

[94]

M.Sc. Semester-IV (Organic Chemistry) Examination

Tuesday, 26th March 2019

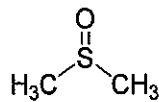
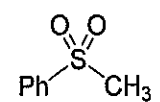
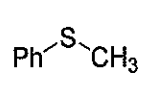
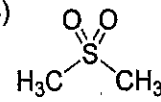
Topics in Organic Chemistry: PS04EORC21

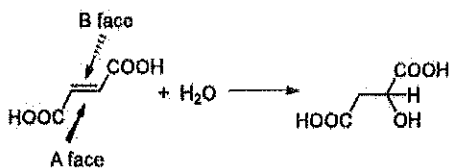
Time: 02:00 p.m. to 05:00 p.m.

Marks: [70]

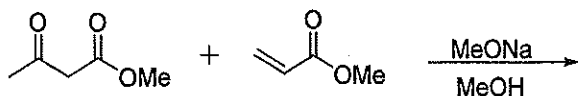
Note: Right hand figures indicate marks

Q-1 Select the correct answer from the options given below. [08]

- Which of the following cross coupling reactions uses terminal alkyne as one of the starting material?
(a) Suzuki (b) Stille (c) Sonogashira (d) Kumada
- Which of the following reagent/reaction proceeds via radical pathway?
(1) TEMPO (2) Ritter reaction (3) McMurry reaction (4) Luche reagent
(a) 1 & 2 (b) 1 & 3 (c) 3 & 4 (d) 2 & 4
- The haptic number and number of electrons donated by π -allyl cation for formation of π -complex with palladium metal are _____.
(a) η^2 and 3 (b) η^3 and 4 (c) η^2 and 2 (d) η^3 and 2
- Which of the following complex do not obey 18 electron rule?
(a) ferrocene (b) $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (c) $\text{Pd}(\text{PPh}_3)_4$ (d) $\text{Fe}(\text{CO})_5$
- Which one of the following reagents is not used for selective protection of unhindered primary alcohols in the presence of secondary alcohols?
(a) TMS (b) TBDMS (c) TBDPS (d) TIPS
- The correct order of acidity for the following molecules is _____.
(1)  (2)  (3)  (4) 
(a) 1>3>2>4 (b) 2>4>1>3 (c) 2>1>4>3 (d) 2>4>3>1
- Hydration of fumaric acid gives malic acid as shown below. Assume that addition of water takes place specifically from A face or B face. The correct statement pertaining to stereochemistry of malic acid formed is

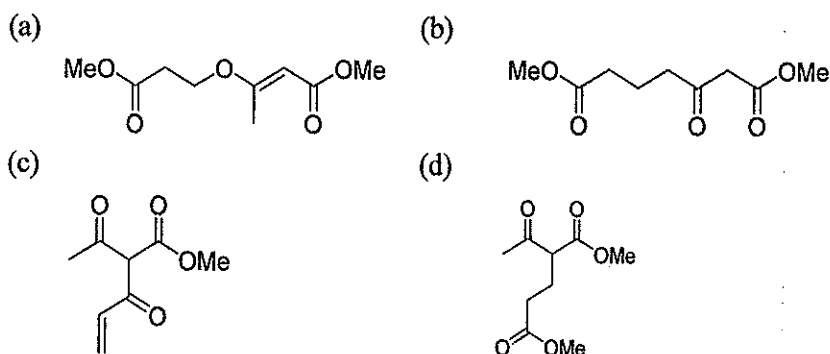


- addition specifically from B face gives S-isomer of malic acid
 - addition specifically from A face gives S-isomer of malic acid
 - addition specifically from B face gives a racemic mixture of malic acid
 - addition specifically from A face gives R-isomer of malic acid
- The major product formed in following reaction is



(1)

(PTO)



Q-2 Answer the following (Any Seven).

[14]

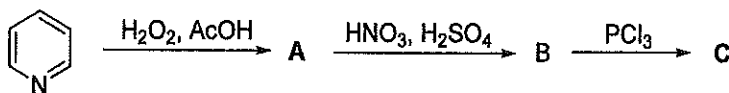
- Why oxidative additions of MeI and H₂ to the Vaska's complex follow different pathway?
- Deduce the structure of A, B and C in following reaction.



- Explain the Sharpless dihydroxylation of *trans*-stilbene.
- Write a short note on bonding interactions in transition metal complexes.
- Explain Hiyama coupling with reaction mechanism.
- Explain Stereoselectivity in dehydrobromination reaction of 2-bromopentane with NaOEt.
- Deduce the structure of A and B in the following reaction scheme.



- Complete the following reaction scheme.



- Predict multiplicity and approximate δ ppm values for ¹H-NMR spectrum of methyl-5-bromopentanoate.

