

Total number of printed pages-12

14 (CHM-2) CH 202

2018

CHEMISTRY

Paper : CH-202

(Organic Chemistry 2)

Full Marks : 80

Time : Three hours

The figures in the margin indicate full marks for the questions.

Unit 1

(Photochemistry)

Answer Q. 1 and **any three** from the rest.

4×5=20

1. a) A mixture of benzopenone and naphthalene is irradiated at a wavelength, where only benzophenone absorbs. Triplet energy of benzophenone is greater than that of naphthalene. Which of the following statements will be true about the photochemistry of this system? 1
- I. The naphthalene will exhibit fluorescence.

Contd.

II. Benzophenone phosphorescence will be enhanced.

III. The naphthalene will exhibit phosphorescence.

IV. Neither benzophenone nor naphthalene will give rise to phosphorescence.

b) A molecule exhibits delayed fluorescence and the intensity of fluorescence increases with the rise of reaction temperature. Identify the type of delayed fluorescence.

c) A molecule (X) exhibits phosphorescence. If the solvent is changed from benzene to bromobenzene, what will happen to the value of quantum yield of phosphorescence?

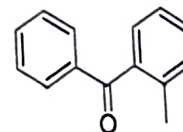
d) The energy difference (ΔE_{ST}) between the S_1 and T_1 state of three molecules X, Y and Z are 5, 30 and 70/kcal/mole respectively. Which of these three is most likely to show E-type delayed fluorescence?

e) The singlet and triplet energy of a molecule B are 80 and 65 kcal/mole respectively. If the B is produced from A as a result of chemical reaction, such that the enthalpy of activation for the reaction is 30 kcal/mole and the enthalpy change for the reaction $A \rightarrow B$ is -40 kcal/mole. Will the reaction be chemiluminescent?

2. Answer **either (a) or (b)** and (c): $1 \times 5 = 5$

a) (i) When benzophenone is irradiated in presence of isopropanol, benzopinacol is formed? How was it proved that the triplet excited state of benzophenone was involved in the reaction? 1.5

(ii) Show the products of the following photochemical reaction, with the intermediates involved, if any. Justify your answer. 1.5

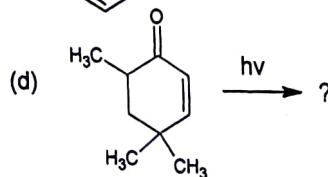
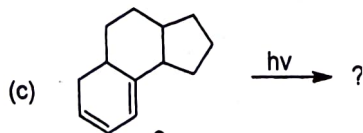
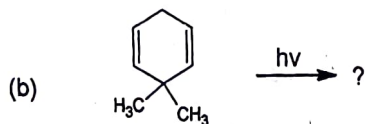
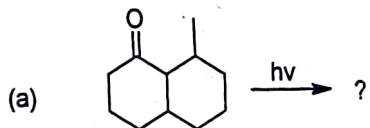


Or

(b) What happens when norbornene () is separately irradiated in presence of acetone and benzophenone? Justify the formation of different products. 3

- (c) The $\lambda_{\max}$ of photoexcitation and the energy of the triplet excited states of the *cis*- and *trans*- isomers of an alkene are (280 nm, 60 kcal/mole) and (320 nm, 50 kcal/mole) respectively. Comment on the photostationary state of *cis-trans* isomerization of that alkene, if it is irradiated in presence of sensitizer with a triplet energy of 62 kcal/mole. 2

3. Give the products of the following photochemical reactions with intermediate steps where necessary. 1.5+1.5 +1+1=5

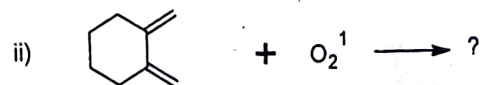
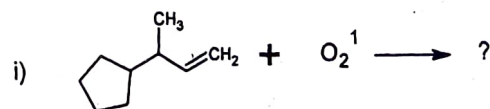


4. What is Paterno-Büchi reaction ? Comment on the products formed when excited state benzophenone reacts with *cis*- and *trans*-2-butene separately. How does it help in suggesting a reaction mechanism for the Paterno-Büchi reaction ?

