RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2012

THIRD YEAR

Date : 19/12/2012 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : V (Gr. B) Full Marks : 50

[Attempt **one** from each unit]

Unit-I

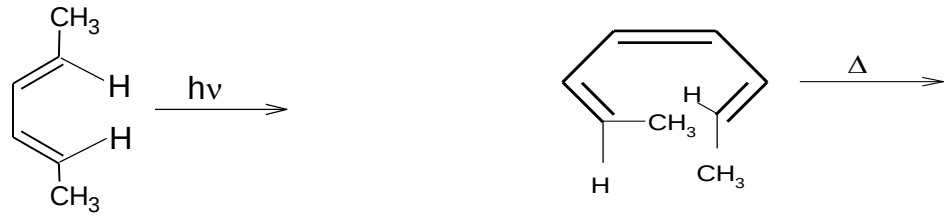
1. a) Draw all possible chair conformations of any one enantiomer of trans –1,2–dimethylcyclohexane. Although the conformation of cis –1,2–dimethylcylcohexane is chiral yet it is optically inactive – explain. Compare the heat of combustion values of cis– and trans –1, 2–dimethylcyclohexane. [3]

   b) Predict, with reasons, which of the following will undergo faster oxidation with chromic acid.
   (i) trans –4–t–butylcyclohexanol, (ii) cis–4–t–butylcyclohexanol. [2½]

   c) Draw the most stable conformation of trans–1, 3–ditertiary–butylcyclohexane. [1½]

   d) Predict the products in the following electrocyclic reactions and explain them on the basis of FMO interactions. [3+3]

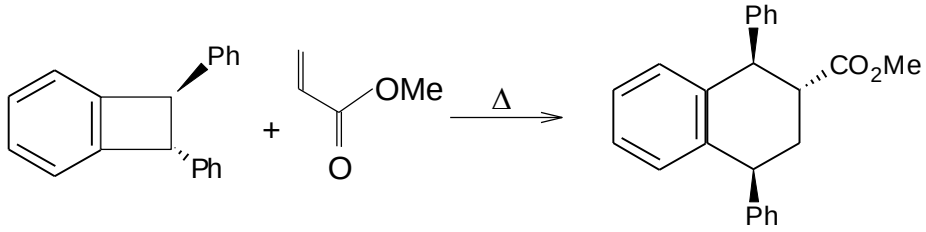
   (i) (ii)



2. a) The relative proportions of *a, a* : *e, e* conformations of the trans –1, 2–dibromocyclohexane in gaseous and liquid phases are 95:5 and 52:48 respectively. Explain the difference in conformational populations in the two phases. [3]

   b) The trans isomer of ethyl 4–t–butylcyclohexanecarboxylate undergoes base induced hydrolysis 20 times faster than the cis–isomer whereas the trans isomer of 4–t–butylcyclohexyl 4–nitrobenzoate hydrolyses only 2.5 times faster than the cis–isomer under similar condition — explain. [3]

   c) Rationalise the following reaction by FMO interactions showing the steps. [3]



   d) The rate of S_N1 solvolysis of cis–4–t–butylcyclohexyl p–toluenesulphonate is faster than the trans-isomer – explain. [2]

   e) Cis–4–hydroxycyclohexanecarboxylic acid readily forms a lactone but the trans-isomer fails to do so – explain. [2]

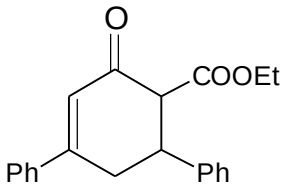
Unit-II

3. a) Give the synthetic equivalents corresponding to the following synthons: [1]

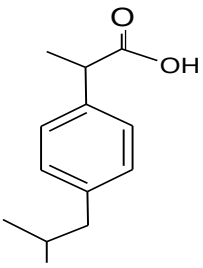
   (i) $\overset{+}{C}H_2CH_2OH$ (ii) $\overset{-}{C}H_2COOH$

b) Give retrosynthetic analysis and an efficient synthesis of each of the following (**any two**): [3x2]

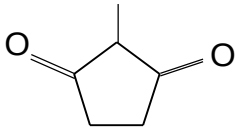
(i)



