M. Sc. Chemistry Examination, 2019

(4th Semester)

Organic Chemistry Special

Paper - XIII-O

Time : Two hours Full Marks : 50

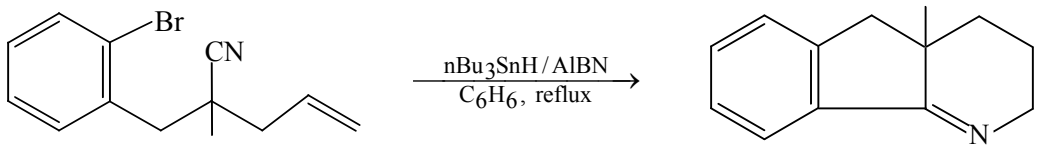
(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - O - 4131

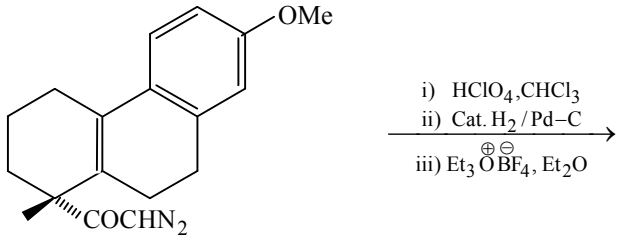
1. a) The somo energy of a radical determines its properties as electrophilic and/or nucleophilic. Explain your answer. 2

   b) Discuss the mechanism of the following transformation. 2

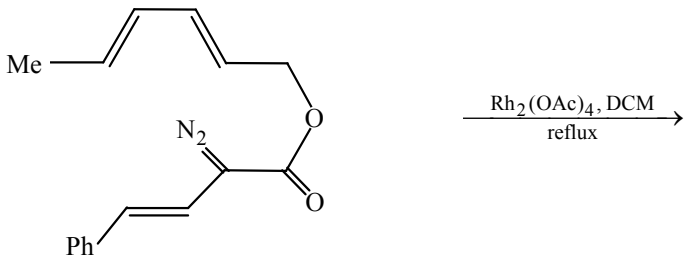


   c) Predict the product of the following reactions and explain with probable mechanism ***(any two)***. $2\frac{1}{2}\times2$

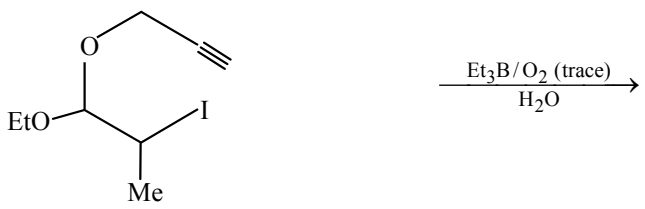
   i)



   ii)

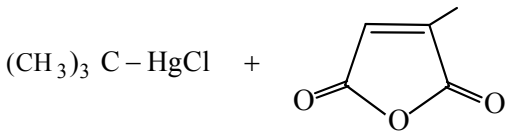


   iii)



d) Ascertain the structure of the products **A** – **C** and suggest plausible mechanism in each step. $2\frac{1}{2}$

e) Identify the products in the following reaction and explain their formations.

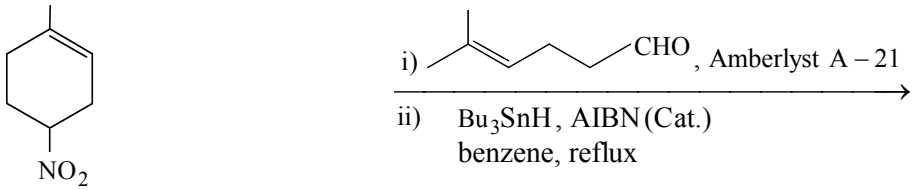


1

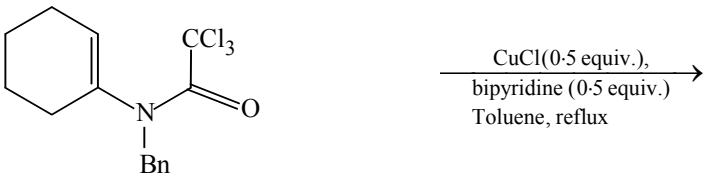
2. Draw the structure of the product(s) with proper stereochemistry of the following reactions and explain with mechanism ***(any five)*** : $2\frac{1}{2}\times5$

a)

