

[60]

Printed pages: 03

SARDAR PATEL UNIVERSITY
SEMESTER-II EXAMINATION
M.Sc. (CHEMISTRY)
Thursday, 23rd April, 2015
ORGANIC CHEMISTRY [PS02CCHE02]

Time: 02:30 p.m. to 05:30 p.m.

Total marks: 70

Q-1. Select the correct answer from the options given below for each of the following question. [08]
 Mention the answers only e.g. (a) - (ii) in the given answer book.

- (a) IUPAC name of [15]-Crown-5 is _____.
- (i) 1,4,7,10,13-pentaoxocyclohexadecane (ii) 1,4,7,10,13-pentaoxocyclooctadecane
 (iii) 1,4,7,10,13-pentaoxocycloheptadecane (iv) 1,4,7,10,13-pentaoxocyclopentadecane
- (b) Oppenauer oxidation is the reverse reaction of _____.
- (i) Clemensen reduction (ii) Complex hydride reduction
 (iii) Birch reduction (iv) Meerwein Ponderoff Verly reduction
- (c) Active methylene groups can be selectively oxidised by _____.
- (i) SeO₂ (ii) MnO₂ (iii) DMSO/PTS (iv) Al(O-terbutyl)₃
- (d) Periodic oxidation of a compound consumes 2 moles of HIO₄ to give 2 mole of formic acid and 1 mole of formaldehyde. This compound may be _____.
- (i) 1,2-propanediol (ii) 2,3-dihydroxypropanal (iii) glycerol (iv) 2-hydroxypropanal
- (e) Which of the following reagents is used for anti-hydroxylation?
- (i) Lead tetraacetate (ii) Woodward reagent
 (iii) HIO₄ (iv) Prevost Reagent
- (f) Wolff Kischner reduction is used for reduction of _____.
- (i) base sensitive substrates (ii) acid sensitive Substrates
 (iii) acyl halides to aldehydes (iv) alkenes and alkynes
- (g) Arrange the following mechanistic steps in order of their occurrence for reduction using Wilkinson catalyst.
- (1) Reductive elimination
 (2) Oxidative addition of H₂ to the metal
 (3) π -complexation of alkene
 (4) Intramolecular hydride transfer
- (i) 1,2,4,3 (ii) 1,4,3,2 (iii) 2,3,4,1 (iv) 2,4,3,1
- (h) Which of the following is one of the twelve principles of Green Chemistry?
- (i) The energy requirement for a chemical synthesis should be the lowest.
 (ii) Waste treatment and its disposal should be efficient.
 (iii) Use of catalysts should be discouraged.
 (iv) Use of protecting groups should be encouraged.

Q-2. Answer ANY SEVEN of the following questions.

[14]

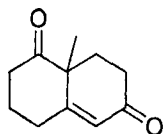
- How does Bamford-Stevens reaction differ from Shapiro reaction?
- Give mechanism for oxidation of benzylic alcohol using MnO_2 .
- Why Wittig reaction should be performed under dry and inert conditions?
- Calculate oxidation number for carbon-1 in 1-pentanol, pentanal and pentanoic acid.
- Why Horner-Emmons reaction is more advantageous over Wittig reaction?
- Give synthesis of $\text{N,N}'$ -dicyclohexylcarbodiimide which is used as a dehydrating agent.
- What precautions are to be observed in using Grignard reagents?
- Explain the differences in migratory aptitude in the intermediates of Baeyer Villiger oxidation and hydroboration reaction.
- Describe reduction of 2° and 3° amides by LiAlH_4 .

Q-3.

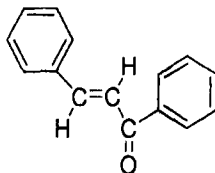
3(a) Suggest synthesis of following compounds by the reaction mentioned against them.

[06]

i)



ii)



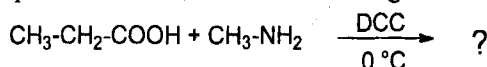
Robinson annulation

Stork enamine Reaction

3(b) (i) Why does stabilized ylide preferentially lead to the formation of *E*-alkene in Wittig reaction?

