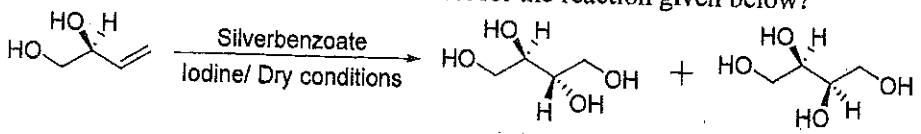
[34] SEAT No._____ Total No. of pages: 03

SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-II) EXAMINATION
WEDNESDAY, 20th MARCH 2019
TIME: 10.00 a.m. to 01.00 p.m.
ORGANIC CHEMISTRY–II: PS02CCHE22

Note: Figure to the right indicate full marks. **Total marks: 70**

Q.1 **Select the correct option for the following questions from (i) to (iv) options given below each question.** Mention the question number and answer only in your answer book e.g. (a)-(iii) **(08)**

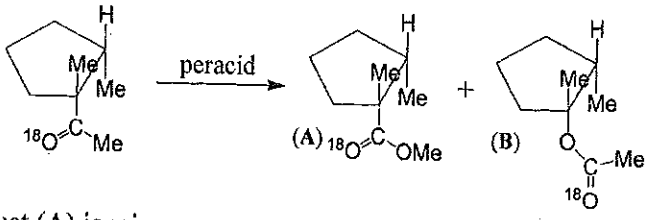
(a) Which of the following statements are correct for the reaction given below?



1. Only product A is formed.
2. Products A and B are formed in equal amount.
3. Product A is a threo isomer and Product B is an erythro isomer.
4. Product A is an erythro isomer and Product B is a threo isomer.

(i) 1, 2 and 3 are correct. (ii) 1, 2 and 4 are correct.
(iii) 2 and 3 are correct. (iv) 2 and 4 are correct.

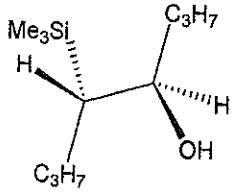
(b) Which of the following statements are correct for the shown reaction?



1. Product (A) is minor.
2. Methyl group has less migratory aptitude than 1° carbon, 2° carbon and 3° carbon.
3. The reaction occurs by retaining the original geometry of the substrate.
4. Carbonyl oxygen of the substrate is inserted between carbonyl carbon and the alkyl group.

(i) 1, 2 and 3 (ii) 1, 3 and 4 (iii) 2, 3 and 4 (iv) 2 and 3

(c) In Peterson reaction, the following β-hydroxyalkyltrimethylsilane in the presence of BF_3 will yield _____.



(i) Z-3-hexene (ii) *E*-4-octene
(iii) Z-4-octene (iv) *E*-3-hexene

(d) Optical purity of an isomer (+) - A produced in a reaction is 79%. The amount of its enantiomer (-) - A in the product mixture should be_____.

(i) 10.5% (ii) 21% (iii) 68.5% (iv) 89.5%

C.P.T.O.

(e) Which of the following statements are correct for Brown's hydroboration of alkene?
1. The overall addition is syn and occurs from the most hindered side.
2. It is regioselective and boron adds to less substituted olefinic carbon.
3. Addition of H-B to alkene gives anti-Markonikoff's product.
4. It occurs through a four membered transition state.
(i) 2 and 4 are correct. (ii) 1, 2 and 4 are correct.
(iii) 1, 3 and 4 are correct. (iv) 2, 3 and 4 are correct.

(f) The oxidation state of carbon-1 in propanoic acid is _____.
(i) +3 (ii) +2 (iii) +1 (iv) -3

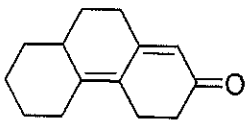
(g) 1-methylcyclohexene upon hydroboration with 9-BBN and then carbonylation in presence of $LiAlH(OCH_3)_3$ followed by alkaline H_2O_2 oxidation gives_____.
(i) *cis*-2-methylcyclohexane carboxaldehyde
(ii) *trans*-2-methylcyclohexane carboxaldehyde
(iii) *trans*-2-methylcyclohexanol
(iv) 1-methylcyclohexanecarboxaldehyde

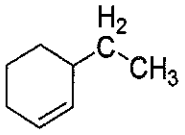
(h) **Assertion** A: 2-pentanone upon treatment with lithium diisopropylamide produces thermodynamic enolate.
Reason R: Enolate ion formation is irreversible as LDA is a strong and bulky base.
(i) **A** is true and **R** is the correct reason for it.
(ii) **A** is true but **R** is NOT the correct reason for it.
(iii) **A** is false and **R** is true.
(iv) Both **A** and **R** are false.

