

Name:

Enrolment No:



UPES

End Semester Examination, December 2023

Course: Organic reaction mechanism

Program: BSc (H) Chemistry with research

Course Code: CHEM4013

Semester: VII

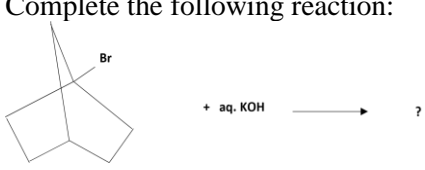
Time: 03 hrs.

Max. Marks: 100

Instructions: Read all the below mentioned instructions carefully and follow them strictly:

- 1) Mention Roll No. at the top of the question paper.
- 2) Do not write anything on the question paper except roll number.
- 3) Attempt all the parts of a question at one place only.
- 4) Internal choice is given only in Q 9 and 10.

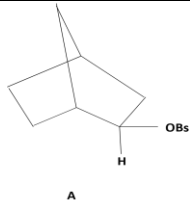
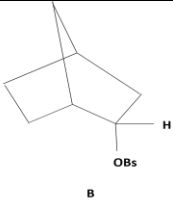
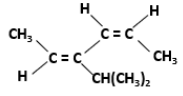
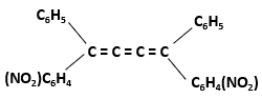
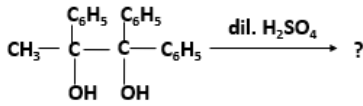
SECTION A
(5Qx4M=20Marks)

| S. No. | | Marks | CO |
|--------|--|-------|-----|
| Q 1 | Suggest a mechanism for the following reaction: $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2\text{Cl} + \text{KOH} \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2\text{OH} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$ (15 %) (85 %) | 4 | CO3 |
| Q 2 | Which intermediate is formed during the hydrolysis of mustard gas? How does it impact the rate of reaction? | 4 | CO2 |
| Q 3 | Carry out following conversions: a. Pyrrole to 3-chloropyridine. b. Phenol to o-hydroxy benzaldehyde. | 4 | CO1 |
| Q 4 | If dissociation constants of two substituted benzoic acids are 3.1×10^{-3} and 4.3×10^{-2} . Predict which of the two is substituted with electron donating group in it. | 4 | CO3 |
| Q 5 | Complete the following reaction:  | 4 | CO2 |

SECTION B
(4Qx10M= 40 Marks)

Question nos. 6, 7 and 8 are compulsory; internal choice is given in Q 9.

| | | | |
|-----|--|-----|-------------|
| Q 6 | a. Compare the rates of solvolysis of the following compounds: | 5+5 | CO3, CO2 |
|-----|--|-----|-------------|

| | <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>A</p> </div> <div style="text-align: center;">  <p>B</p> </div> </div> <p>b. What are long-lived free radicals? The dissociation percentage of central bond of few compounds is given below:</p> <table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 5px;">Compound</th> <th style="text-align: left; padding: 5px;">Dissociation</th> </tr> </thead> <tbody> <tr> <td style="padding: 5px;">1,2-(diphenyl-p-anisyl) ethane</td> <td style="padding: 5px;">20 – 25 %</td> </tr> <tr> <td style="padding: 5px;">1,2-(tri-o-anisyl) ethane</td> <td style="padding: 5px;">95 – 100 %</td> </tr> <tr> <td style="padding: 5px;">1,2-(phenyl-di-p-biphenyl) ethane</td> <td style="padding: 5px;">18 %</td> </tr> <tr> <td style="padding: 5px;">1,2-(tri-p-biphenyl) ethane</td> <td style="padding: 5px;">10 %</td> </tr> </tbody> </table> <p>Arrange these compounds in the increasing order of the stabilities of the free radicals generated from them.</p> | Compound | Dissociation | 1,2-(diphenyl-p-anisyl) ethane | 20 – 25 % | 1,2-(tri-o-anisyl) ethane | 95 – 100 % | 1,2-(phenyl-di-p-biphenyl) ethane | 18 % | 1,2-(tri-p-biphenyl) ethane | 10 % | | |
|-----------------------------------|---|-----------------|---------------------|--------------------------------|-----------|---------------------------|------------|-----------------------------------|------|-----------------------------|------|--|--|
| Compound | Dissociation | | | | | | | | | | | | |
| 1,2-(diphenyl-p-anisyl) ethane | 20 – 25 % | | | | | | | | | | | | |
| 1,2-(tri-o-anisyl) ethane | 95 – 100 % | | | | | | | | | | | | |
| 1,2-(phenyl-di-p-biphenyl) ethane | 18 % | | | | | | | | | | | | |
| 1,2-(tri-p-biphenyl) ethane | 10 % | | | | | | | | | | | | |
| Q 7 | <p>a. Which reactive intermediate is analogous to carbenes? Write two reactions where this intermediate is applied, and also name these reactions.</p> <p>b. Write the product of the reaction when o-bromoanisole and m-bromoanisole are individually treated with sodamide. Provide a suitable explanation to your answer.</p> | 5+5 | CO1 | | | | | | | | | | |
| Q 8 | <p>a. Define plane of symmetry. Mention the number of vertical and horizontal planes of symmetry in benzene, cyclopropane and naphthalene.</p> <p>b. Which type of stereoisomerism applies in the following compounds:</p> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <p style="margin-top: 10px;">Specify in both the compounds at possible positions.</p> | 5+5 | CO1 | | | | | | | | | | |
| Q 9 | <p>Complete the following reaction with mechanism:</p> <div style="text-align: center; margin: 10px 0;">  </div> <p>Name the reaction and mention its important features also.</p> <p style="text-align: center; margin: 20px 0;">OR</p> <p>What happens when:</p> <ol style="list-style-type: none"> a. Acetamide is treated with bromine in alkaline medium? b. 2-chloro cyclopentanone is treated with sodium ethoxide? c. Benzyl trimethyl ammonium chloride is treated with sodamide? d. Neo-pentyl alcohol is treated in the presence of concentrated sulfuric acid? | 10 | CO3 | | | | | | | | | | |

SECTION-C
(2Qx20M=40 Marks)

Internal choice is given in Q 10, while Q 11 is compulsory.

| | | | |
|------|--|--------------|------------|
| Q 10 | <p>a. Discuss the order of stability of various cycloalkane rings. Why is cyclohexane extraordinarily stable despite of the ring strain in it?</p> <p>b. Differentiate decalols and decalones. Compare them on the basis of their stabilities.</p> <p style="text-align: center;">OR</p> <p>Elaborate conformation in following category of molecules:</p> <p>i. Cyclohexanones</p> <p>ii. Substituted cyclohexenes</p> | 10+10 | CO3 |
| Q 11 | <p>a. Assign D/L and R/S configurations to the following compounds:</p> <div style="display: flex; align-items: center; justify-content: center;"><div style="text-align: center;">$\begin{array}{c} \text{COOH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{COOH} \end{array}$</div><div style="margin: 0 10px;">and</div><div style="text-align: center;">$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} - \text{C} - \text{Cl} \\ \\ \text{Cl} - \text{C} - \text{H} \\ \\ \text{CH}_3 \end{array}$</div></div> <p>b. Write short notes on the following:</p> <p>i. Axial chirality</p> <p>ii. Spiranes</p> | 10+10 | CO2 |