[41]

No. of printed pages 04

SARDAR PATEL UNIVERSITY

M. Sc. (Chemistry)
Semester-I, Examination
December 03, 2012 Monday
Time: 10:30 am – 1:30 pm
ORGANIC CHEMISTRY-I [PS01CCHE02]

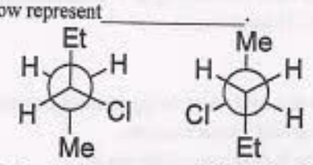
Maximum Marks – 70

Q-1 Select the correct answer from the choices given below for each of the following questions. Write only the correct code of answer in the answer book; **e.g. 1(a)-(iii).** **[08]**

(a) Neomenthyl chloride gives 3-menthene in 75 % of yield upon dehydrochlorination because
(i) two axial hydrogens are available on both sides of axial chlorine
(ii) axial hydrogen is only available on position-2 for elimination
(iii) axial hydrogen is only available on position-4 for elimination
(iv) it is a Saytzeff product

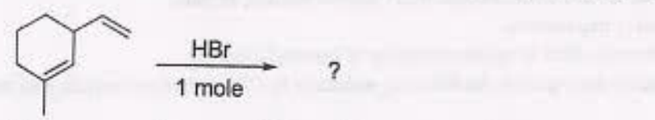
(b) Assertion A: A bulky base like potassium ter-butoxide is used in Darzen Glycidic ester condensation.
Reason R: It prevents the chances for S_N2 type displacement.
(i) Both **A** and **R** are true and **R** is the correct explanation.
(ii) Both **A** and **R** are true but **R** is not the correct explanation.
(iii) **A** is true and **R** is false
(iv) **A** is false and **R** is true

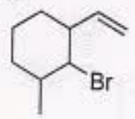
(c) The pair of structures given below represent_____.



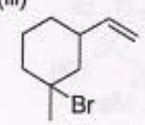
(i) enantiomers (ii) diastereomers (iii) homomers (iv) positional isomers

(d) The major product formed upon addition of 1 mole of HBr in the following reaction is_____.



(i)


(ii)


(iii)


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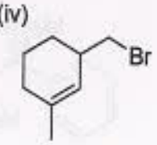
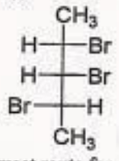
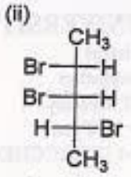
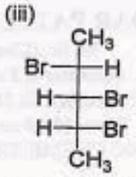
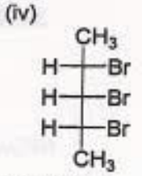


(e) In which of the following isomers carbon-3 is achirotopic and stereogenic?

(i) 

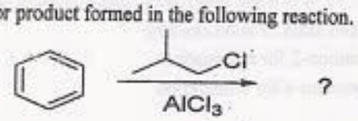
(ii) 

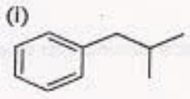
(iii) 

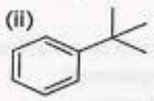
(iv) 

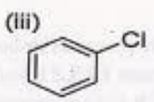
(f) Which is the correct route for preparing 1,3-dibromopropane from 3-bromopropene?
(i) hydrobromination in presence of UV light
(ii) bromination in presence of $FeBr_3$
(iii) hydrobromination in presence of peroxide
(iv) acid catalyzed hydrobromination

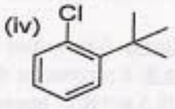
(g) Predict the major product formed in the following reaction.



(i) 

(ii) 

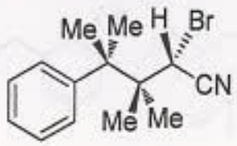
(iii) 

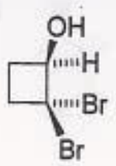
(iv) 

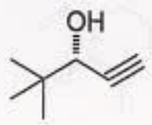
(h) E1cb mechanism involves_____.
(i) simultaneous bond breaking of C-H and C-Y bonds
(ii) breaking of C-H bond in a reversible step followed by C-Y bond breaking
(iii) irreversible breaking of C-H bond followed by C-Y bond breaking
(iv) C-Y bond breaks first then C-H bond breaks

Q-2 Answer **ANY SEVEN.** **[14]**

(a) Explain the formation of ethane as a byproduct during photochlorination of methane.
(b) Explain umpolung approach by giving proper example.
(c) Explain ipso substitution. List the factors responsible for it.
(d) Give necessary requirements for an ansa compound to be chiral.
(e) Hoffmann rearrangement is intramolecular, explain.
(f) Cope reaction is more stereoselective than Chugaev reaction, explain.
(g) Give method to trap nitrenes.
(h) Explain: Peroxide effect in hydrobromination of 2-methyl-1-butene.
(i) Assign chirality descriptors to the following molecules by CIP method and explain your answer.







