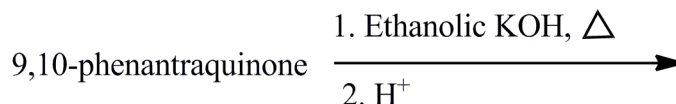


SEMESTER-V (Hons)

CEMACOR12T: ORGANIC CHEMISTRY-V

Carbocycles and Heterocycles

1. What are polynuclear aromatic hydrocarbons? Give examples.
2. Outline the synthesis of Phenanthrene.
3. Outline Bardhan Sengupta Synthesis of phenanthrene.
4. 1, 2-bond of naphthalene has greater double bond character than 2,3- bond. Explain.
5. Write the product with plausible mechanism of the following reaction:



6. Outline Haworth synthesis of naphthalene
7. Anthracene is more reactive than naphthalene
8. Anthracene can participate in Diels-Alder reaction, whereas phenanthrene does not. Explain.
9. Devise an experiment to show whether the rearrangement of naphthalene-1-sulphonic acid to 2- sulphonic acid is intramolecular or intermolecular.
10. Phenanthrene reacts with dichlorocarbene in its C-9/C-10 positions but anthracene does not. Explain this observation.
11. How many methylphenanthenes are possible?
12. Show would you synthesize these methylphenanthenes starting from naphthalene?
13. How would you prepare the following compounds by the Haworth synthesis?
(a) 7-chloro-1-methylnaphthalene (b) 2-Methylnaphthalene (c) 1-Ethyl-4- methylnaphthalene
14. Electrophilic substitution and addition reaction of anthracene occur preferentially at the 9 and 10-positions. Explain.
15. How one can get pyrrole ring by taking EAA as one of the starting materials? Write the mechanistic details.
16. Electrophilic attack takes place at C-2 in pyrrole but C-3 in indole. Explain.
17. In the Fischer indole synthesis a phenylhydrazone is converted to an indole by action of acid. Write the mechanism involved.
18. Discuss the following methods of synthesis

(i) Hantzsch synthesis of pyridine

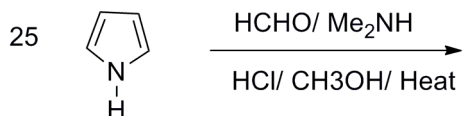
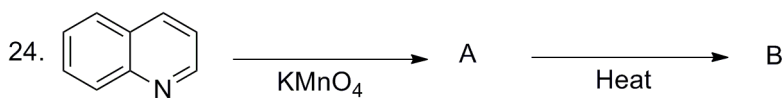
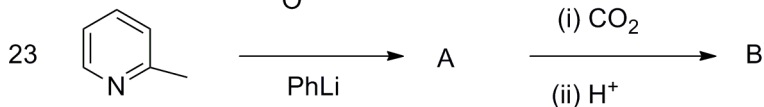
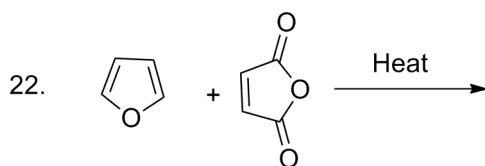
19. (ii) Skraup synthesis of quinoline

20. How would you carry out the following transformation?

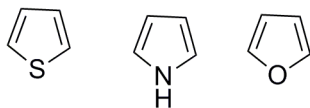


21. Arrange furan, pyrrole and thiophene in order of increasing aromaticity and explain your reasoning.

22. Identify the products of the following reactions with proper explanation;



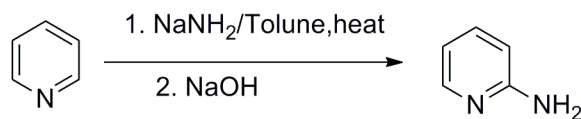
27. Compare the value of dipole moment of following heterocycles:



28. Outline the Bischler-Napieralski synthesis of isoquinoline.

29. Pyridine N-oxide not only is reactive towards electrophilic substitution, but also seem to be reactive towards nucleophilic substitution.

30. Amination of pyridine occurs on heating it heating with sodamide in dry toluene at 1100C. This is referred to as the Chichibabin reaction.



Discuss the mechanism of the reaction.

