2022

CHEMISTRY — HONOURS

Paper : CC-8

(Organic Chemistry - 4)

Full Marks : 50

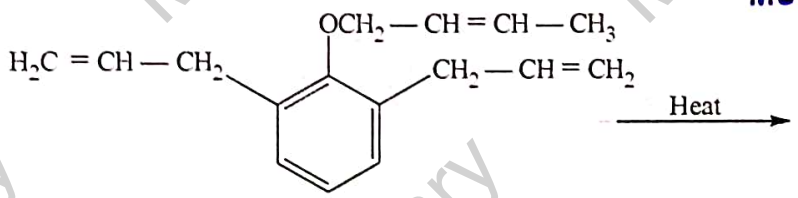
The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** questions from the rest (***question no.*** **2** to **13**).

1. Answer ***any ten*** questions : 1×10

(a) Give the product(s) of the following reaction :



(b) The IR spectrum of benzene shows many peaks but its UV spectrum is very simple. Explain.

(c) Phenol is directly converted to anisole on reaction with diazomethane but an aluminium alkoxide catalyst is required to convert ethanol to ethyl methyl ether with the same reagent. Explain.

(d) $[B] \xleftarrow{Na/ether} CH_3CH_2CN \xrightarrow[2.\ H^{\oplus}/H_2O]{1.\ CH_3Mg\ I/dry\ ether} [A]$

Give the structures of [A] and [B] (structures only).

(e) The difference in precessional frequency of a proton from TMS is 186 Hz in a 60 MHz NMR machine. Find its δ value.

(f) How do you protect propane–1,3-diol? Write down also the deprotecting agent.

(g) Explain why the normal isotope of carbon, ^{12}C is NMR inactive.

(h) Write down the products (only write down the structures of the products) obtained by diazocoupling of benzenediazonium chloride with alkaline 2-naphthol and aniline separately.

(i) Explain why *cis*- cinnamic acid absorbs at a higher frequency than its *trans*- isomer in the IR spectrum.

(j) Give *one* example of each of the following :

(i) Illogical electrophile

(ii) Illogical nucleophile

(k) Write down the structures of the products when RCOOH and $R_2C = O$ are separately subjected to Schmidt reaction.

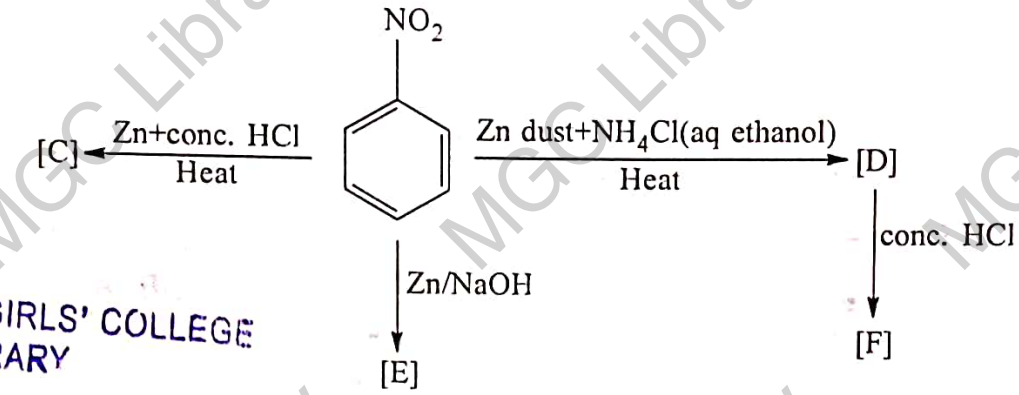
(l) Write down the synthetic equivalents corresponding to the following synthons :

(i) $:\overset{\ominus}{C}HO$ (ii) $\overset{\ominus}{Ph}$

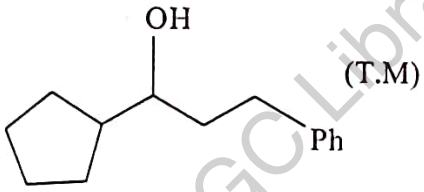
2. (a) How is *threo* (active) isomer of butane-2,3-diol be distinguished from its *erythro* (*meso*) isomer by IR spectroscopy?