Q-3 [A] Answer the followings

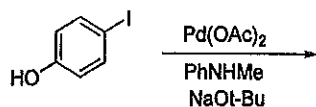
[06]

- Explain hydroformylation of alkene by oxo process proceeds via two migratory insertions.
- Explain Heck reaction with catalytic cycle.

[B] Answer the followings

[06]

- Explain-hydropalladation and dehydropalladation can lead to alkene isomerization.
- Give the product with appropriate mechanism.



OR

[B] Answer the followings

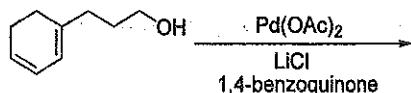
[06]

- Explain-nucleophilic substitution reaction to the π -allyl cation

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complex of palladium gives product with retention of configuration.

2. Give the product with appropriate mechanism.

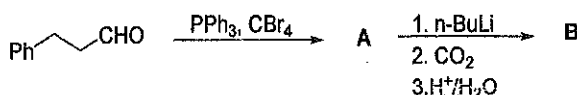


Q-4 [A] Explain the following statements. [06]

1. In Nef reaction primary nitroalkanes produce aldehydes while secondary nitroalkanes produce ketones.
2. Wacker oxidation involves three steps in catalytic cycle.

[B] Answer the following. [06]

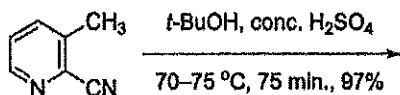
1. Write note on McMurry reaction.
2. Give the product with suitable mechanism.



OR

[B] Answer the following. [06]

1. Give applications of TEMPO reagent with suitable mechanism.
2. Give the product with suitable mechanism.

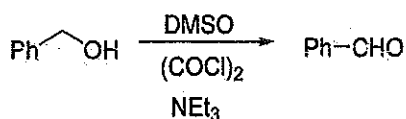


Q-5 [A] Justify the following statements. [06]

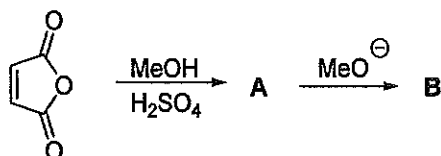
1. Peterson Olefination gives opposite geometrical isomers from the same diastereoisomer of the starting material.
2. With α,β -unsaturated ketones the non-stabilized sulfonium ylide favors 1,2-addition while the stabilized sulfonium ylide favors 1,4-addition.

[B] Answer the following. [06]

1. Give the mechanism for following transformation.



2. Complete the reaction scheme with appropriate mechanism.



OR

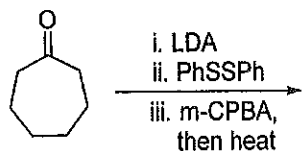
[B] Answer the following. [06]

1. Give synthesis of sulfenyl chloride from sulfuryl chloride with mechanism. Show that sulfenyl chloride is good soft electrophile.

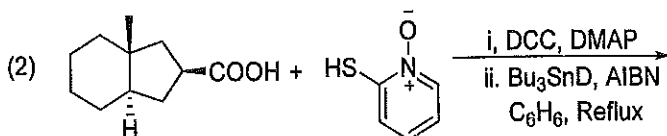
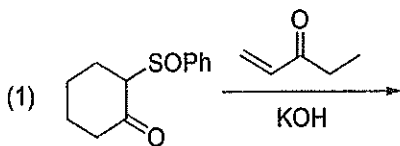
(3)

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2. Give the product with appropriate mechanism.

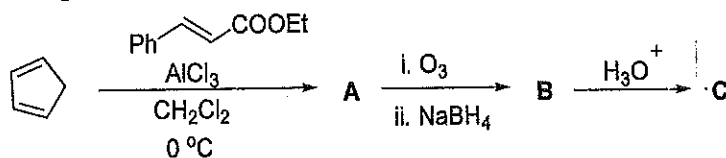


Q-6 [A] Complete the following reactions with appropriate reaction mechanism. [06]



[B] Answer the followings. [06]

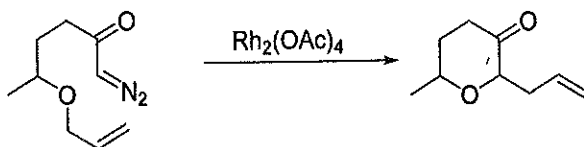
1. "The reaction of 3-methylindole with MeLi in dichloromethane involves carbene as a reactive intermediate", justify the statement.
2. Complete the following reaction scheme.



OR

[B] Answer the followings. [06]

1. Show that the following reaction involves [2,3]-sigmatropic rearrangement.



2. Complete the following reaction scheme.

