M. Sc. Chemistry Examination, 2018

(4th Semester)

Organic Chemistry Special

Paper - XIII-O

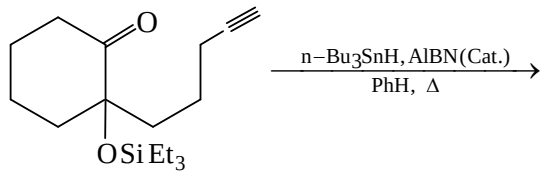
Time : Two hours Full Marks : 50

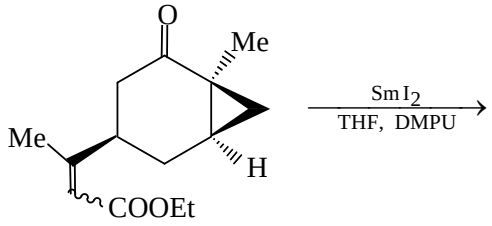
(25 marks for each Unit)

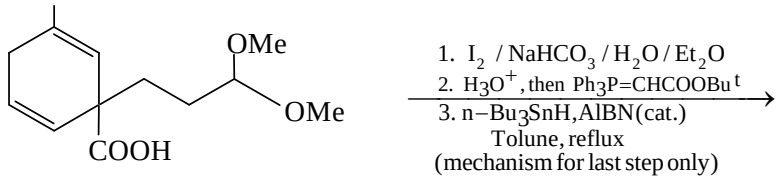
Use a separate answerscript for each Unit.

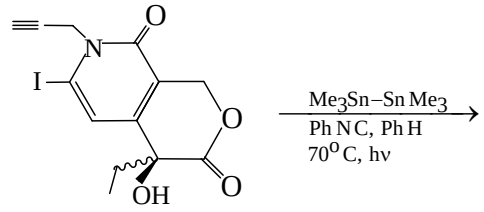
UNIT - O - 4131

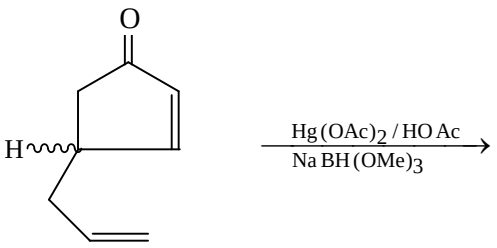
1. Predict the product(s) in the following reactions with proper stereochemistry and explain their formation with mechanism. (***Any five***). $2\frac{1}{2}\times5$

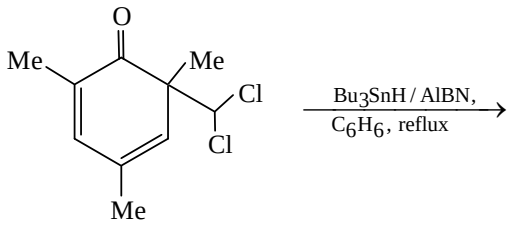
i) 

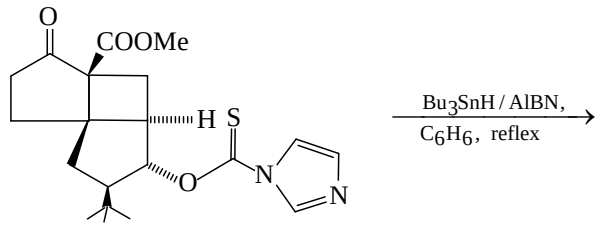
ii) 

iii) 

iv) 

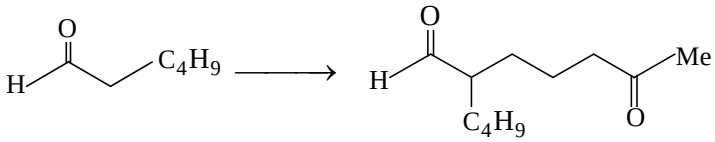
v) 

vi) 

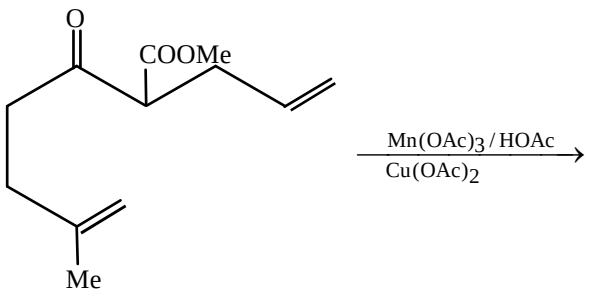
vii) 

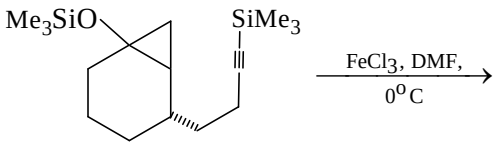
2. a) Radical initiated polymerisation of a mixture of dimethyl fumerate and vinyl acetate takes place efficiently in a definite sequence. Suggest the structure of the polymer chain and explain with mechanism. $2\frac{1}{2}$