(b) Explain why is tetramethylsilane (Me_4Si) (TMS) used as an internal standard in NMR spectral studies. Write down the unit used to measure coupling constant. 3+2

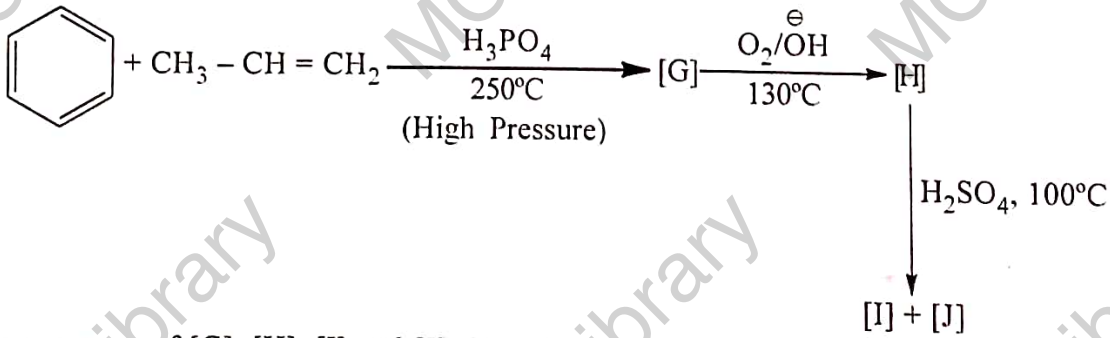
3. (a)



(b) Show the retrosynthetic pathway and the synthesis of target molecule (TM) as follows : 3+2

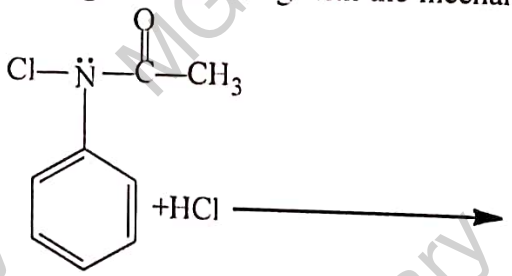


4. (a)



Give the structures of [G], [H], [I] and [J]. Show the mechanism involved in conversion of [H] to [I] and [J]

(b) Give the product(s) of the following reaction along with the mechanism involved. 3+2



5. (a) Define stereospecific and stereoselective reactions and justify the difference between the two terms with the example of addition of singlet and triplet carbene to *Z*-2-butene.

   (b) Primary and secondary nitroalkanes can take part in Nef carbonyl synthesis, but tertiary nitroalkanes can not. Explain. 3+2

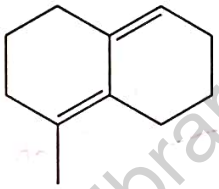
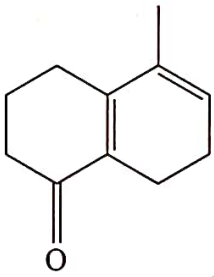
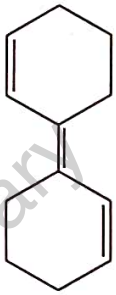
6. (a) Explain why anisole with a mixture of nitric and sulphuric acid gives *o*-nitroanisole in 31% yield whereas with $HNO_3 - Ac_2O$ gives the same product in 71% yield. Provide a suitable mechanism to justify the above observation.

   (b) Show how a single reagent can be used to distinguish between primary, secondary and tertiary aromatic amines (No mechanism is needed). 3+2

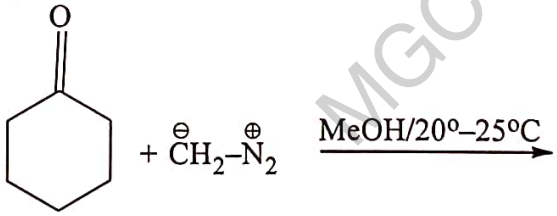
7. (a) Account for the following trends in λ_{max}(nm) : ethylene (175), 1,3-butadiene (217); and 1,3,5-hexatriene (250). Explain why 1,5-hexadiene (λ_{max} = 185 nm) does not absorb light above 200 nm.

   (b) Discuss the difficulties of synthesising $Me_3C - NH_2$ by Gabriel phthalimide synthesis. Show how Me_3CNH_2 can be prepared from $Me_3C - OH$. 3+2

8. (a) Using Woodward-Fieser rule, calculate λ_{max} of the UV absorption for the following compounds :

(i)  (ii)  (iii) 

   (b) Give the product(s) of the following reaction along with the mechanism involved. 3+2



9. (a) An organic compound with molecular formula $C_6H_{12}O$ gives positive iodoform test. Its IR and ^1H NMR spectral data are as follows.

