STUDY MATERIAL

Dumkal College
Basantapur Dumkal

Course Code: CHEMHT-14

Semester: VI (Hons)

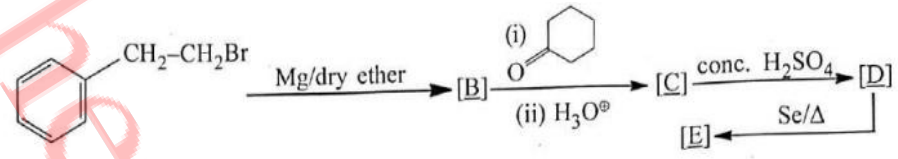
Name of the Teacher: Md Muttakin Sarkar

Name of the Department: Chemistry

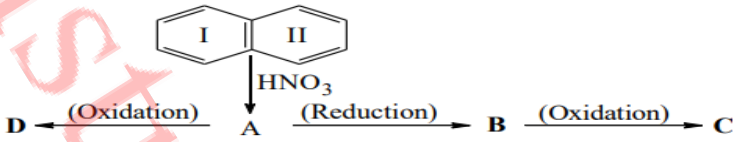
B.Sc 6th Sem Organic Chemistry Question paper

Carbocycles

1. Anthracene is more reactive at what positions and why?
2. Why 1,2-bond of naphthalene is shorter than 2,3-bond?
3. Why 9 or 10 position of anthracene is more reactive than any other position?
4. Identify [B] to [E] of the following sequence of reactions



1.(a) Complete the following series of reactions and indicate at what conclusion would you achieve from it regarding the structure of naphthalene :

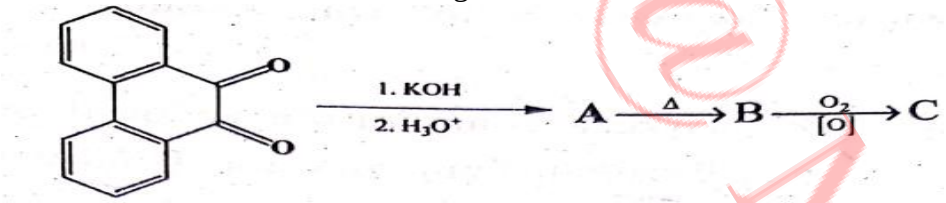


(b) How would you synthesise anthracene taking Diels-Alder reaction as one of the steps involved in the synthesis? 3+2

1.a) Explain why anthracene cannot be prepared by succinolation of naphthalene.

b. How can you convert naphthalene into 2-bromonaphthalene? Explain with mechanism. 2+3

3. What are A, B, C of the following reactions?



4. Give a comparative account on the Bardhan-Sengupta and Bogert-Cook methods of synthesis of Phenanthrene. What is the side product of them?

5. (a) How is phenanthrene synthesised using cyclohexanone and bromobenzene as starting materials? Mention all the steps.

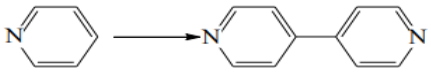
(b) 'Naphthalene undergoes electrophilic substitution preferentially at 1-position.' Jusitfy the statement. 3+2

6.(a) Explain why anthracene cannot be prepared from naphthalene by Friedel-Crafts reaction with succinic anhydride.

(b) Write down the mechanism of bromination of phenanthrene. 3+2

Heterocycles

1. Write the structure of the product when 2-methylfuran is treated with DMF-$POCl_3$.
2. Write appropriate reagent for the following conversion :



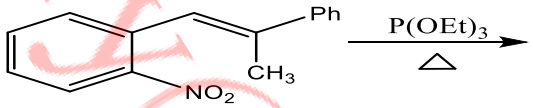
3. Generally, pyridine does not allow Friedel-Craft reaction. Explain.
4. Decarboxylation of quinoline-2-carboxylic acid is far easier than quinoline-3-carboxylic acid - Explain.
5. Directions of dipole moments in furan and pyrrole are different. Explain.
6. Compare the reaction of pyrrole and pyridine with peroxybenzoic acid.
7. Explain why pyrrole undergoes protonation on carbon instead of nitrogen in presence of acid.
8. 'Pyridine is completely soluble in water'. Justify the statement.
9. Furan undergoes Diels-Alder reaction, but pyrrole does not. Explain
10. Why indole-3-aldehyde cannot undergo Cannizzaro reaction?
11. What happens when pyridine-N-oxide is heated with acetic anhydride followed by hydrolysis of the product?
12. Write down the mechanism of the following reaction with plausible mechanism :

