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14 (CHM-2) 202

2022

CHEMISTRY

Paper : CH-202

(Organic Chemistry 2)

Full Marks : 80

Time : Three hours

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

Part-A : Answer the following questions.

1. For acetone, the absorption at λ_{max} 278nm ($\epsilon = 15$) is due to _____. 2
(a) $n - \pi^*$
(b) $\pi - \pi^*$
(c) $\pi - \sigma^*$

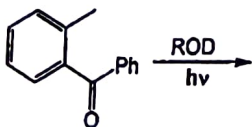
Contd.

2. How do you define a molecular triplet excited state during a photophysical process? Give *two* methods by which molecular triplet excited states can be generated. Write the expression for Beer-Lambert law and state the significance of the parameter ' ϵ ' appearing herein. 1+2+2=5

OR

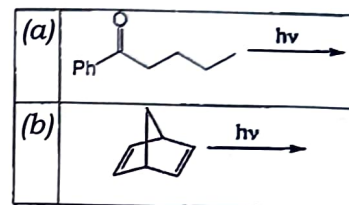
When does an electronic transition become space forbidden? Illustrate your answer with a suitable example. Using a Jablonski diagram, examine the process of resonance fluorescence? 1+2+2=5

3. What happens when a mixture of benzophenone and benzhydrol is irradiated? Suggest a mechanistic pathway for the reaction process. Comment on the quantum yield of the reaction. Identify the products for the following reaction and suggest a mechanistic explanation. 1+2+2=5

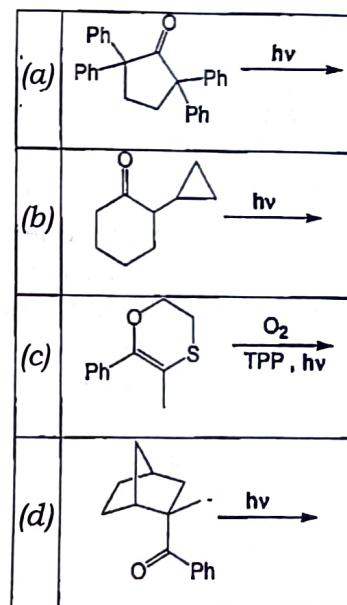


OR

Show the major products for the following reactions along with the intermediates where required: 2.5×2=5

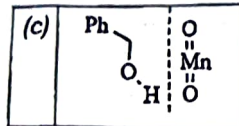
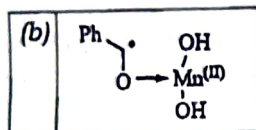
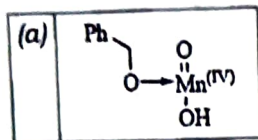


4. Complete the following reactions (*any three*), and show the important intermediate steps. 3×3=9



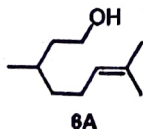
Part-B : Answer the following questions.

5. Which of the following intermediate species is unlikely to be formed during the oxidation of an alcohol with MnO_2 in a non-polar solvent : 2



6. Compare the reactivity of Jones reagent, Collins reagent, pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC). Show how citronellol (6A) reacts with PCC and PDC in dichloromethane solvent.

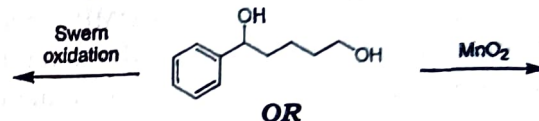
3+3=6



OR

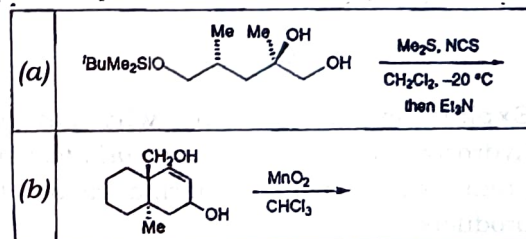
How does *cis*- and *trans*-2-*tert*-butyl-cyclohexanol react with $HCrO_4$? Write the mechanism of the reaction, show the intermediates and compare the rate determining step of the reaction. 3+3=6

