

2020

## CHEMISTRY — HONOURS

Paper : CC-7

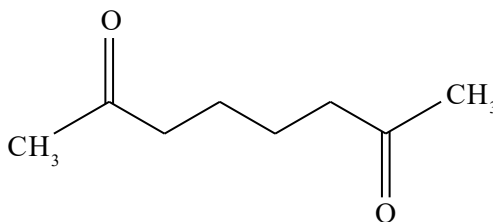
(Organic Chemistry-3)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question no. 1** (compulsory) and **any eight** questions from the rest (**Q. 2** to **Q. 12**).1. Answer **any ten** questions :

1×10

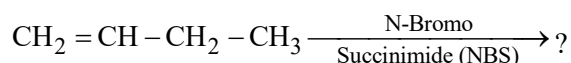
(a) Give the structural formula for the alkene that gives the following ozonolysis product :

(b) Convert acetophenone to  $\text{PhCOCH}=\text{CH}_2$  via a Mannich base.

(c) Define an ylide.

(d) Why does chloral exist normally as a chloral hydrate?

(e) Write down the structure of the major product in the following reaction :



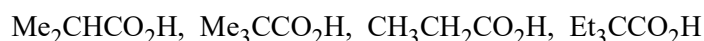
(f) How can you convert HCHO to methyl formate in a one step reaction?

(g) Why are ethers such as dry  $\text{Et}_2\text{O}$  used as solvent for  $\text{RMgBr}$ ?(h) Which alkylating agent is needed for the synthesis of  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$  from  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{Et}$  (EAA)?

(i) Give the product from acid catalysed reaction of cyclohexanone with pyrrolidine.

(j) Prepare (Z)-2-butene from 2-butyne.

(k) Give the order of the rate of esterification of the following acids with MeOH (No explanation needed).



(l) Which of the following esters undergo the Dieckmann condensation under usual condition?

Adipate and glutarate.

Give the product.

Please Turn Over

(m) Why does *p*-nitrobenzaldehyde fails to undergo benzoin condensation?

(n)  $\text{Ph}_3\text{P}^{\oplus} - \text{CPh}_2^{\ominus}$  does not react with carbonyl compounds. Explain.

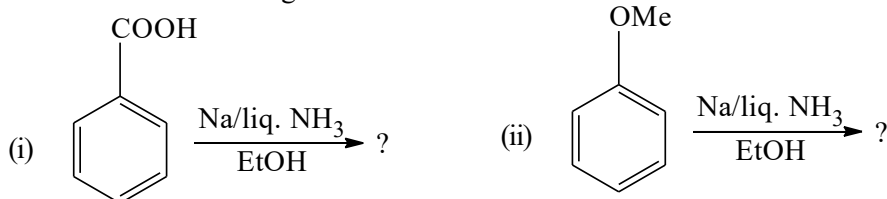
2. (a) Nitration of anisole with the conventional nitrating mixture gives *ortho* and *para*-nitroanisoles in the ratio 31 : 67 whereas the same reaction when carried out with  $\text{N}_2\text{O}_5$  ( $\text{HNO}_3 - \text{Ac}_2\text{O}$ ) gives *ortho* and *para*-nitroanisoles in the ratio 71 : 28. Explain the above observation with plausible mechanism in each case.

(b) 3-Hydroxybenzaldehyde undergoes Cannizzaro reaction; however 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde fail to react. Explain. 3+2

3. (a) Give the mechanism of Friedel-Craft acylation of benzene with acid anhydrides. Explain why more than 2 equivalents of  $\text{AlCl}_3$  are needed for this reaction.

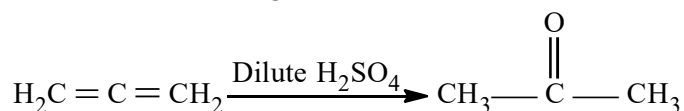
(b) Reaction between  $\text{PhCHO}$  and  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2\text{CH}_3$  gives  $\text{PhCH} = \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2\text{CH}_3$  in base and  $\text{PhCH} = \text{C}(\text{CH}_3)\text{COCH}_3$  in acid. Give mechanistic explanation. 3+2

4. (a) Give the products of the following with mechanism :

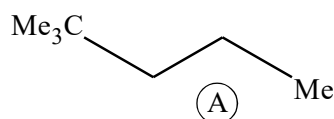


(b) Give the mechanism of the following reaction :

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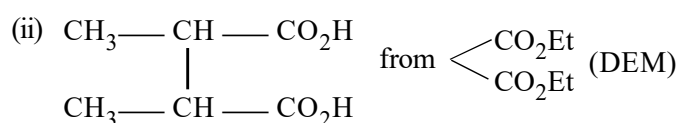
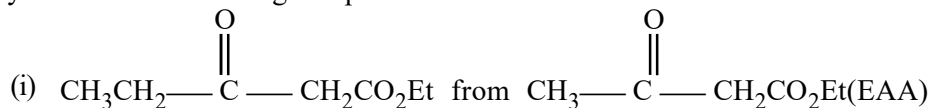


5. (a) Apply Corey-House method to synthesize compound (A) using two suitable substrates having four carbon and three carbon units, respectively. Give argument for your favour.



