ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27
M.Sc. (Chemistry) - III SEMESTER
SEMESTER EXAMINATION: OCTOBER 2022
(Examination conducted in December 2022)
OCH9122: ORGANIC SYNTHESIS-I

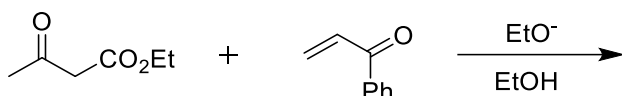Time: 2 ½ hours   Maximum Marks: 70

This question paper contains 3 printed pages and 3 parts

Part-A

Answer any SIX of the following: **(6 x 2 = 12)**

1. What is Bamford-Steven's reaction? Give an example.
2. Write down the product for the following reaction.

3. Mention any two applications of chromium trioxide in organic synthesis.
4. Give any two advantages of a supported catalyst.
5. What is a pre-catalyst and an active catalyst in a catalytic cycle? Give example for each.
6. What is Henry reaction? Give an example.
7. Give the structure of Grubbs generation II catalyst
8. What is ortholithiation? Give an example.

Part-B

Answer any FOUR of the following: **(4 x 12 = 48)**

9. (a) Outline the mechanism for the synthesis of Mannich base from acetophenone and formaldehyde.   (4+3+5)
   (b) Explain the mechanism of acyloin condensation with a suitable example.
   (c) Write down the mechanism for the following reaction
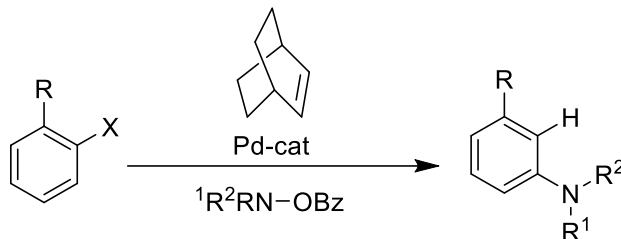

10. (a) Give the product(s) of C-H lithiation of (i) benzene, (ii) toluene, (iii) o-xylene and (iv) dimethylamine using an alkyllithium reagent.   (4+4+4)
    (b) Discuss the Schlenck equilibrium observed in organomagnesium compounds.
    (c) What is a Gilman reagent? How is it generated? Give any two of its applications in organic synthesis.

11. (a) Discuss the mechanism of the following reactions: (9+3)
    (i)   Wolf-Kishner reduction
    (ii)   Dess-Martin oxidation
    (iii)   Benkeser reduction
    (b) Predict the missing reagent(s) for the following reactions

(i)

(ii)

(iii)
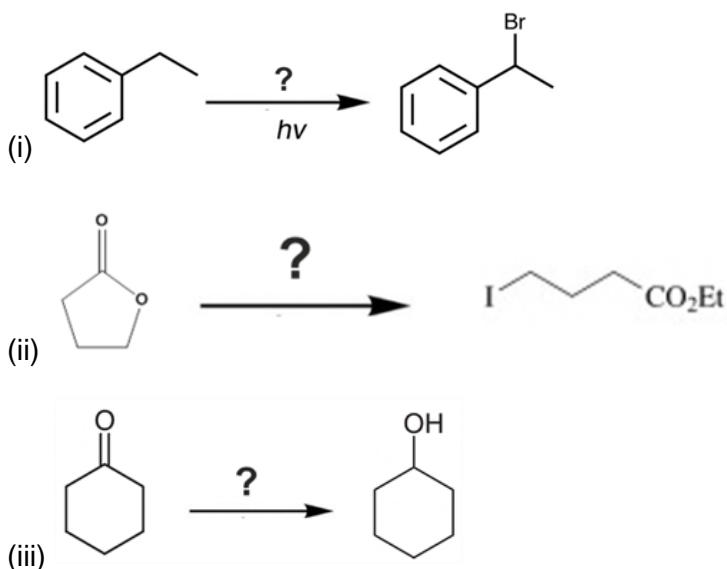
12. Describe a suitable catalytic cycle for the following: (4+4+4)
    (a) Assymmetric transfer hydrogenation of prochiral ketone using [(mesitylene)Ru{(R,R)-TsDPEN}Cl] (Noyori catalyst).
    (b) Alkene metathesis (general mechanism).
    (c) Mizaroki-Heck Coupling
13. (a) Write down the general mechanism for metal mediated C-H activation reaction.
                                                                              (3+6+3)
    (b) Explain the following individual steps using suitable examples for each. (i) Migratory insertion and (ii) β-hydrogen elimination.
    (c) Give the suitable reagent(s) for the following conversions

