M. Sc. Chemistry Examination, 2017

(4th Semester)

Organic Chemistry (Special)

Paper - XIII-O

Time : Two hours Full Marks : 50

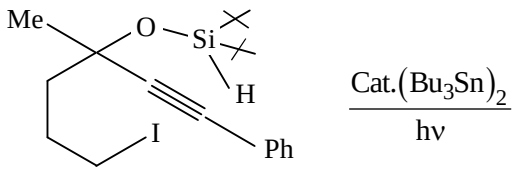
(25 marks for each unit)

Use a separate answerscript for each unit.

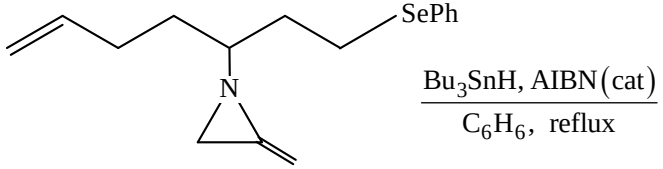
UNIT - O - 4131

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

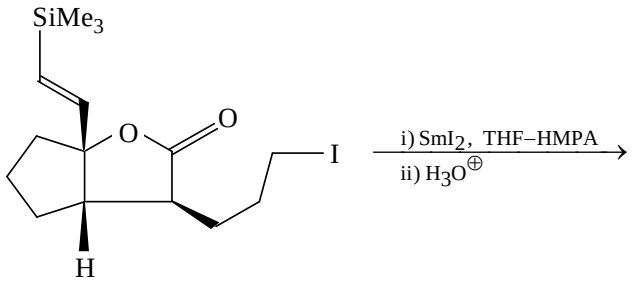
a)



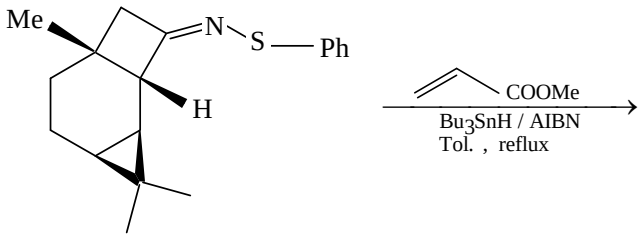
b)



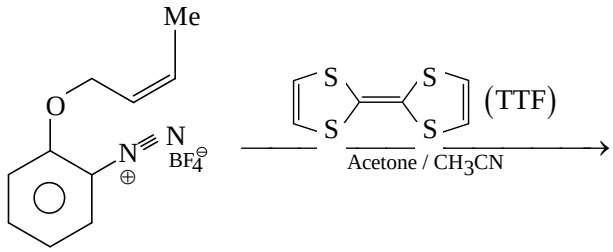
c)



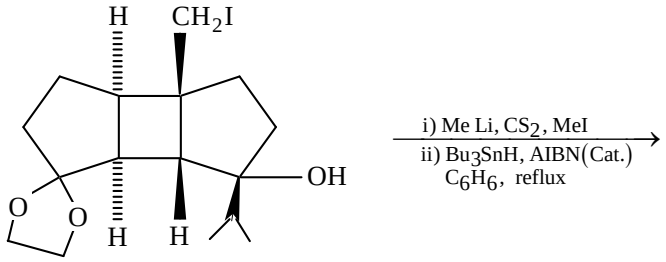
d)



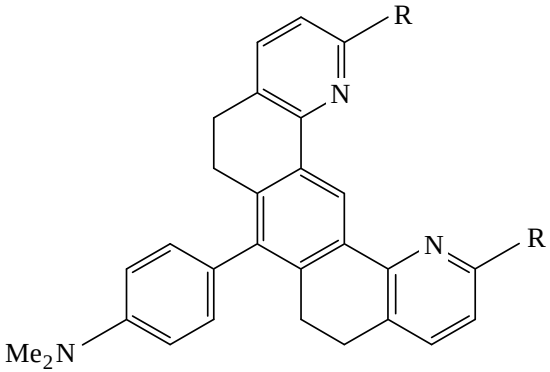
e)



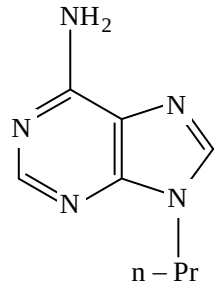
f)



B) Molecule **E** acting as a host for molecule **F**.