Cyclic Stereochemistry

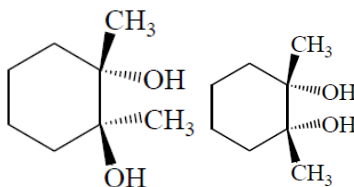
1. Draw the conformational structures for *cis* and *trans* 1,3-dimethylcyclohexanes.
2. “Cyclopropane is highly strained”—account.
3. Write down the preferred conformation of *cis* 1,3- cyclohexane diol.
5. Explain what will happen when *p*-toluene sulphonates of *cis* and *trans* 2-*p*- toluene sulphonyl cyclohexanol is reacted with NaOH?
6. Acetolysis of both *cis*- and *trans*-tosylate shown below give the same diacetate. Explain



7. *trans*-1,3-Di-*tert*-butylcyclohexane prefers twist boat conformation and readily passes to its *cis*-isomer on heating with Pd/C. Explain
8. The *cis*-1,2-dimethylcyclohexane is less stable than its *trans* isomer, but *cis*-1,3-dimethylcyclohexane is more stable than its *trans* isomer. Draw the most stable conformations of both and explain.
9. Both *cis*- and *trans*-1,2-dibromocyclohexanes give the same product when heated with iodide ion. Identify the product and explain the reactions.
10. Explain the fact that *trans*-4-*tert*-butylcyclohexyltosylate undergoes bimolecular elimination with thiophenate, but not with much stronger base ethoxide.
11. State Baeyer’s angle strain theory. Limitation of Baeyer’s angle strain theory.
12. Compare the acid strength of *cis* and *trans* isomer of cyclohexane-1,2-dicarboxylic acid
13. Compare the rate of chromic acid oxidation of *cis* and *trans* 4-*t*-butylcyclohexanol.
14. Compare the rate of hydrolysis of *cis* and *trans* isomer of ethyl 4-*t*-butylcyclohexane carboxylate.
15. What will happen when *cis* and *trans* isomer of 4-*t*-butylcyclohexyl amine is treated with NaNO₂/HCl?
16. Compare the rate of reaction of *cis* and *trans* isomer of 1,2-dibromocyclohexane with NaI.
17. Explain the reaction of 2-bromo-4-phenylcyclohexanol with either NaOH or Ag₂O.

18. What is the proof of NGP?

19. Predict the products when different isomers of 1,2-dimethylcyclohexane-1,2-diol reacted with 60% H_2SO_4 ?



20. Indicate symmetry properties of cyclohexane chair and cyclohexane boat.

21. Draw the conformational structures for cis and trans 1,2-dimethylcyclohexanes. Compare enthalpy contents and state optical properties of the conformers.

22. Propose a mechanism for interconversion of cyclohexane chair.

23. Write down the preferred conformation of cis-4-hydroxyl cyclohexane carboxylic acid. What happens when it is heated?

24. Indicate the preferred conformation of 2-bromo cyclohexanone.

25. Draw assigning reason the preferred conformation of cis- and trans-1,4-tert-butyl cyclohexane carboxylic acid. Comment on the relative strength of the two acids in the aqueous medium.

26. Draw the preferred conformation of trans-1,3-ditertiary butyl cyclohexane. Explain.

27. What is anomeric effect?

28. Cyclopropane is more reactive than cyclobutane and cyclopentane.

29. Compare the dipole moment of 1,2-dibromocyclohexane.

30. Compare the basicity of cis and trans isomer of 4-t-butylcyclohexyl amine.

Pericyclic reaction

1. What is pericyclic reaction?

2. Write down the characteristics of pericyclic reaction.

3. Draw molecular orbital representation of ethylene.

4. Draw molecular orbital representation of but-1, 3-diene.

5. Draw MO's of 1,3, 5 -hexa triene.

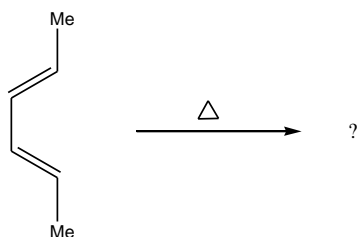
6. What is electrocyclic reaction?

7. Describe stereoselectivity of electrocyclic reaction.

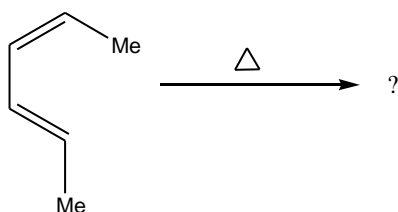
8. Define stereoselectivity of 4 pi system under photochemical and thermal condition.

