

2020

CHEMISTRY — HONOURS

Sixth Paper

(Group - A)

Full Marks : 75



Candidates are required to give their answers in their own words as far as practicable.

Answer **any six** questions, taking **one** from each Unit.

All questions carry equal marks.

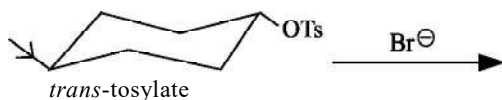
CHT - 32a

Unit - I

1. (a) Both  and  produce same product on acetolysis. Explain.

- (b) On treatment with nitrous acid, *trans* isomer of 4-*t*-butylcyclohexyl amine gives corresponding alcohol with retention of configuration, but in the case of the *cis*-isomer, cyclohexene derivative is obtained. Explain this with mechanism.

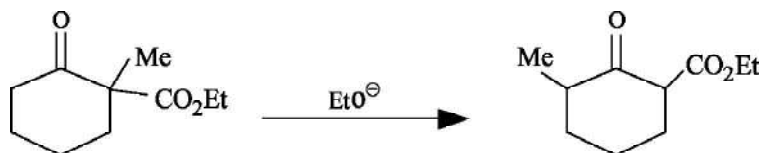
2. (a) Write down the product of the reaction with mechanism :



Instead of Br^\ominus , strong base like EtO^\ominus has no effect on this *trans* isomer. Why? On similar treatment with Br^\ominus , what will be the product in case of *cis*-isomer

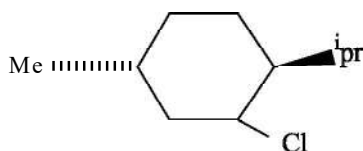


- (b) Outline a mechanism for the following conversion :



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3. (a) Two diastereoisomers of the following compound differ in the orientation of Cl. One isomer undergoes E_2 dehydrohalogenation 200 times faster than the other. Draw the conformations of the two diastereoisomers and explain the observation.

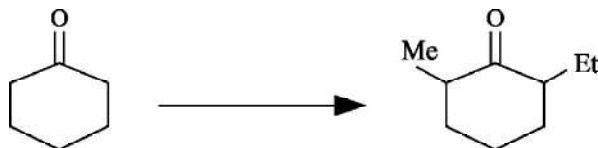


- (b) Between the two isomers of 4-tert-butylcyclohexane carboxylic acid, which is the stronger acid and why?
4. (a) Compare the rate of chromic acid oxidation of



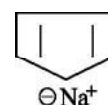
- (b) *Cis* -1, 2 - dimethylcyclohexane exist as a non-resolvable dl-pair, why?

5. (a) Discuss the factors that influence C-alkylation vs. O-alkylation during base catalysed alkylation of enolates.
- (b) Outline the following conversion :



Unit - II

6. (a) Mesityl oxide shows λ_{\max} 230 nm and 329 nm in hexane while in water, λ_{\max} 243 nm and 305 nm is observed. Explain.
- (b) Arrange CH_3F , CH_3Cl and CH_3Br in increasing order of chemical shift and account for the trend.
7. (a) An organic compound of molecular formula, $\text{C}_9\text{H}_{10}\text{O}_2$ showed the following spectral pattern :
- UV : λ_{\max} 270 nm, IR 1680 cm^{-1}
- $^1\text{H NMR}$: δ 7.6 (2H, d, $J = 8\text{ Hz}$); 6.9 (2H, d, $J = 8\text{ Hz}$); 3.9 (3H, s) and 2.0 (3H, s). Identify the compound explaining the above spectral data.
- (b) Explain why :
- (i) $^1\text{H-NMR}$ signal for O-H proton in *ortho* hydroxyacetophenone shifts upfield when temperature is increased.
- (ii) $^1\text{H NMR}$ spectrum of sodium salt of cyclopentadiene consists of a singlet

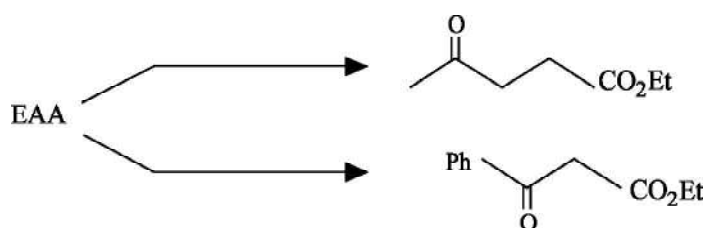


8. (a) How can you distinguish the following pairs of compounds by IR spectroscopy :
- Phenyl acetate and Methyl benzoate
 - O*-nitrophenol and *p*-nitrophenol.
- (b) Why is TMS chosen as the universal internal standard for ^1H NMR spectroscopy?

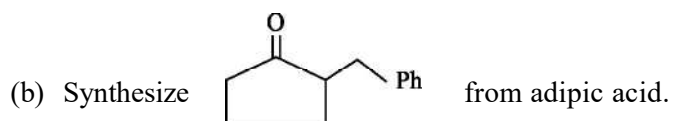
CHT - 32b

Unit - I

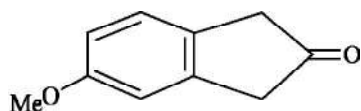
9. (a) Outline the following conversions :



- (b) Define donor and acceptor synthons with example.
10. (a) With help of Felkin-Anh model, predict the product when (R)-Benzoin is reduced with LiAlH_4 .