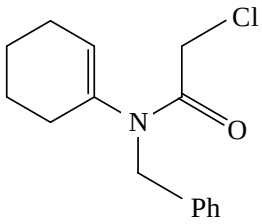
E : R = 9 – Anthryl

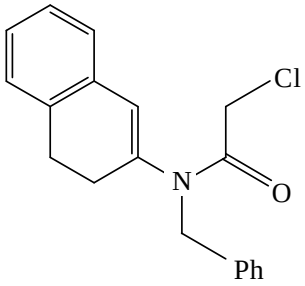


F

ii) Explain why α-cyclodextrin and β-cyclodextrin show different effects on the rate of cycloaddition of cyclopentadiene and acrylonitrile. (1×2)+1

b) The following two compounds behave differently towards tributyltin hydride in presence of AIBN(cat.) under refluxing in toluene. Draw the structure of the product(s) and explain your answer. 3





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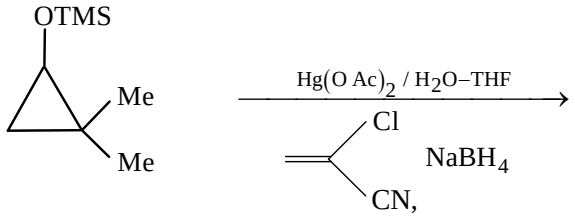
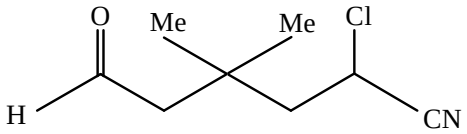
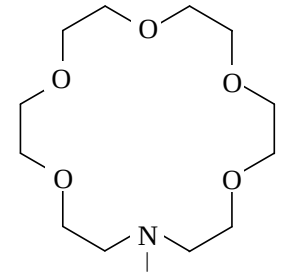




Discuss the mechanism of the above reaction. $2\frac{1}{2}$

R^2 =



ii) Write the structure of the molecular self-assembly formed by hydrogen bonding interaction involving three molecules of 5, 5-diethylbarbituric acid and three molecules of 2, 4, 6-triamino-5-n-butylpyrimidine. $1\frac{1}{2}+1\frac{1}{2}$

b) Give one example of each of the following types of receptors (***attempt any three***) 1×3

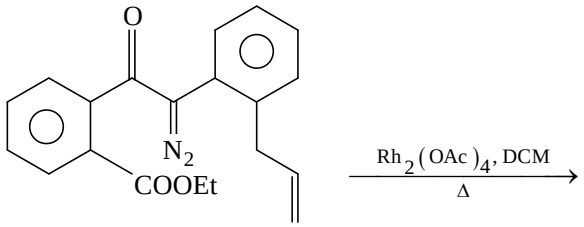
i) Two-dimensional molecular cleft.

ii) Hemispherand

iii) 3-Cryptand

iv) Azide binding cryptand.

c) i) Show how a receptor synthesized from the following two compounds can effectively catalyze the exchange of C-2 hydrogens of quinuclidinone (1-azabicyclo [2.2.2] octan-3-one) in $CDCl_3$ saturated with D_2O.

ii) 

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3. Attempt ***any four*** of the following questions : 4×4

a) i) Give one method for determination of σ_α^+ and σ_β^+ values of thiophene and furan.

