

(6 pages)

MAY 2016

P/ID 40124/PCHD

Time : Three hours

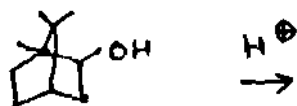
Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. Draw the oxaphosphatane intermediate proposed for the Wittig reaction. Adduce evidence for its existence.
2. Explain the $A - S_E2$ mechanism of olefin addition.
3. Indicate the conditions under which E2 process prefers syn elimination over anti elimination.
4. Discuss the stereochemistry of addition of bromine to maleic acid.
5. *t*-Butyl chloride and $t\text{-Bu}S^{\otimes}Me_2$, both give nearly 36% 2-methyl -1-propene, but at different rates. Explain.
6. What is the connection between Arndt Eistert synthesis and Wolf rearrangement?

7. Write the product in the following reaction :



8. What is "memory effect" in rearrangement reactions?

9. What is Huang Minlon modification of Wolf Kishner reduction?

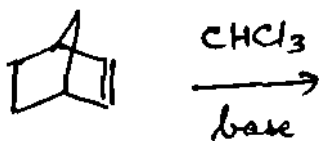
10. How can it be proved that alcohols are not intermediates in the reduction of $RCOR$ to RCH_2R by Clemenson method?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) What is cyano ethylation? Explain how that can be effected.

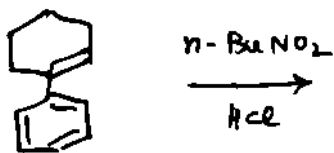
(ii) Write the product in the following reaction and explain the mechanism.



- (iii) Discuss how carbenes react with alkynes.
- (iv) Illustrate that Simmon Smith reaction is useful in α - methylation of ketones.
- (v) Propose the mechanism for Stobbe condensation. Describe the scope of this reaction. (4 + 3 + 3 + 5 + 5)

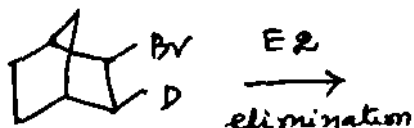
Or

- (b) (i) Write a note on 1, 3 - dipolar addition reactions.
- (ii) Discuss the mechanism of benzoin condensation and Mannich reaction in detail.
- (iii) Give a detailed account of hydroboration reaction.
- (iv) Give the product in the following reaction with correct stereochemistry: (4 + 8 + 5 + 3)



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12. (a) (i) Indicate the product in the following reaction, explaining its formation :



- (ii) What are the evidences that support the E, CB mechanism during an elimination process? Discuss in detail.
- (iii) Explain how the orientation of double bond during HX elimination is being influenced by various factors. (4 + 6 + 10)

Or

- (b) (i) Discuss the features of E1, E2 and E, CB mechanisms in detail and compare their characteristics.
- (ii) There is substantial ^{14}C isotope effect in cope Elimination. Why?
- (iii) The erythro isomer on pyrolytic elimination gives a transolefin. Account.
- (iv) Explain how ketene can be obtained from carboxylic acid.
- (v) Strong bases benefit elimination against substitution. Account. (10 + 2 + 3 + 2 + 3)

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[P.T.O.]

13. (a) (i) Discuss different methods of preparing nitrenes and explain their reactions.
- (ii) With adequate evidences, prove the mechanism of Von Richter rearrangement.
- (iii) Indicate how Sommelet Hauser rearrangement is a competitive process for Stevens rearrangement. When both rearrangements are possible in a substrate, how can one divert the substrate to undergo Stevens rearrangement? (12 + 4 + 4)

Or

- (b) (i) Discuss the scope, mechanism and applications of the following rearrangement reactions :
- (1) Demjanov rearrangement
 - (2) Dienone - Phenol rearrangement
 - (3) Pinacol - Pinacolone rearrangement.
- (ii) Explain how both $\text{Ph CH}_2 \text{CO CH}_2 \text{Cl}$ and Ph CH Cl CO CH_3 yield the same product on base treatment. (15 + 5)

14. (a) (i) Electron donating and electron withdrawing groups present in the aryl ring plays a vital role in determining the rate of the reaction as well as the nature of the product during Birch reduction. Illustrate these points with examples.
- (ii) Explain the course of hydride reduction on 4-t-butyl cyclohexanone indicating the correct stereochemistry of the final product.
- (iii) Discuss the methods available to oxidise the allylic positions without disturbing the double bonds.
- (iv) Explain the role of Cr VI reagents in oxidising alcohols. (6 + 4 + 5 + 5)

Or

- (b) Write notes on :
- (i) Role of DMSO in oxidation reactions.
- (ii) Oxidation aryl methanes
- (iii) Selectivity in manganese dioxide reactions. (7 + 7 + 6)