Q.2 **Answer ANY SEVEN of the following.** **(14)**

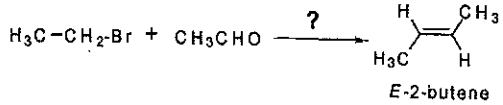
(a) How 1,4-pentadiene can be converted to cyclohexanone?
(b) Give mechanism for the action of dimethylsulphoxide on 2-pentanol in the presence of *p*-toluenesulphonyl chloride.
(c) How does DCC work in the formation of methylbenzoate from benzoic acid?
(d) Explain mechanism for oxidation of benzyl alcohol using MnO_2.
(e) Give reaction of excess of methyl lithium with diethyl carbonate.
(f) Predict the product of ozonolysis of 2,3-dimethyl-1,3-butadiene.
(g) How propanamide reacts with $LiAlH_4$?
(h) Predict the structure of a polyhydric compound which gives two moles of formic acid and one mole of glyoxalic acid by consuming 2 moles of periodic acid.
(i) How trimethylsilylhalide can be used in purification of enolates?

Q.3 (a) Suggest synthesis of following molecules by the mentioned reaction. **(06)**
(i) Robinson Annulation (ii) Shapiro Reaction





(b) (i) Give synthesis for the following molecule by using Wittig reaction. **(06)**



E-2-butene

(ii) How replacement of phenyl sulfones with heteroaryl sulfones alters the reaction pathway for classical Julia olefination?

OR

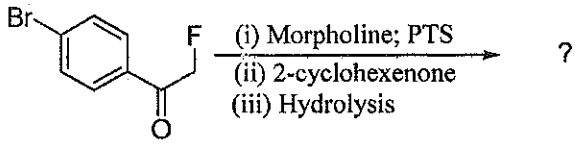
(b) Justify following statements: **(06)**

(i) The nature of solvent decides pathway for Bamford-Stevens reaction.

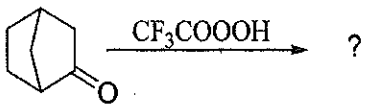
(ii) In Wittig reaction using stabilized ylide, the product ratio is governed by rate of decomposition of betaine intermediate.

Q.4 **(a)** Complete and explain following reactions. **(06)**

(i)



(ii)



(b) (i) Which steps are involved in mechanism of Buchwald–Hartwig amination? **(06)**

(ii) Explain the stereochemistry involved in Woodward hydroxylation of fumaric acid.

OR

(b) Justify following statements. **(06)**

(i) Migratory aptitudes from carbon to oxygen in Bayer Villiger reaction and from boron to oxygen in alkaline hydrogen peroxide oxidation of alkylboranes are different.

(ii) Hindered boron reagents have special role in carbonylation reaction of alkylboranes.

Q.5 **(a)** Complete following transformations. **(06)**

(i) (ii)

(b) Attempt following as suggested. **(06)**

(i) Oxidation of 2-butene with OsO_4 is a stereospecific reaction, explain.

(ii) Why different enolates are formed in the base abstraction reaction of 2-methyl cyclopentanone by using LDA and by triethylamine?

OR

(b) Justify following statements. **(06)**

(i) Sharpless asymmetric epoxidation is highly enantioselective reaction.

(ii) N-bromosuccinimide reacts differently with cyclohexene in aprotic polar solvent, non-polar solvent and under aqueous conditions.

Q.6 **(a)** Justify following statements by citing proper examples. **(06)**

(i) CH_3Li, CH_3MgBr and $(CH_3)_2CuLi$ react differently with pent-3-ene-2-one.

(ii) $NaBH_4$ is a more selective reagent than $LiAlH_4$.

(b) (i) How to increase the rate of Meerwein Pondroff Verley reduction? How does MPV reduction and Cannizzaro reaction differ from each other? **(06)**

(ii) Using Cram's rule, show that nucleophilic addition of methyl magnesium bromide to acetophenone is enantioselective.

OR

(b) (i) Give the importance of Tributyl tin hydride as a reagent in organic synthesis. **(06)**

(ii) Explain with suitable example that Wilkinson's hydrogenation is superior over heterogeneous hydrogenation.