U.G. 3rd Semester Examination - 2019

CHEMISTRY

[HONOURS]

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

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

The figures in the right-hand margin indicate marks.

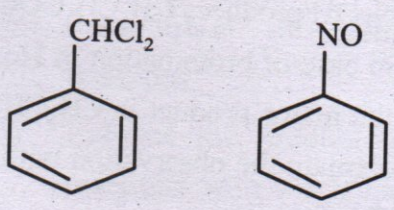
Candidates are required to give their answers in their own words as far as practicable.

1. Answer any **five** questions: $2\times5=10$

a) Why acetylene is less reactive than ethylene towards bromine addition?

b) What are $\pi-$ and $\sigma-$ complexes in aromatic electrophilic substitution?

c) Predict the favoured position of electrophilic substitution of the following compounds and justify your answer.



d) Why $Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}Ph_2$ does not react with carbonyl compounds?

e) O-chloronitrobenzene gives O-nitrophenol when treated with Na_2Co_3 solution, but the m-isomer does not react even with conc. KOH solution– explain.

f) What kind of compounds act as Michael acceptors in reaction with carbanions? Draw an orbital picture of carbanion-enolate ion.

g) Explain why potassium phenoxide is not suitable for the synthesis of salicylic acid by Kolbe-Schmidt reaction.

h) What type of Grignard reagent is formed when $BrPhCH_2CH_2Br$ is treated with one mole of Mg in dry ether? Other an explanation.

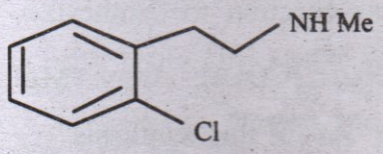
2. Answer any **two** questions: 5×2=10

a) i) How can you convert HCHO to methyl formate in one step?

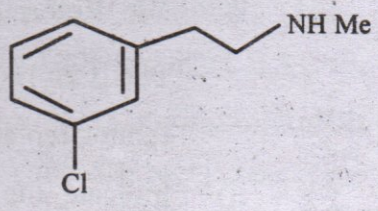
ii) Butanone on bromination in presence of NaOH produces $CH_3CH_2COCBr_3$ whereas in case of bromination in HoAc medium, the major product is $CH_3CH(Br)COCH_3$. Explain the observation with mechanistic details. 2+3=5

b) i) Why dimethoxy carbene does not react with $CH_3CH=CH_2$?

ii) Both compounds (I) and (II) give the same product when treated wih a strong base. Indicate the product and explain with proper mechanistic details.



(I)

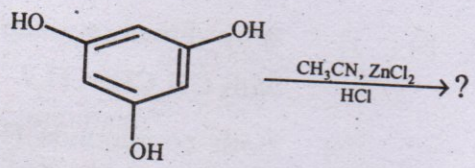


(II)

iii) Discuss the mechanism of Claisen condensation reaction. Why is an adequate amount of NaOEl is necessary for the successful completion of the reaction? 1+2+2=5

c) i) Two ozonides are formed when $(CH_3)_2C=C(CH_3)_2$ is treated with ozone in presence of HCHO. Give the mechanism of formation of two ozonides.

ii) Indicate the product of the following reactions with mechanism:

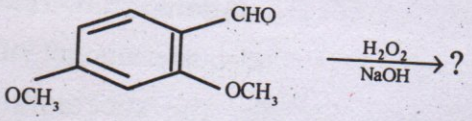
a) 

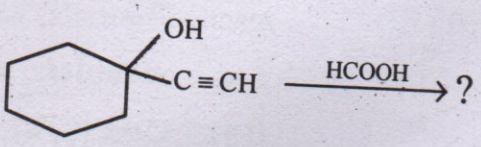
b) $Ph-C\equiv CH \xrightarrow[H_2O]{SeO_2} ?$

$2+(1\frac{1}{2}+1\frac{1}{2})=5$

d) i) Use Reformatsy reaction to synthesize $PhC(CH_3)=C(CH_3)COOH$. Why 'Mg' cannot replace 'Zn' in this synthesis?

ii) Indicate the products of the following reactions and rationalize with mechanism (any one):

A) 

B) 

