CSM – 17 / 15

Chemistry

Paper – II

Time : 3 hours

Full Marks : 300

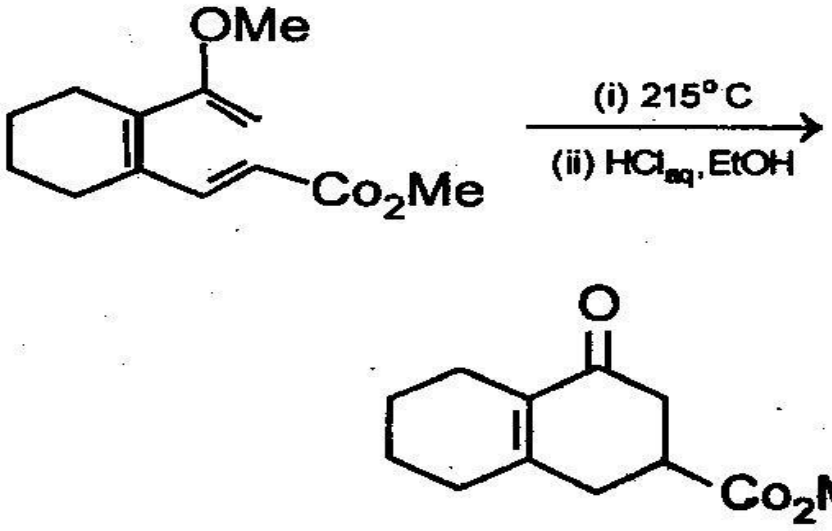
The figures in the right-hand margin indicate marks.

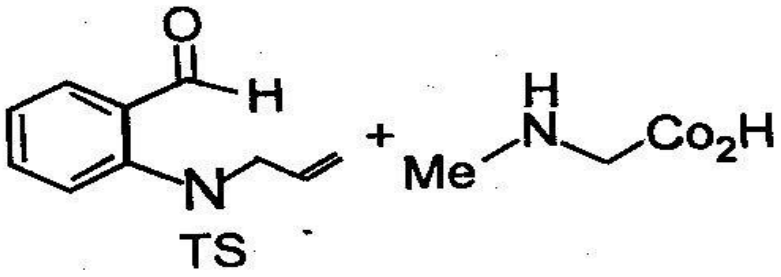
*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and **three** of the remaining questions, selecting at least **one** from each Section.*

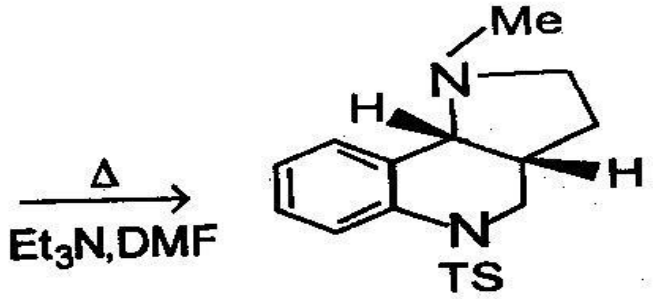
Section – A

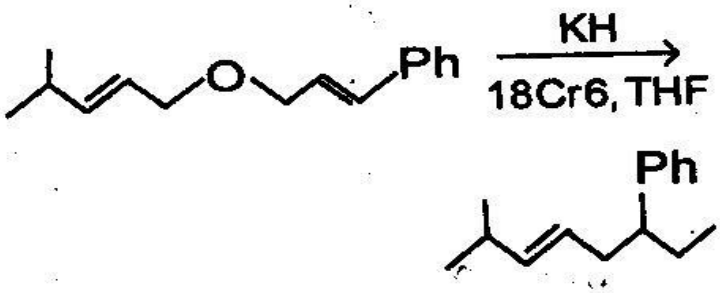
1. Answer any **three** of the following questions : 20×3 = 60

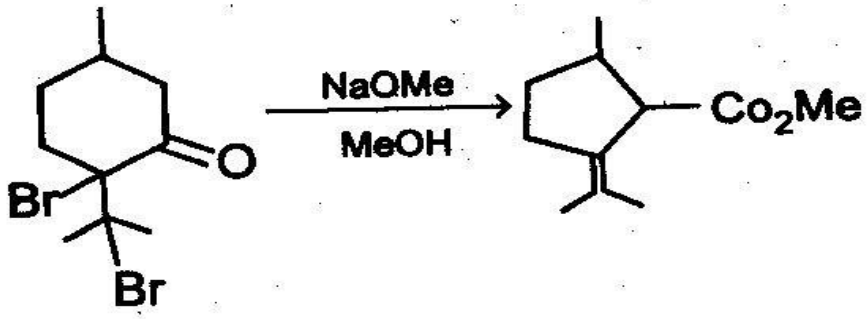
   (a) Explain the following and provide mechanism :

