.

Unit–I

Answer **any one** question : 10x1=10

1. a) The chemical shifts for three vinyl protons of p-chlorostryrene appears at $\delta_{6.70}$, 5.70 and 5.45. Assign each of them. To which type of coupling pattern does this vinyl system belong? Also draw the coupling patterns of the vinyl protons separately showing all the coupling constants. 5

   b) Give one example each of the following types of coupling patterns. Label the type of protons in each case.
   i) ABX ii) ABC iii) AA'BB' iv) A_2B_2 4

   c) Distinguish between  and  by ^1H NMR spectroscopy. 1

2. a) In which type of coupling system do the vinylic protons of vinyl acetate belongs to? Label the protons according to this type. Also draw the coupling patterns separately for each of the vinylic protons showing the coupling constants for all the individual sets. 4

b) An organic compound having molecular formula $C_9H_{10}O_2$, gave the following spectral data :

UV; λ_{max} 274 nm (ε = 2050)

IR; $\bar{\nu}_{max}$ 3031, 2941, 1724, 1608, 1504, 1060, 830 cm^{-1}

^1H NMR; δ; 2·35 (3H, s), 3·82 (3H, s),
7·20–7·85 (4H, m)

Mass; (m/z) : 150, 145, 119

What is the probable structure of the compound?

c) How NOE is used to identify citral-a and citral-b. 2

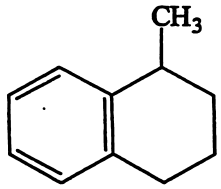
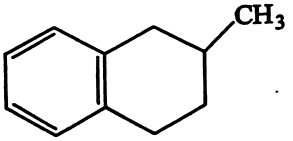
Unit II

Answer **any one** question : 10x1=10

3. a) How would you distinguish between the following pairs of isomeric compounds from their mass spectral fragmentations? 3x2=6

i) CH_3CH_2–$\underset{\displaystyle CH_3}{\underset{|}{CH}}$–$CH_3$ and $CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}$–$\underset{\displaystyle CH_3}{\underset{|}{CH}}$–$CH_3$

ii) $CH_3CH_2CD_2COOC_2H_5$ and
$CH_3CD_2CH_2COOC_2H_5$

iii)  and 

b) The three isomeric xylenes gives identical mass spectra, all showing the base peak at m/z 91. Explain. 4

4. a) What is nitrogen rule? Explain with suitable example its importance in mass spectral analysis. 4

b) Predict the mass spectral fragmentation pattern of diethyl ether. 2

c) Briefly discuss the basic principle of Chemical ionization mass spectrometry. 4

Unit III

Answer **any one** question : 10x1=10

5. a) Define Gel. Classify different types of gels. Give some examples of law molecular weight mass organogelators. 2+2+2=6

b) What are the techniques used for studying gel morphologies? 2

c) Give applications of gel. 2

6. a) Write the working principle of gel electrophoresis. 4

b) Write various applications of gel electrophore. 3

c) What is gel transition temperature? 2

d) Give an example of naturally existing hydrogel. 1

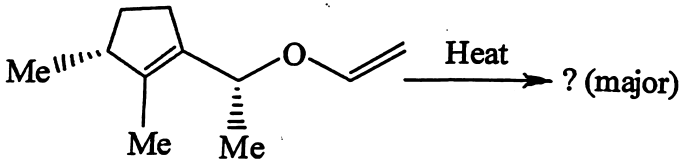
Unit IV

Answer **any one** question : 10x1=10

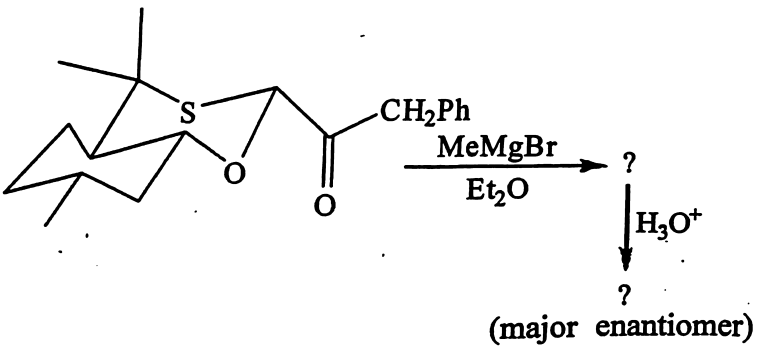
7. a) What are the 'player' and 'spectator' ligands in respect of a synthesis? Cite an example. 2

   b) Write the stereostructure of the major products in the following reactions. Explain the stereoselectivity. Name the stereogenic units of the products with appropriate notations. (Answer any two). 4+4

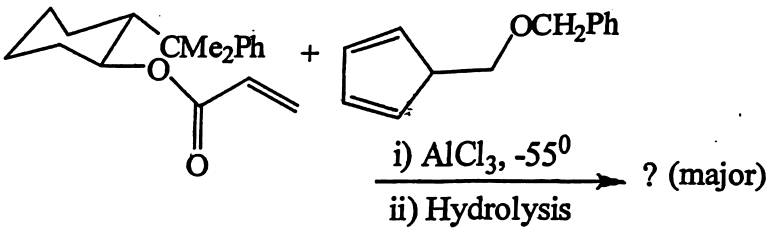
i)



ii)



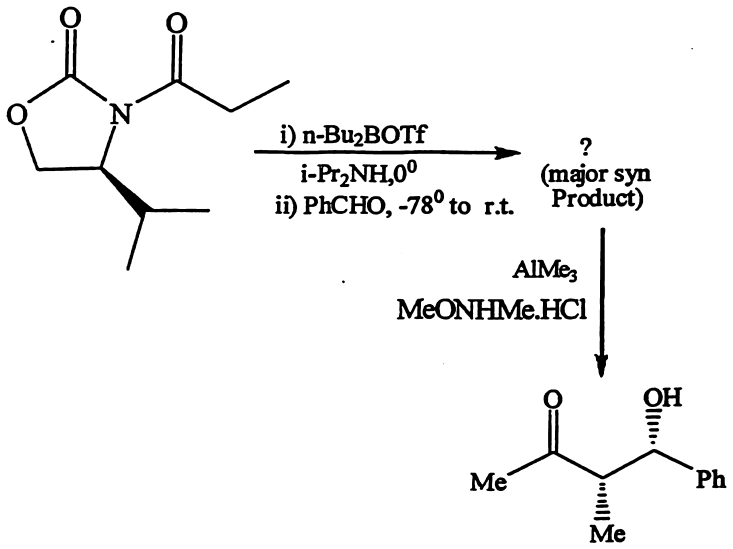
iii)



8. a) Discuss the principle of stereoselective synthesis using a Chiral auxilliary. $2\frac{1}{2}$

b) State the criteria to be fulfilled in a good stereoselective synthesis as mentioned by Eliel. $2\frac{1}{2}$

c) Fill up the blanks (marked?) with appropriate reagent/ reaction condition / intermediate in the following diastereo-selective synthesis. 3



d) Account for the low kinetic acidity of the methane H in the following compound. 2