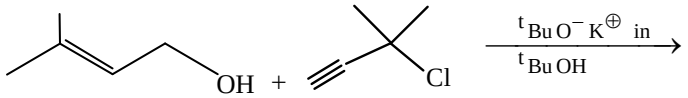
b) Carry out the following conversion and explain with mechanism. $2\frac{1}{2}$

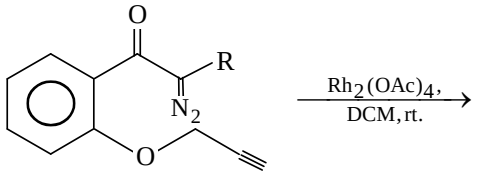


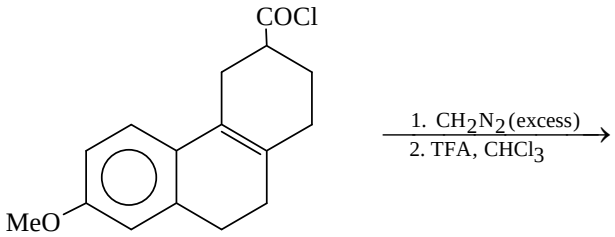
c) Suggest the product(s) and justify your answer with proper mechanism ***(Any Three)*** : 2×3

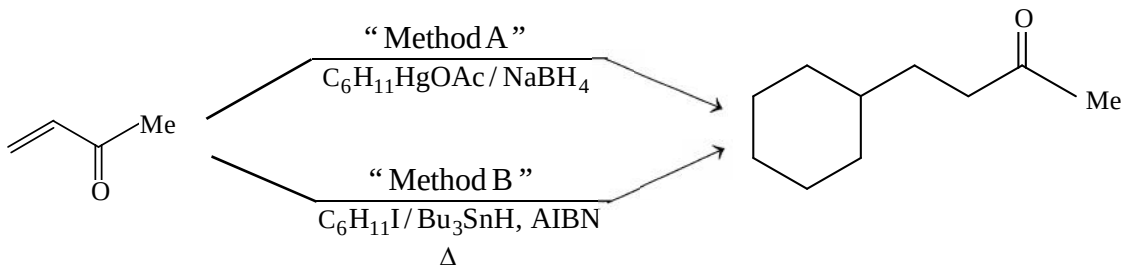
i) 

ii) 

iii) 

iv) 

v) 

d) 

Which of the above two methods will be used to get the better yield of the product ? Give reason for your answer. $1\frac{1}{2}$

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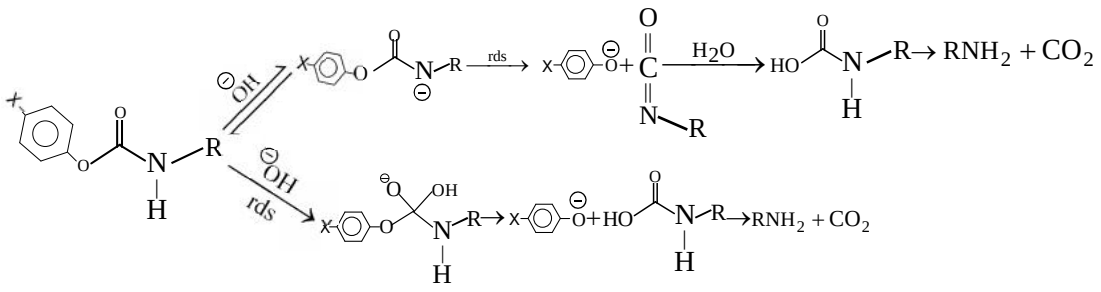
3. a) Write down Yukawa-Tsuno equation for the following solvolysis reaction. Solvolysis of P-substituted cumyl chloride exhibits 'r = 1' and '$\rho = -4.52$' – explain the mechanism. 1+2

b) i) What should be the relative magnitude of ρ value(s) for path A and path B in the following reaction ? Which path is favourable ?

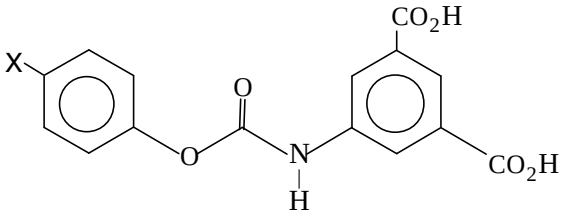
Path A



Path B

1+1

ii) Write down the structure of a 'Catalytic antibody' which is expected to hydrolyse the following compound via path B. 1