   (i) 

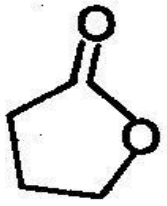
(ii) 



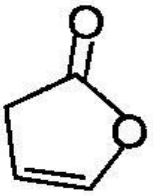
(iii) 

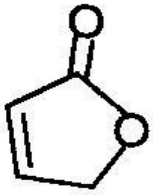
(iv) 

(b) Correctly match the structure and the carbonyl stretching frequency in IR absorption from the following :

(A) 

(i) 1750 cm^{-1}

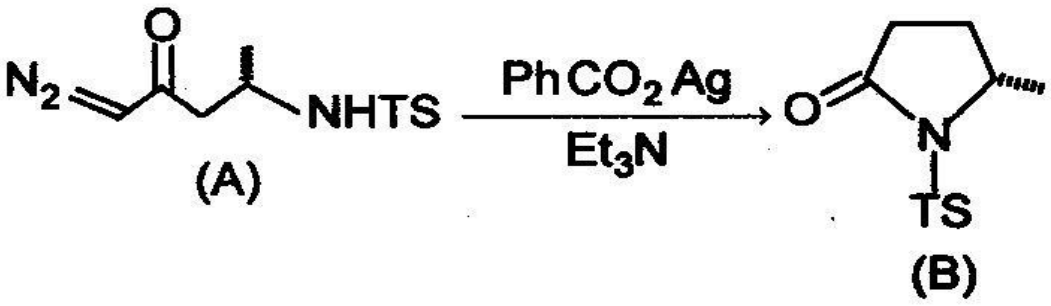
(B)  (ii) 1770 cm^{-1}

(C)  (iii) 1800 cm^{-1}

Give reasons for your matching.

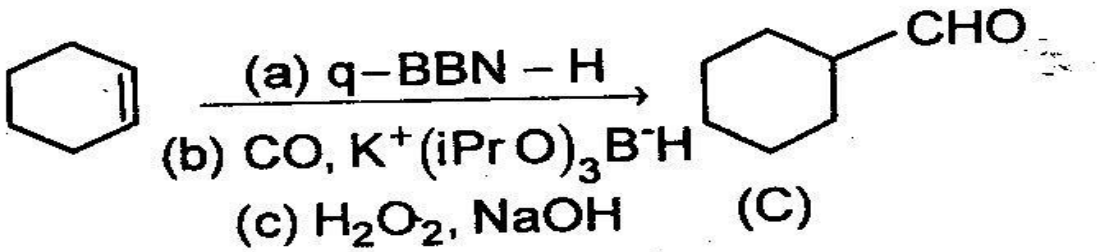
(c) Rationalize the following giving mechanism :

(i) Explain the formation of the lactan (B) on treatment of the diazoketone (A) with silver (I) benzoate :

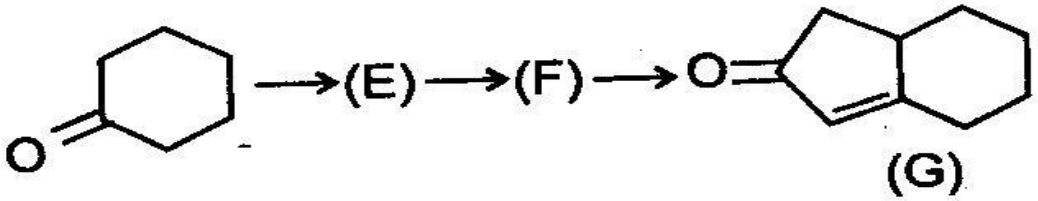


(A) (B)

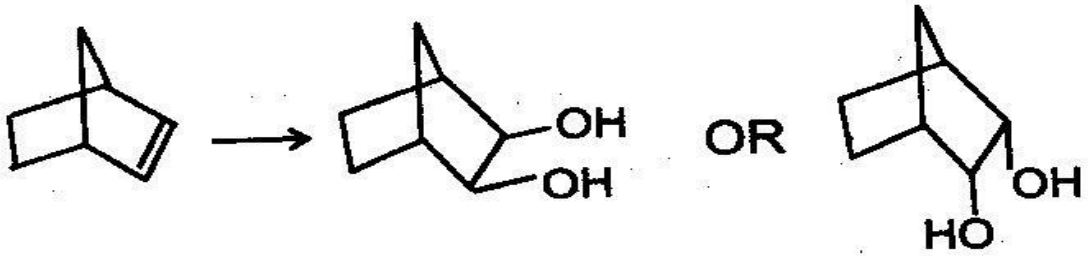
(ii) Draw the structures of the intermediates in the Carbonylation of cyclohexene to give the aldehyde (C) :



