2024

4th Semester Examination

CHEMISTRY (Honours)

Paper : C 10-T

[Organic Chemistry-IV]

[CBCS]

Full Marks : 40   Time : Two Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers
in their own words as far as practicable.

Group - A

Answer any *five* questions from the following :

$2 \times 5 = 10$

1. Account for the fact that pure primary amine can't be prepared by the reaction between alkyl halide and concentrated ammonia solution.

2. What are the common features of Hofmann, Curtius, Lossen and Schmidt rearrangement?

3. How relaxation time is related to signal broadening in NMR spectroscopy?
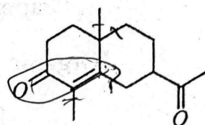
P.T.O.

4. How does the number of neighbouring protons affect the splitting of NMR signals? Provide examples to illustrate.

5. A natural product is known to have either structure **A** or **B**. The ultraviolet spectrum in alcohol has λ_{max} 252 nm. Which is the most likely one?
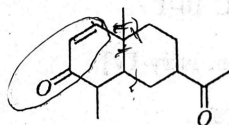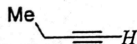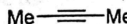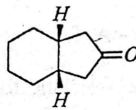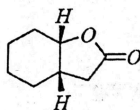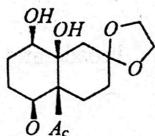

(A)   (B)

6. What are the characteristic values of IR absorptions for the following compounds?

7. Why excess diazomethane is required in Arndt-Eistert synthesis? Explain with suitable mechanism.

8. Provide the structures of **(A)** and **(B)**?   1+1

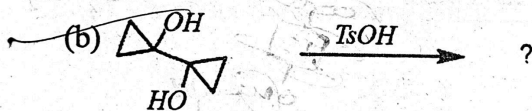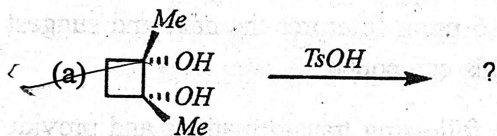$\xrightarrow{TsCl,\ Pyridine}$ **(A)** $\xrightarrow{KOH}$ **(B)**

(3)

Group - B

9. Give the mechanism of the Hofmann rearrangement. On the basis of mechanism, explain why the reaction cannot be used to prepare secondary and tertiary amines? 3+2

10. What are the major products for these reactions? Provide mechanisms explaining the selectivity in the migration. $2\frac{1}{2} + 2\frac{1}{2}$

(a) $\xrightarrow{\text{TsOH}}$?

(b) $\xrightarrow{\text{TsOH}}$?

11. Provide the structures of (A) and (B) with proper stereochemistry. Draw the energetically favourable transition states for these reactions. $2\frac{1}{2} + 2\frac{1}{2}$

(*R*)-3-methylpentan-2-one $\longrightarrow$
$\xrightarrow{\text{LiAlH}_4}$ (A)
$\xrightarrow{\text{mCPBA}}$ (B)
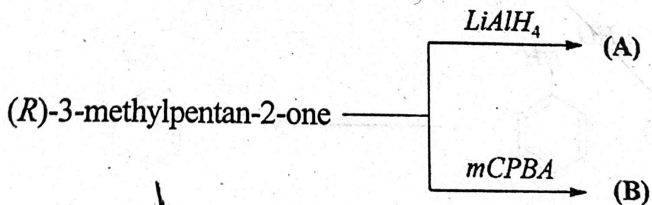
12. (a) Explain the fundamental principle behind nuclear magnetic resonance (NMR) spectroscopy. How does it use the magnetic properties of atomic nuclei to provide structural information about molecules?

   (b) Define the term finger print region in Infrared spectroscopy.   3+2

13. A $C_9H_{10}O_2$ compound has strong infrared adsorption at 1690 and 1100 cm^{-1}. Its ^1H NMR spectrum has sharp singlet peaks at δ 2.8 and 3.8 ppm ($3H$ each) and two doublets at δ 6.9 and 7.8 ppm ($2H$ each, J = 8 Hz). Its ^{13}C NMR spectrum shows peaks at 197, 165, 130, 129, 114, 56, 26 ppm. Interpret the data and suggest a structure for this compound.

14. Accomplish the following transformations and provide mechanism in each case. $2\frac{1}{2}+2\frac{1}{2}$
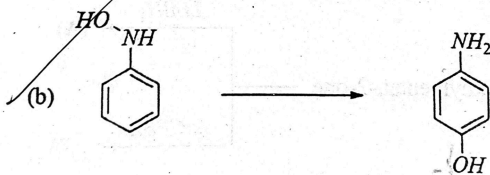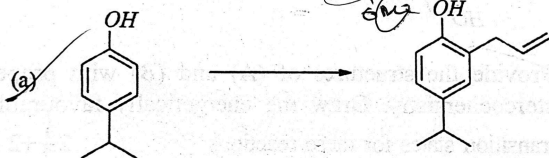
(5)

Group - C

Answer any *one* question from the following :

$$10 \times 1 = 10$$

15. (a) An organic compound [X] $(C_{12}H_{16}O_3)$ exhibits the following spectral data :

IR 1720 cm^{-1}, ^1H NMR : 2.35 (*s*, 6*H*); 3.30 (*s*, 3*H*), 3.83 (t, 2H); 4.42 (*t*, 2*H*); 7.07 (*s*, 1*H*), 7.58 (*s*, 2*H*). The compound [X] with an excess of MeMgBr gives 1:1 mixture of compounds [Y] and [Z]. The compound [Z] exhibits the following NMR data 2.0 (*bs*,1*H*); 3.30 (*s*, 3*H*); 3.56 (*t*, 2*H*); 3.70 (*t*, 2*H*).

Predict the structure of [X], [Y] and [Z].   6

(b) Carry out the following transformations :

(i)

(ii)

·2+2

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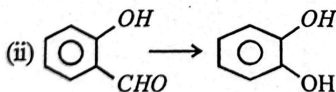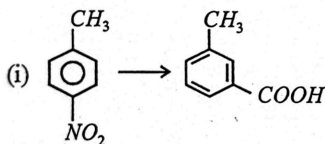
16. Propose syntheses for the following compounds, explaining the retrosynthetic pathways. $2\frac{1}{2} \times 4 = 10$

(i)

(ii)

(iii)

(iv)