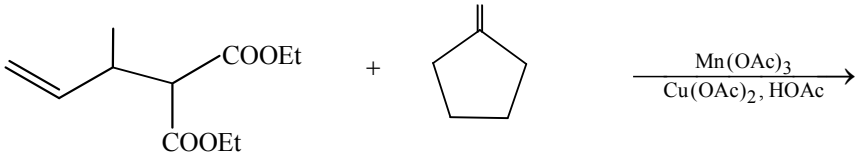
b)



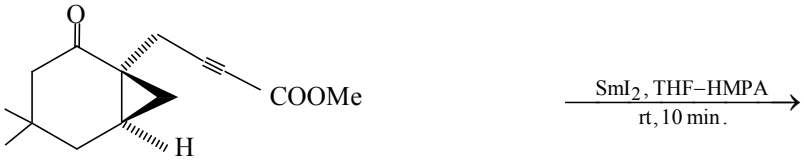
c)

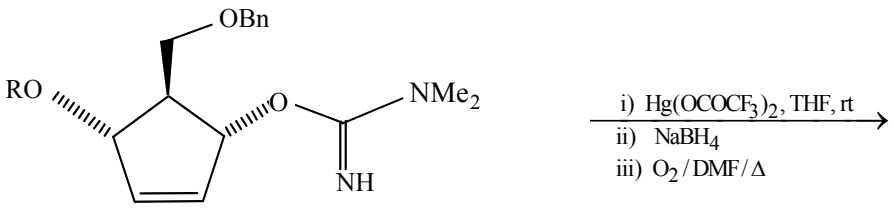


d)



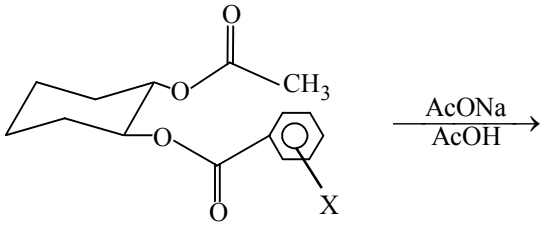
e)



f) 

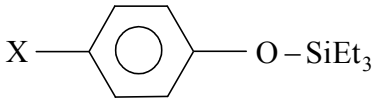
UNIT - O - 4132

3. a) The rates of acetolysis of the following reaction, give a linear plot against σ with a ρ value of $-1{\cdot}00$. Predict the product with mechanism.



If the carbonyl oxygen of substituted benzoyloxy group is labelled with ^{18}O, and the reaction product after acetolysis is reduced with $LiAlH_4$, the *trans*-1, 2,–cyclohexanediol retain 50% of the labelled ^{18}O – explain. 1+1+2

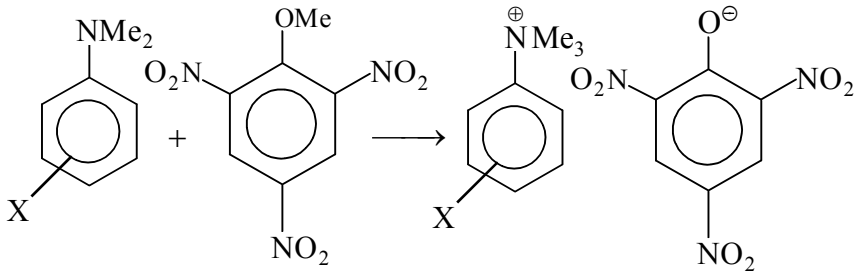
b) Write down Yukawa-Tsuno equation for the base-catalysed hydrolysis of the compound **D** in 60% aqueous dioxane at 30°C. This reaction exhibits 'r = 0·5' and 'ρ = + 3·52'. Explain the mechanism.