(iii) Draw the structures of the compounds (E) and (F) and suggest reagents for the conversion of (E) to (F) and for (F) to the cyclopentenone (G) :



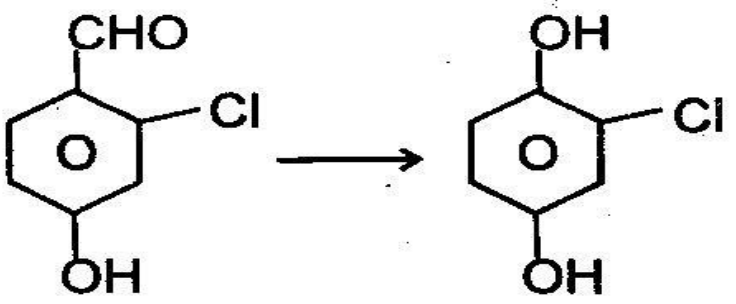
(iv) Suggest reagents and conditions for the formation of the exo-cis-diol and reagent and conditions for the formation of the endo-cis-diol product by oxidation of the alkene (H) :



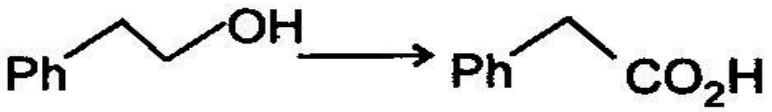
(H) exo

(d) How will you carry out the following conversions ?

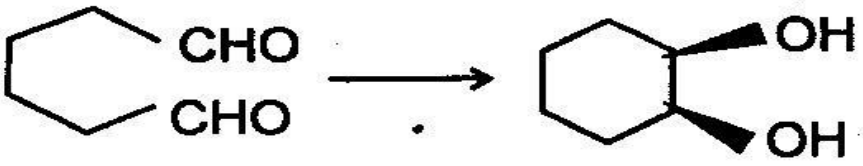
(i)



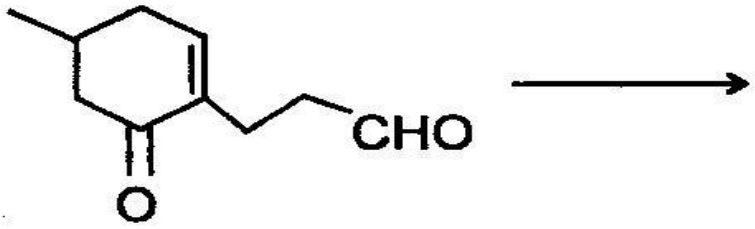
(ii)

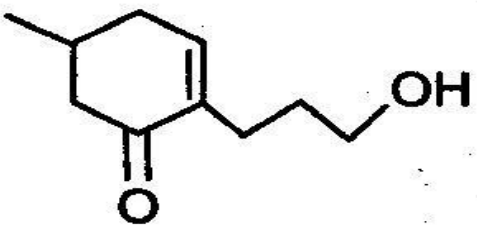


(iii)



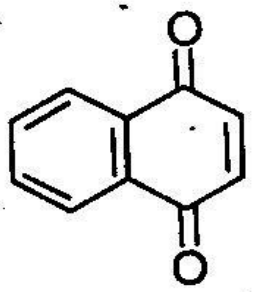
(iv)





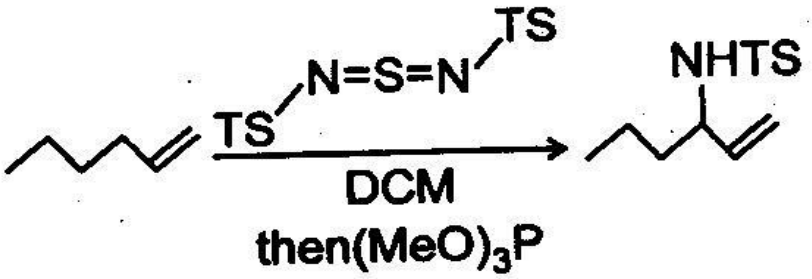
2. Answer the following :

(a) Suggest a method for preparation of naphthaquinone : 5

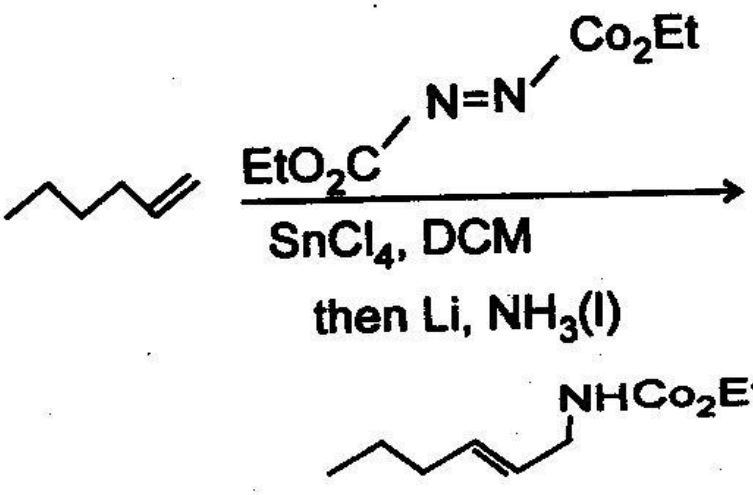


(b) Draw the structure of the intermediates in the following allylic amination reactions and hence explain the difference in the outcome of these two reactions : 5+5 = 10

