2025

CHEMISTRY — HONOURS

Paper : DSCC-12

(Organic Chemistry – IV)

Full Marks : 75

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Question nos.* 1, 2, 3, 4** (compulsory) and attempt ***any four questions from the rest (***Question nos.* 5** to **10**).

1. Answer ***any ten*** questions : 2×10

(a) Give the synthetic equivalent of $\overset{\ominus}{C}H_2NH_2$ and $H_2\overset{\oplus}{C}-CH_2-OH$.

(b) "C_1 of naphthalene is more reactive compared to C_2 towards electrophilic substitution reaction."— Why?

(c) Which one is more basic and why— pyrrole or pyridine?

(d) Name the reagent for protection of ROH and reagent for its deprotection.

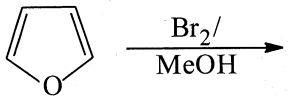
(e) Discuss the optical activity of *cis*- and *trans*-1, 3-dimethylcyclohexane.

(f) 'Furan and pyrrole have the opposite directions of the dipole moment.'— Justify.

(g) Mention the product formed when Ethylacetoacetate (EAA) is treated with *n*-Buli (2 eq) followed by MeI (1 eq). Explain.

(h) What happens when *cis*- and *trans*-4-hydroxycyclohexane-1-carboxylic acids are separately heated? Justify your answer.

(i) Identify the product(s) of the following reaction with mechanism.



(j) Electrophilic substitution in pyrrole takes place at 2-position but in pyridine at 3-position— why?

(k) Draw the resonating structures of naphthalene and apply Fries rule to identify the most stable structure.

(l) Discuss FGA with reference to retrosynthesis with a proper example.

2. Write short note on :

(a) Retrosynthesis (using the following points) :

(i) Define illogical electrophile with one example.

(ii) Define illogical nucleophile with one example.

(iii) Define functional group interconversion (FGI) with an example. 1½+1½+2

Or

(b) Umpolung (using the following points) :

(i) Definition

(ii) Synthesize $PhCOCH_3$ from PhCHO using umpolung technique

(iii) Mention two criteria for choosing a good protecting group. 1+2+2

3. Write short note on :

(a) Bardhan Sengupta synthesis of Phenanthrene (using the following points) :

(i) Synthetic pathway showing all the steps involved.

(ii) Write down the mechanism of bromination of Phenanthrene. 3+2

Or

(b) Skraup synthesis of quinoline (using the following points) :

(i) Synthetic pathway mentioning all the steps involved.

(ii) Explain the following facts :

(I) Why can't $H_2C = CH - CHO$ be directly used instead of glycerol?

(II) What is the role of $FeSO_4$ in the above reaction? 3+1+1

4. Write short note on :

(a) Dynamic stereochemistry of cyclohexane (using the following points) :

(i) Chiral pathway of cyclohexane ring flipping.

(ii) Comparison of conformational free energy of mono halogen substituted cyclohexanes (Cl, Br, I). 3+2

Or

(b) Anancomeric effect of substituted cyclohexane (using the following points) :

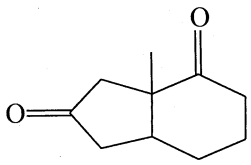
(i) Definition with one example.

(ii) Draw the most stable conformation of the following compounds with justification.

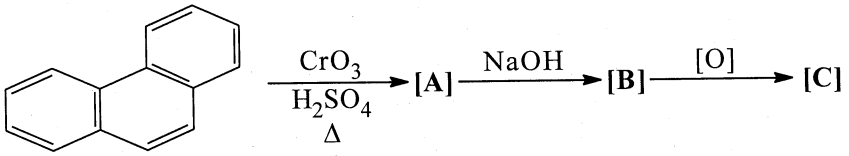
I. *cis*- 1,4-di*tert*-butylcyclohexane

II. *trans*- 1,3-di*tert*-butylcyclohexane. 2+3

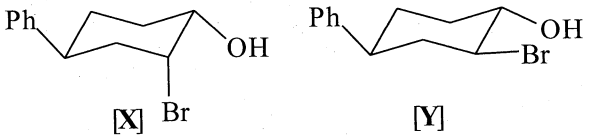
5. (a) Give a plausible retrosynthetic pathway for the molecule shown below along with its forward synthesis.



(b) Complete the following sequence :



(c) "[X] gives a cyclohexanone derivative with Ag_2O but [Y] undergoes ring contraction."— Why? 4+3+3

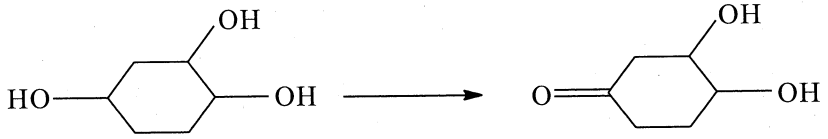


6. (a) (i) Outline Hantzch synthesis of diethyl-2,6-dimethyl pyridine-3,5-dicarboxylate.