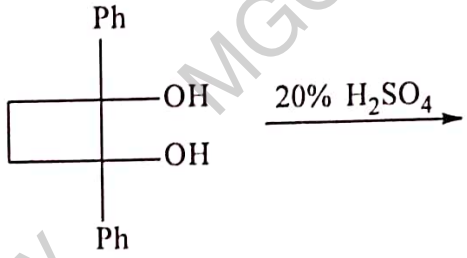
   IR : $\nu_{cm^{-1}} = 1710\ cm^{-1}$ (strong)

   ^1H NMR : $\delta_{\underset{(ppm)}{2.1}}$ (3H, s) and 1.1 (9H, s).

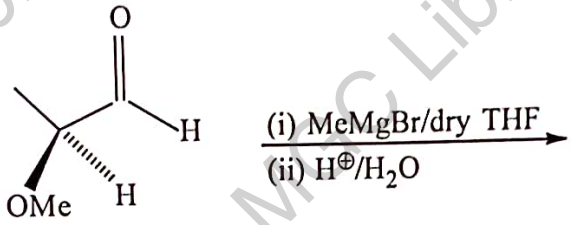
   Deduce the structure of the molecule with proper justification.

   (b) What is the range of 'finger print region' in IR spectroscopy in cm^{-1}? Justify the naming of this range. 3+2

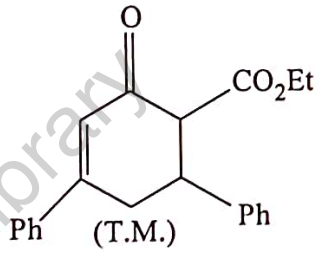
10. (a) The following reaction gives a single product. Give the structure of the product and also explain mechanistically why the other isomeric product is not formed.



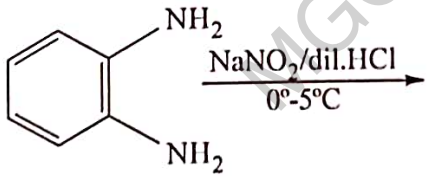
(b) Use Felkin-Anh's model to determine the stereochemistry of the major product of the following reaction : 3+2



11. (a) Give the retrosynthetic pathway followed by the synthesis of the following target molecule (TM) :



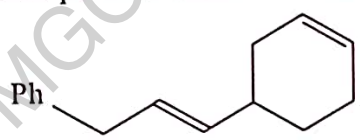
(b) Give the product(s) of the following reaction along with the mechanism involved : 3+2



12. (a) $Ph_2C(OH)-C(OH)Me_2$ (I) + $Ph_2C(OH)-C(OH)Et_2$ (II) $\xrightarrow{H^{\oplus}}$ [K] + [L]

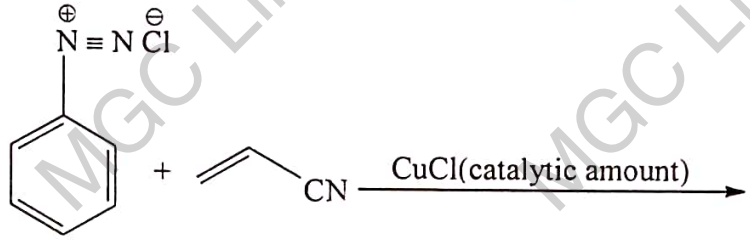
Explain the products of the reaction mechanistically.

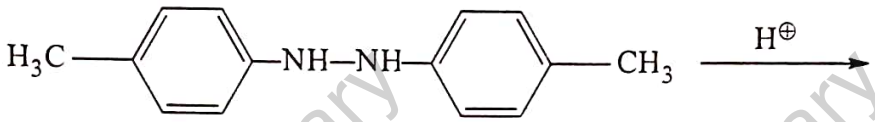
(b) Give possible modes of retrosynthetic analysis and efficient synthesis for



Which mode is better choice? 3+2

13. (a) Give the products of the following reactions along with plausible mechanism :

(i) 

(ii) 

(b) Define the terms 'chemically equivalent' and 'magnetically equivalent' used in ^1H NMR spectroscopy. Give an example of a molecule with chemically equivalent but magnetically non-equivalent protons with proper justification. 3+2