(i)

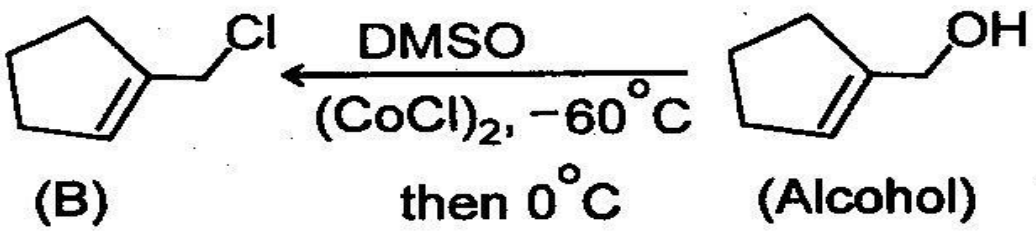


(ii)

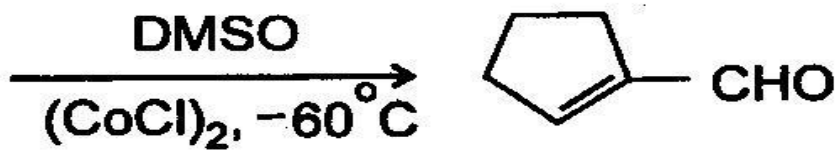


(iii) Explain the fomation of the products (A) and (B) formed from the alcohol in the presence and absence of a base :.

5×2 = 10



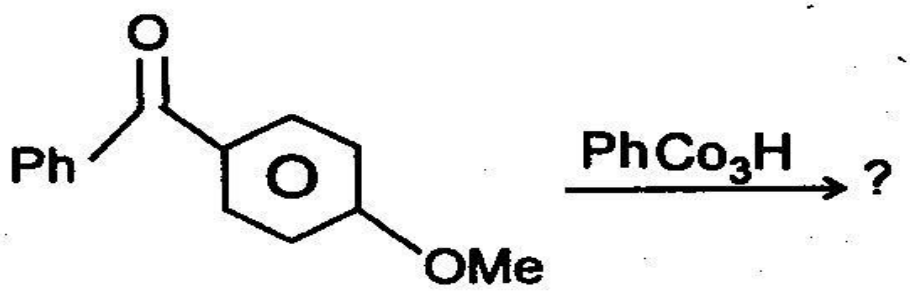
(B) (Alcohol)



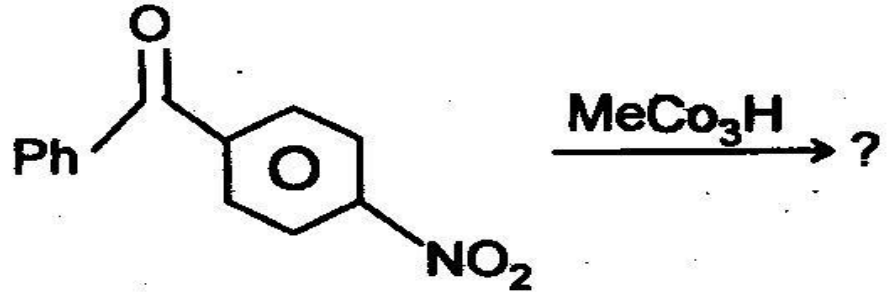
(A)

(c) Predict the product(s) of the following reactions and give mechanisms : 5+5 = 10

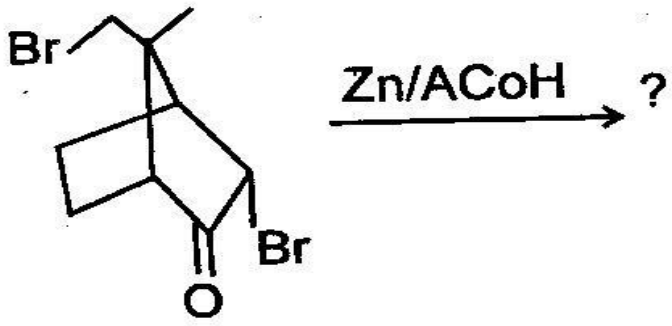
(i)

