



WEST BENGAL STATE UNIVERSITY B.Sc. Honours 2nd Semester Examination, 2021

# CEMACOR04T-CHEMISTRY (CC4)

# **ORGANIC CHEMISTRY-II**

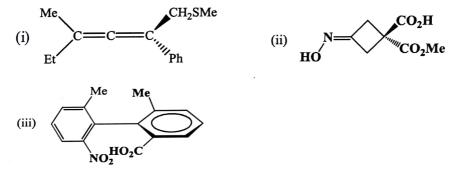
Time Allotted: 2 Hours

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 three questions taking one from each unit

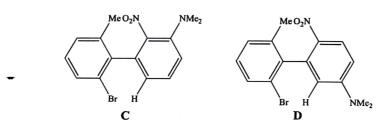
## <u>Unit-I</u>

1. (a) Assign (R/S) configurational descriptors to the following molecules.



(b) Explain the following observations.

- (i) Cyclopentadiene exists only in the *s*-*cis* form whereas 1,3-pentadiene can exist both in *s*-*cis* and *s*-*trans* forms.
- (ii) (2R, 3S)-2,3-Dibromobutane is more stable than (2S, 3S)-2,3-Dibromobutane.
- (iii) Compound C undergoes racemisation at a slower rate than compound D.



- (c) Explain Buttressing effect with an example.
- (d) Account for the following observations.
  Dipole moment of *meso-1,2-dichloro-1,2-diphenyl* ethane is less than that of the active isomer.

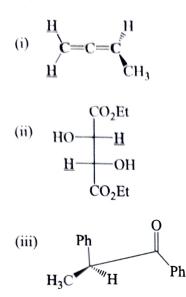
Full Marks: 40

 $1 \times 3 = 3$ 

2+2+2

2

2. (a) Find out the topic relationship between the underlined 'H' atoms and the mentioned faces in the following and describe the process by which the relationships are determined.

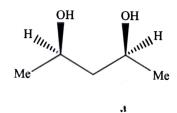


(Two faces of carbonyl)

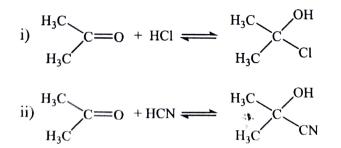
- (b) What is the product obtained from the reduction of (2S, 3R)-2,3dichlorocyclobutanone with LiAlH<sub>4</sub> by attack from the *Re* face?
- (c) What type of stereoisomerism (enantiomerism / diastereomerism) is expected for the following compounds? Explain your answer.

(i) MeCH = C = C = C = C = CHEt (ii) PhCH = C = C = C = CHMe

- (d) Explain the stereoisomerism of 6,6'-dinitro-diphenic acid and draw the energy profile for racemisation of its enantiomers.
- (e) Write down the compound obtained by substitution of *pro-s* hydrogen of the following compound by Cl. Also find out the configuration of the centre at which the substitution is done.



#### Unit-II



2

3+1

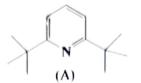
2

2

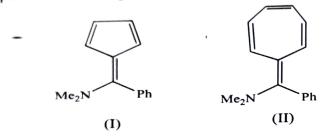
3

2

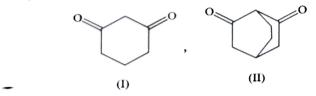
(b) (A) is known as an excellent scavenger of protons. — Explain.



- (c) Treatment of conc.  $H_2SO_4$  with naphthalene yield 1-derivative at low temperature and 2-derivative at higher temperature. Draw the mechanism and energy profile of those reactions. Explain the terms "kinetic controlled" and "thermodynamic controlled" reaction in connection with the above reaction.
- (d) Compare the basic strength of (I) and (II).



- (e) Explain the following statements.
  - (i) Cyclic 1,2-diketones exist mainly in the enol form.
  - (ii) In aqueous alkali, cyclohexane-1,3-dione (I) is readily soluble, while bicyclo
    [2.2.2] octane-2,6-dione (II) is poorly soluble.