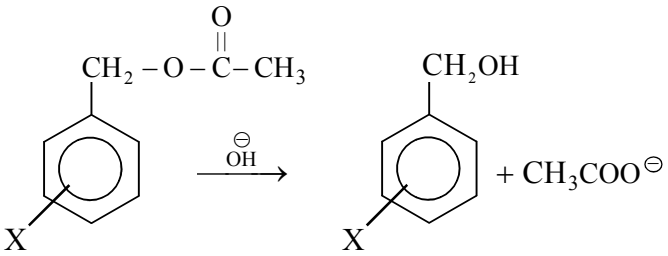
D

1+2

c) Explain ρ value of the following reaction. 1+1

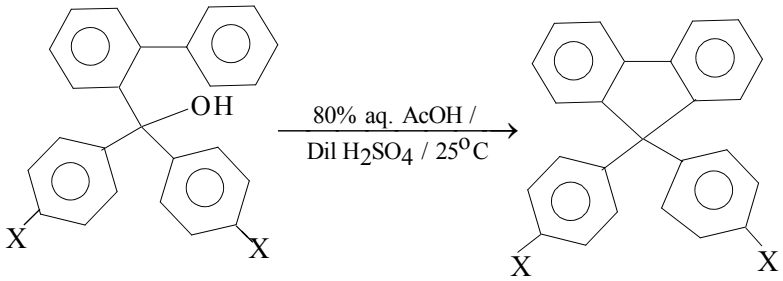
i) 

$\rho = -2{\cdot}72$ (benzene, 25°C)

ii) 

$\rho = +0 \cdot 47$ (60% aq acetone, 25°C)

d) Predict the mechanism of the following reaction and identify the rate determining step (rds) for each substituent.



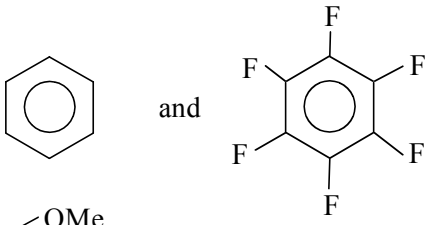
X = OMe $\rho = +2 \cdot 67$

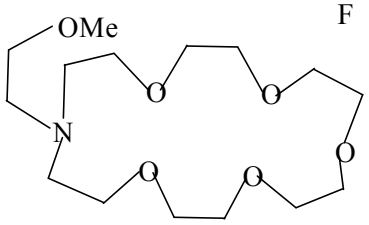
X = Cl $\rho = -2 \cdot 51$

1+1+1

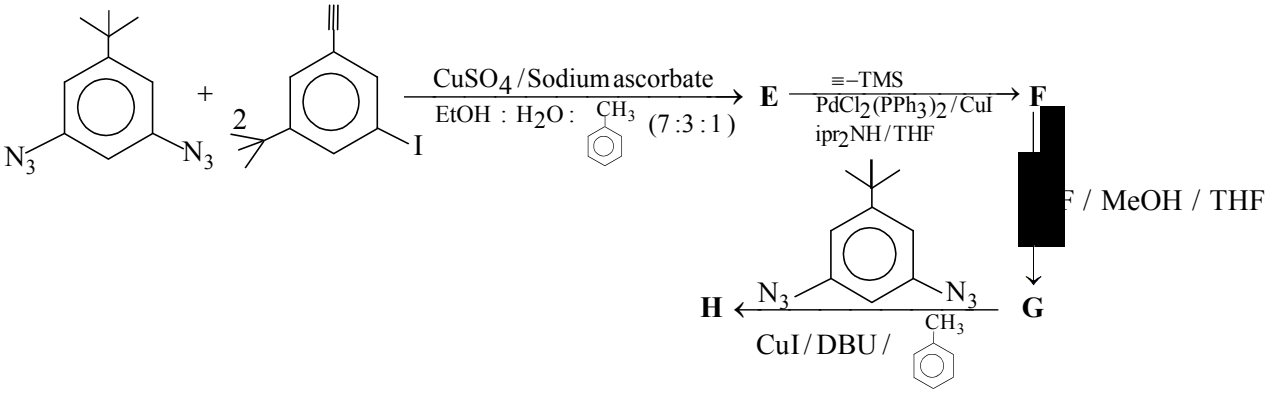
4. a) What is halogen bonding - explain with a suitable example. 2