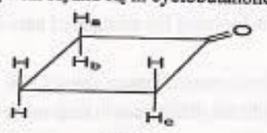
Q-3

(a) Draw all the possible stereoisomer of pentane-1,2,3,4,5-pentaol. How many of them are chiral? Assign chirality descriptors to all. **[06]**

(b) **Answer the following.** **[06]**

(i) Draw the structure of (S)-6,6'-diacetamidobiphenyl-2,2'-dicarboxylic acid. Why does it lose optical activity upon saponification?

(ii) Explain the topic relationship of H_a with H_b and H_c in cyclobutanone using symmetry criteria.

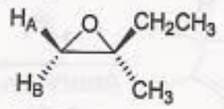


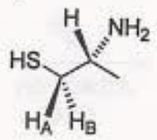
OR

(b) **Answer the following.** **[06]**

(i) Explain: Dissymmetry is the minimum requirement to exhibit chirality.

(ii) Assign prochirality descriptors to the designated hydrogen atoms (H_A and H_B) in following molecules by CIP method and explain your answer.



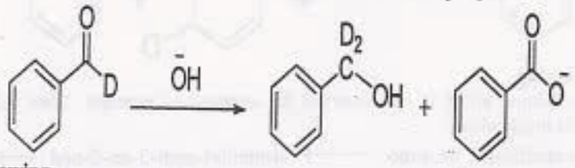


Q-4

(a) **Comment on the mechanism of following reactions.** **[06]**

(i)

(ii)



(b) **Explain the following.** **[06]**

(i) The stereochemical outcome of aldol condensation can be controlled by base strength.

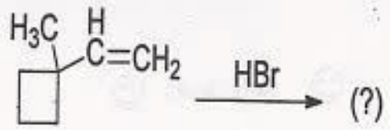
(ii) Favorskii rearrangement involves cyclopropanone as the intermediate.

OR

(b) **Answer the following.** **[06]**

(i) Explain: Sommelet Hauser rearrangement involves 2,3-sigmatropic shift.

(ii) Complete following conversion and explain its mechanism.



Q-5

(a) Answer the following. [06]

(i) Ph-CH_2-CH_2-Br does not show any deuterium exchange when subjected to β-elimination in the presence of EtOD/EtO^-. Explain the information obtained from this observation.

(ii) Show that any increase in the bulk, irrespective of its origin, increases the yield of Hoffman Elimination.

(b) Answer the following. [06]

(i) Explain Curtin Hammett principle by citing the example of base induced dehydrobromination from 2-(R)-bromobutane.

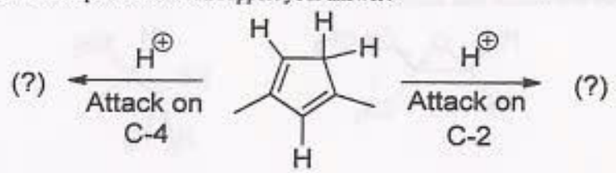
(ii) The product of hydroxylation from *trans*-2-butene using OsO_4 is a dl pair whereas use of per acid yields a meso compound. Highlight the differences in their mechanisms.

OR

(b) Discuss the following. [06]

(i) Iodide ion induced debromination in erythro-1,2-dibromo-1,2-dideutereoethane.

(ii) In following reaction write the product formed by attack on C-2 and C-4. Which path is more favorable? How NMR spectral data can support your answer?

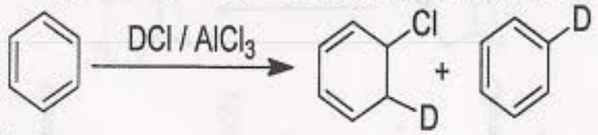


Q-6

(a) Answer the following. [06]

(i) Show that molozonide is involved as the intermediate in ozonolysis. How is it converted to ozonide?

(ii) Which of the following products do you expect in the given reaction? Justify your choice.



(b) Answer the following. [06]

(i) Primary kinetic isotope effect is not observed for nitration of benzene. What information can be obtained about its mechanism?

(ii) Complete the synthesis : acetone ⟶ 4-methyl-pent-3-en-2-one ⟶ dimedone

OR

(b) Explain the following statements. [06]

(i) Amino group is an activating group towards electrophilic aromatic substitution even though nitration of aniline gives significant amount of *meta* derivative.

(ii) In naphthalene attack of electrophile on 1st position is more favorable than 2nd position.

☺ *Best Luck* ☺