

C 4757

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Name.....

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2016

(CUCSS)

Chemistry

CH 2C 07—REACTION MECHANISM IN ORGANIC CHEMISTRY

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

Answer all questions.

Each question carries 1 weightage.

1. Which product(s) would form by the hydrolysis of 3-bromo-1-butene by aqueous sodium carbonate ? Explain.
2. Which alkene(s) would form in the EtONa/EtOH promoted elimination of $\text{Me}_3\text{C}-\text{CH}_2-\text{CMe}_2-\text{Br}$? If more than one forms, which one would be the major product ?
3. Which product would form if $1,2-(\text{N}\equiv\text{C}-\text{H}_2\text{C})-\text{C}_6\text{H}_4-(\text{CH}_2-\text{C}\equiv\text{N})$ is subjected to intramolecular Thrope condensation followed by hydrolysis ? Write the mechanism.
4. Which product would form from $\text{Ph}-\text{CO}-\text{Cl}$ on reaction with $n\text{-BuLi}$ at $(-)$ 78°C followed by hydrolysis ? Which other organoLi reagent can be used to react with the above product to form $n\text{-Bu}-\text{CMe}(\text{OH})-\text{Ph}$?
5. Identify the starting acyclic product arising from :
 - (i) Thermolysis ; and
 - (ii) Photolysis respectively dimethyl ester of *cis*-cyclohexa-1,3-diene-5,6-dicarboxylic acid.
6. Show that antarafacial thermal [1,3] migrations are allowed by Woodward-Hoffmann rules. Such rearrangements are however, rare. Why ?
7. 2-Nitrobenzaldehyde isomerizes on photolysis. Identify the product and show how does it form.
8. What is Patterno-Buchi reaction ? What is its use ?
9. Identify the photoproduct(s) that would arise by irradiating cyclohex-2-en-1-one.

Turn over

10. Describe the method to estimate the number of active hydrogens in a natural product.
11. Explain the classification of alkaloids and terpenes.
12. Describe the Emde degradative method.

(12 × 1 = 12 weightage)

Section B

Answer any **eight** questions.

Each question carries 2 weightage.

13. Describe the effect of :
 - (a) The substrate ; and
 - (b) The leaving group in S_N1 and S_N2 reactions.
14. Explain the mechanism and stereochemical course of S_E1 and S_E2 reactions.
15. How can the nitrenes Ph-N: and Ph-CO-N: be formed as reactive intermediates ? Write examples of their subsequent reactions.
16. Explain the mechanism and stereochemistry of pyrolytic eliminations.
17. (a) Isopropoxide anion in isopropanol can be used to convert a ketone to a secondary alcohol. Explain with mechanism.

(b) Stobbe condensation of acetone with diethyl succinate does not give either $\text{HOOC-C(=CMe}_2\text{)-CH}_2\text{-COOH}$ or $\text{EtOOC-C(=CMe}_2\text{)-CH}_2\text{-COOEt}$, but only $\text{HOOC-C(=CMe}_2\text{)-CH}_2\text{-COOEt}$. Explain why mechanistically.
18. Write an example each for esters that would hydrolyze by
 - (i) $A_{Al}1$; and
 - (ii) $B_{AC}2$ mechanism respectively.

Write the mechanism of each of these hydrolysis reactions.

19. Describe the mechanism of Mannich and Prins reactions.

20. Identify the products of the following concerted reactions:
- Thermal isomerization of 3-hydroxyhexa-1,5-diene ; and
 - Thermolysis of 1-methylcyclohexene . Write mechanisms.
21. Apply FMO method to derive the selection rules for the $[4n]$ and $[4n+2]$ electron, thermal and photochemical electrocyclisations.
22. Write the mechanism of :
- Claisen rearrangement.
 - Cope rearrangement .
 - Diels-Alder reaction ; and
 - Ene reaction.
23. Which products would form by the photolysis of
- $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$; and
 - $\text{H}_2\text{C}=\text{CH}-\text{C}(\text{Me})_2-\text{CH}=\text{CH}_2$? Write the mechanism of the product formation.
24. Discuss the conversion of cholesterol to testosterone.

(8 × 2 = 16 weightage)

Section C

Answer any two questions.

Each question carries 4 weightage.

25. Discuss the important mechanisms of aromatic nucleophilic substitutions.
26. Discuss the factors that control the orientation and stereochemistry of the C=C bond formation in E2 eliminations. Consider the size and nature of nucleophile and leaving group as well as substrate structure in your answer.
27. Write brief notes on :
- Norrish I and II photocleavages ; and
 - Hoffmann-Loeffler-Freytag reaction.
28. Write the salient steps in the synthesis of longifolene.

(2 × 4 = 8 weightage)