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SEAT No. _____

No of Printed Pages: 04

SARDAR PATEL UNIVERSITY
M.Sc. (CHEMISTRY) Semester -II, Examination
April 12, 2018 Thursday
ORGANIC CHEMISTRY - II [PS02CCHE02]

Time: 10:00 am - 01:00 pm

Maximum Marks - 70

Q.1 Select the correct answer from the option given below for each of the following questions. Write [08]
ONLY ANSWERS in the provided answer book. [e.g. Q.1 (1)-(a)]

(1) Pent-3-ol on reaction with $\text{Al}[\text{O}-\text{C}(\text{CH}_3)_3]_3$ in presence of acetone gives _____.

- (a) Pentane (b) Pentanoic acid
 (c) Pentanal (d) Pentan-3-one

(2) Which of these reagents could accomplish the following reaction?



- (a) NaBH_4 (b) LiAlH_4
 (c) H_3O^+ (d) None of these

(3) What ylide is needed to make 3-ethyl-3-heptene from 3-pentanone in a Wittig reaction?

- (a) $\text{Ph}_3\text{P}=\text{CH}-\text{CH}_2-\text{CH}_3$ (b) $\text{Ph}_3\text{P}=\text{C}(\text{CH}_2\text{CH}_3)_2$
 (c) $\text{Ph}_3\text{P}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (d) $\text{Ph}_3\text{P}=\text{CH}-\text{CH}_3$

(4) Which of the following is the correct pair of reagents to get 2-pentanone from pentyne?

- (a) Disiamylborane + Acetic acid (b) Disiamylborane + Alkaline H_2O_2
 (c) Hydrochloric acid + Water + Mercuric Sulfate (d) Tetrylborane + Carbon monoxide

(5) In the hydrogenation of alkene using Wilkinson's catalyst, The first step in the catalytic cycle is _____.

- (a) alkene coordination (b) oxidative addition of H_2
 (c) loss of PPh_3 (d) loss of chloride ion

(6) Which of the following statements are not true for Stork-Enamine reaction?

- (i) It is used for the alkylation and acylation of a carbonyl compound.
 (ii) Alkylation usually occurs on the more substituted side of the original ketone.
 (iii) Aldehyde can't be alkylated.
 (iv) Self condensation of carbonyl compound is possible.

- Option: (a) i, iii & iv (b) i, ii & iv
 (c) ii, iii & iv (d) i, ii & iii

- (7) The reaction of N-Bromosuccinamide (NBS) with cyclohexene in the presence of a radical initiator leads to which one of the following products?
- (a) 1,2-dibromocyclohexene (b) 3-Bromocyclohexene
 (c) Bromocyclohexene (d) 3,3-dibromocyclohexene
- (8) Which of the following statement correct for Bamford Stevens reaction?
- (a) Carbene is generated as an intermediate in presence of protic solvent
 (b) Carbocation is generated as an intermediate in presence of aprotic solvent
 (c) Highly substituted alkene obtained in a good yield
 (d) Highly substituted alkene obtained in a poor yield

Q.2 Answer ANY SEVEN of the following

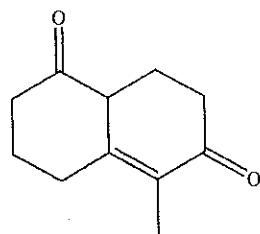
[14]

1. Explain: Umpolung approach in dithiane reagent.
2. How will you extend the alkyl chain by one & two carbon atoms using Grignard reagent?
3. Why KMnO_4 oxidation in presence of dicyclohexano-18-crown-6 is superior to the routine method?
4. 2S-Bromobutane has specific rotation $+23.1^\circ$. A mixture of enantiomeric bromobutane has observed specific rotation of $+9.24^\circ$. Find out enantiomeric excess and %age of S isomer in the mixture.
5. Explain: Chemoselectivity of the hydroborating reagents by citing proper example.
6. Give the mechanism for the oxidation of 2^o-alcohol using Oppenauer oxidation.
7. Compare the reactivity of LiAlH_4 and NaBH_4 .
8. How higher homologous of cyclic ketone can be synthesized by Wittig reaction?
9. Give the mechanism for the reaction of α -hydroxy carboxylic acid with leadtetraacetate.

