WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2021

CEMACOR04T-CHEMISTRY (CC4)

ORGANIC CHEMISTRY-II

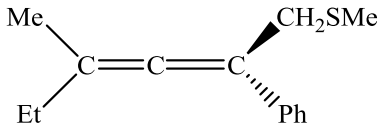
Time Allotted: 2 Hours | Full Marks: 40

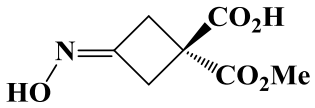
The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

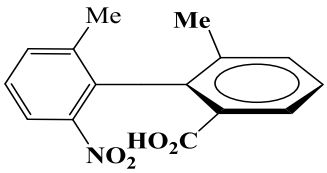
Answer any *three* questions taking *one* from each unit

Unit-I

1. (a) Assign (R/S) configurational descriptors to the following molecules. 1×3 = 3

(i) 

(ii) 

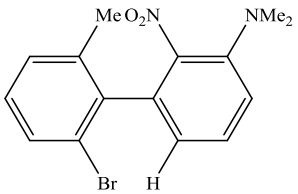
(iii) 

(b) Explain the following observations. 2+2+2

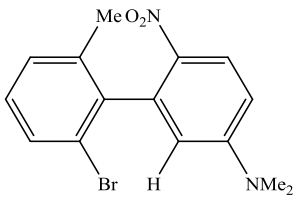
(i) Cyclopentadiene exists only in the *s-cis* form whereas 1,3-pentadiene can exist both in *s-cis* and *s-trans* forms.

(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



D

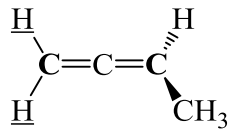
(c) Explain Buttressing effect with an example. 2

(d) Account for the following observations. 2

Dipole moment of *meso*-1,2-dichloro-1,2-diphenyl ethane is less than that of the active isomer.

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. 3+1

(i)



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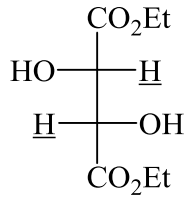

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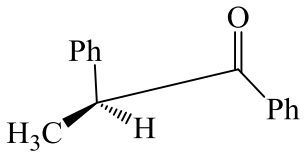


(Two faces of carbonyl)

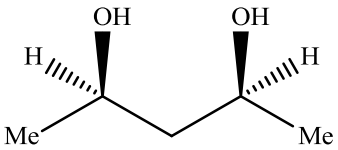
(b) What is the product obtained from the reduction of (2S, 3R)-2,3-dichlorocyclobutanone with $LiAlH_4$ by attack from the *Re* face? 2

(c) What type of stereoisomerism (enantiomerism / diastereomerism) is expected for the following compounds? Explain your answer. 2

(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. 3

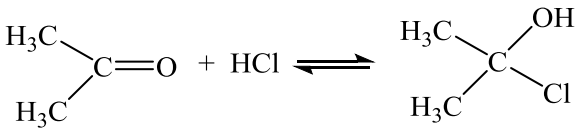
(e) Write down the compound obtained by substitution of *pro-s* hydrogen of the following compound by Cl. Also find out the configuration of the centre at which the substitution is done. 2



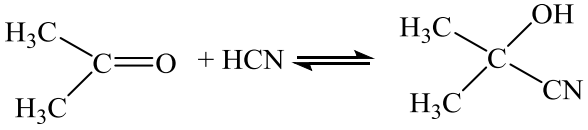
Unit-II

3. (a) Which of the following reaction is thermodynamically more favourable? — Why? 3

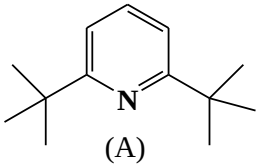
i)



ii)



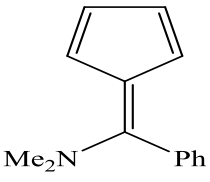
(b) (A) is known as an excellent scavenger of protons. — Explain. 2



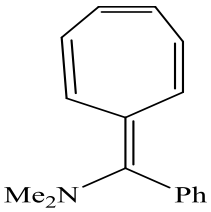
(A)

(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. 2+2

(d) Compare the basic strength of (I) and (II). 2



(I)

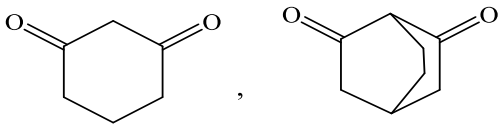


(II)

(e) Explain the following statements. 1+2

(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.

