

(6 pages)

MAY 2015

**P/ID 40124/PCHD**

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Time : Three hours

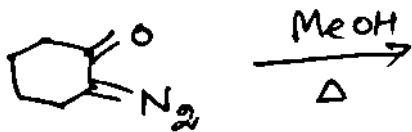
Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

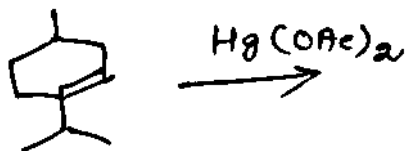
Answer ALL questions.

1. Propose a method of preparing methyl ketones from terminal alkynes.
2. Explain how wittig reagent is generated.
3. What happens when nitrile oxide reacts with an activated olefin? Write the equation.
4. In the case of chugaev reaction, the chances of isomerisation of resultant olefins are minimum, compared to the pyrolysis of acetates. Explain why?
5. During E2 elimination, diaxial elimination is more facile than axial equatorial or equatorial-equatorial elimination. Explain.
6. Pyrolysis of sec-butyl acetate gives 1-butene and 2-butene in 3:2 ratio. Account for this.

7. What happens when an  $\alpha$ -diketone is subjected to Baeyer villiger oxidation?
8. Write the product in the following reaction:



9. Indicate the reagent of choice for the conversion of acetophenone to phenylglyoxal.
10. Write the product in the following reaction

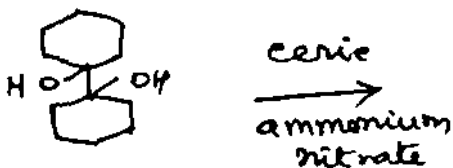
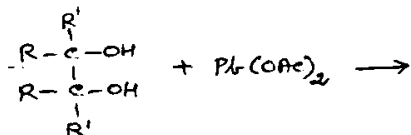


PART B – (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) Discuss the importance of selenium dioxide in allylic oxidation.
- (ii) NBS is the best brominating agent for allylic system. Illustrate this statement with example.

- (iii) Indicate the position of attack of bromine in the NBS reaction of  $CH_3CH_2CH_2CH=CHCH_3$ .
- (iv) Explain how oxalyl chloride helps in the oxidation of alcohols by DMSO.
- (v) Write the products in the following reaction.



(5+3+3+5+4)

Or

- (b) (i) Discuss the role of metal hydrides in reduction reactions.
- (ii) Explain how birch reduction can be used to partially reduce aromatic rings.

- (iii) Explain how MPV reduction is very selective for the reduction to secondary alcohol.
- (iv) Indicate how clemenson reduction and wolff kishner reduction are complimentary to each other. (5+5+5+5)
12. (a) (i) Explain the role of carbenes in simmon smith reaction.
- (ii) Discuss how hydroboration can be considered as a stereochemical alternate for hydration of olefins by mineral acid.
- (iii) Explain the stereochemical outcome of the bromination of cis and trans-2-butene.
- (iv) Highlighting the specificity of cyanide as the reagent, discuss the mechanism of benzoin condensation. (5+5+5+5)

Or

- (b) Write notes on
- (i) Mannich reaction
- (ii) Darzen reaction
- (iii) Michael addition (7+6+7)

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[P.T.O.]

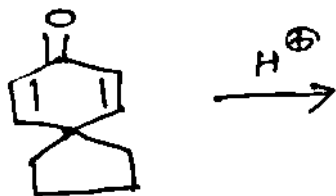
13. (a) (i) Account for the fact – that the first step of E<sub>1</sub>CB mechanism is reversible and presence of an electron withdrawing group at  $\beta$ -carbon increases the rate of E<sub>2</sub> elimination.
- (ii) Write an account of E<sub>1</sub>-E<sub>2</sub>-E<sub>1</sub>CB spectrum.
- (iii) Discuss the factors that decide the extent of branching in the olefins formed during elimination. (6+8+6)

Or

- (b) (i) Substitution is a competitive process for elimination both under acidic and basic conditions. Illustrate with examples. Discuss the factors that decide the ratio of substitution vs elimination.
- (ii) Write notes on
- (1) Cope elimination
- (2) Stereo chemical factors in elimination. (10+10)
14. (a) (i) Nitrogen is the by product in Von Richter rearrangement. In what way, this information is useful to analyse the mechanism of the reaction? Explain.
- (ii) Indicate how crossover experiments are useful in establishing the mechanism of Stevens rearrangement.

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- (iii) How can you ascertain the involvement of cyclopropanone intermediate in Farorski rearrangement? Discuss how both  $PhCH_2COCH_2Cl$  and  $PhCHClCOCH_3$  yield the same product on Farorski rearrangement?
- (iv) Predict the product in the following reaction with mechanism. (5+5+6+4)



Or

- (b) (i) Demjanov rearrangement can lead to ring expansion or ring contraction. Explain.
- (ii) Tricyclic alkanes with molecular formula  $C_{10}H_{16}$  are converted to adamantane on lewis acid treatment. Account for this transformation.
- (iii) Explain how nitrenes are generated. Discuss their stability and reactivity. (5+5+10)