

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2023

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

Time Allotted: 2 Hours

Full Marks: 40

The figures in the margin indicate full marks. Candidates should answer in their own words and adhere to the word limit as practicable. All symbols are of usual significance.

Answer any four questions taking one from each unit

Unit-I

- 1. (a) Although N, N-dimethylaniline couples with benzenediazonium chloride, its 2 2,6-dimethyl derivative does not. Explain. (b) Predict the product with suitable mechanistic course when p-bromonitrobenzene is 2 treated with potassium cyanide in aqueous ethanol medium. (c) How can you chemically distinguish between o-phenylene diamine and 2 *m*-phenylene diamine? 2
- 2. (a) How can you chemically distinguish between the isomers 4-nitro toluene and PhCH₂NO₂? 2
 - (b) Carry out the following conversion using Mannich reaction in one of the steps:

(c) Predict the product in the following reaction

$$\begin{array}{c}
OH \\
\hline
OH \\
\hline
ArN_2CI^- \\
H^+
\end{array}
?$$

Unit-II

3. (a) Carry out the following conversion and suggest plausible mechanism of the ring 2 expansion step:

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- (b) Two isomeric α-halo ketones A and B on treatment with NaOMe (separately) gave the same product PhCH₂CO₂Me. Identify A and B.
 (c) Show how each of the following conversions could be accomplished by using a
- 2+2

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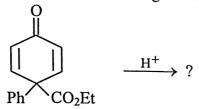
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- sequence of reactions involving a rearrangement reaction:

 (i) Benzophenone ______ Aniline
 - (ii) Ph Me Me Ph Me Me Me Me Me

- 4. (a) In the Hofmann degradation of benzamide, small amounts of PhNHCONHPh and PhNHCONHCOPh are sometimes obtained along with aniline. Explain.
 - (b) Identify the product of the following reaction and suggest plausible mechanism for its formation.

- (c) Suggest a mechanism of the following reaction
- \sim NH—NH— \sim SO₃H \xrightarrow{HCl} H₂N— \sim NH₂
- (d) Find out the product in the following reaction



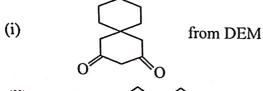
Unit-III

5. (a) Explain with suitable examples: (i) synthon; (ii) illogical electrophile.

2+2

(b) Synthesize following compounds using retrosynthetic analysis:

2+2



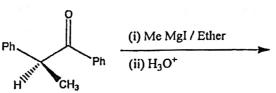
(ii) HO_2C CO_2H from DEM

DEM = Diethyl malonate

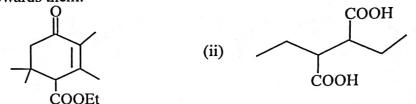
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(i)

(c) Use Felkin-Anh model to explain the formation of major product in the following reaction:



6. (a) Analyse the following molecules retrosynthetically and suggest plausible synthetic routes towards them:

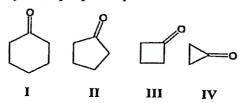


- (b) Write down the synthetic equivalents of the following: (any two)
- (i) $\stackrel{\ominus}{\text{CHO}}$ (ii) $\stackrel{\ominus}{\text{CH}}_2 \text{COOH}$ (iii) $\text{CH}_3 \stackrel{\ominus}{\text{C}} = \text{O}$
- (c) Synthesis of large rings is kinetically favourable but thermodynamically unfavourable Justify or contradict with reasons.
- (d) Which synthon does the following compound represent when it reacts with benzaldehyde and the product is hydrolysed by acid?



Unit-IV

7. (a) Consider the following cyclic ketones. Suggest the correct increasing order of C = O stretching frequency with proper explanation.



- (b) The position of UV absorption maxima of aniline and benzene is different in aqueous medium but they give identical absorption maxima in acidic solution. Explain this observation.
- (c) A compound having molecular formula C₈H₁₀O shows the following spectroscopic data:

IR: 1170, 2950, 3080 cm⁻¹

¹H-NMR: δ 2.2 (3H, s), 3.5 (3H, s), 7.3 (2H, d, J = 8 Hz), 7.6 (2H, d, J = 8 Hz) Find out the structure of the compound and explain the spectroscopic data as far as practicable.

(d) How would you distinguish 1,1-dichloroethane and 1,2-dichloroethane using NMR spectroscopy?

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2+2

2

2

3

2

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- (e) How can you distinguish between the members in each of the following pairs of $1\frac{1}{2}+1\frac{1}{2}$ compounds by the spectroscopic technique mentioned within parenthesis?
 - (i) p-Cresol and anisole (by UV spectroscopy)
 - (ii) cis-stilbene and trans-stilbene (by ¹H-NMR spectroscopy)
- (f) How can you monitor the progress of the following reaction using IR spectroscopy?

2

4

2

1+1

8. (a) A compound having molecular formula $C_{10}H_{12}O_2$ shows the following IR and 1H -NMR data.

IR: 3050, 2950, 1730 cm⁻¹

¹H-NMR: δ 1.3 (6H, d), 5.2 (1H, septet), 7.2 (3H, m), 8.0 (2H, m)

Find out the structure of the compound and explain the spectroscopic data as far as practicable.

(b) Which of the following nuclei are NMR active?

 $_{5}B^{11}, _{6}C^{13}, _{1}H^{2}, _{9}F^{19}$

- (c) Distinguish the following pairs of compounds on the basis of IR spectroscopic data (any *two*):
 - (i) Acetone and hexamethyl acetone
 - (ii) Salicylic acid and p-hydroxy benzoic acid
 - (iii) Phenyl acetate and methyl benzoate
- (d) Define the following terms in connection with UV spectroscopy with suitable example (any *two*):
 - (i) Auxochrome
 - (ii) Blue shift
 - (iii) Chromophore.
- (e) Find out the number of signal(s) in NMR spectroscopy (any *two*):

