This question paper contains 7 printed pages]

L-113-2019

FACULTY OF SCIENCE

M.Sc. (First Year) (Second Semester) EXAMINATION MARCH/APRIL, 2019

(CBCS Pattern)

CHEMISTRY

Paper II (CH-422)

(Organic Chemistry)

(Thursday, 25-4-2019)

Time: 10.00 a.m. to 1.00 p.m.

Time—3 Hours

Maximum Marks—75

- N.B. := (i) Attempt All questions.
 - (ii) Figures to the right indicate full marks.
 - (iii) Use of logarithmic table and calculator is allowed.
 - (iv) Multiple Choice Questions (MCQs) should be attempted only once on Page No. 3 of answer-book with complete answer.
- 1. Attempt any three of the following:

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- (a) Describe the mechanism and synthetic uses of Reformatsky reaction.
- (b) Interconversion of 1, 3, 5-hexatriene \(\) 1, 3-cyclohexadiene under thermal and photochemical condition can be explained by FMO method.
- (c) Discuss the stereochemistry of spiranes and allenes.
- (d) Discuss the mechanism of E^2 reaction.
- (e) Cycloaddition of 1, 3-butadiene and ethylene by FMO and PMO method. Explain.

P.T.O.

- 2. Answer any three of the following:
 - (a) Why on thermal reaction cis 3, 4-dimethyl cyclobutene gives (2E, 4Z), 2, 4-hexadiene while the trans isomer gives the (2E, 4E) 2, 4-hexadiene.

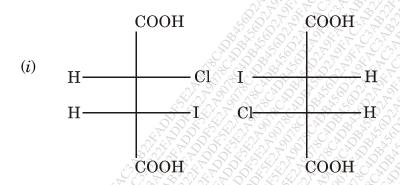
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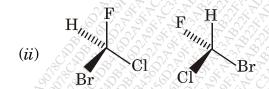
- (b) Explain witting reaction. Give its mechanism. How would you synthesis C_6H_5 —CH=CH— CH_3 ?
- (c) Trans (ee) 1, 3-dimethyl cyclohexane is more stable than trans (ee) 1, 2-dimethyl cyclohexane.
- (d) The relative rates of reaction of 1-bromo-2, 2-dimethyl propane and bromo ethane is 4.2×10^{-6} and 1.0 respectively with EtO \ominus in EtOH at 55°C.
- (e) What are sigmatropic rearrangement? Explain 1, 3-sigmatropic rearrangement by FMO and PMO method.
- 3. (a) Construct correlation diagram and FMO method for the following transformations. Predict whether these transformations are thermally or photochemically allowed:

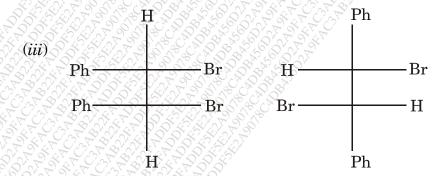
Illustrate the mechanism for the following reactions with suitable examples:

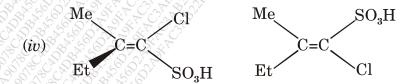
- (i) Michael addition
- (ii) Benzoin condensation.

(b) Indicate whether the relationship in each pair of compounds below is identical, enantiomeric or distereomeric by assigning R & S and E & Z configurations:



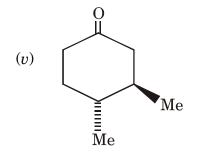


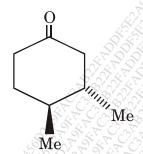




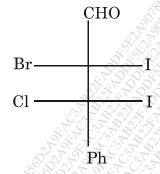
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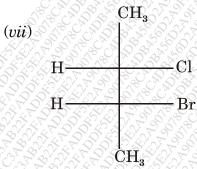


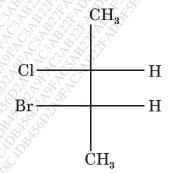


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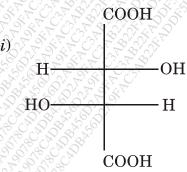
-Ph

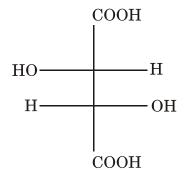






(viii)





4. (a) Give the order of stability of different conformational isomers in chair form of 1, 4 dimethyl cyclohexane by drawing their chair conformations and Newmann's projection formula of each and illustrating 1, 3 diaxial interaction.

Or

- (i) Addition of HX on alkenes is regioselective. Why?
- (ii) Write a note on stereochemistry of addition reactions.
- (b) Predict the product(s) with appropriate mechanism of the following (any four):

(i)
$$\begin{array}{c} O \\ + CH_2 = CH - C - CH_3 \xrightarrow{(i) \ CH_3 \overline{O}K}^+ ? \end{array}$$

$$(ii) \qquad \stackrel{\Delta}{\longrightarrow} ?$$

$$(iii) \quad \text{CH}_2 = \text{CH} - \text{C} - \text{CH}_3 + \text{CH}_2 \xrightarrow{\text{COOC}_2\text{H}_5} ?$$

(iv)
$$\begin{array}{c|c} H & COOC_2H_5 \\ + & C \\ COOC_2H_5 \end{array} ?$$

P.T.O.

$$(v) \qquad \qquad \underbrace{ (i) \ \text{RCO}_3\text{H}}_{(ii) \ \text{H}^{\dagger}/\text{H}_2\text{O}} ?$$

(viii)
$$Ph$$
— C — $CH_3 + Br$ — CH_2 — $COOEt$ — $?$

- 5. (A) Select the *correct* answer from the given options for each of the following:
 - (i) Stobbe reaction involves base catalysed condensation between:
 - (a) Benzaldehyde and KCN
 - (b) Benzaldehyde and diethyl malonate
 - (c) Aldehyde or ketone and diethyl succinate
 - (d) None of the above
 - (ii) Cycloaddition reaction between 1, 3-butadiene and ethylene under thermal condition is:
 - (a) supra-supra
- (b) antra-antra
- (c) supra-antra
- (d) both (a) and (b)
- (iii) Pyrolytic elimination of acetates, xanthates and amine oxides exhibits:
 - (a) Anti stereoselectivity
 - (b) Syn stereoselectivity
 - (c) Enantio selectivity
 - (d) Diastereo selectivity

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- (iv) The optically active allene among the following:
 - (a) 3-methyl but-1, 2-diene
 - (b) 1, 2-butadiene
 - (c) 1, 2-pentadiene
 - (d) 2, 3-pentadiene
- (v) [1, 3] sigmatropic rearrangement is symmetry allowed under :
 - (a) thermal
 - (b) photochemical
 - (c) presence of non-polar solvent
 - (d) presence of catalyst
- (B) Write notes on (any two):
 - (a) Pyrolytic elimination
 - (b) 1, 3-dipolar cycloaddition reaction
 - (c) Stereochemistry of Biophenyls.

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