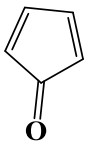


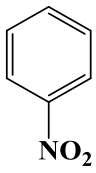
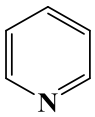
(I) (II)

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

$CH_3COCH_2COCH_3$, $CH_3COCH_2CO_2Et$, $PhCOCH_2COCH_3$ and $CH_3COCH(Ph)CO_2Et$

(b) Compare the basicity with explanation. 4

i)  and 

ii)  and 

(c) Compare the acidity of the following compounds 2+2

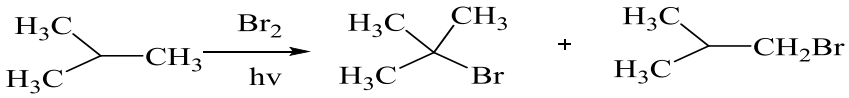
(i) *p*-chlorophenol and *p*-fluorophenol.

(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-dichlorobut-2-ene. At 200°C, the yields are 30% and 70% respectively. Explain these observations with energy profile diagram. 3

(e) What is nucleophilic catalysis? 1

Unit-III

5. (a)  3

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

(b) Explain the following observations. 2×4 = 8

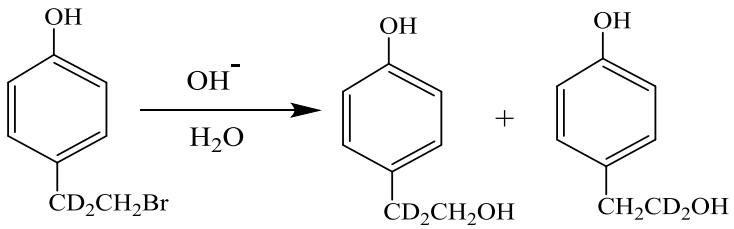
(i) Iodide induced debromination occurs faster for *meso*-2,3-dibromobutane than for its active isomer.

(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.

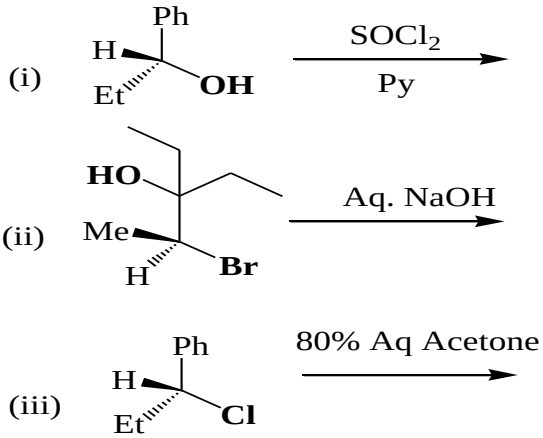
(iv) Rate of the reaction between methyl iodide and NaN_3 at 0°C increases 4.5×10^4 fold when the solvent is changed from methanol to dimethyl formamide.

(c) Account for the following observation. 2



6. (a) When the elimination of HF from 1,1-dichloro-2,2,2-trifluoroethane is carried out with sodium methoxide in CD_3OD, 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. 2

(b) Identify the product/s in the following reactions with proper stereochemistry and show the plausible mechanisms 2×3 = 6



(c) For the synthesis of CH_3-O-$C(CH_3)_3$, two plausible reaction routes are given below. Find out the favourable reaction route with explanation. 2

Route-I $H_3C—Br + (CH_3)_3COK \longrightarrow$

Route-II $(CH_3)_3CBr + H_2C—OK \longrightarrow$

(d) In the following reaction, the order of nucleophilicity is $I^- > Br^- > Cl^-$ when LiX is used as source of halide ions, but the order is reversed when $Bu_4N^+X^-$ is used. — Why? $1\frac{1}{2}$

$$CH_3CH_2CH_2CH_2OBs + X^- \xrightarrow{\text{Acetone}} CH_3CH_2CH_2CH_2X + BsO^-$$

(e) E2 and $E1_{CB}$ eliminations cannot be distinguished kinetically — Justify the statement. $1\frac{1}{2}$

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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