1+2+2=5

5. What is singlet oxygen? How is it generated chemically ? — Illustrate with *two* examples. Give the products of the following reactions :

1+2+2=5

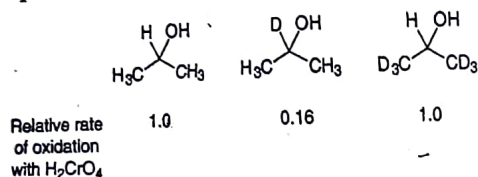


Unit 2

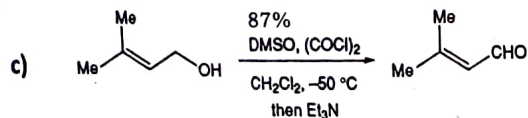
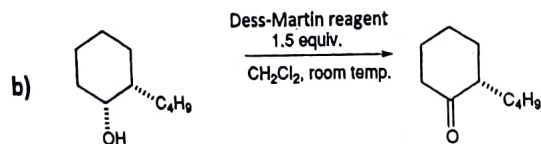
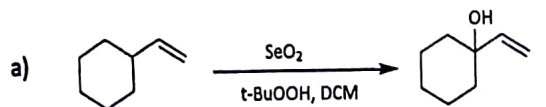
(Oxidation reaction)

Answer Q. 6 and **any two** from the rest: $6 + (5 \times 2) = 16$

6. Provide a mechanistic rationale for the oxidation of 2-propanol with chromic acid. The relative rates of 2-propanols with chromic acid are as follows. How do you explain the rate variation? $3 + 3 = 6$



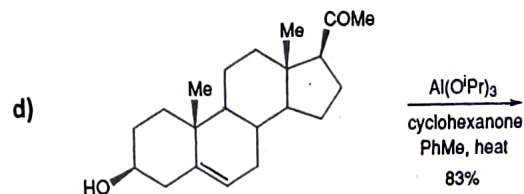
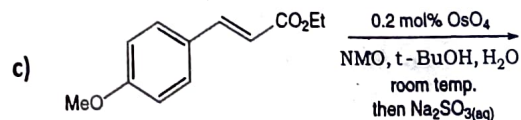
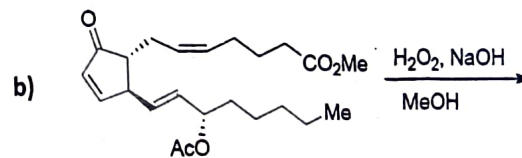
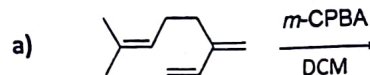
7. Propose mechanistic description for the following transformations: (**any two**)



$2.5 + 2.5 = 5$

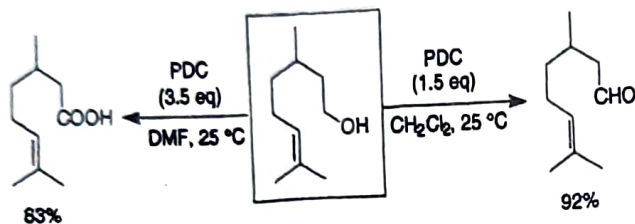
8. Give a schematic outline of the $\text{Ti}(\text{O}i\text{-Pr})_4$ catalysed asymmetric epoxidation of an allylic alcohol using (+/-)- diethyl tartrate as catalyst and *t*-BuOOH as the co-oxidant. Draw the structure of the active catalyst and identify the essential features. $3 + 2 = 5$

9. Predict the major products for the following reactions, and comment on the selectivity: (**any two**) $2.5 + 2.5 = 5$



10. Compare the acidity of Jones reagent, Collins reagent, pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC). How do you account for the reactivity and selectivity of PDC in the following reactions?

3+2=5



Unit 3

(Reduction reactions)

Answer **any two** from (Question 11 to Question 14)

2×5=10

11. Explain the stereochemistry of heterogeneous catalytic hydrogenation reaction with suitable examples. What are the major disadvantages of heterogeneous catalytic hydrogenation reactions?

3+2

12. Explain the reduction of conjugated ketones by sodium in ammonia with detailed mechanism. Why isolated double bonds cannot be reduced by sodium in ammonia?

3+2

13. Explain the stereochemistry of hydrogenation of ketones having one asymmetric centre by transfer hydrogenation reagents with detailed mechanism. How the reactivity of lithium aluminium hydride can be reduced, explain with suitable example?

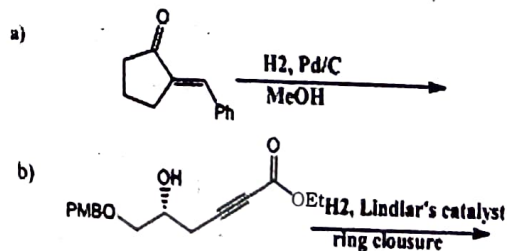
3+2

14. Explain the mechanism of reduction of a keto compound by NADPH. In case of reduction of ketones having prochiral centre how the stereochemistry is governed?