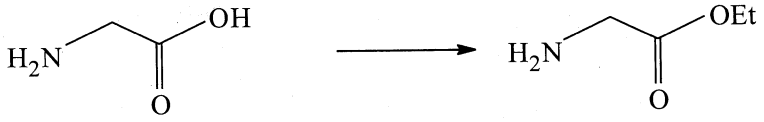
(ii) Write the structure of the final product formed when pyridine is treated with $NaNH_2$ in toluene and then quenched with water (No mechanism required).

(b) Using suitable protecting group, how will you bring about the following transformations?

(I)



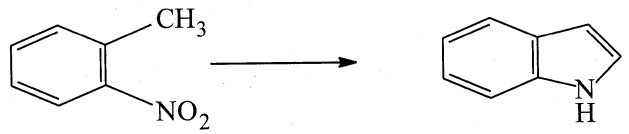
(II)



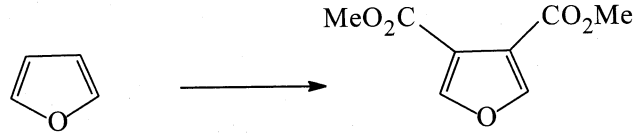
(c) "Equal amounts of (*a, a*) and (*e, e*) conformers of *trans*-1,2-dibromocyclohexane exist in non-polar solvents but the (*e, e*) conformer prevails in polar solvents."— Explain. 4+3+3

7. (a) Carry out the following transformations :

(i)

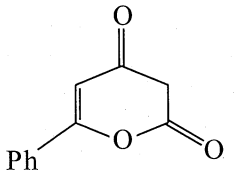


(ii)



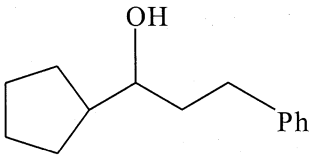
Please Turn Over

(b) Propose a synthetic route for the following target molecule taking EAA and benzoyl chloride as possible synthetic equivalents produced after retrosynthesis.



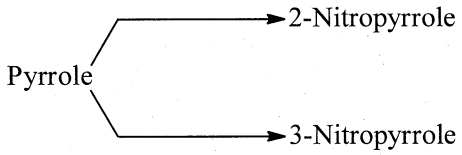
(c) Explain why anthracene cannot be prepared from naphthalene by Friedel-Craft reaction with succinic anhydride. 4+3+3

8. (a) Show the retrosynthetic pathway and the forward synthesis of the following molecule.



(b) "*trans*-2-Aminocyclohexanol on treatment with aq. $NaNO_2$ and dil. HCl gives cyclopentane carboxaldehyde while its *cis*-isomer gives a mixture of products."— Explain.

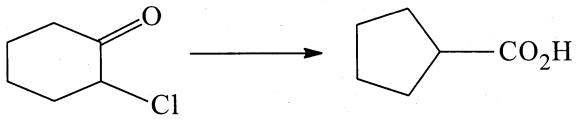
(c) Convert :



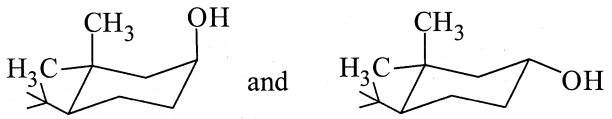
4+3+3

9. (a) "Pyridine-*N*-oxide is more reactive towards both electrophiles and nucleophiles."— Explain.

(b) How can you convert? Give mechanism.



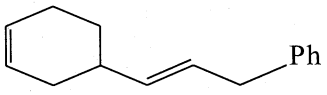
(c) Compare the rates of chromic acid oxidation of the following compounds with explanation.



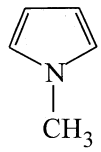
4+3+3

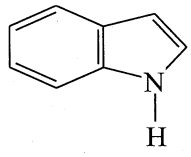
10. (a) "Acetolysis of both *cis*- and *trans*-isomers of 2-acetoxycyclohexyltosylate give the same product." —Explain.

(b) Give the retrosynthetic analysis and the forward synthesis of the following molecule :



(c) Predict the products of the following reactions with mechanism.

(i)  $\xrightarrow[\text{Cu-Bronze}]{N_2CHCO_2CH_3}{}^{100\ ^\circ C}$?

(ii)  $\xrightarrow[2.\ H_2O/NaOAc]{1.\ DMF/POCl_3}$? 4+3+3
