

2025

CHEMISTRY — HONOURS

Paper : DSCC-9

(Organic Chemistry - III)

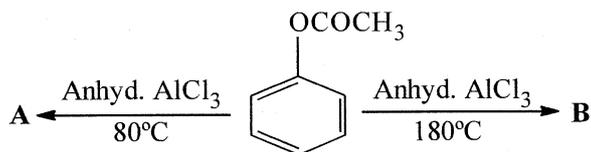
Full Marks : 75

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question nos. 1, 2, 3, 4** (compulsory) and **any four** questions from the rest (**question nos. 5 to 10**).1. Answer **any ten** questions :

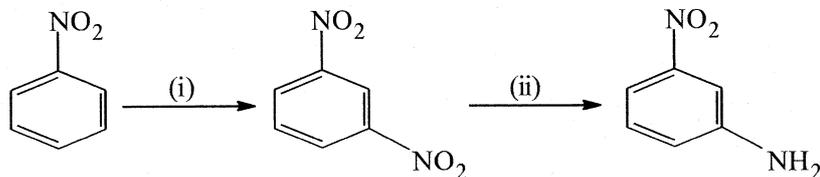
2×10

(a) Define the following terms with example :

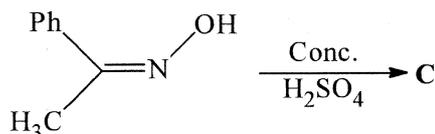
(i) Chromophore (ii) Auxochrome.

(b) Identify **A** and **B** in the following reaction :

(c) Identify the reagents in the following transformations :



(d) "The IR spectrum of benzene shows many peaks but its UV-spectrum is very simple."— Explain.

(e) Identify **C** with mechanism :

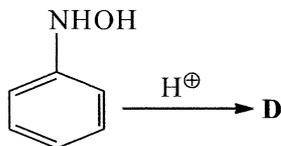
(f) Write the products of reduction of nitrobenzene under acidic and neutral conditions.

(g) "Ethylene fails to show any IR signal around 1600 cm^{-1} ." — Explain.

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(h) Identify **D** with mechanism :



- (i) "Tertiary amine of the type $R^1R^2NCH_3$ can be prepared using formaldehyde and formic acid as the reagents." Show the mechanism of the reaction.
- (j) Two peaks appeared at δ 4.0 ppm and δ 4.4 ppm in the NMR spectrum of a compound. Calculate their chemical shift values in Hz in a 100 MHz instrument and 1000 MHz instrument.
- (k) Both $Ph_2C(OH)C(OH)CMe_2$ and $Ph(Me)C(OH)C(Me)(OH)Ph$, give the same ketone on separate treatment with H_2SO_4 . Write down the structure of the product.
- (l) What differences in chemical shift values are expected for proton of CH_3F and CH_3Cl ?

2. Write short note on :

(a) Effect of hydrogen bonding in IR spectroscopy (using following points) :

- (i) Intramolecular and intermolecular hydrogen bonding.
- (ii) Examples (one for each). 3+2

Or

(b) Claisen Rearrangement (using following points) :

- (i) Statement.
- (ii) Mechanism taking a suitable substrate. 2+3

3. Write short note on :

(a) Solvent effect on λ_{max} values of α, β -unsaturated carbonyl compounds (using following points) :

- (i) General trend of shift of λ_{max} values on increasing solvent polarity.
- (ii) Explanation of the change of λ_{max} values using energy diagram. 2+3

Or

(b) Pinacol-Pinacolone Rearrangement (using following points) :

- (i) One example.
- (ii) Mechanism.
- (iii) Comment on the migratory aptitude of the migrating groups. 1+2+2

4. Write short note on :

(a) Internal standard in NMR spectroscopy (using the following points) :

- (i) Reason for its use.
- (ii) Common internal standard used.
- (iii) Reason for using a specific compound as internal standard (*any two points*). 2+1+2

(3)

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Or

(b) Diazocoupling reaction (using the following points) :

- (i) Substrate and condition for diazotization reaction.
 (ii) Mechanism of formation of diazonium salt.
 (iii) Coupling reaction of diazonium salt with alkaline β -naphthol solution. (1+1)+2+1

5. (a) (i) An organic compound with molecular formula $C_6H_{12}O$ gives positive iodoform test. Its UV, IR and NMR spectral data are given below :

UV : λ_{max} 282 nm (ϵ_{max} 22)

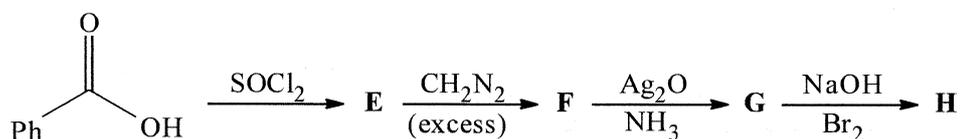
IR : $\bar{\nu}$ 1710 cm^{-1}

1H NMR : δ 2.1 (3H, s) and 1.1 (9H, s)

Identify the compound with explanation.