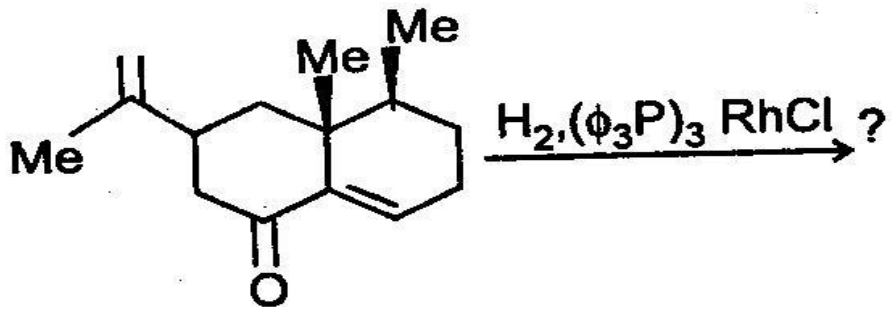


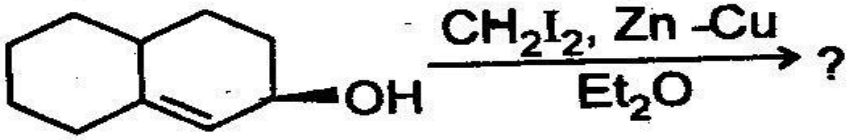
(ii)

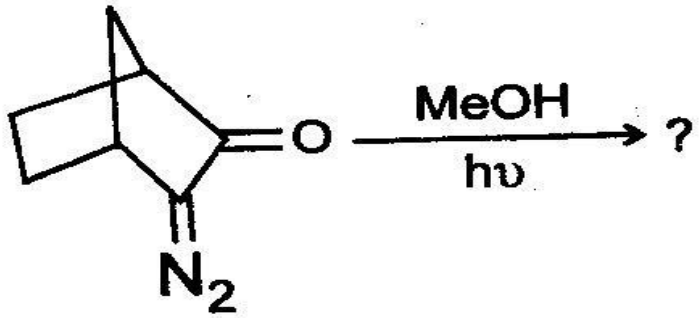


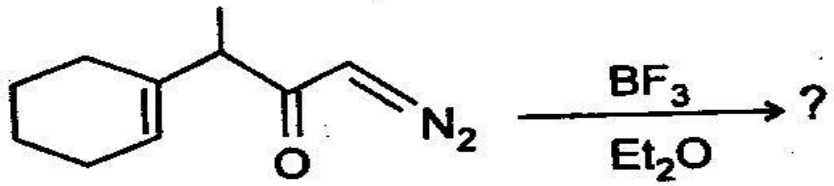
(d) Predict the product(s) and give the mechanisms : 5×5 = 25

(i) 

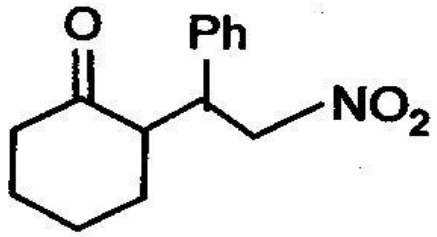
(ii) 

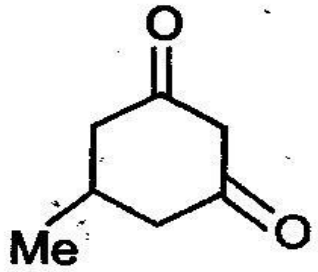
(iii) 

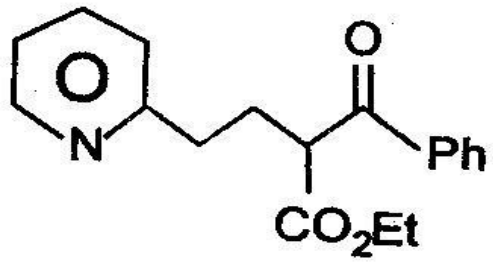
(iv) 

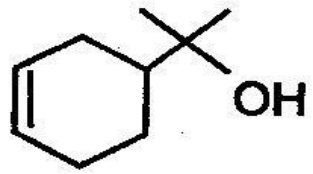
(v) 

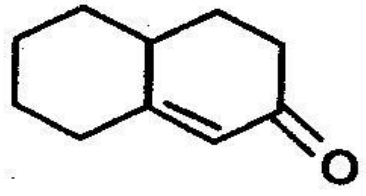
3. Suggest a method for the preparation of the following compounds (any **ten**) : 6×10 = 60

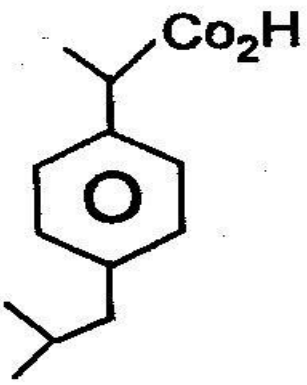
(a) 