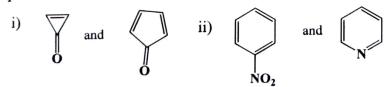


4. (a) Arrange the following compounds in the increasing order of enol content. Explain 2 your answer.

 $CH_3COCH_2COCH_3$ ,  $CH_3COCH_2CO_2Et$ ,  $PhCOCH_2COCH_3$  and

CH<sub>3</sub>COCH(Ph)CO<sub>2</sub>Et

(b) Compare the basicity with explanation.



- (c) Compare the acidity of the following compounds
  - (i) *p*-chlorophenol and *p*-fluorophenol.
  - (ii) *p*-nitro benzoic acid and *p*-methoxy benzoic acid.
- (d) The addition of chlorine (1 mol) to 1,3-butadiene at 25°C produces 60%
  3,4-dichlorobut-1-ene and 40% 1,4-4ichlorobut-2-ene. At 200°C, the yields are 30% and 70% respectively. Explain these observations with energy profile diagram.
- (e) What is nucleophilic catalysis?

3

3

2

1+2

2+2

2

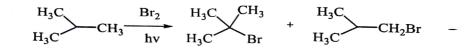
Strine

4

2+2

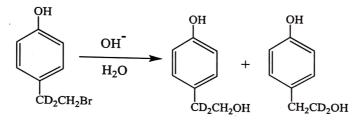
#### <u>Unit-III</u>

5. (a)

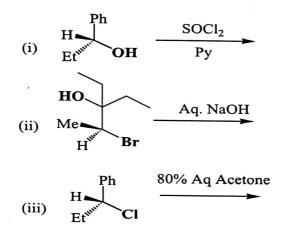


Show the mechanism of the reaction and predict the product composition with proper justification.

- (b) Explain the following observations.
  - (i) Iodide induced debromination occurs faster for *meso-2*,3-dibromobutane than for its active isomer.
  - (ii) Potassium permanganate dissolves in benzene in presence of 18-crown-6 to form a purple solution.
  - (iii) Bromination of propane is more regioselective than chlorination of the same compound.
  - (iv) Rate of the reaction between methyl iodide and NaN<sub>3</sub> at 0°C increases  $4.5 \times 10^4$  fold when the solvent is changed from methanol to dimethyl formamide.
- (c) Account for the following observation.



- 6. (a) When the elimination of HF from 1,1-dichloro-2,2,2-trifluoroethane is carried out with sodium methoxide in CD<sub>3</sub>OD, 1,1-dichloro-1-deuterio-2,2,2-trifluoroethane can be recovered from the reaction mixture. How can this result be interpreted for the elimination reaction? Offer an explanation.
  - (b) Identify the product/s in the following reactions with proper stereochemistry and  $2 \times 3 = 6$  show the plausible mechanisms



 $2 \times 4 = 8$ 

3

(c) For the synthesis of CH<sub>3</sub>-O-C(CH<sub>3</sub>)<sub>3</sub>, two plausible reaction routes are given below. Find out the favourable reaction route with explanation.

6

Route-I  $H_3C$ —Br + (CH<sub>3</sub>)<sub>3</sub>COK  $\longrightarrow$ 

Route-II (CH<sub>3</sub>)<sub>3</sub>CBr + H<sub>2</sub>C-OK

(d) In the following reaction, the order of nucleophilicity is Γ > Br<sup>-</sup> > CΓ when LiX is used as source of halide ions, but the order is reversed when Bu<sub>4</sub>N<sup>+</sup>X<sup>-</sup> is used. — Why?

 $CH_{3}CH_{2}CH_{2}CH_{2}OBs + X^{-} \xrightarrow{Acetone} CH_{3}CH_{2}CH_{2}CH_{2}X + BsO^{-}$ 

- (e) E2 and E1<sub>CB</sub> eliminations cannot be distinguished kinetically Justify the  $1\frac{1}{2}$  statement.
  - N.B.: Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.

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