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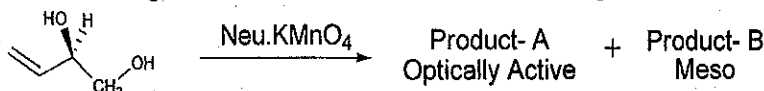
SARDAR PATEL UNIVERSITY
M.Sc. (SEMESTER-II) EXAMINATION
THURSDAY, 12th APRIL 2018
TIME: 10.00 a.m. to 01.00 p.m.
ORGANIC CHEMISTRY-II: PS02CCHE22

Note: Figure to the right indicate full marks.

Total marks: 70

Q.1 Select the correct option for the following questions from the 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. It is a case of anti hydroxylation.
2. Products A and B are formed in equal amount.
3. Product A is an erythro isomer and Product B is a threo isomer.
4. Product A is a threo isomer and Product B is an erythro isomer.

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

(b) The oxidation state of carbon-1 in acetic acid is _____.

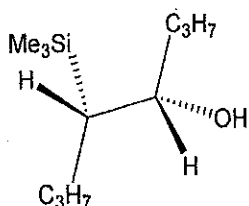
- (i) +3 (ii) +2
 (iii) +1 (iv) -3

(c) **Assertion A:** Lithium diisopropylamide produces kinetic enolate of 2-pentanone.

Reason R: Enolate ion formation is reversible 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.

(d) In Peterson reaction, the following β -hydroxyalkyltrimethylsilane in the presence of sodium hydride will yield _____.



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

(e) Bamford Stevens reaction when performed using a protic solvent produces _____.

- (i) high yield of terminal alkene.
 (ii) high yield of internal alkene without any side products.
 (iii) internal alkene with many other by-products.
 (iv) terminal alkene through carbocationic intermediate.

(f) 1 mole of a compound gives 2 mole of formic acid and 2 mole of glyoxalic acid upon oxidative cleavage using periodic acid oxidation. How many moles of H_5IO_6 will be consumed during this reaction?

- (i) 1 mole (ii) 2 mole (iii) 3 mole (iv) 4 mole

①

[P.T.O.]

- (g) Match the following listed **Reagents (A)** and the **Names (B)** associated with them. Find the correct answer from the codes given below.

	<u>Reagents (A)</u>	<u>Associated Names (B)</u>
I	HIO ₄	(a) Criegee oxidant
II	SeO ₂	(b) Moffatt oxidant
III	DMSO-PTS	(c) Reilly oxidant
IV	Pb(OAc) ₄	(d) Malaprade oxidant
		(e) Kornblum oxidant
		(f) Jones Reagent

- (i) I-(d) ; II-(c) ; III-(e) ; IV-(a) (ii) I-(c) ; II-(d) ; III-(e) ; IV-(a)
 (iii) I-(e) ; II-(f) ; III-(b) ; IV-(d) (iv) I-(d) ; II-(a) ; III-(b) ; IV-(c)

- (h) **Assertion A:** In Stork enamine reaction primary amine is not used.

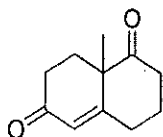
Reason R: Primary amines favour formation of conjugated enamines over the non-conjugated isomers.

- (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 true and R are false.
 (iv) A is false and R is true

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

- (a) How symmetrical alkenes can be synthesized by Wittig reaction?
 (b) Give mechanism for Moffatt oxidation of 2-butanol.
 (c) Explain the differences in migratory aptitude in the intermediates of Baeyer Villiger oxidation and hydroboration reaction.
 (d) Give the mechanism of amide formation from benzoic acid and methylamine using dicyclohexylcarbodiimide.
 (e) Show that 9-BBN is more regioselective and chemoselective than B₂H₆.
 (f) Why Grignard reagents should be protected from carbon dioxide, water and oxygen?
 (g) Explain mechanism for the conversion of tetralin to naphthalene using DDQ.
 (h) How do Grignard and Gilman reagents differ in their reactivity towards the given molecule, hex-3-en-2-one?
 (i) Give mechanism for oxidation of benzylic alcohol using MnO₂.

Q.3 (a) (i) Give complete synthesis for the following molecule by using Robinson ring annulation reaction. (06)



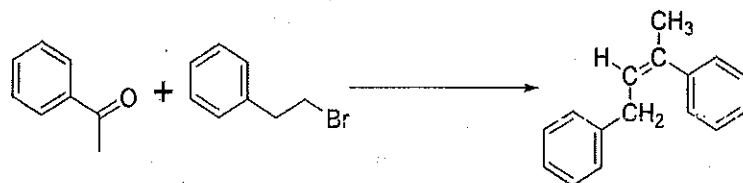
- (ii) How replacement of phenyl sulfones with heteroaryl sulfones alters the reaction pathway for classical Julia olefination?
 (b) Explain the following statements: (06)
 (i) The mechanism of Bamford-Steven's reaction is dependent on nature of solvent.
 (ii) In Wittig reaction employing stabilized ylide, the ratio of E-Z alkenes in product mixture is governed by decomposition rate of betaine intermediate.