3+2

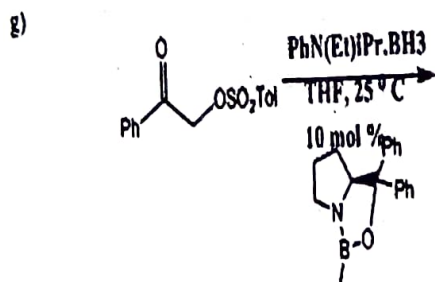
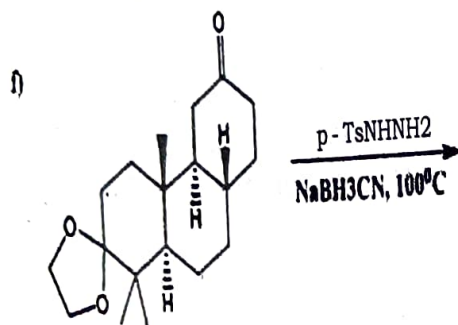
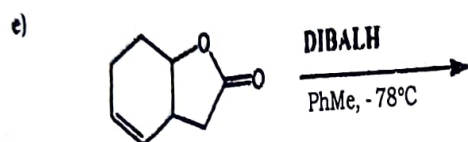
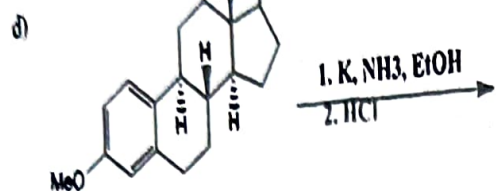
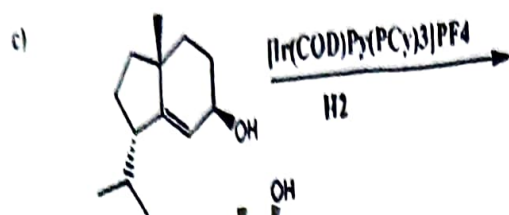
15. Predict the product(s) with plausible mechanism: (**any four**)

2.5×4=10



Unit 4

(Pericyclic reactions)

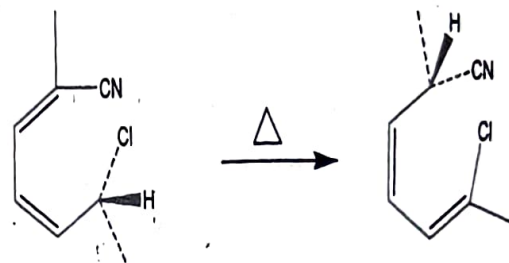


Answer **any six** :

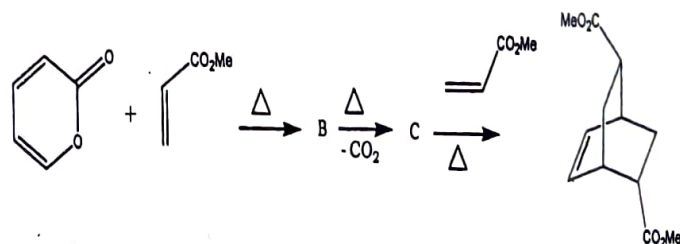
6×4=24

16. Based on symmetry correlation diagram discuss whether $\pi 2a + \pi 2a$ cycloaddition is thermally allowed or not? 4

17. Discuss the suprafacial and antarafacial modes of interaction in [1,5] sigmatropic rearrangement. Based on symmetry conservation rule explain the formation of product. 2+2=4



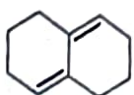
18. Discuss the mechanism of formation of products and identify the pericyclic reaction. 1+1+2=4



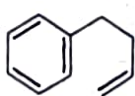
19. What do you mean by Huckel type and Mobius type of ring in pericyclic reactions? Discuss using suitable basis orbitals. Write the Woodward-Hoffmann pericyclic selection rules for ground-state thermal reactions. 3+1=4

20. Draw the disrotatory ring closure of 1,3,5-hexatriene and discuss the reaction whether thermally allowed or not. 4

21. Answer the following: 1+1+2=4

(i) Explain why the conjugate diene  can not undergo [4+2] cycloaddition reaction?

(ii) What is meant by "inverse electron demand cycloaddition reaction"?

(iii) What do you mean by Cope rearrangement? Explain why  cannot undergo Cope rearrangement.

22. Explain formation of the product:

3+1=4