Indole-2-acetic acid $\xrightarrow{\text{Acidulated water}}$

1.(a) Identify the starting materials and show the mechanism of the reaction to obtain the following product involving reaction indicated in the parantheses : 3-Methylindole (Fischer indole synthesis)
(b) Quinoline-2,3-dicarboxylic acid smoothly forms only quinoline-3-carboxylic acid via a selective decarboxylation. — Explain. 3+2

2. (a) How will you prepare 3-nitropyrrole exclusively from pyrrole?
(b) Carry out conversion of pyridine to 4-nitropyridine. 3+2

3.a) In the Fischer indole synthesis, a phenyl hydrazone is converted into an indole by the action of. an acid through [3, 3]- sigmatropic rearrangement. Explain.
b. Outline an experiment to decide which of the two nitrogens of phenylhydrazone is lost during the above reaction. c. Predict the product in the following reaction:



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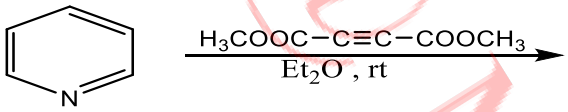
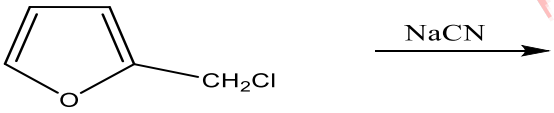
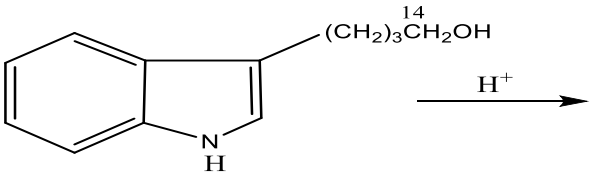
d. Predict the product(s) with plausible mechanism:



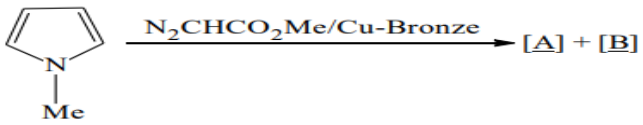
3+2+3+2

4. How would you prepare 2-methyl-4- hydroxyquinoline and 4-methyl-2-hydroxyquinoline using aniline and ethylacetoacetate (EAA)? Give mechanisms of the reactions involved.
5. Write down the product(s) of the following reactions:

a) 

b) 

6.(a) Outline Hantzch synthesis of diethyl – 2,6-dimethylpyridine – 3,5-dicarboxylate.
(b) Identify [A] and [B] in the following reaction and explain their formation. 3+2



7.(a) Explain the difference in behaviour when 1– and 3–methylisoquinoline are treated with n-Buli. Identify [G] in the following reaction. 1–Methylisoquinoline $\xrightarrow[2.PhCHO]{1.BuLi}$

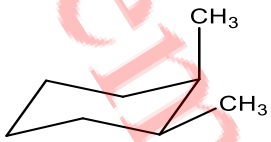
(b) How 4-nitropyridine is prepared from pyridine? 3+2

8. (a) Show the steps of the following reaction along with plausible mechanism.

$PhNH_2 + PhNO_2 + HOCH_2 - CH(OH) - CH_2OH \xrightarrow{H_2SO_4\ /FeSO_4}$ Quinoline + $PhNH_2 + H_2O$

Why can't $CH_2 = CH - CHO$ itself be used instead of $HOCH_2 - CH(OH) - CH_2OH$?