(ii)

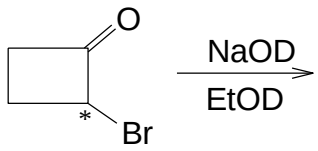


(iii)



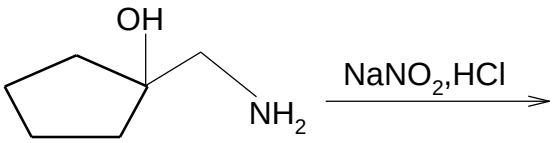
c) Complete the following reactions with plausible mechanism (**any two**): [2½x2]

(i)

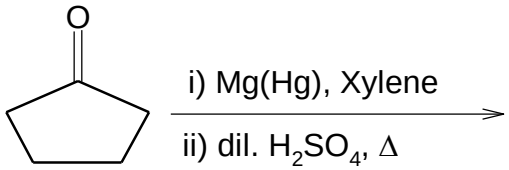


[$*C \equiv {}^{14}C$]

(ii)

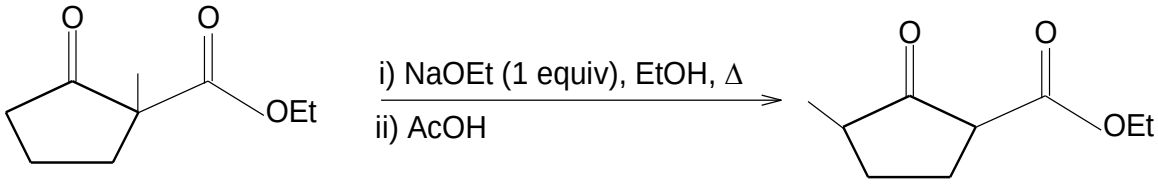


(iii)



4. a) What is meant by 'illogical electrophile' and 'illogical nucleophile'? Give examples. [2]

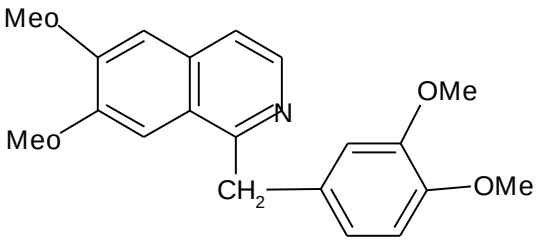
b) Explain the following transformation: [3]



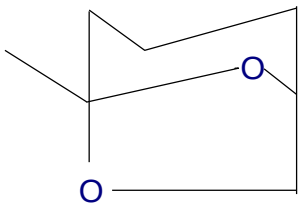
Justify the reason behind use of atleast one equivalent of the base in the above transformation.

c) From retrosynthetic approach find suitable starting materials for the following (<u>any one</u>). Show the synthetic steps also. [4]

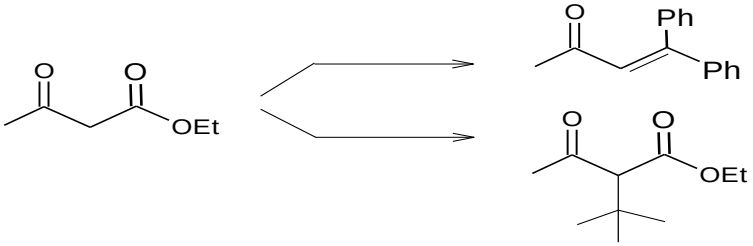
(i)



(ii)



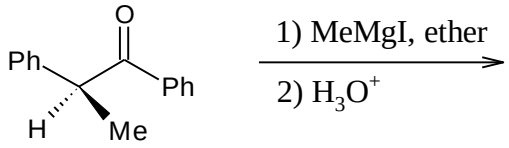
d) How will you carry out the following transformations? [3]



Unit-III

5. a) Outline Bardhan Sengupta synthesis of phenanthrene. [4]

b) Predict the major product in the following diastereo-selective reaction using Felkin-Anh model. [4]



c) Predict the product(s) and explain the stereochemical course of the following reaction. [2]

$$(Z)\text{-}PhCH=CHSiMe_3 \xrightarrow{DCl}$$

d) Outline the steps for the preparation of 2-chloronaphthalene from naphthalene. [2]

