



UNIVERSITY OF NORTH BENGAL

B.Sc. Honours Part-II Examination, 2021

CHEMISTRY

PAPER-III

ORGANIC CHEMISTRY

Full Marks: 60

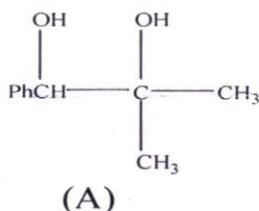
ASSIGNMENT

*The figures in the margin indicate full marks.
All symbols are of usual significance.*

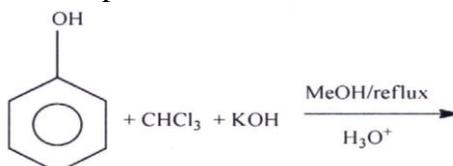
Answer any four questions from the following

15×4=60

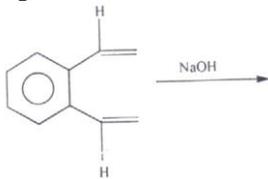
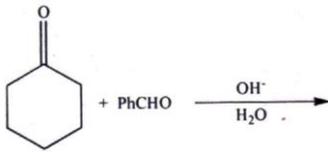
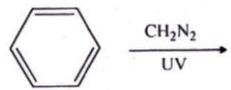
1. (a) Explain the following points of view regarding Pinacol-Pinacolone rearrangement. 2+2+2
+3+3
- (i) Formation of initial carbenium ion intermediate
 - (ii) One synthetic application with mechanism
 - (iii) Concerted nature of migration
 - (iv) Migratory aptitude of the migratory groups
 - (v) Semi Pinacol-Pinacolone rearrangement.
- (b) What happens when (A) is treated with $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ in dilute acetic acid? Illustrate with the mechanism of the reaction. 3



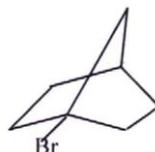
2. (a) Discuss the reactions of primary, secondary and tertiary alcohols with hydrogen halides with mechanism and suitable examples. 4
- (b) (i) Prove that whether Fries rearrangement is intermolecular or intramolecular. 4+4+3
- (ii) What are the effects of temperature and solvent on the Fries rearrangement?
- (iii) Predict the products with plausible mechanism.



3. (a) Illustrate the cleavage of ethers with examples and reaction mechanism at (i) cold and (ii) high temperatures. 2+2

- (b) How will you prepare ether peroxide from ether? How is the presence of peroxides in ether identified? How are the peroxides removed from ether? 2+1+1
- (c) Convert butan-2-ol into butanone. Provide mechanism for the conversion. 3
- (d) Justify with suitable examples that benzaldehyde with electron releasing groups can only act as donor while those with electron withdrawing groups can only act as acceptor in Benzoin condensation. 4
4. Write short notes: 3×5=15
- (a) Mixed Aldol Condensation
- (b) Oppenauer oxidation
- (c) Reimer Tiemann reaction
- (d) Hinsberg method
- (e) Elimination versus Substitution.
5. (a) Justify that the proton exchange is not involved in the rate determining step in the Benzilic acid rearrangement. 3
- (b) Discuss semi Benzilic acid rearrangement with mechanism. 3
- (c) What are the effects of electron withdrawing and electron donating substituents of benzaldehyde in Cannizzaro reaction? Mention with examples. 4
- (d) Predict the products with mechanism: 2½+2½
- (i)  (ii) 
6. (a) Explain with examples that Hofmann, Curtius, Schmidt and Lossen rearrangements are mechanistically allied. 5
- (b) Prepare diazomethane from N-nitroso-N-methyl-p-toluenesulphonamide. 2
- (c) Predict the products: 1+1+1+2
- (i) $C_6H_5OH \xrightarrow{CH_2N_2}$
- (ii) $RCHO \xrightarrow{CH_2N_2}$
- (iii) $RCOCl \xrightarrow{CH_2N_2}$
- (iv) 
- (d) How will you distinguish methyl alcohol and ethyl alcohol chemically? 3
7. (a) Define racemic modification. What are the different types of racemic modification? What do you mean by partial resolution of a racemic modification? 1+2+1
- (b) State the principle of resolution through diastereomer formation and represent the scheme of resolution of a (±) acid. 2+3
- (c) Calculate the specific rotation of an optically active compound in solution containing 0.75 g/10 ml, when measured in a 1 dm tube of a polarimeter at 25° C showing a rotation +1.2°. 3

- (d) Justify that presence of a chiral centre is not the necessary condition for a compound to be optically active. 3
8. (a) How are S_N1 and S_N2 type reactions distinguished by (i) isotope effects and (ii) salt effects? 2+2
- (b) Provide the kinetic evidence in favour of S_N1 mechanism. 3
- (c) The following bicyclic compound is exceedingly unreactive towards nucleophilic substitution by both S_N1 and S_N2 mechanism. — Justify. 3



- (d) Discuss the mechanism and stereochemistry of the following reaction: 3



- (e) Predict the product with suitable mechanism: 2

