TDC (CBCS) Odd Semester Exam., 2020
held in March, 2021

CHEMISTRY

(3rd Semester)

Course No. : CHMHCC-302T

(Organic Chemistry)

Full Marks : 50
Pass Marks : 20

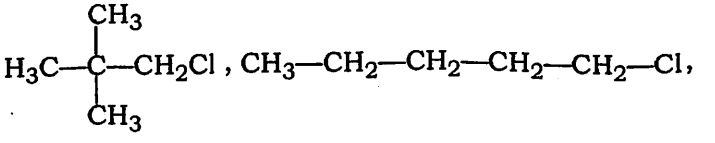
Time : 3 hours

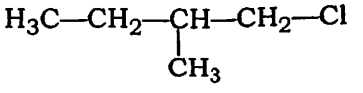
The figures in the margin indicate full marks for the questions

SECTION—A

1. Answer any *ten* of the following questions : 2×10=20

(a) *(i)* Arrange the following compounds in order to reactivity towards NaI in acetone (most reactive first) :



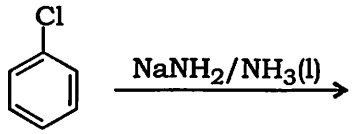


(ii) Arrange the following nucleophiles in order of increasing nucleophilicity :

$I^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$

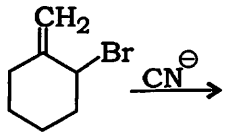
(b) Explain the fact that allyl chloride undergoes substitution reaction by S_N1 mechanism whereas *n*-propyl chloride reacts by S_N2 mechanism.

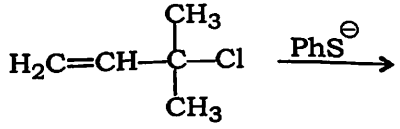
(c) Predict the products of the following reactions :

(i) 

(ii) $H_3C\ COOAg + Br_2 \longrightarrow$

(d) Write the structure of nucleophilic substitution products in each of the following reactions :

(i) 

(ii) 

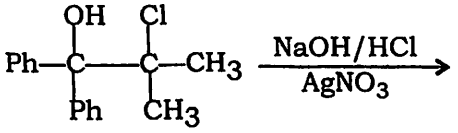
(e) In the following sequence of reactions, identify the compounds *A* and *B* :

$$H_3CCH_2CH_2OH \xrightarrow[180\ ^\circ C]{H_2SO_4} A \xrightarrow{RCOOOH} B$$

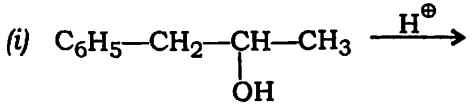
(f) Arrange the following compounds in order of increasing acidity (weakest acid first). Justify your answer.

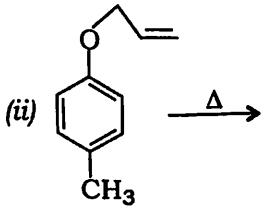
Phenol, cyclohexanol, *p*-bromophenol, *p*-methoxyphenol

(g) Give the mechanism and product of the following reaction :

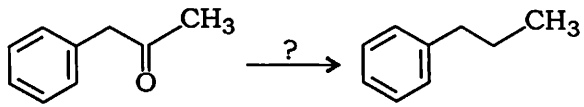


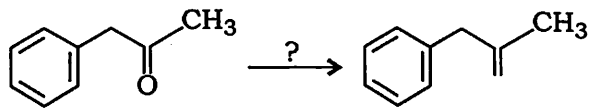
(h) Predict the products in each of the following reactions :

(i) 

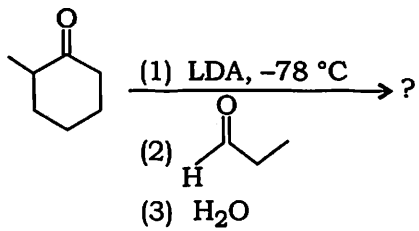
(ii) 