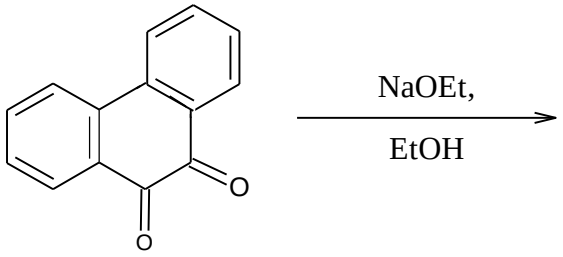
e) Predict the product of the following reaction. [1]

$$Phenanthrene \xrightarrow[t-BuOK]{CHCl_3}$$

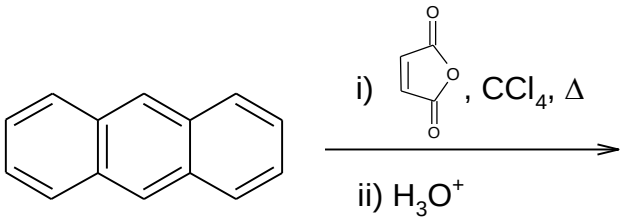
6. a) Outline the steps for the sysnthesis of 1,7–diisopropyl naphthalene from cumene. [4]

b) Predict the products with plausible mechanism. [3x2]

(i)



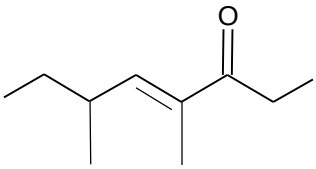
(ii)



c) How will you prepare Ethyl 3-methylbut-2-enoate using Me_3SiCH_2COOEt? Show the steps. [3]

OR

How will you prepare (A) from Pentan-3-one and 2-methylbutanal through the formation of a silylenolether?



(A)

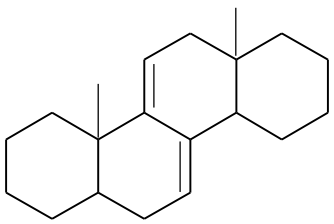
Unit-IV

7. a) Define with examples.

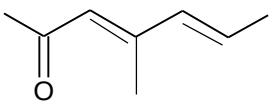
(i) hypsochromic shift, (ii) hyperchromic effect [2]

b) Calculate the λ_{max}^{uv} for the following [2]

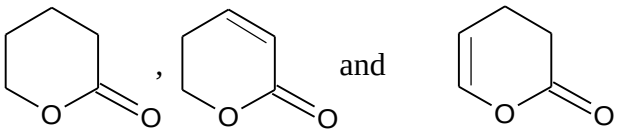
(i)



(ii)



c) Arrange the following lactones in order of increasing $C=O$ stretching frequency with explanation. [3]



d) Draw a clear diagram for ^{1}HNMR spectrum of CH_3CHBr_2 explaining the multiplicities of the proton signals. [3]

e) How will you distinguish between salicylaldehyde and p-hydroxybenzaldehyde by IR spectra? [2]

8. a) An organic compound, C_4H_8O showed the following spectroscopic results:

$\lambda_{max}^{uv}: 275nm, \in_{max} 17$

$\bar{\nu}_{max}^{IR}: 2950-2857\,cm^{-1}(m)$

$1715\,cm^{-1}(s)$

$1460\,cm^{-1}(m)$

$^{1}HNMR\,signals: \delta 2.5(q)[2H]$

$\delta 2.1(s)[3H]$

$\delta 1.1(t)[3H]$

Identify the compound with proper analysis of the data above. [3]

b) Why is TMS used as reference compound for ^{1}HNMR spectrum? [2]

c) The position of *uv* absorption maxima of 2-hydroxypyridine shifts to shorter wavelength with increase in pH of the medium, but that of aniline hydrochloride shifts to longer wave length if pH is increased – explain the observations. [4]

d) Ethylenic protons absorb at lower field than either alkane hydrogen or acetylenic hydrogen — why? [3]