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B.Sc./4th Sem (H)/CHEM/23(CBCS)

2023

4th Semester Examination

CHEMISTRY (Honours)

Paper : C 10-T

(Organic Chemistry-IV)

[CBCS]

Full Marks : 40

Time : Two Hours

The figures in the margin indicate full marks.

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

Group - A

Answer any *five* questions : $2 \times 5 = 10$

1. Explain the following :

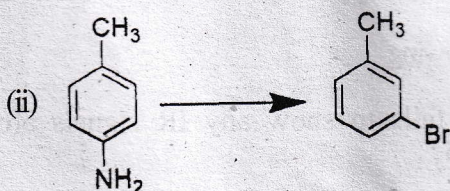
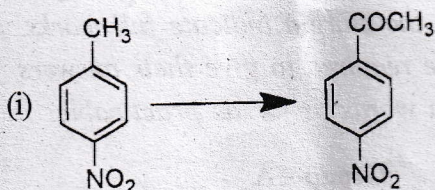
(i) Ethylene fails to show any IR signals around 1600 cm^{-1} .

(ii) Can D_2O be used as a solvent in $^1\text{H-NMR}$ studies?

2. Write a note on symmetry restriction in electronic transition.

P.T.O.

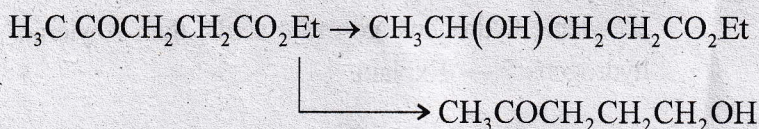
3. How can you distinguish chemically between N-methylaniline and N, N-dimethylaniline?
4. In the Arndt-Ester synthesis two equivalents of diazomethane is used. — Explain the statement showing mechanism of the reaction.
5. Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of H_2O_2 an amide is formed — Explain.
6. Transform the following :



7. How you can distinguish between the following pairs :
 - (i) $\text{CH}_3\text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}_2\text{OH}$ (ordinary grade) by NMR.
 - (ii) Methylbenzoate and Phenylacetate by IR.

(3)

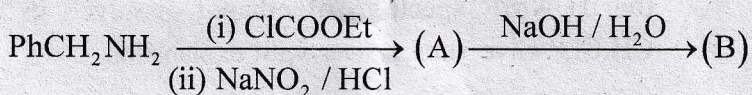
8. Convert the following :



Group - B

Answer any *four* questions : $5 \times 4 = 20$

9. (a) Complete the following reaction scheme with plausible mechanism. 3



(b) How can IR spectroscopy distinguish between 1-hexyne, 2-hexyne, and 3-hexyne? 2

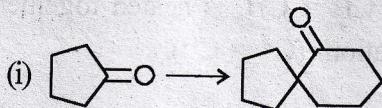
10. (a) An organic compound (S) C_8H_9ON on treatment with H_2SO_4 isomerizes to (T) which on hydrolysis furnishes aniline and acetic acid. What are (S) and (T)? Explain the above fact and show mechanism of isomerization step only. 3

(b) How *o*-nitroaniline can be distinguished from *p*-nitroaniline by UV-spectroscopy? 2

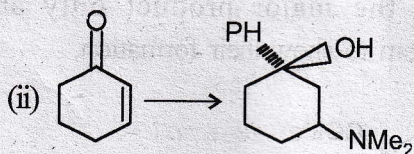
11. (a) Write the structure of all possible products when 1:1 mixture of $\text{PhOCH}_2 - \text{CH} = \text{C}^*\text{H}_2$ and $\text{PhOCH}_2 - \text{CH} = \text{CH}_2$ is heated together. Explain their formation. ($\text{C}^* = \text{C}^{14}$). 2

P.T.O.

- (b) Why do acetylenic protons resonate at upfield region with respect to ethylenic protons though acetylenic hydrogens are more acidic than ethylenic hydrogens ? — Explain. 3
12. (a) Compare the rate of formation of aniline from fluorobenzene and bromobenzene in presence of NaNH_2 and liq. NH_3 . Cite suitable experimental evidence. 3
- (b) Which has a greater chemical shift for the OH proton, the ^1H NMR spectrum of pure ethanol or the ^1H NMR spectrum of ethanol dissolved in CH_2Cl_2 ? Give your answer with explanation. 2
13. (a) Explain with mechanism the rate(s) of nitration of nitrobenzene and pentadeuteronitrobenzene under similar reaction conditions. 2
- (b) How many peaks do you expect for nitrobenzene in its ^1H -NMR spectrum? Draw a rough sketch for the ^1H -NMR spectrum of nitrobenzene assigning the protons in the diagram. (Actual δ values and meta-coupling may be ignored). 3
14. (a) If two signals differ by 90 Hz in a 300 MHz spectrometer, by how much do they differ in a 500 MHz spectrometer? 1
- (b) Convert : 2+2



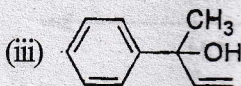
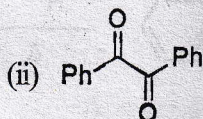
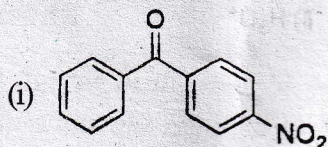
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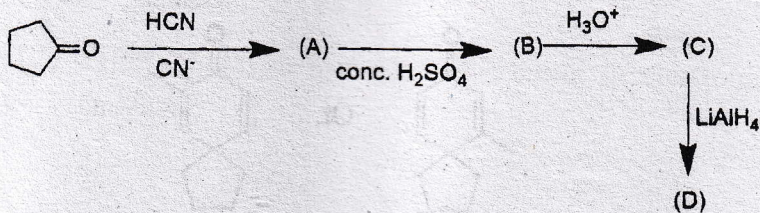
Group - C

Answer any **one** question : $10 \times 1 = 10$

15. (a) Give the retrosynthetic pathways and one efficient synthetic method for the following compound. 3×2



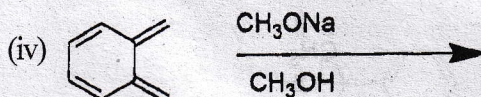
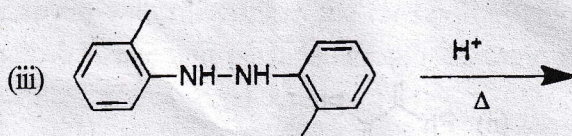
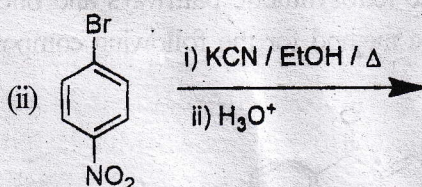
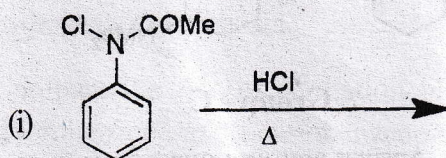
- (b) Write down the structure of the products A, B, C and D 4



P.T.O.

(6)

16. (a) Predict the major product only and write mechanism to show their formation. 2×4



- (b) Which member of the following pair will undergo Dienone-Phenol rearrangement more rapidly and why? 2

