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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 ${\rm O_3}$ 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 γ-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_6H_4 -CO-Ph gets converted to mainly PhCO-O- C_6H_4 -0Me-4. What is the mechanism ?
- 12. What product would form upon Beckmann rearrangement reaction from cyclohexyl methyl ketone ${\rm CH_3\text{-}CO\text{-}C_6H_{11}}$? How ?

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

Section B

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

- 13. Which product would form by the reaction of $\mathrm{CF_3\text{-}CO\text{-}OOH}$ with Me-CO-Chx (where Chx is cyclohex-1-yl) in $\mathrm{CH_2Cl_2}$. What is the mechanism of the reaction ?
- 14. What are the advantages of ${\rm CrO_3}$ -pyridine reagent as an oxidant ? Which product(s) would form in the oxidation of ${\rm Me_2C=CH_2-CH_2-CH_2-OH}$ with ${\rm CrO_3-2Py}$?
- 15. Comment on the reduction of : (i) Cyclohexanone and (ii) Cyclohex-2-en-1-one with one equivalent of NaBH₄. 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?

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



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.

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