U.G. 3rd Semester Examination-2021
CHEMISTRY
[HONOURS]
Course Code : CHEM-H-CC-T-7

Full Marks : 40 Time : $2\frac{1}{2}$ 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

a) When 2-butyne is treated with sodium in liquid ammonia followed by ammonium chloride, E-2-butene is formed as the major product but 1,3-butadiene gives predominantly Z-2-butene under identical conditions. Explain with mechanism.

b) Reaction of allene with 1 equivalent of dry HCl gives mainly 2-chloropropene as the major product though allyl cation is more stable than $[MeC{=}CH_2]^+$. Offer an explanation.

c) How can you convert benzene into 3-nitro propyl benzene?

d) Use of excess active methylene compound is not recommended for Knoevenagel reaction. Why?

[Turn over]

e) When benzene is treated with isobutyl chloride in presence of anhydrous $A1Cl_3$, *tert*-butyl benzene is formed as the major product. Explain with mechanism.

f) Claisen condensation of ethyl acetate occurs better with EtONa in diethyl ether than in ethanol. Explain.

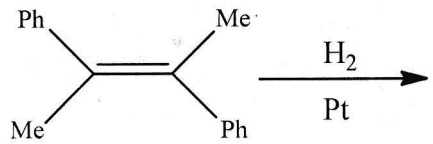
g) What happens when phenyl acetic acid is treated separately with excess CH_3Li and CH_3MgBr and the product is acidified?

h) How can you synthesize MeCH=CHCOMe using directed aldol condensation?

2. Answer any **two** from the following: 5×2=10

a) i) Predict the product(s) in the following reactions with proper configuration:

I)



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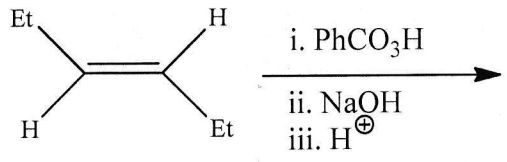
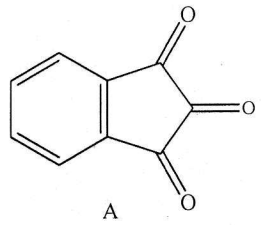
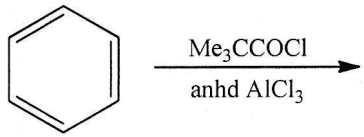


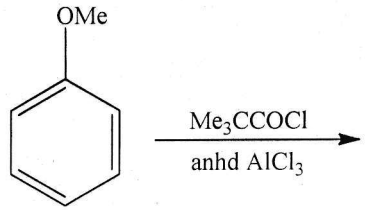
ii) Compound A easily forms hydrate but acetone doesn't. Explain.



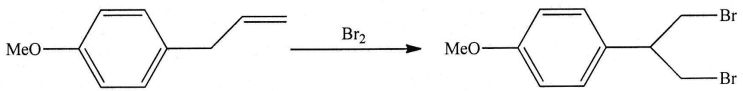
3+2

b) i) Identify the major products in the following reactions and explain your answer with mechanistic rationalization.

I) 

II) 

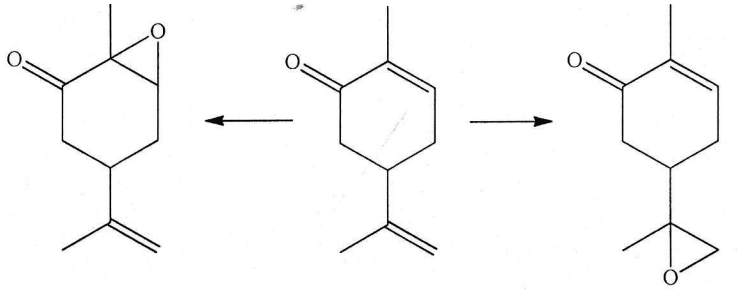
ii) Formulate a plausible mechanism for the following reaction:



3+2

c) i) State with mechanism what happens when benzaldehyde in two moles amounts is treated with one mole of phenyl magnesium bromide.

ii) How can you carry out the following transformations? Suggest mechanism in each case.