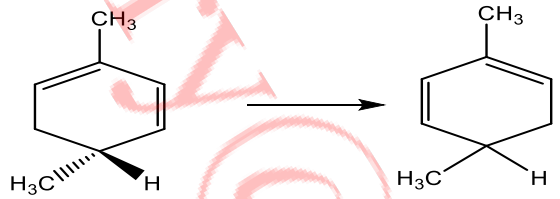
(b) Identify the product(s) of the following reaction with proper explanation : 3+2



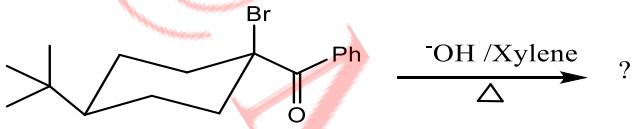
Cyclic Stereo chemistry

1. Write down the preferred conformation of 1-methyl- 1-phenylcyclohexane and justify your answer.

2. Suggest mechanism for the following transformation and depict the absolute stereochemistry of the chiral centre.



3. Give the product of the following reaction along with the mechanism:



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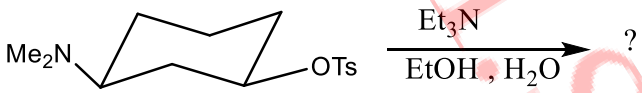
4. Predict the product(s) with stereochemistry of the following reaction:

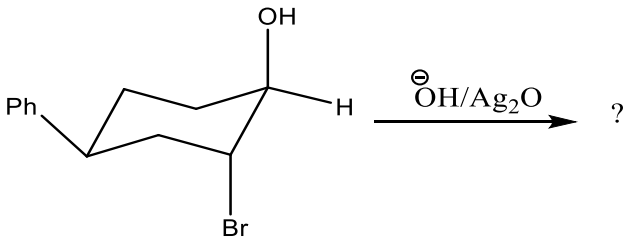


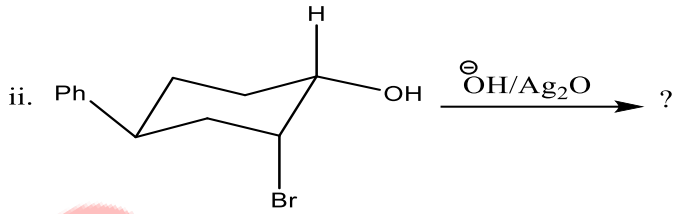
3

5. Write down the most stable conformation of *trans*-1, 4-dimethylcyclohexane.

6.a) Explain the fact that trans-4-tert butylcyclohexyl tosylate undergoes bimolecular elimination with the bases bromide and thiophenolate, although not with the much stronger base ethoxide.

b) Write down the products of the following reactions with plausible mechanism :

i. 

ii. 

2+3

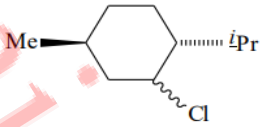
7. (a) Trans-2-aminocyclohexanol on treatment with aqueous NaNO2 and dilute HCl gives cyclopentane carboxaldehyde while its cis-isomer gives mixture of products. — Explain.

(b) Explain why cis-4-hydroxycyclohexanecarboxylic acid lactonises on heating but the trans-isomer does not. 3+2

8. Draw the boat conformation of cyclohexane in Newman projection.

9. Calculate the value of angle strain in cyclopropane employing Baeyer strain theory.

10. (a) Two diastereoisomers of the following compound differ in the orientation of Cl atom. One isomer undergoes E_2 dehydrohalogenation 200 times faster than the other. Draw the conformations of the two diastereoisomers and explain the observation.



(b) Predict the product of the above said reaction with mechanism. 3+2

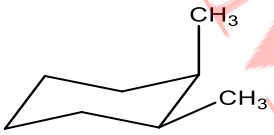
11.a) Predict the product(s) with suitable mechanism :

(b) Which one of the following is stronger acid and why? cis-4-tert butyl-cyclohexanecarboxylic acid or trans-4-tert butyl-cyclohexanecarboxylic acid. 3+2

12. How would you synthesise phenylalanine employing Erlenmeyer azlactone synthesis? Is the synthesis stereospecific in nature?

13. Give an example of a substituted cyclohexane system where the conformation with axial substituent is more stable than the equatorial one.

