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.

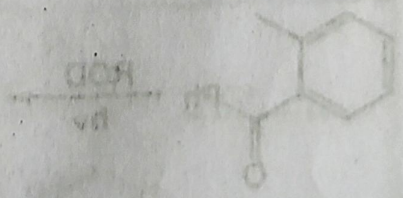
Part–A : Answer the following questions.

1. For acetone, the absorption at $\lambda_{max} 278nm\ (e = 15)$ is due to _____. 2

   (a) $n - \pi^*$

   (b) $\pi - \pi^*$

   (c) $\pi - \sigma^*$

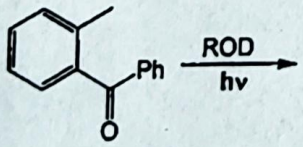


2. How do you define a molecular triplet excited state during a photophysical process ? Give *two* methods by which molecular triplet excited states can be generated. Write the expression for Beer-Lambert law and state the significance of the parameter 'ε' appearing herein. 1+2+2=5

OR

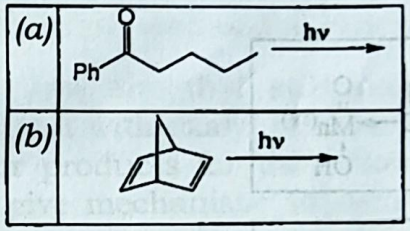
When does an electronic transition become space forbidden ? Illustrate your answer with a suitable example. Using a Jablonski diagram, examine the process of resonance fluorescence ? 1+2+2=5

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

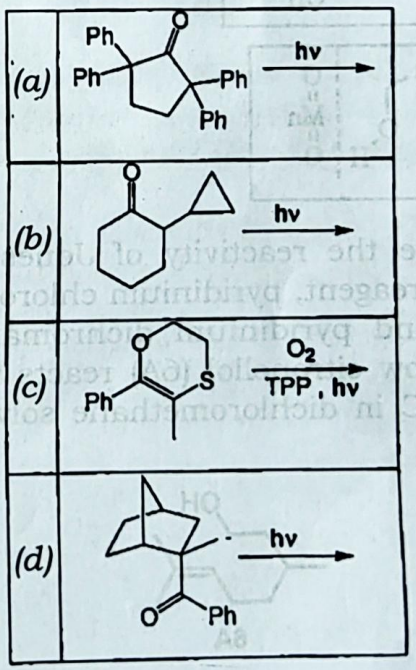


OR

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

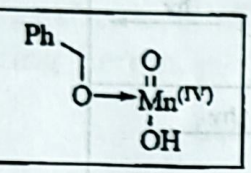


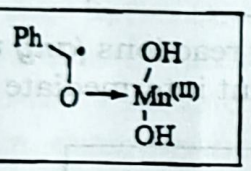
4. Complete the following reactions ***(any three)***, and show the important intermediate steps. 3×3=9

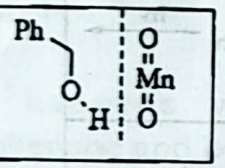


Part–B : Answer the following questions.

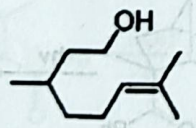
5. Which of the following intermediate species is unlikely to be formed during the oxidation of an alcohol with MnO_2 in a non-polar solvent : 2

(a) 

(b) 

(c) 

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



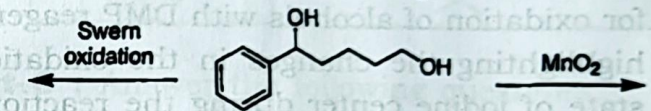
6A

1

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

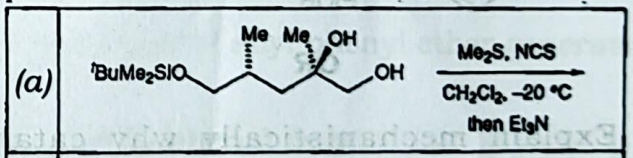
7. How can dimethyl sulfoxide (DMSO) be activated with oxalyl chloride ? Identify the major products for the following reactions and give mechanistic explanations. 2+3=5

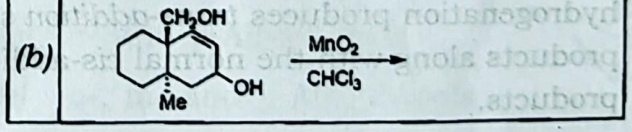


OR

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

(a) 

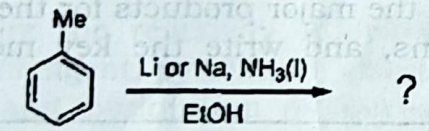
(b) 

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

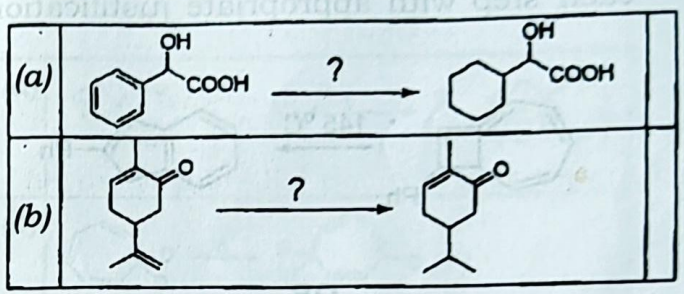
10. Predict the product, and suggest a plausible mechanism for the following reaction : 1+4=5



OR

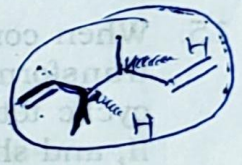
Explain mechanistically why catalytic hydrogenation produces *trans-addition* side-products along with the normal *cis*-addition products.

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

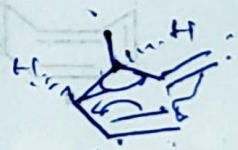


(*a*) (2*Z*, 6*Z*)-Octa-2,6-diene

(*b*) (2*E*, 6*E*)-Octa-2,6-diene

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

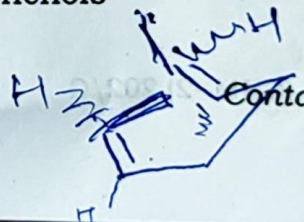
13. Thermolysis of allyl phenyl ether generates : 2



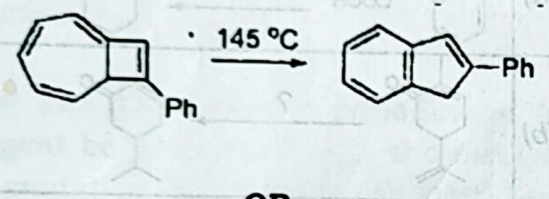
(*a*) o-Allylphenol only

(*b*) o- and p-Allylphenols

(*c*) o-, m- and p-Allylphenols



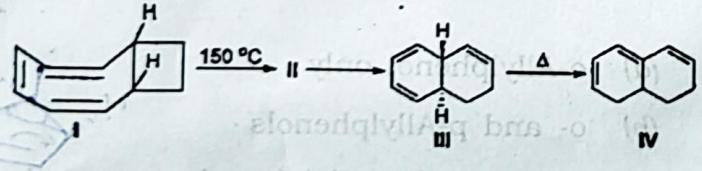
14. The following transformation involves electrocylic ring closing, ring opening reaction followed by a sigmatropic rearrangement. Write the mechanisms for each step with appropriate justification. 5



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 $I \rightarrow II \rightarrow III \rightarrow IV$. 6



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