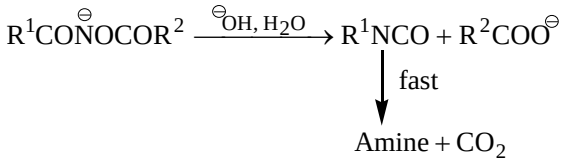
ii) In the pKa vs σ plot for 3-/4-substituted pyridines, the σ values for 4-NO_2, 4-CN and 4-CO_2Et do not show good correlation. Comment on the nature of deviation and give suitable explanation. $2\frac{1}{2}+1\frac{1}{2}$

b) Discuss the approach of Taft for determination of σ* values (which are measures of inductive effect) of different substituents. 4

c) . . . . . *trans*-2-(*m-and p*-substituted benzoyloxy-)-cyclohexyl *p*-toluenesulphonates, in acetic acid in the presence of acetate ions, yield a linear plot with σ with a ρ value of – 1.00. If the carbonyl oxygen is labelled with ^{18}O, and the reaction product is reduced with $LiAlH_4$, the *trans*-1, 2-cyclohexanediol retains 50% of the activity.

Comment on the mechanism of the reaction. 4

d) i) The Lossen rearrangement of the potassium salts of acyl hydroxamic acids

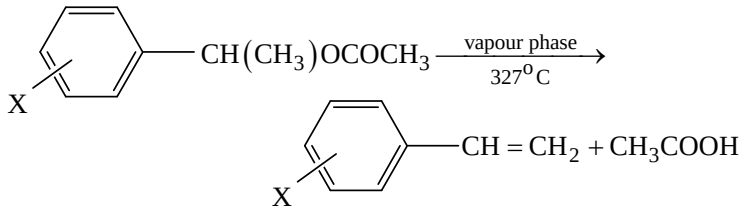


yields the following ρ values :

$R^1 = XC_6H_4,\ R^2 = C_6H_5 :\ \rho = -2.59$
$R^1 = C_6H_5,\ R^2 = XC_6H_4 :\ \rho = +0.87$

Show how the mechanism is consistent with these results.

ii) The log k for the following thermal elimination reaction shows a good correlation with σ^+ with a ρ value of –0.66.



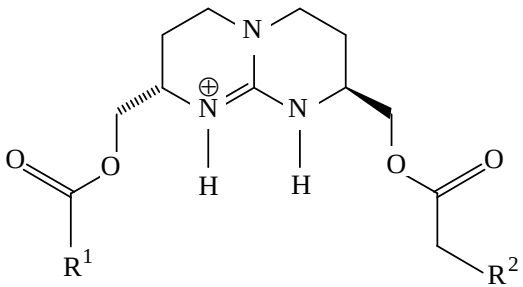
Comment on the nature of the transition state of the reaction. $2\frac{1}{2}+1\frac{1}{2}$

e) i) A Hammett plot for the second order rate constants of urethane formation from ethyl chloroformate and $XC_6H_4NH_2$ in anhydrous acetone has a ρ value of –5.56 for X = *p*-OCH_3, *p*-CH_3, *m*-CH_3 and H using σ values ; a ρ value of – 1.57 is found for x = *p*-Br, *m*-Cl, *m*-NO_2, *p*-$COOC_2H_5$ and *p* -NO_2 using σ^- where appropriate. Comment on the mechanism of the reaction.

ii) Explain how the magnitudes of the ρ values for log f *vs* σ^+ plot for aromatic electrophilic substitution reactions gives an idea about the nature of the transition states of the reactions (f = partial rate factor). $2\frac{1}{2}+1\frac{1}{2}$

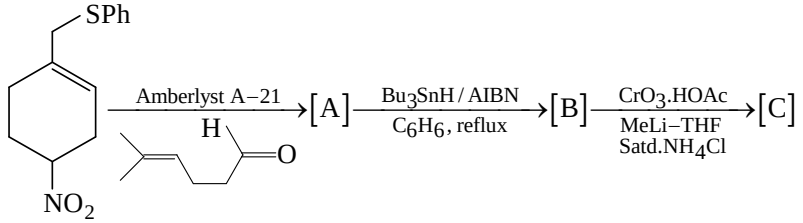
4. Attempt ***any three*** of the following questions : 3×3

a) i) Show how the following molecule can act as a host for *S*-tryptophan.



