1 SEM PG (CBCS) CHM C 2

2025

(December)

CHEMISTRY

Paper : 102

(Core Course)

(Organic Chemistry–I)

Full Marks : 60

Time : Three hours

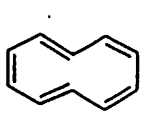
The figures in the margin indicate full marks for the questions.

UNIT–I

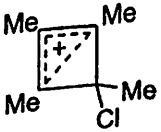
(Marks : 12)

1. Answer ***any six*** questions from the following : 2×6=12

   (a) Comment on the aromaticity of the following : ½×4=2

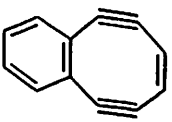


(i)



(ii)

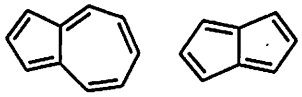
(iii)



(iv)

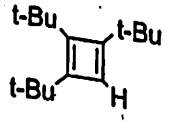
(b) "Cyclopentadiene is more prone to a proton loss, whereas cycloheptatriene losses a hydride rapidly." Justify the statement with proper structure.

(c) Compound **A** is stable and has a dipole moment whereas compound **B** does not have a dipole moment and is relatively unstable. Explain why.

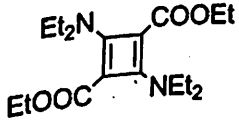


A B

(d) *Cyclobutadienes are antiaromatic and unstable compounds.* Comment on the stability of the following substituted cyclobutadienes (**A** and **B**) with proper explanation.



(A)



(B)

(e) Cyclooctatetraene dissolved in concentrated H_2SO_4 shows the presence of a diatropic ring current with NMR spectra values for proton with $\delta = -0.3$; 5.1; 6.4; and at 8.5 ppm. Based on these findings predict the aromaticity and assign the protons of cyclooctatetraene.

(f) What are addition compounds ? Give an example of each of the four class of addition compounds. 1+1=2

(g) Write a short note on phase transfer catalyst.

(h) Write the Hammet equation. Elaborate the physical significance of substituent constant. 1+1=2

(i) Base catalyzed hydrolysis of ethyl m-nitrobenzoate ester is 63.5 times faster, whereas ethyl p-methoxybenzoate ester is 0.21 times slower under same condition. Given the value of $\sigma_m - NO_2$ as 0.71, calculate the value of $\sigma_p - OMe$.

UNIT–II

(Marks : 12)

2. Answer ***any four*** questions from the following : 3×4=12

(a) What is crossover experiment ? Discuss the mechanism of Fries rearrangement with the help of crossover experiment. 1+2=3

(b) Write and identify the kinetic and thermodynamically stable products for the addition reaction of *HBr* with 4-methyl-1,3-pentadiene. Draw their energy profile diagram. 1+1+1=3

(c) Explain neighbouring group effect. Compare the rate hydrolysis of 2-phenylthioethyl chloride and 1-chloropropane. 1+2=3

(d) How will you confirm that 1.5+1.5=3

(i) addition of bromine does not take place in a single step ?

(ii) hydride ion transfer takes place in Cannizzaro reaction ?

(e) Define primary and secondary kinetic isotope effects with examples. Discuss the kinetic isotope effect of Cope rearrangement. 1+1+1=3

(f) What is isotope labelling ? Discuss the mechanism of Cannizzaro reaction with the help of isotope labelling. 1+2=3

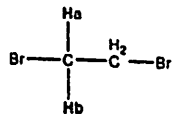
UNIT–III

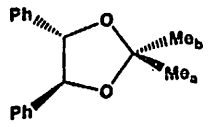
(Marks : 12)

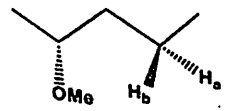
3. Answer ***any four*** of the following : 3×4=12

(a) What do you understand by enantioselective and diastereoselective reactions ? State *three* methods of asymmetric induction in an organic molecule. 2+1=3

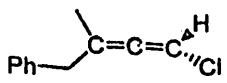
(b) Label the ligands marked as *a* and *b* in the following compounds as homotopic, enantiotropic, and diastereotopic :



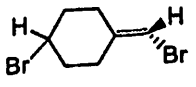




(c) Assign *R* or *S* for the following compounds :



(i)



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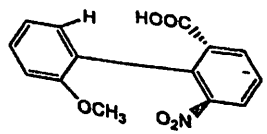
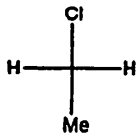
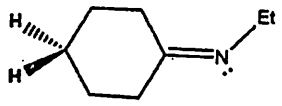


(iii)

(d) Label the pairs of ligands shown in bold face in each of the following compounds as *Pro-R* or *Pro-S*.