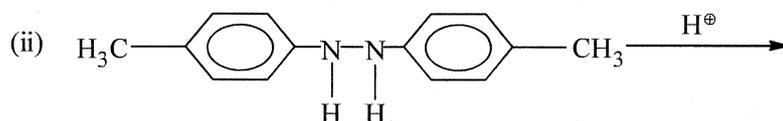
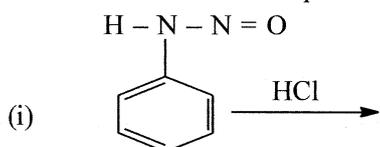
(ii) In the structure of aniline, point out the chromophore and auxochrome components.

(b) Identify **E**, **F**, **G** and **H** and give mechanism for the conversion of **G** to **H** :



(c) Explain what happens when cyclopentanone is treated with diazomethane. (3+1)+3+3

6. (a) Give the structure of the products of the following reactions with mechanism :



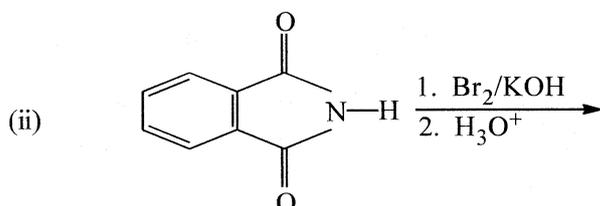
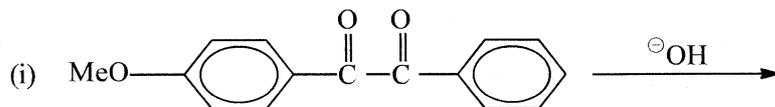
(b) Arrange *E*-Stilbene and *Z*-Stilbene in order of their increasing λ_{max} with justification.

(c) "Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed." — Explain. (2+2)+3+3

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7. (a) Predict the products of the following reactions with proper mechanisms :



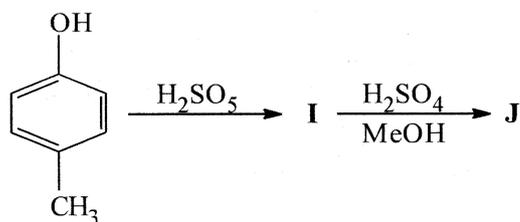
(b) A compound with molecular formula C_8H_8O gives the following spectra :

IR : $\bar{\nu}$ 3100, 1700 (s), 1640, 1680 cm^{-1} .

1H NMR : δ 7.3 – 8.2 (complex multiplet), δ 2.5 (3H, s)

Identify the compound with proper justification.

(c) Identify **I** and **J** :



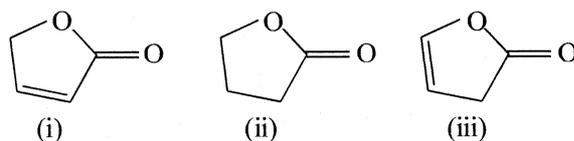
Give mechanism for the formation of **J** from **I**.

(2+2)+3+3

8. (a) (i) Label the different types of non-equivalent hydrogens of propene.

(ii) "As the ring size increases from cyclopropanone (1815 cm^{-1}) to cyclohexanone (1715 cm^{-1}), the carbonyl stretching frequency decreases."— Explain the observation.

(b) Arrange, with explanation, the following molecules in order of increasing C = O stretching frequency :



(c) Carry out the following transformations :

(i) Aniline \rightarrow 1, 3, 5-Tribromobenzene

(ii) *p*-Nitrotoluene \rightarrow *p*-Aminobenzoic acid.

(1+3)+3+3

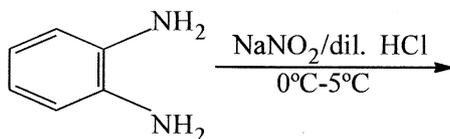
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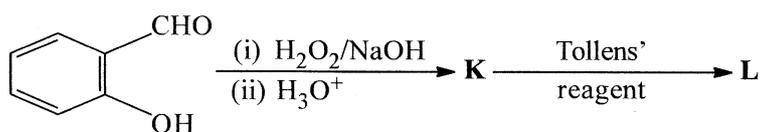
9. (a) Define the following terms with one example of each :

(i) Hyperchromic shift and (ii) Hypsochromic shift.

(b) Predict the product with mechanism :



(c) Identify **K** and **L**. Write the mechanism for formation of **K** :

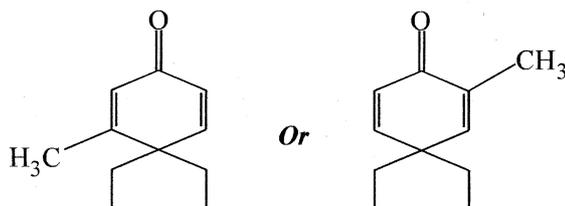


4+3+3

10. (a) (i) Toluene is oxidized to benzaldehyde. What changes in ^1H NMR spectral features would you expect for the product with respect to starting material?

(ii) Compare λ_{max} value of *s-cis* and *s-trans*-1,3-butadiene.

(b) Which member of the following pair will undergo dienonephenol rearrangement more rapidly and why?



(c) How would you chemically distinguish between the following pairs of compounds?

(i) Methyl cyanide and methyl isocyanide

(ii) *p*-Chloroaniline and aniline hydrochloride.

(2+2)+3+3

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