

Reg. No. :

Code No. : 8398

Sub. Code : HCHM 31

M.Sc. (CBCS) DEGREE EXAMINATION,
NOVEMBER 2016.

Third Semester

Chemistry

ORGANIC CHEMISTRY – III

(For those who joined in July 2012 – 2015)

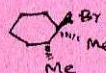
Time : Three hours

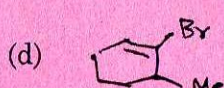
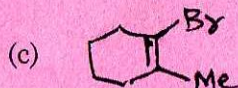
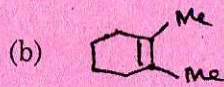
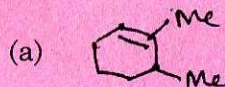
Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. The E2 elimination product of  is



20. (a) Compare the structural features of the disaccharides sucrose, maltose and lactose.

Or

(b) Write notes on :

(i) Structure of quercetin

(ii) Nucleoproteins

(iii) Amylose and amylopectin.



2. $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ undergoes nucleophilic substitution reaction at a faster rate than $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ because of

- (a) the electro negativity of sulfur
- (b) mesomeric effect of sulfur
- (c) the inductive effect of sulfur
- (d) neighbouring group participation

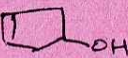
3. Which of the following reagents is not suitable to convert phosphonium salts to ylides?

- (a) Phosphorous oxychloride
- (b) Sodamide
- (c) Sodium hydride
- (d) n - butyl lithium

4. Which of the following is the intermediate in the Birch-reduction?

- (a) Anion radical (b) Cation radical
- (c) Carbene (d) Benzyne

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5. The conversion of  to  can be effected by

- (a) Methyl magnesium iodide
- (b) Zinc - copper couple in CH_2Cl_2
- (c) Chloroform in sodium hydroxide
- (d) None of these

6. Favorski rearrangement involves a

- (a) three membered ring intermediate
- (b) four membered ring intermediate
- (c) five membered ring intermediate
- (d) six membered ring intermediate

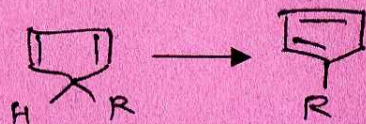
7. The number of nodes present in Ψ_3 of butadiene is

- (a) 1 (b) 2
- (c) 3 (d) 0

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8. The $[i, j]$ value for the following conversion is



- (a) [1, 3] (b) [1, 5]
 (c) [1, 7] (d) [3, 3]
9. The enzyme that cuts starch into maltose unit is
- (a) α - amylase
 (b) β - amylase
 (c) glucan dikinase
 (d) water dikinase
10. The electrophilic substitution in thiazole can take place at position
- (a) 2 (b) 3
 (c) 4 (d) 5

PART B — ($5 \times 5 = 25$ marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Explain the importance of Hoffmann and Saytzeff rules.

Or

- (b) Describe the mechanisms of S_N1' , S_N2' and S_Ni reactions.

12. (a) Compare the course catalytic reduction and metal - ammonia reduction over terminal non terminal alkynes. Provide the mechanisms of the reactions, highlighting the stereochemical outcome in each case.

Or

- (b) Explain how the attack of nucleophiles to enones can be tuned to yield either 1, 2 - addition product or 1, 4 - addition product. Write a note on Michael addition reaction.



13. (a) Write notes on :

- (i) Carbene rearrangement
- (ii) Cine substitution.

Or

- (b) Explain why triplet carbene has radical character and singlet carbene has ionic character. Distinguish between electrophilic and nucleophilic radicals with examples.

14. (a) Draw the orbital correlation diagram of con rotatory ring closure of 1, 3 - butadiene and show that the reaction is thermally allowed.

Or

- (b) What are frontier molecular orbitals? How are frontier orbital theory is helpful in explaining the pericyclic processes? Find out whether (i) the con rotatory ring closure of allyl cation and (ii) $\pi 2a + \pi 2a$ addition reaction are thermally allowed or not using frontier molecular orbital theory.

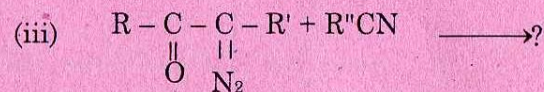
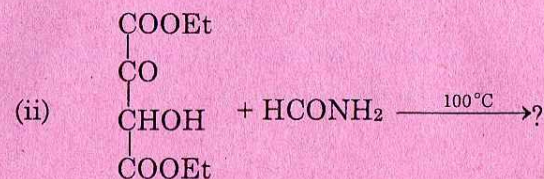
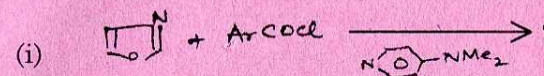
15. (a) Write a note on the biosynthesis of flavanoids.

Or

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(b) Complete the following reactions :



PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Explain why (i) $\text{S}_{\text{N}}\text{i}$ reaction and NGP involved reaction lead to the same stereochemical outcome (ii) E1 reaction and $\text{S}_{\text{N}}\text{1}$ reaction involves same intermediate (ii) Bridge head halides do not undergo nucleophilic substitution (iv) the leaving group need not be a powerful one in E1CB reaction.

Or

- (b) Explain the role of solvent polarity and nucleophilicity of the attacking species on the nucleophilic substitution reaction.

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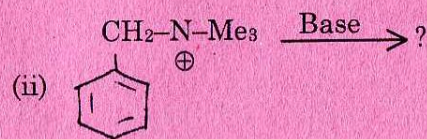
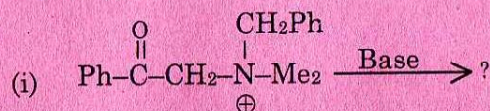
17. (a) Discuss the mechanism of nucleophilic aromatic substitution reactions involving benzyne intermediate. Discuss the course of the treatment of sodamide on 1, 2 - dichloro benzene, 1, 3 - dichloro benzene and 1, 4 - dichloro benzene. Indicate the regiochemical outcome in each case.

Or

- (b) Write notes on :

- (i) Sharpless asymmetric epoxidation
- (ii) Mannich reaction.

18. (a) Describe the mechanism of Stevens rearrangement and Sommelet Hauser rearrangement. Write the products in the following reactions :



Or

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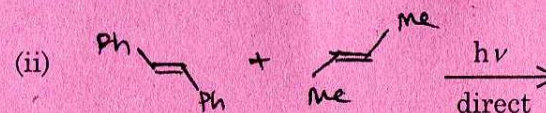
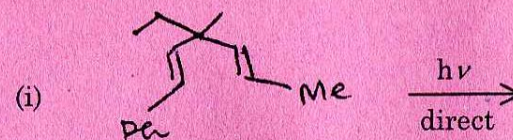
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- (b) (i) Describe the mechanism of Schmidt rearrangement.
(ii) Indicate how nitrenes can be involved in insertion, addition and rearrangement reactions.

19. (a) Describe the Norrish Type I and Norrish Type II reactions. Indicate these two reactions are important reactions of excited carbonyl compounds.

Or

- (b) Write the products in each case describing the mechanism.



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