

[26]

SARDAR PATEL UNIVERSITY

M.Sc. (Chemistry), Semester – I

April 11, 2018 :: Wednesday

Time: 10:00 A.M. – 1:00 P.M.

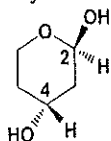
ORGANIC CHEMISTRY-I [PS01CCHE22]

Note: Figures to the right indicate full marks.

Total marks: 70

Q-1 Select the correct answer and mention only the code of correct answer against their question numbers. [08]

a. Which is the correct assignment of chirality at C2 and C4 of the following molecule?



(i) 2S,4S

(ii) 2R,4R

(iii) 2S,4R

(iv) 2R,4S

b. Which of the following is *wrong* statement regarding elimination reaction?

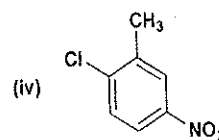
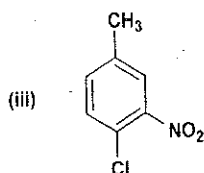
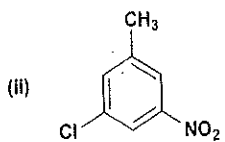
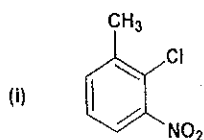
(i) The E2 mechanism generally occurs under highly basic condition.

(ii) The E2 mechanism is stereospecific.

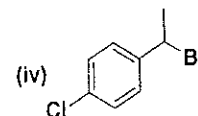
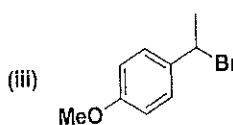
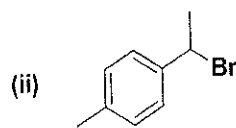
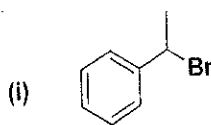
(iii) The E1 mechanism does not require a base.

(iv) The E1cB mechanism is usually unimolecular in the rate determining step.

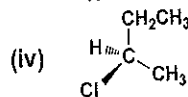
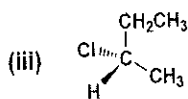
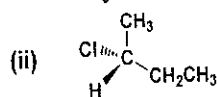
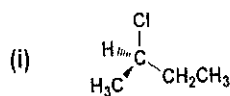
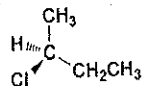
c. Suggest the major product upon chlorination of m-nitrotoluene with Cl₂ / AlCl₃



d. Which is the most reactive compound for the E1 elimination?



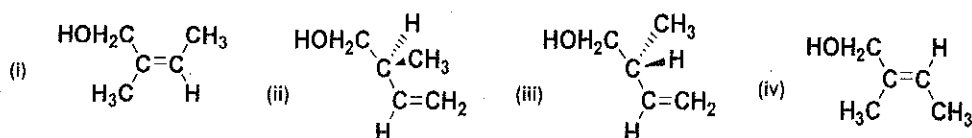
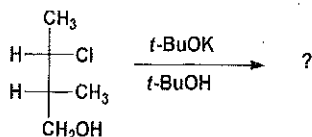
e. Which of (i)-(iv) shows the same compound as the following?



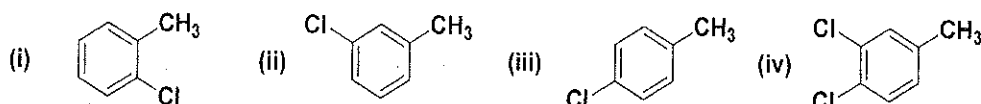
f. Which combination of carbonyl compounds gives phenyl vinyl ketone by an aldol condensation?

- (i) acetophenone + formaldehyde (iii) benzaldehyde + acetaldehyde
 (ii) acetophenone + acetaldehyde (iv) benzaldehyde + formaldehyde

g. Suggest the main product of the following reaction?



h. Which gives about 1:1 *p*- and *m*-methyl aniline as the main products when treated with sodium amide in liquid ammonia?



Q-2 Answer ANY SEVEN of the following in short.