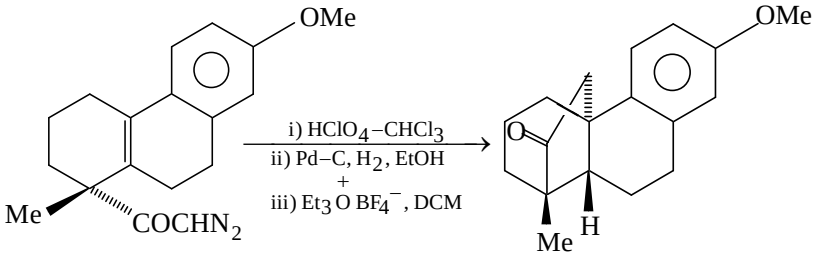
R^1 = 2 – Naphthyl

d) Identify [A], [B] and [C]. Discuss the mechanism for the radical step only. $1\frac{1}{2}+1\frac{1}{2}$



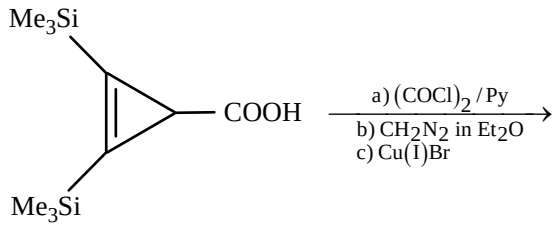
OR

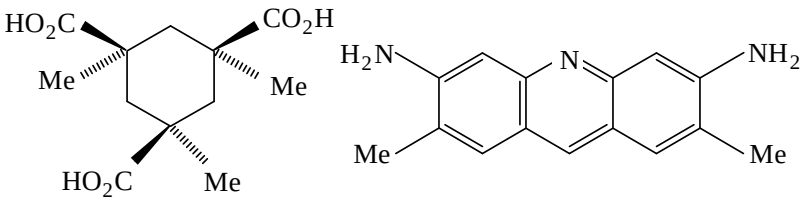
Discuss the mechanism of the following reaction.



e) Predict the product in the following reactions and explain with mechanism (***answer any one***). 2

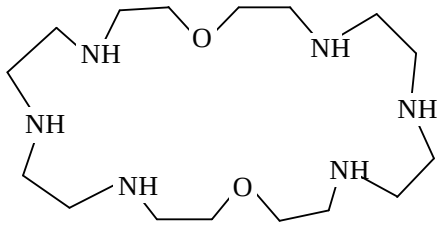
i)





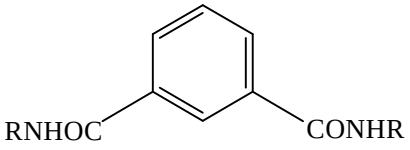
ii) Show how a pentaprotonated form of the following compound catalyzes the conversion of ATP to ADP.

$1\frac{1}{2}\times 2$

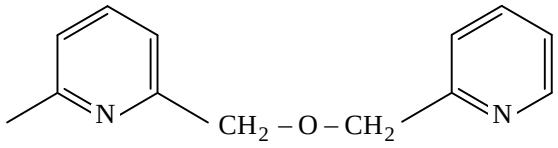


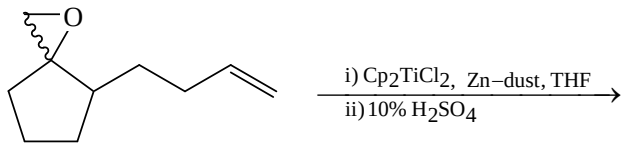
d) i) Show the molecular interactions in the following cases:

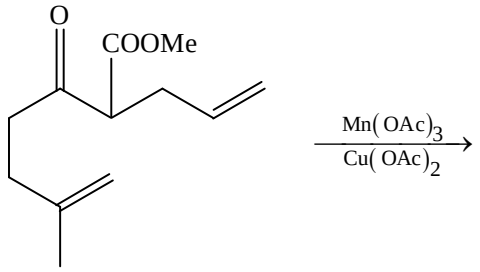
A) Molecule **D** acting as a host for urea.



D

R = 

g) 

h) 

2. a) Account for the stereo chemical preference of the *cis*-isomer over the *trans*-isomer in the following reaction.

2