2+3

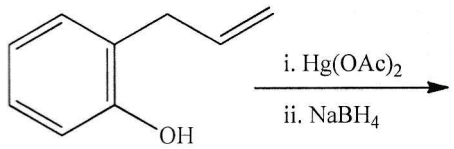
d) i) When benzaldehyde is heated with acetic anhydride in presence of sodium acetate, a small amount of styrene ($PhCH=CH_2$) is sometimes obtained. Explain the observation with a plausible mechanism.

ii) Arrange PhMe. PhOMe. PhCl and $PhNO_2$ in the decreasing order of reactivity towards nitration with a mixture of conc. nitric acid and conc. sulfuric acid and explain your answer. 2+3

3. Answer any **two** from the following: 10×2=20

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

I)



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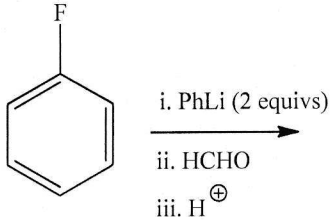
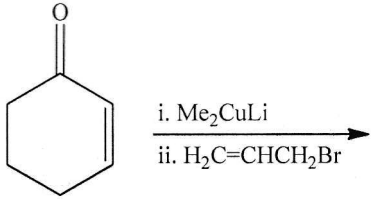


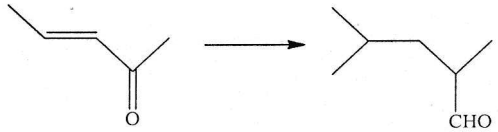
III)



ii) Alkaline hydrolysis of $MeCOOCH_2CH=CHMe$ gives only $MeCH=CHCH_2OH$ but acid hydrolysis of the same ester produces a mixture of $MeCH=CHCH_2OH$ and $MeCH(OH)CH=CH_2$. Explain with mechanism. $(2\frac{1}{2}\times3)+2\frac{1}{2}$

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

I)



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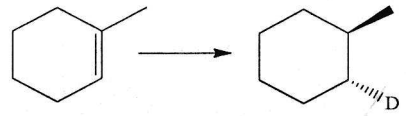
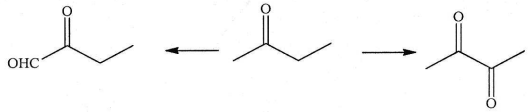
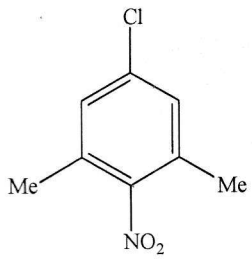
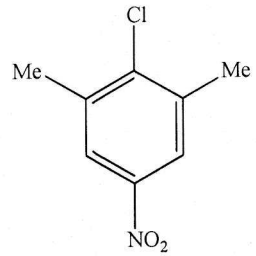


III)



ii) Compare the reactivity of the following compounds towards nucleophiles with reasons.



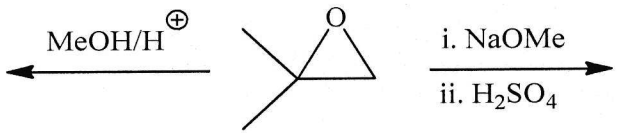


iii) State with mechanism what happens when $PhCH_2OMe$ is treated with butyl lithium followed by dimethyl formamide.

(2+2+2)+2+2

c) i) Anisole affords *o*-nitroanisole with HNO_3–Ac_2O mixture but phenylboronic acid [$PhB(OH)_2$] undergoes *meta* nitration with mixed acid. Explain.

ii) Predict the major products in the following reactions and suggest mechanism in each case.



iii) Mechanism of hydrolysis of *p*-substituted benzoyl chloride depends on the nature of substituent. Explain.

iv) In Stobbe condensation the enolate of diethyl succinate reacts with ketone but in the base catalysed reaction between ketone and a monoester, the enolate of ketone preferentially reacts with the ester. Explain. 2+(2+2)+2+2

d) i) How can you convert bromobenzene into $PhCH_2COMe$?

ii) 1,2,4,5-Tetramethyl benzene (Durene) can form its *p*-diacetylated compound when treated with acetyl chloride in presence of anhydrous $AlCl_3$. Explain.

iii) Base and acid catalysed bromination of acetone furnish different products. Explain with a suitable mechanism.

iv) When allyl bromide is treated with lithium, 1,5-hexadiene is obtained but use of magnesium instead of lithium gives allyl magnesium bromide. Explain.

v) How can you convert diethyl adipate into cyclohexanone? 2+2+2+2+2

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