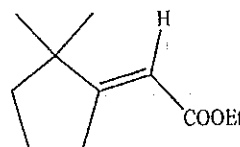
Q.3

(a) Synthesize the following compounds by the reaction mentioned against them.

[06]



(Robinson Annulation Reaction)



(Wittig reaction)

- (b) Describe the role of DCC in the formation of following compounds: [06]
1. Benzoylperoxide from benzoic acid
 2. β -lactam from β -aminocarboxylic acid

OR

- (b) Justify the following statements: [06]
1. Low temperature modification of Wittig reaction predominantly yields E-alkene even with non-stabilized ylide.
 2. Stork Enamine reaction is regioselective.

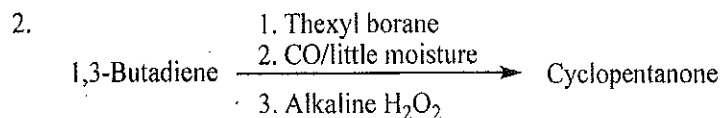
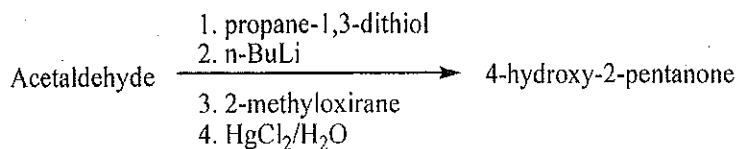
Q.4

- (a) Justify the following statements: [06]
1. Bamford Stevens reaction in presence of protic solvent involves carbocationic intermediate.
 2. Acid catalyzed decomposition of *erythro*- β -hydroxy-silane gives E-alkene in Peterson olefination reaction.

- (b) Answer the followings: [06]
1. Give the experimental proof for [3,3]-sigmatropic rearrangement in a reaction of allyl borane with aldehyde.
 2. Give the synthesis of 3-methyl-1-cyclohexene from 2-methyl cyclohexanone using Shapiro reaction.

OR

- (b) Explain the following transformation: [06]



Q.5

- (a) Explain the followings: [06]
1. Reaction of mono and bis-hydrazones of α -diketones with mercuric oxide.
 2. Reaction of 3(R)-phenyl-2-butanone with PhMgBr using Cram's rule.

(b) Explain the following with appropriate mechanisms: [06]

1. Oxidation of toluene using alkaline KMnO_4 .
2. Prevost hydroxylation of *trans*-2-butene.

OR

(b) Explain the following transformation with appropriate mechanism: [06]

1. 2-hydroxybenzaldehyde to 1,2-dihydroxybenzene using alkaline H_2O_2 .
2. 2-bromo-1-phenylethanone to 2-oxo-2-phenylacetaldehyde using DMSO.
3. 1,1-dimethyltetraline to 1,2-dimethylnaphthalene using DDQ.

Q.6

(a) Answer the followings: [06]

1. What is Green Chemistry? Draw the structure & IUPAC name of i) bicyclohexyl-18-crown-6 and ii) 24-crown-8
2. Discuss the mechanistic differences of Meerwein Ponndrof Verly reduction with Cannizzaro reaction.

(b) Answer the followings: [06]

1. Elaborate the mechanism for conversion of halogeno compounds to hydrocarbons by TBTH.
2. Write a short note on: Wilkinson catalyst.

OR

(b) Discuss the mechanism for reduction of following compounds by LiAlH_4 . [06]

- i) Propanoic acid ii) N,N-dimethylpropanamide iii) Ethylacetate