14. What are the number of gauche-butane interactions present in the following compound?



15.(a) cis-cyclohexane-1,3-diol is oxidized by HIO_4, more rapidly than corresponding trans-isomer. Explain.

(b) What happens when cis- and trans- isomers of 3-hydroxycyclohexanecarboxylic acid are heated separately? 3+2

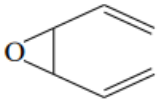
16. Provide an explanation for the fact that under the same condition (NaOEt/EtOH at 75°C), the cis-isomer of 4-tertiarybutylcyclohexyl tosylate undergoes a facile E2 elimination reaction, but the trans-isomer does not.

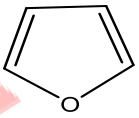
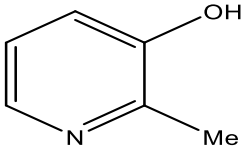
Pericyclic Reaction

1.Define pericyclic reaction.

2. [2+2] Cycloaddition reaction is not a thermally favourable process— why?

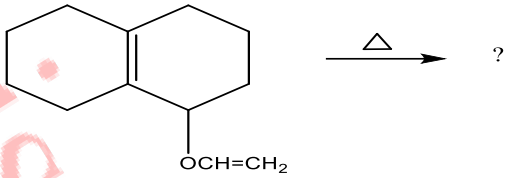
3. Write down the product of thermal sigmatropic reaction of the following molecule :



4. Transform  into 

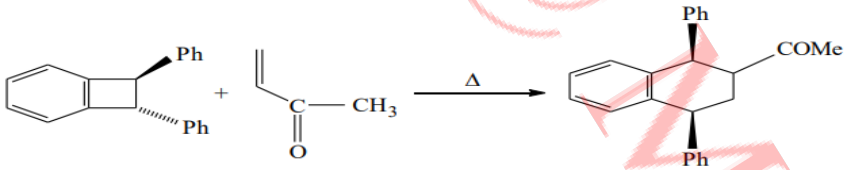
5. Explain endo-selectivity in the Diels-Alder reaction with proper example.

6. Predict the product with mechanism:



7. Explain the following observation:

8. Rationalize the following reaction by FMO , showing the steps of the reaction.

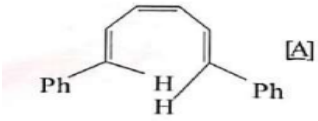


9. Why is the conrotatory ring closing of butadiene thermally allowed?

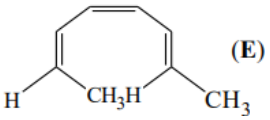
10. Why 2, 3-ditertiarybutyl-buta-1, 3-diene does not undergo Diels-Alder reaction?

11. Why is conrotatory ring closure of (4n+2)π system photochemically allowed?

12. Write the products when [A] is cyclised thermally and photochemically separately. Show FMO interaction and Woodward-Hoffman rule to explain the formation of products.



1.(a) Predict the fate of the following compound E in the case of photochemical electrocyclic ring closure and explain the reaction on the basis of FMO theory :



(E)

(b) Thermal [1, 5] – H shift is facile but thermal [1, 3] – H shift is not observed. — Explain. 3+2

2. Using frontier orbital overlap, explain why Diels-Alder reaction between 1, 3-butadiene and ethylene is thermally allowed but not catalysed by UV light.

3(a) (2E, 4E)-Hexadiene is being separately cyclised by thermal and photochemical processes. Explain the formation of products showing FMO interaction.

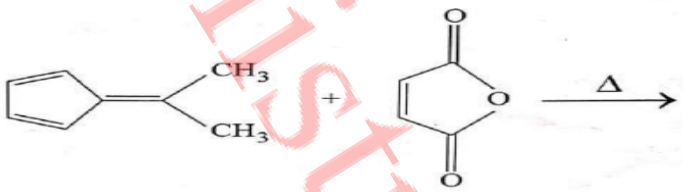
(b) Account for the fact that, in cycloaddition reaction of cyclopentadiene with maleic anhydride the less stable endo adduct predominates. 3+2

4. Depict the FMO interactions for $[\pi_S^4 + \pi_S^2]$ involving thermally allowed process. Explain why the reaction does not take place under photochemical conditions.

