D 6819-A

(Pages : 3)

Name..

### Reg. No

# THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2016

(CUCSS)

### Chemistry

# CH 3C 11-REAGENTS AND TRANSFORMATIONS IN ORGANIC CHEMISTRY

# (2015 Admissions)

Time : Three Hours

### Maximum : 36 Weightage

# Section A

# Answer **all** questions. Each question carries **1** weightage.

- 1. Identify the product arising from the reaction of 1-methoxycyclohex-l-ene with  $0_3$  in presence of dimethylsulfide.
- 2. How can 4-tert-butylcyclohexanone be selectively reduced to trans-4-tert-butylcyclohexanol predominantly ?
- 3. Identify the isomeric products that can be expected from styrene by its reaction with **9-BBN** followed by oxidation with alkaline hydrogen peroxide. Which would be the major product and why **?**
- 4. Write the structure of crown ethers that would complex with Na and K ions selectively. What are the synthetic uses of these complexes ?
- 5. Describe the mechanism of free radical polymerisation reactions.
- 6. Explain the general structure of block and graft copolymers.
- 7. How can 1-azetidine carboxylic acid be obtained from  $\gamma$ -aminobutyric acid ?
- 8. Write a method by which styrene can be converted to 2-phenyloxirane.
- 9. Write a synthesis of indole.
- 10. Write the mechanism of Wolff rearrangement.
- 11. Upon reaction woth perbenzoic acid , 4-MeO-C<sub>6</sub>H<sub>4</sub>-CO-Ph gets converted to mainly PhCO-O-C<sub>6</sub>H<sub>4</sub>-0Me-4. What is the mechanism ?
- 12. What product would form upon Beckmann rearrangement reaction from cyclohexyl methyl ketone CH<sub>3</sub>-CO-C<sub>6</sub>H<sub>11</sub> ? How ?

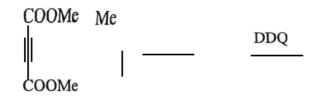
 $(12 \times 1 = 12 \text{ weightage})$ 

### Turn over

#### Section B

# Answer any eight questions. Each question carries weightage 2.

- 13. Which product would form by the reaction of CF<sub>3</sub>-CO-OOH with Me-CO-Chx (where Chx is cyclohex-1-yl) in CH<sub>2</sub>Cl<sub>2</sub>. What is the mechanism of the reaction ?
- 14. What are the advantages of CrO<sub>3</sub>-pyridine reagent as an oxidant ? Which product(s) would form in the oxidation of Me<sub>2</sub>C=CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH with CrO<sub>3</sub>-2Py ?
- 15. Comment on the reduction of : (i) Cyclohexanone and (ii) Cyclohex-2-en-1-one with one equivalent of NaBH<sub>a</sub>. Identify the product in each case.
- 16. Explain Noyori asymmetric hydrogenation with an example.
- 17. Identify the product A and B in the following reaction scheme :



- 18. What are phase transfer catalysts ? What are their typical structure ? Illustrate their application in synthesis with a specific example.
- 19. How can a dithiane be obtained from PhCHO? What would happen this 2-phenyl-1, 3-dithiane is further reacted with MeBr in presence of a n-BuLi followed by hydrolytic work up in presence of HgO?
- 20. Describe the structure and properties of natural and synthetic rubbers.
- 21. Comment on the advantages of solid phase peptide synthesis.
- 22. Describe the amino, carboxyl and **hydroxy** protecting groups used in peptide synthesis. How are these introduced and removed ?
- 23. Comment on the ring susbtitution reactions of pyrrole and pyridine.
- 24. (a) Cycloheptanone was monobrominated and the product was reacted with dry EtOH-NaOEt. What would be the final product ? How does it form ?
  - (b) What is Peterson reaction ?

 $(8 \ge 2 = 16 \text{ weightage})$ 

### Section C

# Answer any **two** questions. Each question carries weightage 4.

25. Describe with examples the mechanism, selectivity and use of the following oxidations :

(i) Dess-Martin oxidation ; (ii) Jacobsen epoxidation ; (iii) Riley oxidation ; and (iv) Swern oxidation.

- 26. Discuss the use of alkali metals in organic reductions in **variuos** reaction media including liquid ammonia.
- 27. What are the general methods to synthesise pyrazole, oxazole and thaizole derivaives?
- 28. Explain the mechanism of : (i) Heck ; (ii) Sonogashira ; (iii) Negishi and (iv) Stille couplings.

 $(2 \times 4 = 8 \text{ weightage})$