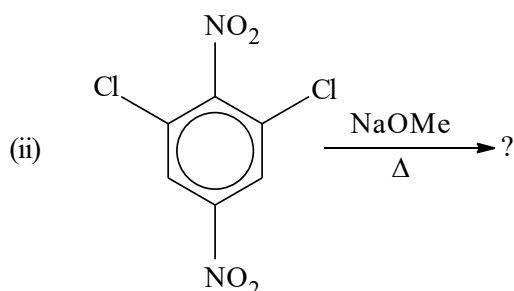
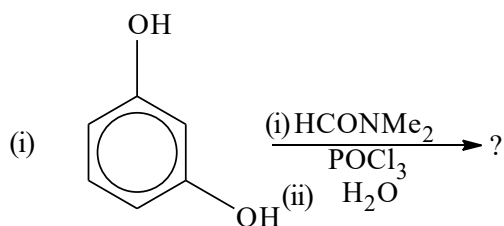
(b) Show the course of Robinson's annulation reaction for synthesizing fused ring in the reaction of cyclohexanone and methyl vinyl ketone. 3+2

6. (a) Synthesize the following compounds :



(b) How will you convert acetylene to  $\text{MeC} \equiv \text{C} - \text{CH}_2\text{CH}_2\text{OH}$  using organomagnesium reagent? 3+2

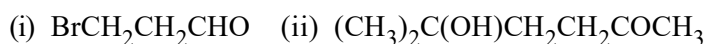
7. (a) Predict the product(s) with plausible mechanism in each case of the following reactions :



- (b) Explain the following : Both  $\text{PhCH}_2\text{COCH}_2\text{Cl}$  and  $\text{PhCHCl}-\text{COCH}_3$  form  $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$  when treated with  $\text{OH}^-$  followed by acidification. 3+2

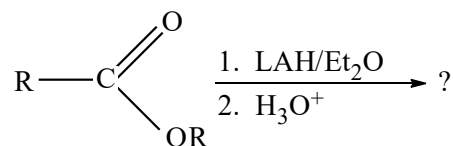
8. (a) Give the product and mechanism for  $\text{OEt}^-$  catalysed Claisen condensation of  $\text{CH}_3\text{CO}_2\text{Et}$ . Account for the inability of methyl 2-methylpropanoate (B) to react. Explain why use of  $\text{NaCPh}_3$  as a base promotes the condensation of (B).  
 (b) The reaction of  $\text{Me}_3\text{CMgCl}$  and  $\text{Me}_3\text{CCOCMe}_3$  after hydrolysis gives a gas (C) and a 2°-alcohol (D); rather than expected tri-*t*-butylcarbinol. Provide structures for (C) and (D) and account for their formation. 3+2

9. (a) Select the best way for reducing the  $>\text{C}=\text{O}$  in each of the following :



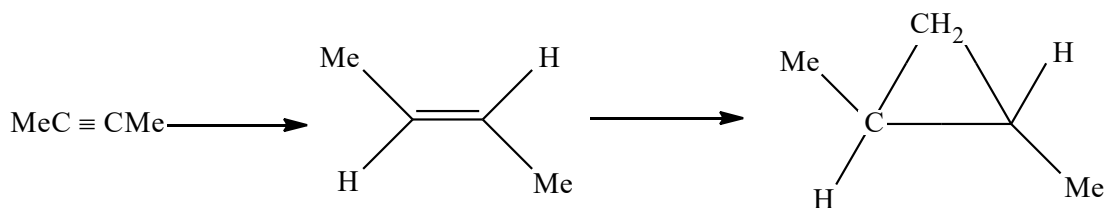
Show steps in each case.

- (b) Suggest the mechanism of the following reaction :



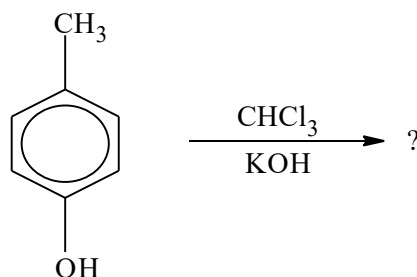
3+2

10. (a) Give the appropriate reagents to carry out the following transformation. Explain your answer.



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(b) Predict the product(s) with plausible mechanism.

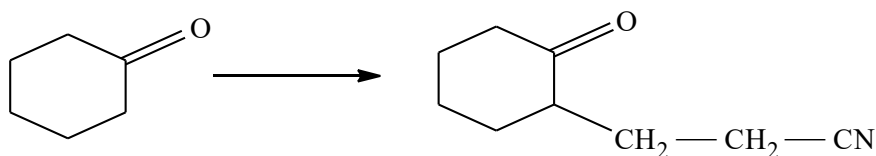


3+2

11. (a) What happens when one equivalent of  $\text{PhCH}=\text{CH}-\text{COPh}$  in ether is separately treated with one equivalent of the following reagent followed by hydrolysis with acid? Explain the mechanism involved.

(i)  $\text{EtMgBr}$  in ether (ii)  $\text{EtLi}$  in ether (iii)  $\text{Et}_2\text{CuLi}$  in ether.

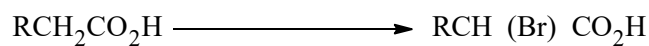
(b) Carry out the following conversion with plausible mechanism :



3+2

12. (a) Two ozonides are formed when  $\text{Me}_2\text{C}=\text{CMe}_2$  is treated with  $\text{O}_3$  in  $\text{CH}_2\text{Cl}_2$  as solvent in the presence of  $\text{HCHO}$ . Give the mechanism of formation of two ozonides.

(b) How can you convert?



Show the plausible mechanism.

3+2

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