2022

CHEMISTRY (Honours)

Paper Code : CEMH DC-T7

[Organic Chemistry]

Full Marks : 25 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.

1. Answer any *five* questions from the following : 1×5=5

(a)  A

In the above reaction, the product "A" is

(i) $PhCH(OH)CO_2H$

(ii) $PhCHO$

(iii) $PhCO_2H$

(iv) $PhCH_2OH$

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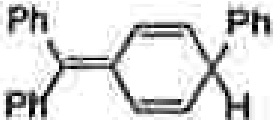
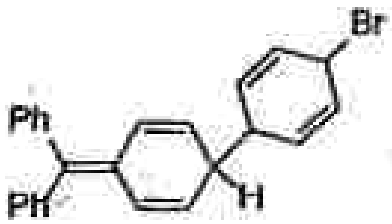
(b)  + $Ph_3\bar{C}Na^+$ $\xrightarrow[\text{liq. } NH_3, -33°C]{KNH_2}$ B

In the above reaction, "B" is

(i) Ph_3CH

(ii) Ph_4C

(iii) 

(iv) 

(c) Which of the following statements is most appropriate for ethylene and 1,3-butadiene ?

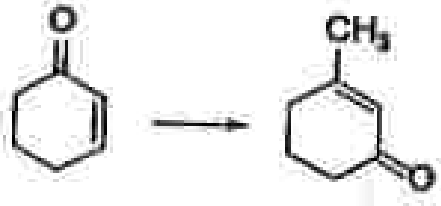
(i) 1,3-Butadiene is more nucleophilic than ethylene

(ii) 1,3-Butadiene is more electrophilic than ethylene

(iii) Both (i) and (ii)

(iv) Neither (i) nor (ii)

(d) Observe the following reaction :



The required set of reagents for this conversion is

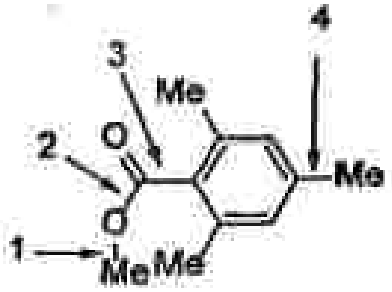
(i) A. CH_3MgBr then H^+, B. H_2SO_4/heat, C. NH_2NH_2, KOH

(ii) A. $(CH_3)_2CuLi$ then H^+, B. $NaBH_4/EtOH$, C. H_2SO_4/heat

(iii) A. CH_3Li then H^+, B. PCC/heat

(iv) A. $NaBH_4 - CeCl_3$ then H^+, B. MnO_2, C. CH_3Li

(e)



The breaking of the bond indicated by an arrow mark is the slowest step in the acid-catalyzed hydrolysis of the above ester. The correct arrow marking is :

(i) 1

(ii) 2

(iii) 3

(iv) 4

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(f) 

The above conversion can be carried out using

(i) An Organomagnesium Reagent

(ii) An Organocuprate Reagent

(iii) An Organolithium Reagent

(iv) An Organozinc Reagent

(g) In the following reaction the correct structures of A & B are :

(i) A: 

B: 

(ii) A: 

B: 

(iii) A: 

B: 

(iv) A: 

B: 

(h) Observe the following reaction :

The required set of reagents for this conversion is

(i) A. SeO_2, B. Conc. $NaOH$ (aq), C. H_3O^+

(ii) A. Conc. $NaOH$ (aq), B. SeO_2, C. H_3O^+

(iii) A. $NaCN$, B. H_3O^+

(iv) A. $Ph_3P=CH(OMe)$, B. H_3O^+

2. Answer any *four* questions : 2×4=8

(a) Formulate a plausible mechanism for the following reaction.

(b) How will you carry out the following conversion ?

(c) Acetals are stable towards bases but easily hydrolysed by acids. Why ?

(d) Bromination of acetophenone in presence of catalytic amount of $AlCl_3$ yields $PhCOCH_2Br$ whereas with excess $AlCl_3$ it yields *m*-bromoacetophenone. Explain.

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(e) Carryout the following conversion :

(f) Propose a mechanism for the following reaction :

(g) What happens when benzoic acid is separately treated with excess of methyl magnesium bromide and excess of methyl lithium? Do the reactions follow the same pattern? If not, why?

(h) How could you carry out the following transformation ?

3. Answer any *two* questions : 6×2=12

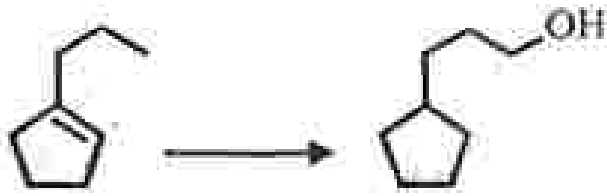
(a) (i) Why lithium aluminium hydride is not used in aqueous or alcoholic medium ?

(ii) Explain the stereochemical aspects of the reaction between *E*-2-butene and bromine with plausible mechanism.

(iii) Account for the following observations :

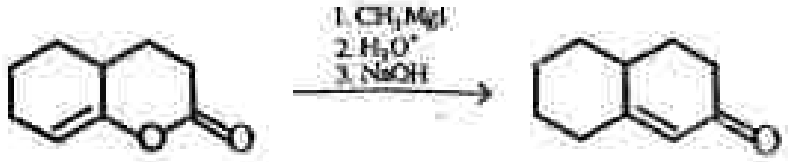
(iv) How would you synthesize the following molecule starting from any organic compound having not more than three carbon atoms: $MeCH(OH)CH_2CH_2NH_2$? 1½+1½+1½+1½

(b) (i) Using hydroboration-oxidation reaction how you carry out the following conversion ?



(ii) Convert : Toluene → *m*-bromotoluene.

(iii) Propose a reasonable mechanism for the following reaction :



2+2+2

(c) (i) Compound **A** (C_8H_{12}) undergoes hydration with a mixture of $HgSO_4$ and H_2SO_4 to produce compound **B** ($C_8H_{14}O$). Compound **B** gives positive haloform reaction. Treatment of **B** with *PhMgBr* followed by acidification with aqueous *HCl* gives compound **C** and **D**. **C** and **D** are isomeric compounds having molecular formula $C_{14}H_{18}$. Ozonolysis of **C** produces cyclohexanone as one of the major

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products. Find the structures of **A, B, C** and **D** and explain the observation.

(ii) Outline the preparation of **A** from acetylene. 4+2

(d) (i) Nitration of phenylboronic acid, $PhB(OH)_2$ with mixed acid at –20°C gives predominantly the *m*-derivative while on treatment with HNO_3/Ac_2O, the predominant product is the *o*-derivative. Suggest an explanation.

(ii) Slow addition of methyl magnesium bromide to a cold, ethereal solution of benzoyl chloride is a better method than addition of methyl magnesium bromide to ethyl benzoate for the preparation of acetophenone. Explain.

(iii) Explain mechanistically why mercuric ion catalysis is better than acid catalysis for the cleavage of 1,3-dithianes.

(iv) Why primary alcohols cannot be oxidized to the corresponding aldehyde by Oppenauer Oxidation? Suggest a methodology to overcome this problem. 1½+1½+1½+1½