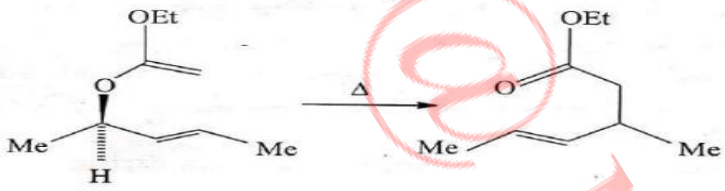
(b) Predict the product(s) with stereochemistry of the following reaction :

(E, E) – $CH_3CH = CHOCH_2CH = CHCH_3 \xrightarrow{\Delta}$ 3+2

5.a) Predict the product of the following reaction and justify the formation in terms of FMO interaction.



b. Suggest mechanism for the following transformation and depict the stereochemistry of the chiral centre.



Carbohydrates

1. How would you distinguish chemically between ribose and 2-deoxyribose?

2. What is the effective structural unit necessary for osazone formation? 3. Name a reagent by which D-glucose and D-fructose can be distinguished chemically.

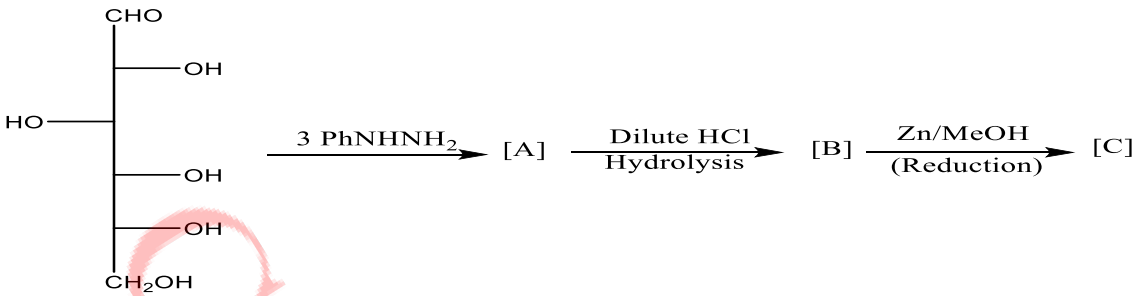
4. Neither the glucose nor the fructose part of sucrose exhibits mutarotation. What information regarding the structure of sucrose is obtained from the above fact?

5.Draw the most stable chair conformation of methyl-D-glucopyranoside.

6. Why fructose remains in equilibrium with glucose in aqueous NaOH?

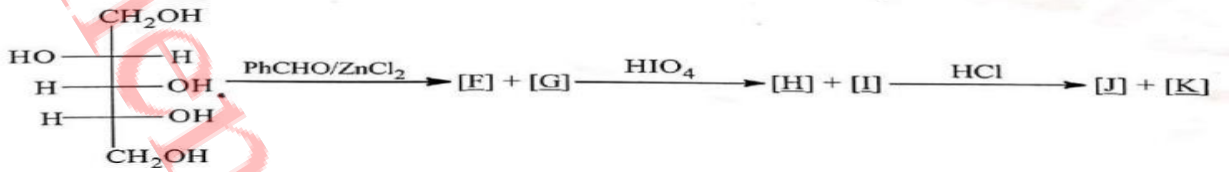
7. Write down the names of two aldohexoses which produce same osazone.

8. Identify [A], [B] and [C] in the following sequence of reactions :



9. Why do glycosides not react with either Fehling's or Tollens' reagent?

10. Give the structures [F] to [K] of the following reaction :



1.(a) Determine whether D-glucose possesses a furanose or a pyranose ring structure from the final product in the following reaction sequence :

D-glucose $\xrightarrow{MeOH/HCl}$ A $\xrightarrow{Me_2SO_4/NaOH}$ B $\xrightarrow{dil.\ HCl}$ C $\xrightarrow{HNO_3\ (Oxidation)}$ 2, 3-Dimethoxysuccinic acid + 2, 3, 4-Trimethoxyglutaric acid

