B.Sc./3rd Sem (H)/CHEM/23(CBCS)

2023

3rd Semester Examination

CHEMISTRY (Honours)

Paper : C 7-T

[Organic Chemistry-III]

[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

1. Answer any ***five*** questions : 2×5=10

(a) How can you convert (*Z*)-2-butene to (*E*)-2-butene?

(b) What happens when one mole of *PhMgBr* is allowed to react with 2 moles of *PhCHO* in anh. ether followed by usual work-up (acidic) of the reaction mixture?

(c) What happens when o-bromoanisole is treated with $NaNH_2/liq.NH_3$? Explain.

P.T.O.

(d) Carry out the following conversion :

$EtC \equiv CH \longrightarrow MeC \equiv CMe$

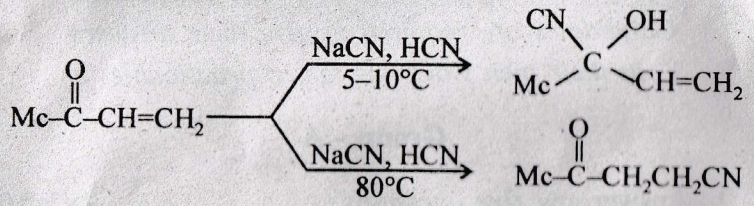
(e) Write the final product(s) in the following case :

$CD_3CHO + 4HCHO \xrightarrow{NaOH}$

(f) Arrange the following compounds in the increasing order of enol content and justify

$MeCOCH_2COCH_3$, $MeCOCH_2CH_2COCH_3$, $(Me_3CCO)_3CH$

(g) Explain the following observation :



(h) Discuss critically with reaction mechanism the easy formation of the oxime of a ketone with hydroxylamine hydrochloride in the presence of sodium acetate.

Group - B

2. Answer any ***four*** questions : 5×4=20

(a) Discuss the mechanism of Cannizzaro reaction. Identify the product(s) formed in each of the following cases. 1+2+2

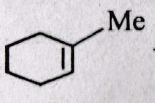
(i) $PhCOCHO \xrightarrow{OH^-}$

(ii) $CH_3CHO + HCHO(\text{Excess}) \xrightarrow{OH^-}$

(b) Explain the following reactions with plausible mechanism and give products). 1½+1½+2

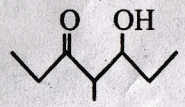
(i) $CH_2 = C = CH_2 \xrightarrow{\text{Dry } HCl\ (1\text{ eqv.})}$

(ii) $CH_3 - C \equiv CH \xrightarrow[HgSO_4,\ 60°C]{\text{dil } H_2SO_4}$

(iii)  $\xrightarrow[\text{then } H_2O_2/aq.\ NaOH]{B_2H_6/THF}$

(c) (i) Work backward to identify the starting material which upon aldol condensation produce the following compounds.

$PhCH = CH - CO - CH = CHPh$,



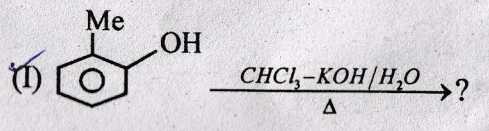
(ii) Write the products *A* and *B* and explain their formation. $1+1+1\frac{1}{2}+1\frac{1}{2}$

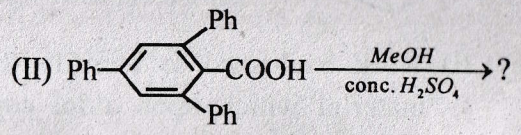
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NaN_3} A \xrightarrow[(ii)\ H_2O]{(i)\ \Delta} B$$

P.T.O.

(d) (i) What would be the product composition if a equimolecular mixture of toluene and chlorobenzene is treated with one molar proportion of bromine in presence of iron powder?

(ii) Predict the fate of the following reactions with proper mechanism.





(e) (i) With suitable examples comment on the selectivity and reactivity of Me_2CuLi and $MeLi$.

(ii) Explain the role of Li^+ in the reduction of carbonyl compounds with $LiAlH_4$. Give the mechanism of the reaction. 2½+2½

(f) (i) Reaction of acetone with equimolecular proportion of bromine yields monobromo-acetone under acid catalysed condition and not under base-catalysed condition. Explain with proper mechanism.

(ii) Give the reagents and reaction conditions for the following with mechanism. 3+2

$$PhCH_2C\equiv CH \longrightarrow PhCH_2\underset{\underset{O}{\|}}{C}-Me$$

Group - C

3. Answer any ***one*** question : 10×1=10

(a) (i) Write the A_{Ac^2} and B_{Ac^2} mechanism for the hydrolysis of methyl benzoate. It is observed that the electron withdrawing, substituent in the *m*- and *p*- positions enhance the rates of B_{Ac^2} hydrolysis of the substituted methyl benzoates while the effect is negligible for A_{Ac^2} reactions. Explain.

(ii) Write down any six principles of green chemistry.

(iii) Reaction of *trans*–2–butene with methylene obtained from diazomethane occurs in a stereospecific way. What happens when the reaction is carried out in the presence of nitrogen? Explain. 4+3+3

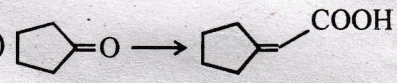
(b) (i) What happens when 2-butyne is treated with *Li* metal in liquid NH_3 and *EtOH*? Give mechanism.

P.T.O.

(ii) Give the product(s) of the following reaction and explain.

$$CH_3CH=CH-CH_2CH_3 \xrightarrow[CCl_4]{NBS(1\,eqv.)}$$

(iii) Carry out the following conversions and give plausible mechanisms :

(i) 

(ii) $MeCOCH_2CH_2CO_2Et \longrightarrow MeCOCH_2CH_2CMe_2OH$

(iv) Acetanilide undergoes nitration by Ac_2O-HNO_3 predominantly at sterically hindered ortho position — Explain.

2+2+(2+2)+2