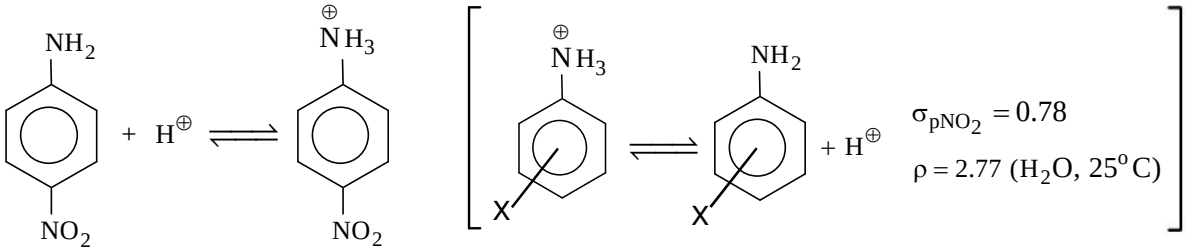


c) The logarithmic values of the relative rates of acid-mediated cleavage in aqueous methanolic $HClO_4$ at 51°C of substituted phenyltrimethylsilanes are as under.

p -NMe_2	7·5	*m* –Me	0·36	*p* – Cl	– 0·87
p -OMe	3·18	H	0·00	*p* – Br	–1·00
p -Me	1·32				

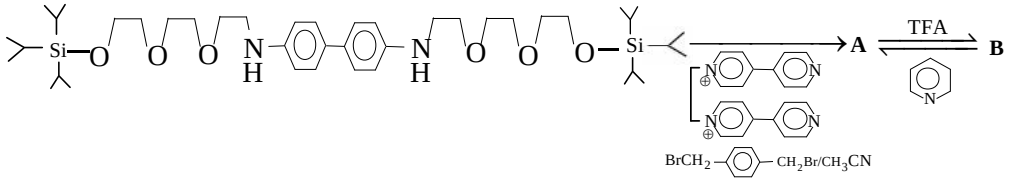
Show that the reaction correlates with $\sigma^{\oplus}$ and thus comment on the mechanism of the reaction. 2

d) Experimental value of $\log K/K_o$ is 3·52 for the following protonation reaction :



Calculate $\sigma^{\ominus}$ (substituent constant) for the protonation reaction. 2

4. a) Write down the structures of **A** and **B** with explanation :



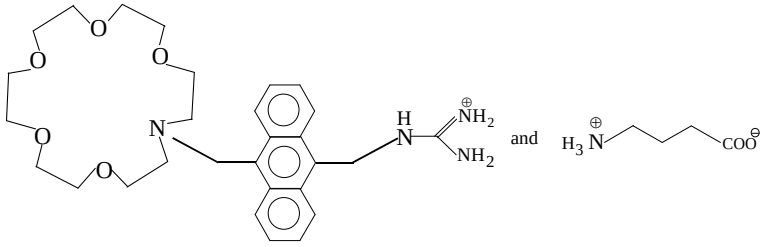
2

b) How will you carry out the following reaction using a supramolecular approach with an appropriate catalyst ? 2

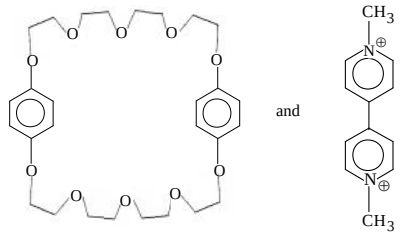
c) What should be the structure of a cyclic peptide that will self-assemble to form nanotube without macrodipole ? 2

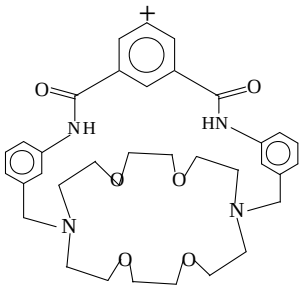
d) Write down the noncovalent interaction(s) present between the following molecules.

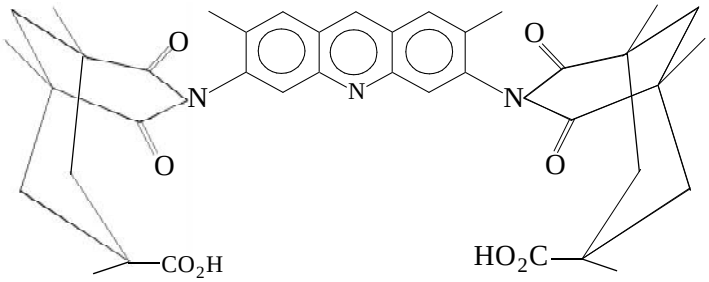
i)



ii)

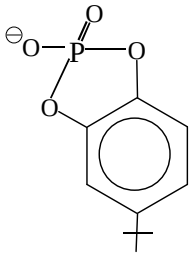


iii)  and NaCl

iv)  and 

1×4

e) Draw the structure of 'Artificial Ribonuclease' that catalyzes hydrolysis of the following phosphodiester molecule.



Explain the regioselectivity of the reaction. 2+1

f) What are 'Cation - π' and 'Anion - π' interactions ? 2