b) Write down the interaction (s) between the following molecules. 2

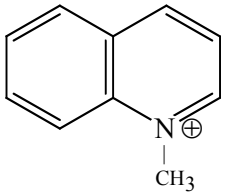
i)  and

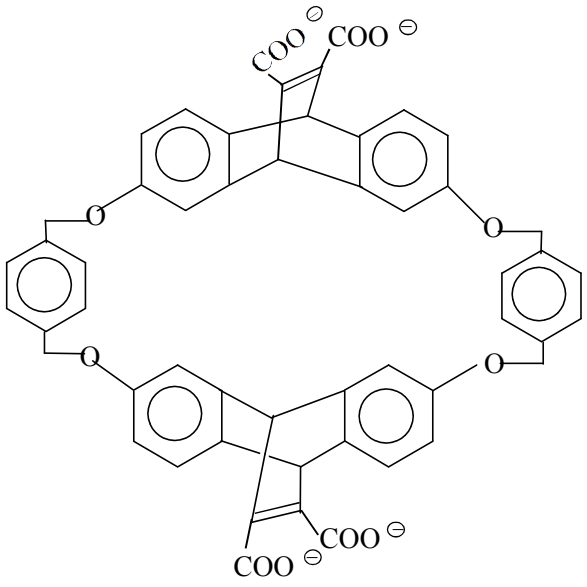
ii)  and $\overset{\oplus}{N}H_4$

c) Predict the product(s) (**E** – **H**) in the following reactions.

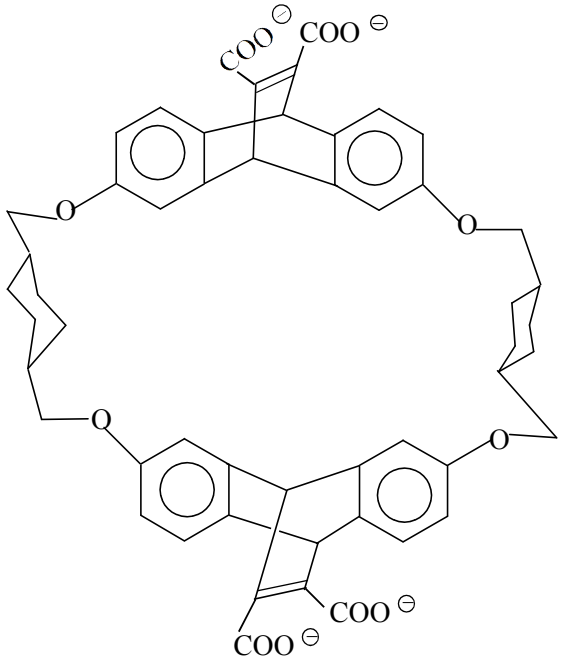


Compound **H** is a preorganized macrocyclic receptor for chloride ion. Write down the noncovalent interactions present between compound **H** and Cl^-. What type of spectroscopic technique(s) can be utilized to identify the above noncovalent interaction(s) ? $\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+1+1$

d) The binding constant of host molecule **I** is greater than that of the host molecule **J** for the guest molecule  – explain. 2



I



J

e) Give one example of 'Rotaxane' which can behave like a pH-driven cable car, and explain the mechanism. 3