(b) The mutarotation of D-glucose in an aprotic solvent does not occur in the presence of pyridine alone or cresol alone; when both cresol and pyridine are present together, mutarotation of glucose takes place. Explain the observation with mechanism. 3+2

2.a) Mutarotation is more rapid when catalyzed by 2-pyridone compared to the mixture of phenol and pyridine - Explain.

b. β-D-glucopyranose undergoes oxidation with bromine-water 250 times as fast as that of α -D-glucopyranose – Explain. 2+3

3. (a) An aldopentose [C] is oxidised by nitric acid to an optically active aldaric acid [D]. On Ruff degradation of [C], an aldotetrose [E] is obtained which is oxidized to optically inactive aldaric acid [F]. Assuming the aldopentose [C] to be a D-sugar, write down the configurations of [C], [D], [E] and [F].

(b) Predict the product(s) and number of moles of HIO4 consumed when HIO4 reacts with methyl-α-D-fructofuranoside and methyl-α-D-glucopyranoside separately. 3+2

4. (a) Convert open chain structure of D-galactose to β-D-galactopyranose and explain which form is more stable between $^4C_1$ and $^1C_4$.

(b) Why specific rotation of B-D-galactopyranose changes rapidly when dissolved in water? 3+2

5.(a) (i) Account for the formation of diketal from the reaction of D-glucose with acetone in sulphuric acid.

(ii) Using the above technique convert D-glucose to D-3-benzylglucose.

(b) Convert D-arabinose to D-mannose. 3+2

Biomolecules

1. dentify the hydrogen bonds between the conjugate base pairs of DNA. 2. What is ninhydrin? Mention its reaction with α – amino acid.

3. Outline a chemical method for the 'determination of N-terminal amino acid of a protein.

4. Draw the complete structure of the peptide Gly-Phe-Ser.

5. Write the different interactions responsible for stabilizing the secondary structure of a protein.

6. Write down the scheme for the synthesis of the dipeptide, Gly-Ala, using DCC promoted peptide bond formation. 7. How does RNA differ from DNA with respect to its structure and function?

8. How lysine (pI = 9·6) can be separated from glycine (pI = 5·97) by electrophoresis?
9. Explain why the compound aspartic acid shows three pKa values.
10. Draw the structure of a purine base mentioning its name.
11. How is the Boc group of an amino acid derivative removed?
12. Designate the structures of possible dipeptides which on hydrolysis afford one mole of glycine and one mole of alanine.
13. What are the bases common both in DNA and RNA? (Structures not needed).
14. Write down the structure of one pyrimidine base present in RNA only.

1. (a) How would you determine the N-terminal residue of a peptide following Edman's degradation method? Why is the method preferred over Sanger's method?
(b) Guanosine is hydrolysed more rapidly than adenosine in dilute acid solution. Explain why. 3+2 2.
(a) Write down a scheme for the synthesis of Gly-Ala using DCC promoted peptide bond formation. Give mechanism for the DCC coupling reaction step. (b)
In an electric field, towards which electrode, would an amino acid migrate at a (i) pH < pI, (ii) pH > pI.
Explain. 3+2
3. (a) How would you synthesise Phe-Gly-Ala applying Merrifield methodology using Boc as N-protecting group?
(b) What happens when alanine is heated with acetic anhydride in pyridine as solvent? Give the mechanism involved in the reaction. 3+2
4.(a) Write down Sanger's degradation method for the N-terminal amino acid determination of the tripeptide ala-gly-phe.
(b) Write down the reaction of proline with ninhydrin. 3+2
5.(a) Synthesise glutamic acid via phthalimidomalonic ester synthesis.
(b) Provide the structures of the nucleosides of
(i) Deoxyribose with cytosine (ii) Ribose with guanine. 3+2
6.(a) Write down the mechanism of hydrolysis of adenosine and uridine. Which one undergoes more rapid hydrolysis in aqueous acid? Give reason in favour of your answer.
(b) Write down the structure of cyclic AMP. When it is treated with aqueous sodium hydroxide, the major product is adenosine-3'-monophosphate rather than adenosine-5'-monophosphate. Explain the observation. 3+2

3+2