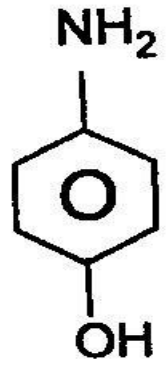
(b) 

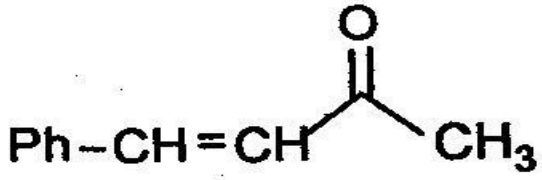
(c) 

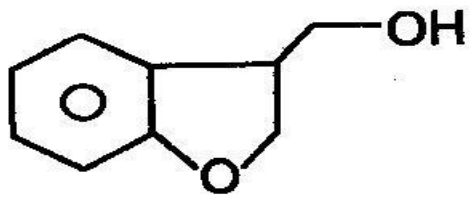
(d) 

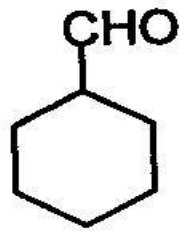
(e) 

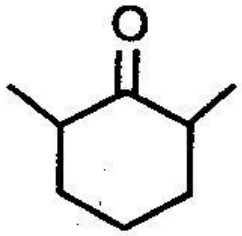
(f) 

(g) 

(h) 

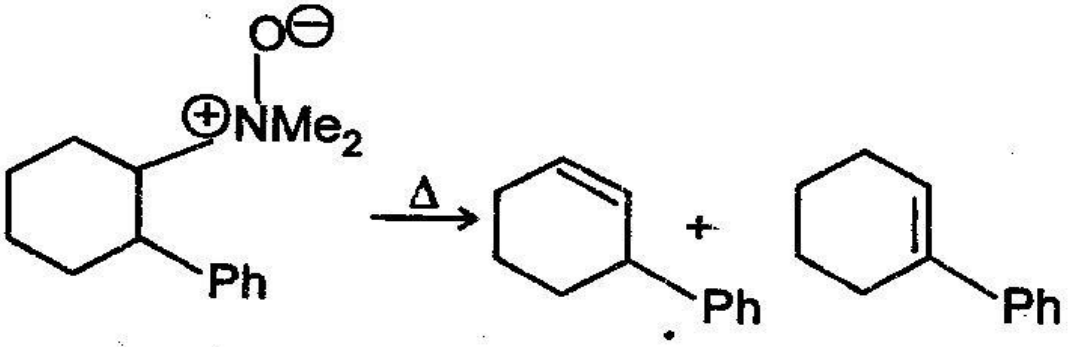
(i) 

(j) 

(k) 

4. Explain the following observations : 10×6 = 60

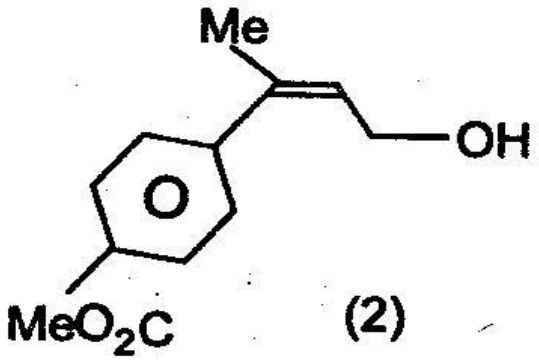
(a) Explain why the two diastereomeric amine N-oxides (1) give, on, heating, two different major regioisomeric alkene products :



(1)

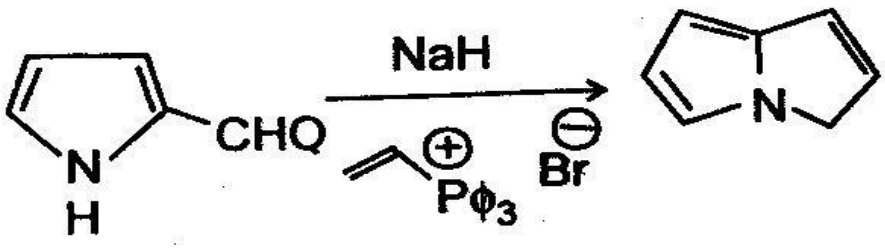
syn	98	:	2
anti	15	:	85

(b) Suggest a method to prepare the allylic alcohol(2) as a single stereoisomer :

