Ex/2CH/2/IX/61/2018

INTER B.SC. EXAMINATION, 2018

(2nd Semester)

CHEMISTRY (HONOURS)

PAPER - IX

ORGANIC CHEMISTRY

Time : Two hours Full Marks : 50

(25 marks for each group)

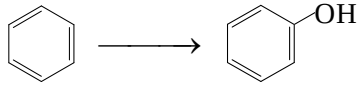
Use a separate answerscript for each group

GROUP - A

1. a) Draw the structure of the major products in the sulphonation of naphthalene at low and elevated temperature. Draw also the energy diagram of this reaction. 3

   b) Suggest reagent(s) for the following transformations : 1×3

   i) $ArCO_2Et \rightarrow ArCHO$

   ii)  (single step)

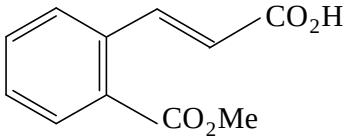
   iii) $ArCH_2OH \rightarrow ArCHO$ (Swern oxidation)

   c) i) What is the effective electrophile in the Vilsmeier-Haack reaction ? How is it generated *in situ* ?

ii) Write down the structure of the compound which on LAH reduction followed by aqueous work up gives benzaldehyde. 2+1

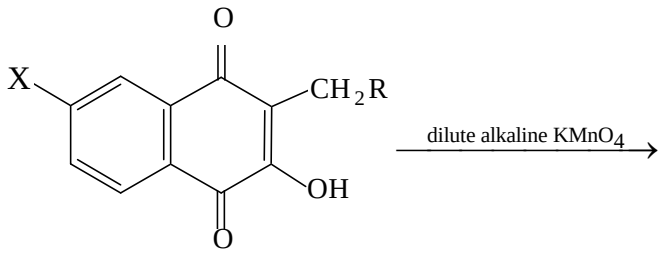
d) Outline the single step synthesis of α-tetralone from benzene and comment on the probable order of bond formation in the reaction. How can you synthesise a hydrophenanthrene skeleton from α-tetralone in two steps ? 4

e) How would you synthesise **A** from phthalic acid ?



A 3

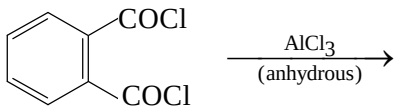
f) Predict the final product of the following reaction indicating the structure of probable intermediates.



3

g) Mechanistically predict the product of the following reactions :

i) $PhN_2^{\oplus}BF_4^{\ominus} \xrightarrow[Cu]{NaNO_2}$

ii) 

2×2

h) What is a persistent radical ? What happens when 2, 4, 6- tri tert-butylphenol is treated with Fe^{+3} in an inert atmosphere ? 2

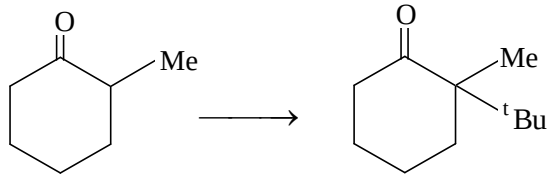
GROUP - B

2. a) What will happen when isopropylmagnesium bromide is treated with diisopropyl ketone ? Explain with mechanism. 2

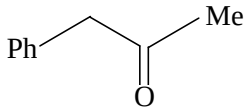
b) Cyanohydrin of benzophenone cannot be prepared by the addition of HCN, but it can be easily prepared using Me_3SiCN in the presence of catalytic amount of KCN. Explain with proper reason. $2\frac{1}{2}$

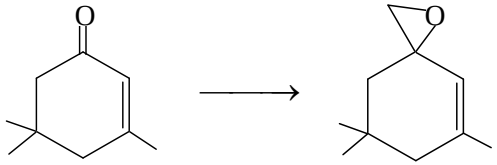
c) What will happen when ^tBuLi and MeLi are sequentially added into CO_2 and then acidified with dil.HCl ? What product would you expect when similar treatment is done using the corresponding Grignard reagents ? Explain with mechanism. $2\frac{1}{2}$

3. How do you carry out the following conversions ? (Mechanism is not required) $1\frac{1}{2}\times4$

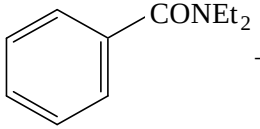
a) 

b) $CH_3CH_2C\equiv CH \longrightarrow CH_3CH_2CH_2CHO$

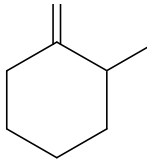
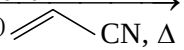
c) $MeCH_2NO_2 \longrightarrow$ 

d) 

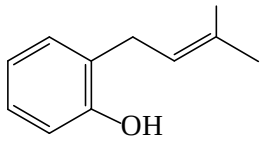
4. a) Identify the products and explain reactions with plausible mechanism of the following :

i) 

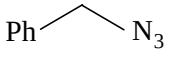
$\xrightarrow[\text{THF / TMEDA}]{\text{i) } {}^{S}BuLi, -78^{O}C}$ ii) DMF iii) $H_3O^{\oplus}$ $2\frac{1}{2}$

ii) 
i) Pyrrolidine
$\xrightarrow[\text{ii)}]{C_6H_6,\ p\text{–TsOH},\Delta}$ 

iii) $H_3O^{\oplus}$ $2\frac{1}{2}$

iii) 

$\xrightarrow[C_6H_6,\Delta]{DDQ}$ $1\frac{1}{2}$

iv) 

$\xrightarrow[\text{ii) } H_2O]{\text{i) } PPh_3}$ $1\frac{1}{2}$

b) What will happen when phenylalanine reacts with ninhydrin ? Give the mechanism. $1\frac{1}{2}$

c) Device a synthesis of the dipeptide Ala-Val. (Mechanism is not required). $2\frac{1}{2}$