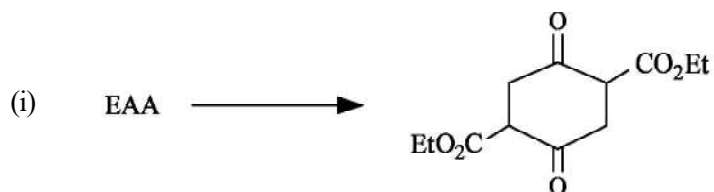


11. (a) Write the possible retrosynthesis of



Mention the forward synthesis also.

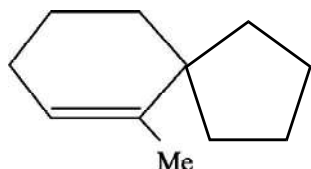
- (b) Predict the product with mechanism when benzophenone reacts with diethyl succinate in presence of potassium tertiary butoxide.
12. (a) Carry out the following conversions :



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(b) Synthesize



from cyclopentanone.

13. (a) PhCHO and $\text{CH}_3\text{COCH}_2\text{CH}_3$ give $\text{PhCH}=\text{CHCOCH}_2\text{CH}_3$ in base and $\text{PhCH}=\text{C}(\text{CH}_3)\text{COCH}_3$ in acid. Give a mechanistic explanation.
- (b) Alcohols are often protected by transforming to OTHP derivative. What advantage does it provide? Mention the protection and deprotection technique.

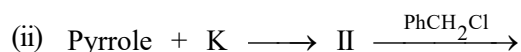
Unit - II

14. (a) How can you show that all methyl- α -D-aldopyranosides have same configuration at C_1 and C_5 ?
- (b) Compare and explain the rates of bromine water oxidation of α -D-glucopyranose and β -D-glucopyranose.
15. (a) Find out the preferred conformation of methyl α -D-glucoside and methyl β -D-glucoside. From the preferred conformations, can you assess their relative stability?
- (b) Predict the product(s) and number of moles of HIO_4 consumed when HIO_4 react with methyl- α -D-fructofuranoside and methyl- α -D-glucopyranoside separately.
16. (a) D-(+) glucose undergoes mutarotation in benzene solution in presence of 2-hydroxypyridine but not in presence of pyridine or cresol alone. Explain mechanistically.
- (b) Both glucose and fructose are reducing sugars but sucrose is not, though it contains a glucose and a fructose unit. Explain.

CHT - 32c

Unit - I

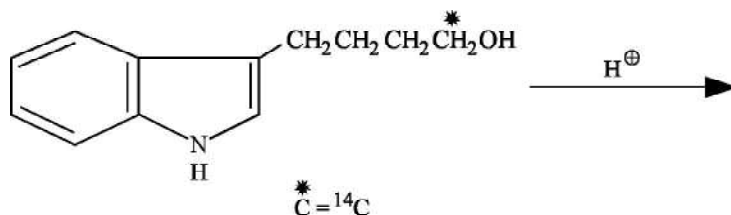
17. (a) Complete the following reactions :



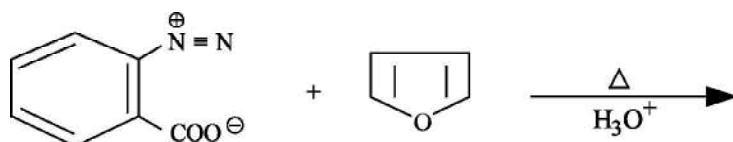
Explain the difference in the nature of the final products obtained in the two reaction sequences.

- (b) Pyridine-N-oxide is more reactive than pyridine towards both electrophiles and nucleophiles – Explain.

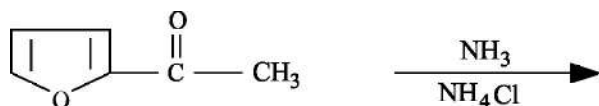
18. (a) Outline Bardhan-Sengupta synthesis of phenanthrene.
 (b) Anthracene can take part in Diels–Alder reaction but naphthalene cannot. Why?
19. (a) How can you prepare ethyl – 2, 5 – dimethyl pyrrole – 3 – Carboxylate using Hantzsch synthesis? Give mechanism.
 (b) Mechanistically predict the product of the following reaction :



20. (a) Predict the product(s) when phenyl hydrazone of ethyl methyl ketone is heated in AcOH. Give mechanism and explain the formation of product(s).
 (b) Predict the product and suggest a mechanism for the following reaction :



21. (a) Why Furan cannot be nitrated with a mixture of conc. HNO_3 and conc. H_2SO_4 ? Write the product and mechanism of reaction of furan with acetyl nitrate at $-10^\circ C$.
 (b) Predict the product(s) with mechanism :



Unit - II

22. (a) How can you determine N-terminal amino acid of a peptide by Edman method? What advantage does it offer over FDNB method?
 (b) Write down the reaction which is used for the identification of amino acids using a spray reagent.
23. (a) Write the structure of cyclic AMP. Explain why it gives adenosine – 5' – monophosphate as the major product on alkaline hydrolysis.
 (b) State the role of DCC in direct coupling of amino acids. Give mechanism.
24. (a) Write the structure of BOC derivative of an amino acid. For which purpose BOC is used? How this group can be removed?
 (b) Write the names and structures of two purine and pyrimidine bases related to the nucleic acid.