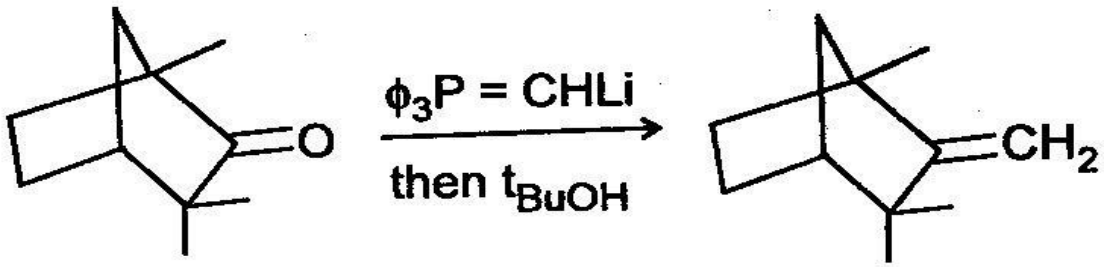


(2)

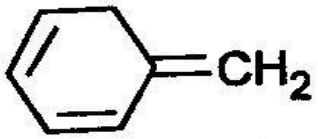
(c) Account for the formation of pyrrolizine (3).



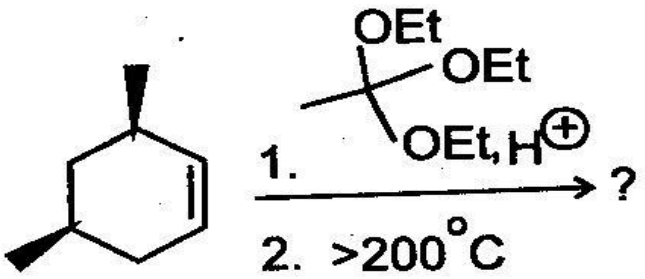
(d) Explain the formation of the adduct (4).



(e) The following isomer of toluene has been prepared. Although it is less stable than toluene, but suprisingly it has a long life . Explain :



(f) Predict the product and write down the stereochem of the product :



Section – B

5. Answer any **three** of the following questions :

(a) (i) What do you mean by number average and weight average molecular mass ?

(ii) How molecular mass of polymer is determined by light scattering method ?

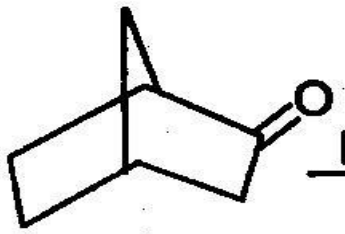
(iii) Calculate $\bar{M}_w$ for a system containing equal number of particles with molecular weight 10,000 and 20,000.

5+10+5 = 20

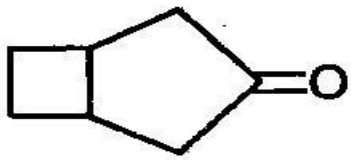
(b) (i) How will you synthesise PVC from acetylene ? What are its commercial applications ? 10

(ii) What do you understand by high polymer ? How can you prove that natural rubber as a high polymer of isoprene ? Discuss the structure and properties of natural polymer. 10

(c) Compound A and B undergo photo-decarboxylation resulting in the formation of I and II from A and III and IV from B. Give the structure of I, II, III, IV and mechanism of their formation : 20

(i) 

A

(ii) 

B

(d) (i) Predict the ESR spectra of the following compounds :

$B_2H_6^-$, $CuSO_4 \cdot 5H_2O$, $C_{10}H_8^-$, $K_4[Fe(CN)_6]$, $[VO\ (d\text{-tartrate})]_2^{4-}$ 15

(ii) Distinguish between 1-pentene and 2-pentene by mass spectra. 5

6. (a) Write two synthetic uses of each of the following reagents : 20

(i) OsO_4

(ii) $LiAlH_4$

(iii) $NaBH_4$

(iv) HIO_4

(b) What is Chemical Shift ? What is its expression ? Discuss three factors affecting chemical shift.

The observed chemical shift of a proton is 300 Hz from TMS and operating frequency of the spectrometer is 100 MHz. Calculate chemical shift in ppm.

5+10+5 = 20

(c) (i) How ESR spectroscopy is used to study the structure of inorganic complexes ?

(ii) An irradiated sample of MgO has a strong ESR line at 0.163T, when spectrometer is operating at 9.4 GHz. What is the g value of the line ?