(i)

(ii)

(iii)
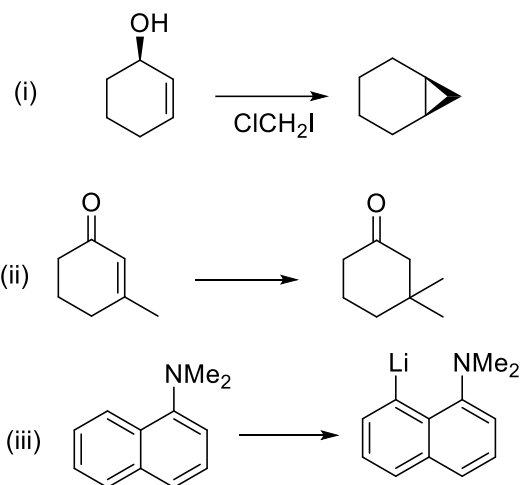
14. (a) Write down the product(s) for the following reaction: (4+4+4)

PG = CN

-2e⁻, 3 F mol⁻¹

PG = CO$_2$Et

PG = Protecting group
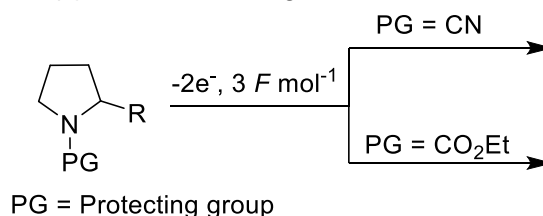
(b) Outline the mechanism of Sharpless asymmetric epoxidation.

(c) Explain the heterogenization of a transition metal based homogeneous catalyst with a suitable example via immobilization on a (i) polymeric and
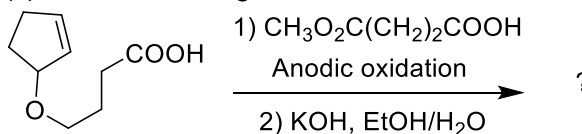(ii) metal oxide supports.

Part-C

Answer any TWO of the following: **(2 x 5 = 10)**

15. a) Write the missing reagent in the following reaction and discuss the mechanism of the formation of the product. (3+2)

H_2C—CO_2Et
|
H_2C—CO_2Et
+
Ph—CHO (Ph, O, H)
?
→
Ph—C=C—CO_2Et (H)
|
H_2C—CO_2H
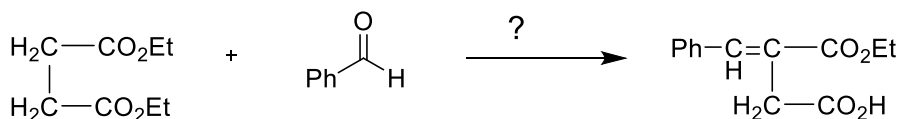
b) Predict the product(s) for the following reaction

1) $CH_3O_2C(CH_2)_2COOH$
Anodic oxidation
2) KOH, EtOH/H_2O
?

16. (a) How would you use organoboranes for the synthesis of 2-hexanone? Discuss the mechanism of the reaction involved. (3+2)

(b) Cyclohexene gives cis-cyclohexane-1,2-diol in the presence of A while it gives trans-cyclohexane-1,2-diol in the presence of B. Identify A and B.

17. (a) Which of the following ligands is more effective in a palladium catalyzed cross coupling reaction with a polar organometallic reagent? Justify your answer. (3+2)

(i)   P(p-tolyl)$_3$,

(ii)   dppf (diphenylphosphinoferrocene).

(b) Addition of excess of PEt$_3$ ligand increases the reductive elimination in [(dppe)Ni(R^1)(R^2)] (dppe = diphenylphosphinoethane). Justify your answer.

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