$3+2=5$

3. Answer any **two** questions: $10\times2=20$

a) i) It is observed that electron withdrawing substituents in the m-and p-positions enhance the rates of BAC2 hydrolysis of substituted methyl benzoates while the

effect is negligible for AAC2 reactions. – explain.

ii) How would you synthesize the following compounds using suitable organometallic reagents?

a) $CH_3CH_2COCH_3$ from CH_3CH_2COCl is one step

b) $(CH_3)_3C–COOH$ from $(CH_3)_3C–Br$

iii) Predict the products giving plausible mechanisms in the following reactions–

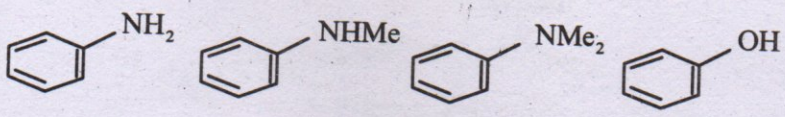
a) $CH_3COCHO \xrightarrow{OH^{\ominus}} ?$

b) $Ph-CH=CH-\overset{\overset{O}{\|}}{C}-Ph$ → MeLi → ?; → Me_2CuLi → ?

3+3+4=10

b) i) Acetals and Ketals regenerate the corresponding carbonyl compounds upon treatment with an aquous acid but they are stable in alkaline medium—justify.

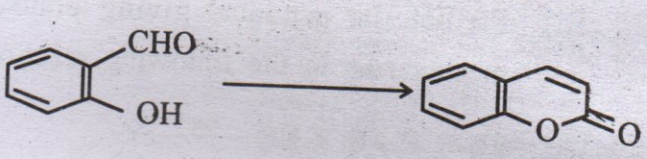
ii) Show the effect of nitrous acid on the following compounds:



iii) Use acetoacetic ester to prepare a β-diketone.

iv) What would be the product composition if equimolecular mixture of toluene and chlorobenzene is treated with 1 molar proportion of bromine in presence of iron powder?

v) How will you convert the following?

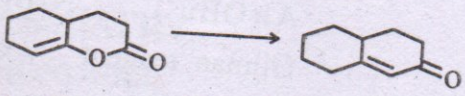


2+2+2+2+2=10

c) i) Can you suggest explanation for the fact that 1, 2-addition reaction of 1, 3-butadiene and HBr occurs faster than 1, 4-addition? How can you account for stability of 1, 4-addition product?

ii) $Hg(OAc)_2$ can be used to convert an alkene to an alcohol without any rearrangement when acid catalysed hydration gives a mixture of alcohols– justify.

iii) Carry out the following conversions (any two):

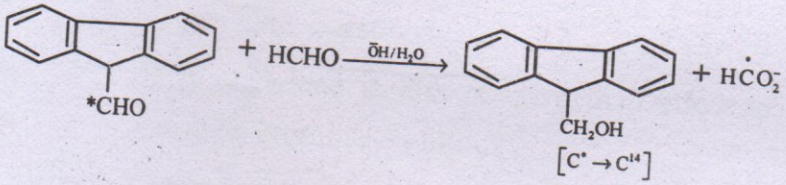
A) 

B) 1-Butene → E-2-butene

C) 

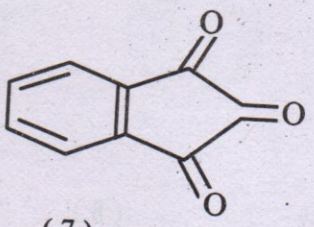
3+3+(2×2)=10

d) i) Provide a reasonable mechanism for the following reaction:



ii) How can you demonstrate that benzoin condensation is a reversible reaction? Why CN^- ion is a very specific catalyst in this reaction?

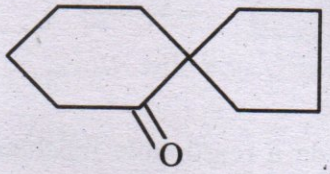
iii) Hydrate forms of the following compounds are stable. Explain

Cl_3C-CHO, 

iv) Give one synthetic use of the following reagents (any **two**):

$Al(OBu^{+})_3$, N-Bromosuccinimide, Gilman reagent

v) Outline the synthesis of the compound (X) from diethyladipate.



(X)

2+2+2(1+1)+2=10