(iii) What is the expression for g in octahedral and tetrahedral crystal field of metal complexes ? 10+5+5 = 20

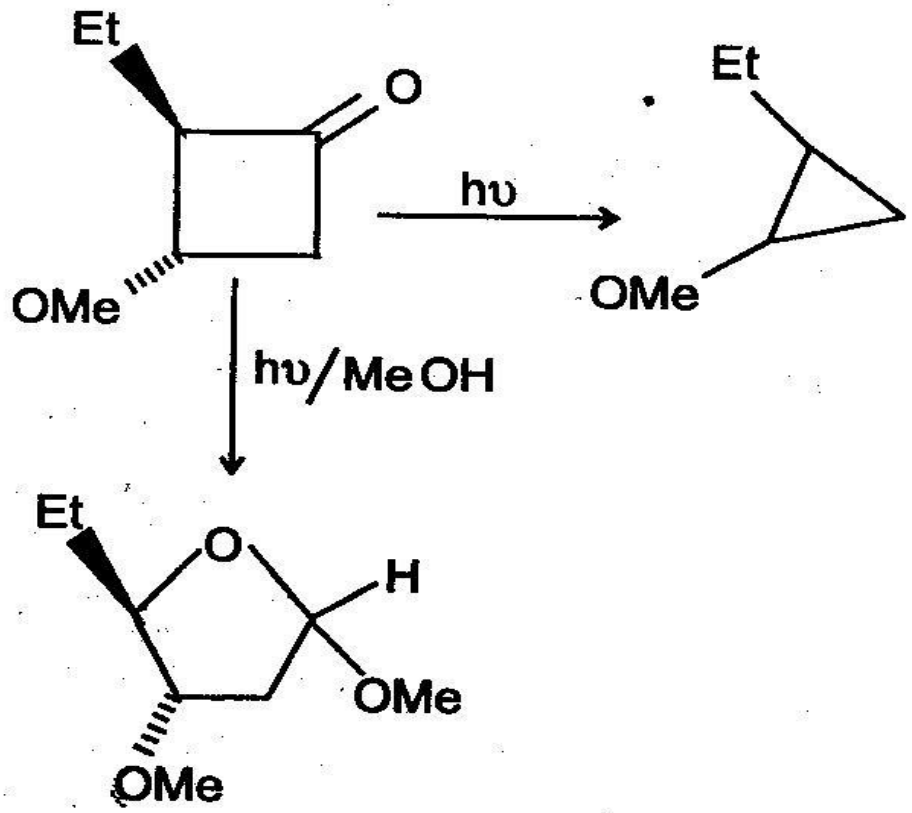
7. (a) Write notes on the following : 21

(i) Norish type II reaction

(ii) Photo fries rearrangement

(iii) Di-π-methane rearrangement

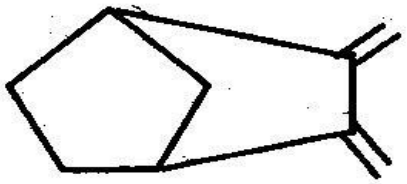
(b) Give the mechanism of the reaction : 15

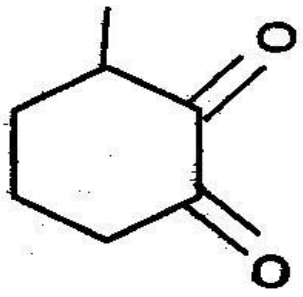


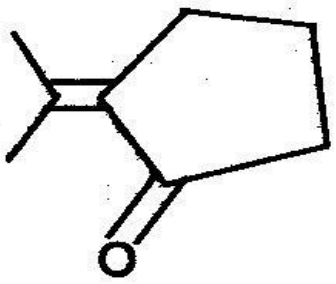
(c) What is McLafferty rearrangement ? How is it used to predict the mass spectra of 1-pentanal. 15

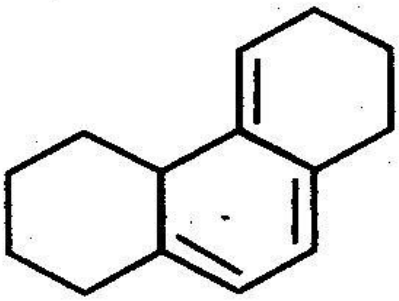
(d) What is Metastable Peak ? What is the significance of metastable peak ? When a parent ion m/e = 77 decomposes by loss of CH ≡ CH to m/e = 51, calculate metastable Peak. 9

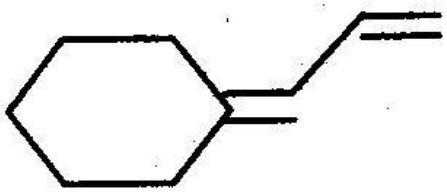
8. (a) Calculate λ_{max} of the following compounds using Woodward-Fisher rule : 20

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(b) Suggest the structure of the compound with molecular formula $C_{10}H_{12}O$ where mass spectra shows peaks at m/e 148, 105, 91, 57, 43. 15

(c) What is Rotational Constant ? What is the change in rotational constant B when hydrogen is replaced by deuterium in hydrogen molecule.

If the rotational constant of carbon-monoxide is 1.9212 cm^{-1}, calculate C–O bond length. 15

(d) Suggest a structure of compound with molecular formula $C_9 H_{12}$, showing NMR signals at 7.2, 2.2 and 0.9 δ ppm. 10