9. Define stereoselectivity of 6 pi system under photochemical and thermal condition.

10.



11.



13. What is cycloaddition reaction? Give examples.

14. Describe selection rule for cycloaddition reaction.

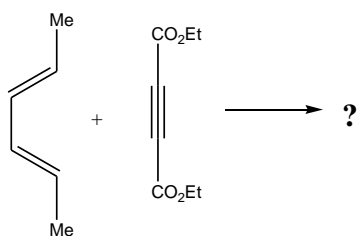
15. Using FMO approach, define stereoselectivity of 2pi + 2pi addition.

16. Using FMO approach, define stereoselectivity of 4pi + 2pi addition.

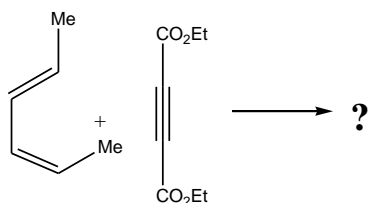
17. Describe the stereochemistry of Diels-Alder reaction of cyclopentadiene with maleic anhydride.

18. Define secondary orbital interaction with an example.

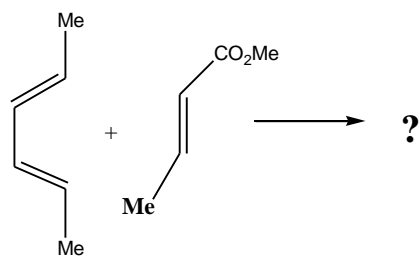
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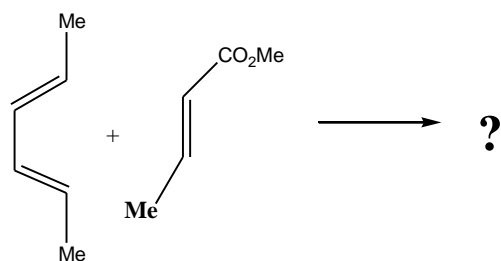
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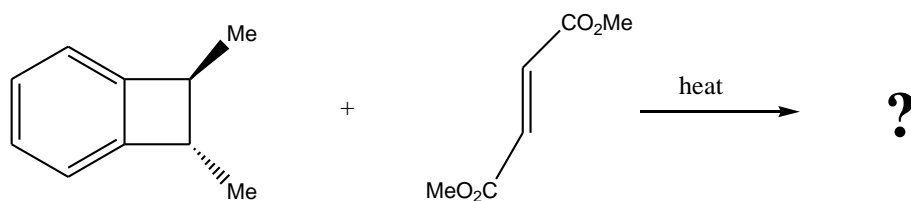
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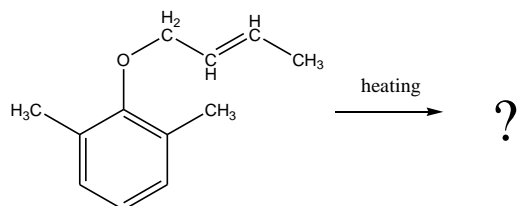
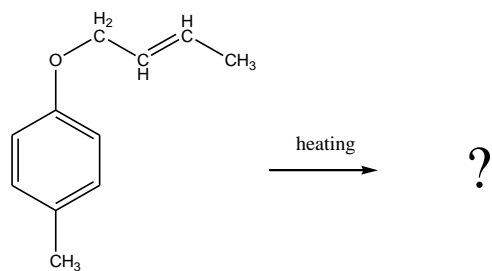
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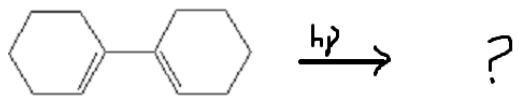
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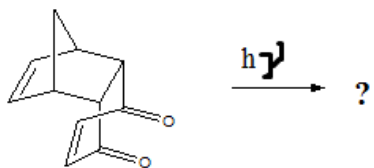
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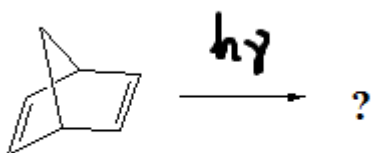
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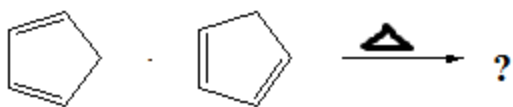
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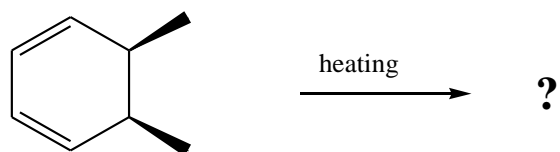
28.



