

U.G. 3rd Semester Examination-2020

CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-07

(Organic Chemistry)

Full Marks : 40

Time : 2½ Hours

The figures in the right-hand margin indicate marks.

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

1. Answer any **five** from the following questions :

2×5=10

- Isobutene fails to react with dimethoxy carbene. Explain.
- Comment on the optical activity of the product in the catalytic hydrogenation of *Z*-3,4-dimethylhex-3-ene.
- Treatment of *p*-bromophenol with sodamide in liquid ammonia at -33°C furnishes *p*-amino phenol. Explain with mechanism.
- Why red phosphorous is used in Hell Volhard Zelinsky bromination of a carboxylic acid?
- How can you convert propyne into propanal?
- Use of magnesium instead of zinc is not

[Turn over]

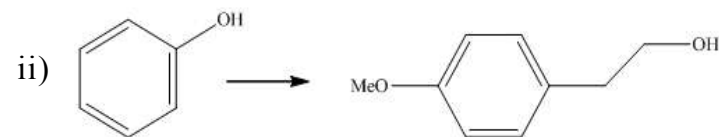
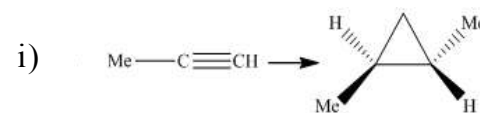
recommended for Reformatsky reaction. Explain.

- Primary alcohols can't be satisfactorily oxidized to aldehydes by Oppenauer oxidation. Explain.
- Write down the major mononitration product of PhCOCH₂Ph with a brief explanation.

2. Answer any **two** from the following questions:

5×2=10

- Addition of bromine to *E*-2-butene gives exclusively the meso dibromide but reaction of *E*-1-phenylpropene with bromine furnishes a mixture of erythro and threo dibromides. Offer an explanation.
 - State, with mechanism, what happens when di isopropyl ketone is treated with *tert*-butyl magnesium bromide. 3+2
- How can you achieve the following transformations? 2½+2½



c) Explain the following observations:

i) Lead tetracetate oxidation of dl-2,3-butane diol occurs faster than that of the meso-isomer.

ii) Bromination of acetophenone in presence of catalytic amount of anhydride aluminium chloride gives PhCOCH₂Br but use of excess anhydride aluminium chloride in the same reaction affords chiefly *m*-bromoacetophenone.

iii) Why α,β -unsaturated carbonyl compounds can't be epoxidised by per acids? 2+2+1

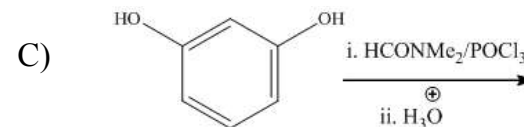
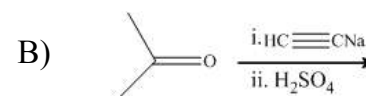
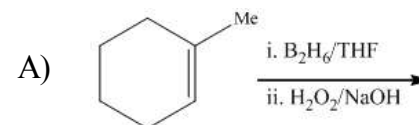
d) i) In Kolbe Schmidt reaction use of sodium phenoxide gives mainly salicylaldehyde but use of potassium phenoxide affords chiefly *p*-hydroxy benzoic acid. Explain.

ii) It is not wise to convert Me₃CCH=CH₂ into Me₃CCH(OH)Me by acid catalysed hydration of the substrate. Why? How this conversion can actually be achieved? 2+3

3. Answer any **two** from the following questions:

10×2=20

a) i) Predict the product(s) in the following reactions and suggest mechanism in each case (any **two**).

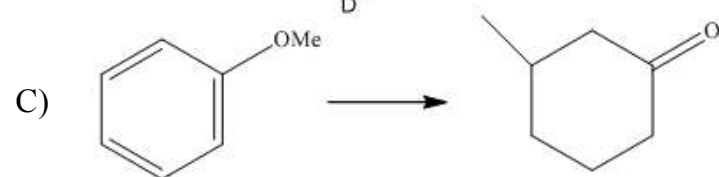
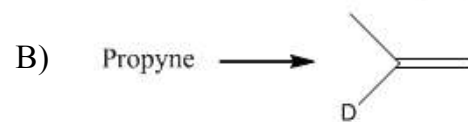


ii) Alkaline hydrolysis of *S*-1-phenyl ethyl acetate gives *S*-1-phenyl ethanol but acid hydrolysis of the same ester forms racemic 1-phenyl ethanol. Explain with mechanism.

iii) For the preparation of ketones slow addition of Grignard reagents to a cold solution of acid chlorides is a much better method than drop wise addition of Grignard reagents to a cold solution of ester. Why?

(3+3)+2+2

b) i) How can you carry out the following transformations?



ii) How does iodine act as a catalyst in the ring bromination of aromatic compounds?

iii) What happens when $\text{MeCOCH}_2\text{COOEt}$ and $\text{MeCOCMe}_2\text{COOEt}$ are separately treated with 1 equivalent of methyl magnesium bromide? (2+2+2)+2+2

c) i) Both *p*-nitro benzaldehyde and *p*-dimethylamino benzaldehyde fail to undergo benzoin condensation but a mixture of these two aromatic aldehydes undergo the reaction. Explain with suitable mechanism.

ii) How can you synthesize 2,2-dimethylpentane by Corey House method?

iii) 2,6-dimethyl acetanilide undergoes nitration mainly at C-3. Explain.

iv) Ozonisation of 2,3-dimethyl-2-butene in presence formaldehyde gives the ozonide of isobutene as one of the products. Explain. 4+2+2+2

d) i) How can you convert $\text{MeCOCH}_2\text{COOEt}$ into
A) PhCH(Me)COOH and
B) $\text{PhCH}_2\text{COCH}_2\text{Me}$?

ii) Nitration of iodobenzene gives a mixture of *o*-nitro iodobenzene and *p*-nitro iodobenzene but nitration of *p*-iodo anisole gives mainly *p*-nitro anisole. Offer an explanation.

iii) 1,3-Butadiene is more reactive than ethylene towards both electrophilic and nucleophilic addition reactions. Explain in terms of elementary molecular orbital approach.

iv) Will the following reaction occur as shown below? If not, why?