7. How can dimethyl sulfoxide (DMSO) be activated with oxalyl chloride? Identify the major products for the following reactions and give mechanistic explanations. 2+3=5



How is Fetizon's reagent prepared? Provide the mechanistic steps involved in the oxidation of primary alcohols with this reagent. 1+4=5

8. Predict the major products for the following reactions, and write the key mechanistic steps. 3+3=6

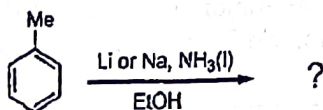


OR

Show the key mechanistic steps in the SeO_2 mediated oxidation of 2-methyl butane. Highlight the aspects of chemo- and regio-selectivity in this reaction. What is the Riley reaction ? $2+2+2=6$

9. How can Dess-Martin periodinane (DMP) reagent be prepared ? Give the mechanism for oxidation of alcohols with DMP reagent, highlighting the changes in the oxidation state of iodine center during the reaction. $2+3=5$

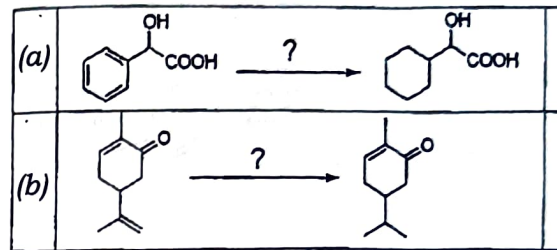
10. Predict the product, and suggest a plausible mechanism for the following reaction : $1+4=5$,



OR

Explain mechanistically why catalytic hydrogenation produces *trans-addition* side-products along with the normal *cis-addition* products.

11. Suggest suitable reagents for the following conversions, and briefly explain the selectivity in each case from mechanistic considerations : $3+3=6$



Part-C : Answer the following questions.

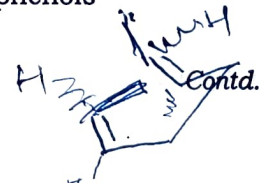
12. The major product formed when (3*R*, 4*S*)-3,4-dimethylhexa-1,5-diene is heated at 240°C is : 2

- (a) (2*Z*, 6*Z*)-Octa-2,6-diene
 (b) (2*E*, 6*E*)-Octa-2,6-diene
 (c) (2*E*, 6*Z*)-Octa-2,6-diene

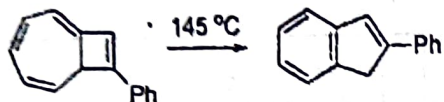


13. Thermolysis of allyl phenyl ether generates : 2

- (a) *o*-Allylphenol only.
 (b) *o*- and *p*-Allylphenols.
 (c) *o*-, *m*- and *p*-Allylphenols



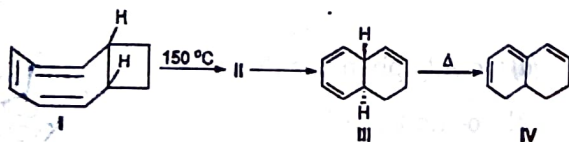
14. The following transformation involves electrocyclic ring closing, ring opening reaction followed by a sigmatropic rearrangement. Write the mechanisms for each step with appropriate justification. 5



OR

Examine the feasibility of the photochemical $\pi 2S + \pi 4S$ cycloaddition reaction using symmetry correlation diagram approach.

15. When compound I was heated at 150°C , it transformed to compounds III and IV, via a cyclic tetraene (II). Propose a structure for II, and show the mechanistic steps involved in the conversion of $\text{I} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \text{IV}$. 6



16. Provide mechanistic interpretations for the following transformation (**any three**), and identify the types of reactions involved in each instance. $3 \times 3 = 9$