(i)



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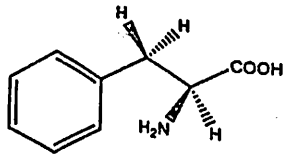
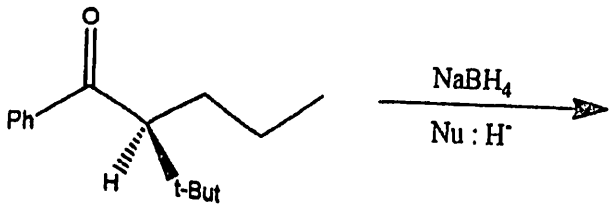


(iii)

(e) Using Felkin-Anh model, identify the major product in the following reaction. Designate the major product as *erythro* or *threo*.



(f) Define enantiomeric excess. If a pure (+) enantiomer has a specific rotation of +90°, what will be the rotation of a mixture containing 25% of the (+) enantiomer and 75% of the (–) enantiomer ? 1+2=3

UNIT–IV

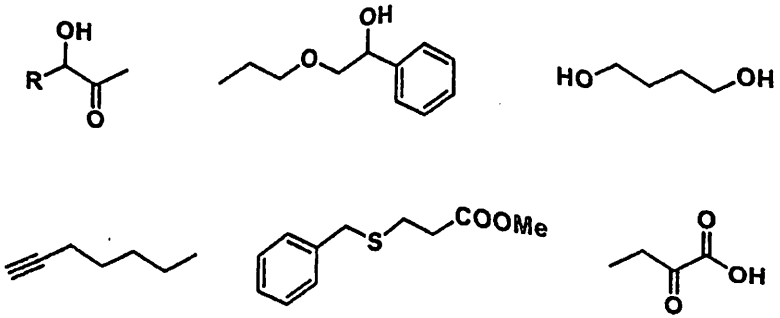
(Marks : 12)

4. Answer the following questions : 2+2=4

(a) Define the terms 'synthons' and 'synthetic equivalents'. Explain with a suitable example.

(b) What is an umpolung. Explain with an example.

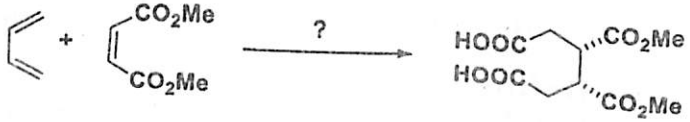
5. Write the retrosynthetic analysis and give the forward synthesis of the following target molecules : ***(any three)*** 2×3=6



6. Answer ***any one*** of the following questions : 2

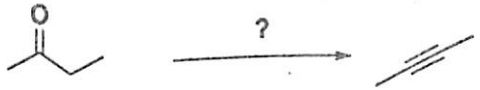
(a) Mention *two* protecting groups for amino functionality. Write the reagents and reaction conditions involved for protection and removal of these groups.

(b) Illustrate how to bring about the following conversions :



(c) Illustrate how to bring about the following conversions :

(i)



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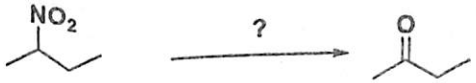


UNIT–V

(Marks : 12)

7. Answer ***any six*** from the following questions : 2×6=12

(a) What is shift and chemical shift in NMR Spectroscopy ? What are the factors that affect the chemical shift ? 1+1=2

(b) What is coupling constant ? Discuss the coupling constants of *cis* and *trans* alkene. 1+1=2

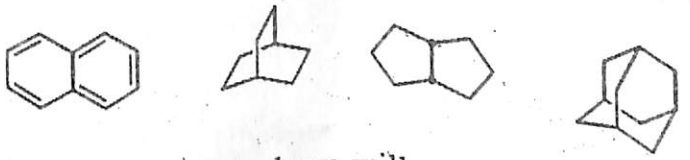
(c) How does radio frequency affect NMR ? What is double resonance in NMR ? 1+1=2

(d) Explain the origin of spin-spin coupling in proton NMR spectroscopy.

(e) Write short note on Magnetic Resonance Imaging (MRI) or Nuclear Overhauser effect (NOE).

(f) What is COSY and HETCOR in NMR spectroscopy ? Explain the COSY spectra of 2-chloropropane.

(g) How many signals would you expect in the ^{13}C NMR of the following compounds ? ½×4=2



(h) Using FTIR, how will you differentiate between the following pairs : 1+1=2

(i) Maleic acid and Fumaric acid

(ii) Ethyl butyrate and Vinyl acetate

(i) The amount of sample required for recording ^{13}C NMR is more in comparison to the amount required for ^{1}H NMR. Explain.