WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2018

CEMACOR01T-CHEMISTRY (CC1)

ORGANIC CHEMISTRY-I

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 ***three*** questions taking ***one*** from each Unit

Unit-I

1. (a) Calculate DBE for the molecule with molecular formula $C_2H_6N_2$. 1

   (b) Draw the orbital picture of $CH_2 = CH - CN$ and indicate the state of hybridisation of carbon and nitrogen in " $-CN$". 2

   (c) Compare with reason the dipole moments of 2

   $\underset{(I)}{CH_3 - CH_2 - Cl}$, $\underset{(II)}{CH_2 = CH - Cl}$ and $\underset{(III)}{CH \equiv C - Cl}$.

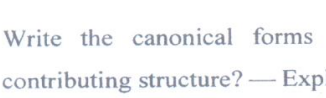
   (d) Draw the Frost mnemonic for the π MO's of square planar cyclobutadiene and hence calculate its delocalization energy in terms of β. 3

   (e) Draw all possible canonical forms of diazomethane CH_2N_2 and justify which one is the most stable and which one is the least stable among them. 3

   (f) Classify the following species as nonaromatic, aromatic, antiaromatic or homoaromatic with reason (***any three***): 3

   (i)  ; (ii)  ; (iii)  ; (iv)  ; (v) 

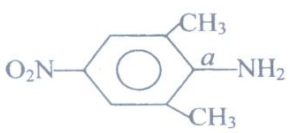
   (g) Between *tert*-butanol and *n*-butanol, which one is more soluble in water and why? 2

2. (a) Write the canonical forms of  Which one is the most contributing structure? — Explain. 2

   (b) Calculate the formal charge on the nitrogen atom of trimethylammonium ion and write the Lewis structure of the species. 2

(c) Bond energy of 'C = C' is less than twice of that of 'C – C' whereas bond energy of 'C = O' is greater than twice of that of 'C – O'. — Explain why. 2

(d) Compare the bond lengths (a vs a') of the following compounds with reason. 2



(e) Arrange the following compounds in order of their increasing heat of hydrogenation values: 2

1-hexene, *cis*-3-hexene, *trans*-3-hexene.

(f) When cyclooctatetraene is reacted with conc. H_2SO_4, a stable species is formed. Again when it is reacted with K metal in THF, another stable species is formed. Show the species formed in the two cases and account for their stability. 3

(g) What is the difference between bond polarity and bond polarisability? 2

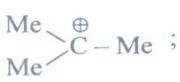
(h) Draw the π-HOMO of buta-1,3-diene in the ground state. 1

Unit-II

3. (a) Write down the product formed in the following reaction. Why is it called a pericyclic reaction? 2

(b) What are singlet and triplet carbenes? Show the orbital diagram of each of them. 3

(c) Compare the stability of the carbocations given below with reason: 2

(i) 

;

(ii) 

(d) Give one example of electrophilic radical. 1

4. (a) Compare the stabilities of the following free radicals 2

$^{\cdot}CH_3$, $\dot{C}H_2F$, $^{\cdot}CF_3$

(b) Give one example of each of pyramidal and planar carbanion. 2

(c) Which of the following species behave as (i) a nucleophile, (ii) an electrophile, (iii) both nucleophile and electrophile and (iv) neither nucleophile nor electrophile? 2

NH_3 , $H_3C-C\equiv\ddot{N}$, $\overset{+}{N}O_2$, $CH_3-\ddot{S}H$

(d) Explain the formation of the different products in the following reactions. 2

$$CH_3CH=CH_2 \xrightarrow{HBr} CH_3\,\underset{\displaystyle Br}{\overset{|}{C}}\,H-\dot{C}H_3$$

$$CH_3CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_2CH_2CH_2-Br$$

Unit-III

5. (a) Draw the Fischer projection formula of (2S, 3R)-3-chlorobutan-2-ol. 2

(b) What is meant by stereogenic center? Are centers of stereogenicity always centers of chirality? Explain with suitable example. 3

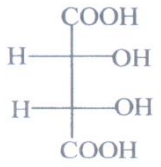
(c) Indicate the symmetry elements and point group of *trans*-1,2-dichloroethylene and chloroform. 3

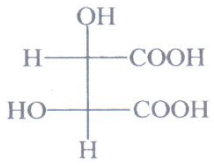
(d) How many stereoisomers will $Me-CH=CH-CH(OH)-Me$ have? Draw the stereostructure of any one of them showing the appropriate configuration in terms of R-/S- and/or E-/Z-. 3

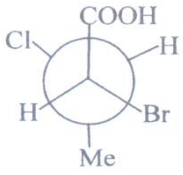
(e) The optically active ketone $Ph-CO-CH\begin{smallmatrix}\diagup Me\\ \diagdown Ph\end{smallmatrix}$ loses its optical activity when treated with a little base. Explain showing the mechanism. 3

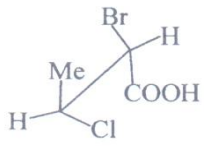
(f) A sample of an optically active compound shows a specific rotation (–)28°. If the specific rotation of its pure dextro form is (+)70°, find the molar ratio of the two enantiomers in the given sample. 2

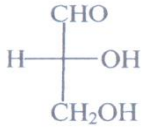
6. (a) Judge whether the following pairs are homomer / enantiomer / diastereomer or constitutional isomer: 3

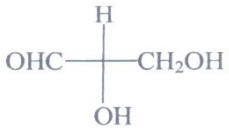
(i)


and


(ii)


and


(iii)


and


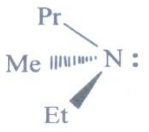
(b) How do you resolve (±) $CH_3CH(OH)CH_2CH_3$? 2

(c) How many active and *meso*-forms are possible for pentane-2,3,4-triol? Draw the Fischer projection formula of one *meso*-form and point out the pseudo asymmetric centre and comment whether it will be chirotopic or achirotopic. 4

(d) Write down the Fischer projection formula of D-glyceraldehyde and L-$C_6H_5CH_2CH(NH_2)COOH$. 2

(e) What are asymmetric and dissymmetric molecules? Explain with suitable examples. 3

(f) State with reason whether the following molecule is resolvable. 2



——×——