OR

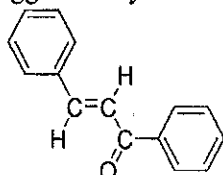
(b) (i) Complete the following reactions and explain. (06)



(ii)



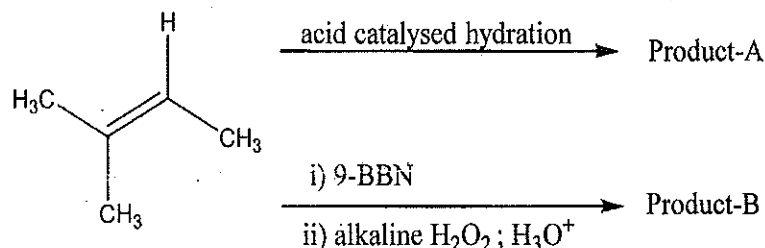
Q.4 (a) (i) Suggest the synthesis of following molecule by Stork enamine reaction. (06)



(ii) How propene can be converted to butanal and 4-heptanol using hydroboration reaction?

(b) (i) Discuss mechanism of Bayer Villiger reaction using isotopic labelling technique. (06)

(ii) Explain the differences in the product formation in following reactions.



OR

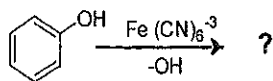
(b) Answer the following. (06)

(i) Explain the stereochemistry involved in Prevost hydroxylation of cis-2-butene.

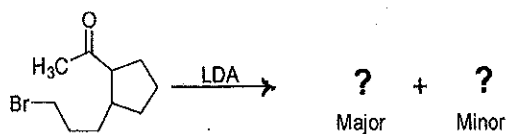
(ii) Which steps are involved in mechanism of Buchwald-Hartwig amination?

Q.5 (a) Complete the following reactions and explain. (06)

(i)



(ii)



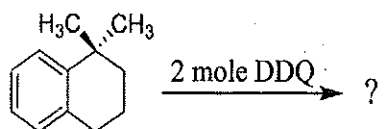
(b) (i) Justify the formation of meso-tartaric acid from maleic acid upon treatment of with neutral KMnO₄. (06)

(ii) Explain reactions of n-BuLi with ethyl orthoformate and diethyl carbonate.

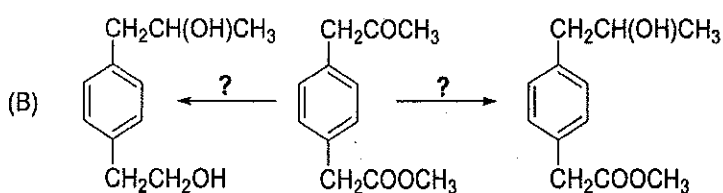
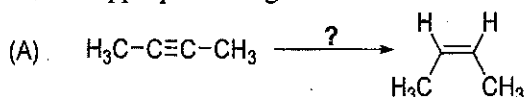
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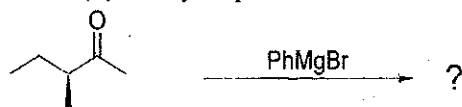
- (b) (i) Give all synthetic applications of mercuric oxide as the reagent. (06)
 (ii) Complete the following transformation.



- Q.6 (a) Justify following statements by citing proper examples. (06)
 (i) The concentration of tributyl tinhydride controls product formation in reduction of haloalkenes.
 (ii) LiAlH_4 and NaBH_4 differ in their reactivity.
 (b) (i) Put the appropriate reagent and reaction condition for following reactions. (06)



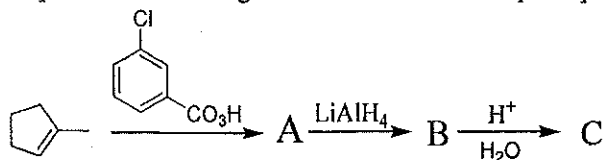
- (ii) Using Cram's rule, show that following nucleophilic addition of phenyl magnesium bromide on 3(S)-methyl-2-pentanone is diastereoselective.



3(S)-methyl-2-pentanone

OR

- (b) (i) How does Meerwein Ponderoff Verley reduction mechanistically differ from the Cannizzaro reduction? How to increase the rate of MPV reduction? (06)
 (ii) Complete the following reaction scheme and explain product formation.



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