29. Write down the major and minor products.



30. Predict the product of the following reaction and show the FMO interactions.



Carbohydrates

1. Draw carbohydrate tree starting from D-Glyceraldehyde
2. Write down furanose structures of D –Glucose.
3. Write down pyranose structures of D –Mannose
4. Write down the Fisher projection of D – Glucose and D – Mannose.
5. What are epimers ? Give examples.
6. Describe anomeric effect.
7. Describe mutarotation of glucose.
8. Define Haworth representations of D-Glucose.
9. Describe Fischer's proof of configuration of (+)-glucose.
10. What happens when glucose is subjected to bromine water oxidation?
11. What happens when glucose is subjected to HNO_3 oxidation?
12. Describe Lobry de Bruyn-van Ekenstein rearrangement.
13. What happens when aldose is subjected reduction?
14. Describe Kiliani-Fischer method for stepping-up of aldose.
15. Describe Ruff's & Wohl's method for stepping-down of aldose.
16. Describe end-group-interchange of aldoses.
17. Define acetonide (isopropylidene) protection of aldose.
18. Define benzylidene protection of aldose.
19. Explain how ring size can be determined for monosaccharides.
20. What is glycosidic linkage of dipeptide.
21. What is Polysaccharides?
22. Write down the structure of starch?
23. Describe use of starch as an indicator in titrimetric analysis.
24. Write down the structure of sucrose.
25. Describe inversion of cane sugar.
26. Give example of C-2 epimers.
27. What happens when D-fructose is subjected to NaBH_4 reduction?
28. Why glucose and fructose both gives positive test with Tollen's reagent.

29. E, F and G are the three aldohexoses. E and F yield D-sorbitol when they are catalytically hydrogenated. E and F yield different osazones when treated with excess phenyl hydrazine. F and G give the same osazone but different alditols. Give structures of E, F and G assuming that F and G are D-aldohexoses.

30. An aldopentose [P] can be oxidized with dil HNO_3 to an optically active aldaric acid. A Kiliani-Fischer synthesis starting with [P] gives two new aldoses [Q] and [R]. Aldose [Q] can be oxidized to an optically inactive aldaric acid, but aldose [R] is oxidized to an optically active aldaric acid. Assuming the D-configuration, give the structures of [P], [Q] and [R] and also justify the assignments.

Biomolecules

1. Make a table for 20 natural alpha amino acids capturing their name, structure, nature, three letter symbol & one letter symbol.
2. Describe Gabriel synthesis for alpha amino acid with suitable example.
3. Describe Strecker synthesis for alpha amino acid with suitable example.
4. Write down the reaction of ninhydrin with amino acid.
5. What is isoelectric point?
6. What are zwitterions?
7. Write the full structure of N-Boc -valine
8. Write down full structure of N-CBz -Phenyl alanine.
9. Draw the full structure of the peptide Ala-Phe.
10. Design a suitable chemical synthesis for the peptide Ala-Phe in details showing all chemical reactions
11. Describe solid phase synthesis (using Merrifield resin) for the peptide Ala-Phe-Val-Leu in details showing all chemical reactions (No mechanism required)
12. Describe Sanger method of protein sequencing.
13. What is Dansyl chloride method of protein sequencing
14. Describe Edman method of protein sequencing.
15. Compare advantage and disadvantages of Sanger method, Dansyl chloride method and Edman method of protein sequencing.
16. Describe use of CNBr in specific cleavage of peptides

17. Write down the name and structure of pyrimidine bases.
18. Write down the name and structure of purine bases.
19. Differentiate nucleosides and nucleotides.
20. Describe double helical structure of DNA.
21. Explain complimentary base-pairing in DNA.
22. Differentiate between DNA and RNA
23. Write down the names of different types of RNA.
24. Describe the basic structure of a nucleotide.
25. What types of bases are present DNA and RNA respectively?
26. Differentiate between endopetidase and exopeptidase.
27. Describe secondary structure of DNA.
28. What is Watson and Crick double helix model?
29. Compare alkaline hydrolysis of DNA and RNA.
30. Write down the mechanism for acid catalysed hydrolysis of nucleosides.