[14]

- cis*-1,2-Dimethylcyclohexane is optically inactive even though it has two chiral centers. Explain.
- Which factors favour ipso substitution?
- Acetophenone on Beckmann rearrangement do not give *N*-methyl benzamide.
- Addition of HBr to 1-phenylpropene yields only (1-bromopropyl)benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.
- Why does menthyl chloride give a single product in elimination reaction?
- Define (i) chiral axis and (ii) homomorphous ligand.
- Friedel-Crafts reaction of benzene with (R)-2-chlorobutane produces optically active or racemic product. Explain.
- Justify that chirality is neither necessary nor the sufficient condition for the occurrence of diastereotopic ligands in molecule.
- How topicity can be decided by symmetry operation?

Q-3 [A] Explain the following statements.

[06]

- 1,2-Dichlorocyclopropane has two stereogenic carbon atoms, comment on its stereoisomerism.
- Define prochiral centre. Assign prochiral descriptors to methylene hydrogens in 2S-chloro butane

Q-3 [B] Discuss in detail.

[06]

- Show that carbon-3 is pseudo-chiral in 2,3,4-trihydroxypentane
- How many stereoisomers are possible for 2,3-dibromopentane? Draw their structure and give R/S notation to them.

OR

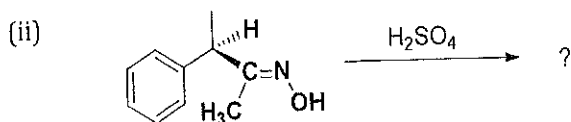
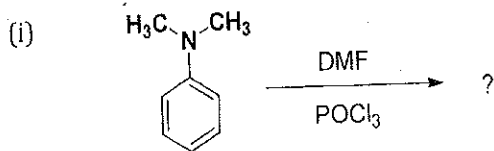
Q-3 [B] Do as directed.

[06]

- (i) Show that rotation of 90° is not allowed to Fischer projection formula.
(ii) Discuss Klyne-Prelog terminology by citing suitable example.

Q-4 [A] Complete the following transformation with detail mechanism

[06]



Q-4 [B] Answer the following

[06]

- (i) Sommelet Hauser rearrangement involves 2,3-sigmatropic shift.
(ii) Dieckmann condensation is an intramolecular Claisen condensation

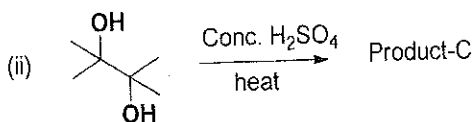
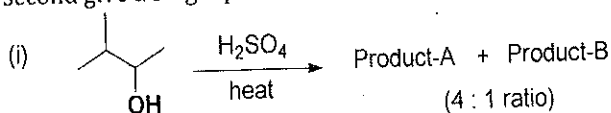
OR

Q-4 [B] Explain in detail.

[06]

- (i) 1, 2-hydride shift in Wagner Meerwein rearrangement does not change molecular skeleton.
(ii) Schmidt reaction is more advantageous over Curtius reaction

Q-5 [A] Suggest mechanisms for these eliminations. Why does the first give a mixture and the second give a single product? [06]



Q-5 [B] Answer the following.

[06]

- (i) Explain the factors favouring E1 elimination.
(ii) Show that hydroxylation of alkene by using peracid is stereospecific.

OR

Q-5 [B] Do as directed.

[06]

- (i) Give the difference between Cope and Chugaev elimination
(ii) Explain Markonikoff's rule by taking example of reaction between HBr and 1-methylcyclohexene

Q-6 [A] Explain in detail.

[06]

- (i) Primary kinetic isotope effect is not observed for nitration of benzene.
(ii) Benzene does not give the product of hydrochlorination with HCl in presence of $AlCl_3$ but it undergoes substitution reaction.

Q-6 [B] Describe in brief.

[06]

- (i) Electrophilic substitution of Naphthalene is more favoured at position - 1 rather than position - 2.
- (ii) Nitration of aniline gives meta derivative as a major product.

OR

Q-6 [B] Answer the following.

[06]

- (i) Discuss the sulphonation of Naphthalene.
- (ii) Electrophilic substitution reaction of pyridine occurs at position-3. Explain.

.....X.....