[06]

(ii) Explain the role of DCC in following reaction.

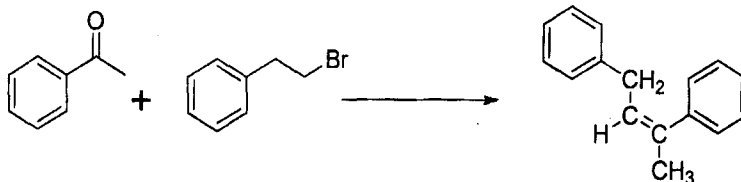


OR

3(b) (i) Explain regioselectivity of Stork enamine reaction by citing suitable example.

[06]

(ii) Mention the required reagents and describe reaction conditions to complete following reaction.



Q-4.

4(a) (i) Explain the role of 1,3-dithiane in organic synthesis. What is the usefulness of Mozingo method of reduction?

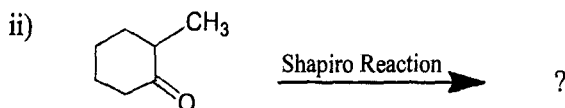
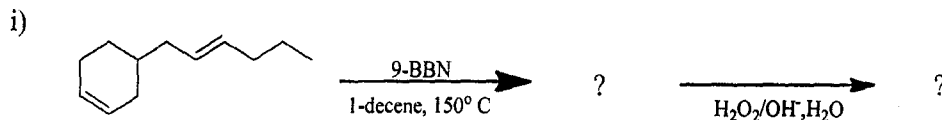
[06]

(ii) Highlight the differences in the reactivity of internal & terminal alkynes in hydroboration reaction followed by alkaline hydrogen peroxide oxidation.

- 4(b) i) Show the importance of carbonylation of organoborane compounds in organic synthesis. [06]
 ii) Show that Peterson olefination follows anti elimination under acidic conditions.

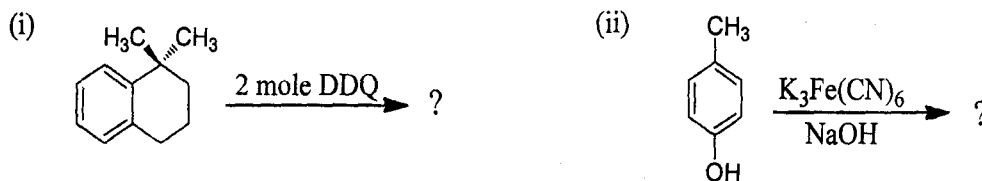
OR

- 4(b) Write the product of the following reactions and suggest probable mechanism. [06]



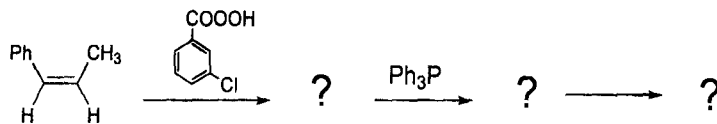
- Q-5(a) (i) What are the characteristics of good oxidizing agents? [06]
 (ii) Give all synthetic applications of mercuric oxide as the reagent.

- 5(b) Predict the product of following reactions with appropriate mechanism: [06]



OR

- 5(b) (i) Complete the following reaction scheme and explain. [06]



- (ii) Show that Prevost hydroxylation of *trans*-2-butene gives meso-2,3-butanediol.

- Q-6(a) (i) Give the importance of Tributyl tin hydride as a reagent in organic synthesis. [06]
 (ii) How do LiAlH_4 and NaBH_4 differ in their reactivity? Explain with suitable examples.

- 6(b) (i) Discuss the effects on outcome of Birch reduction by presence of electron donating and electron withdrawing groups on the substrate. [06]

- (ii) Describe mechanism of Wolff-Kischner reduction. What modifications are suggested in it?

OR

- 6(b) i) What are the advantages of phase transfer catalysts? Give synthesis of 18-crown-6. Discuss working mechanism of 18-crown-6 as the phase transfer catalyst in KMnO_4 oxidation of a water immiscible substrate performed in aqueous medium. [06]

- ii) Give an example of a reaction having 100% atom economy.