(i) Suggest the best suitable reagents for the following reactions and provide the name of the reactions :

(i) 

(ii) 

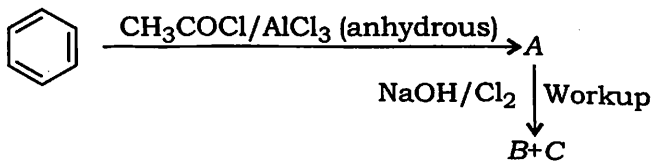
(j) Predict the major products of the following reaction and suggest mechanism :



(k) Carry out the following transformation and provide mechanism of the following reaction :

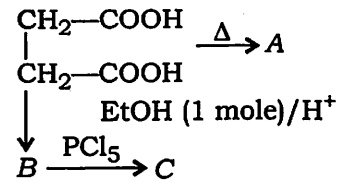
Ph—CHO to Ph—CH=CH—COOH

(l) Complete the following reactions :



(m) Why is acetic acid weaker than formic acid and *p*-methoxybenzoic acid is weaker than benzoic acid?

(n) Complete the following reactions :

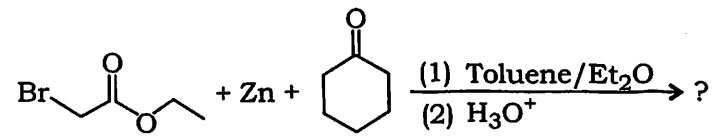


(o) Predict the products of the following reactions :

(i) $HOCH_2COOH \xrightarrow{H^+}$

(ii) $R—CH(OH)CH_2COOH \xrightarrow{H^+}$

(p) Predict the major product of the following reaction and suggest mechanism :



(q) Suggest the reagents for the following transformations :

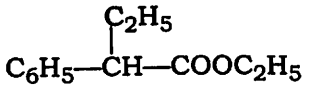
(i) $CH_3—Br$ to $CH_3—SH$

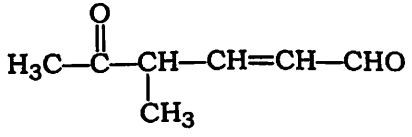
(ii) $PhCH_2Br$ to $PhCH_2COOH$

(r) Offer a suitable explanation for the following observation :

$CH_3CSCH_2COOC_2H_5$ enolizes to a greater extent than $CH_3COCH_2COOC_2H_5$

(s) Underline the most acidic hydrogens in each of the following structures and give reasons of your choice :

(i) 

(ii) 

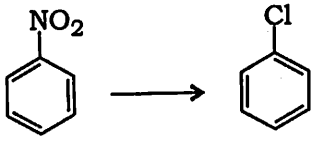
(t) Outline the synthesis of $C_2H_5CH(Br)COOH$ from malonic ester.

SECTION—B

Answer *any* **five** questions

2. (a) How do you account for the racemization of (+)-2-iodobutane when it is allowed to react with iodide ion? 2

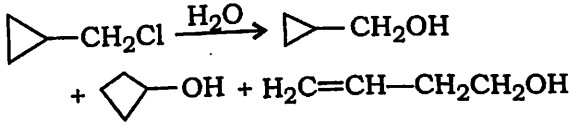
(b) Carry out the following trans-formations : 1½×2=3

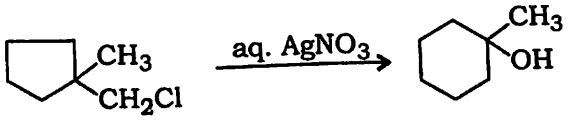
(i) 

(ii) $CH_3—CH_2—OH \longrightarrow CH_3—CH_2—Cl$

(c) Why are the nucleophilic substitution reactions of allylic halides often accompanied by rearrangements? 1

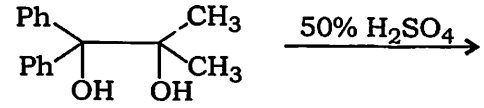
3. (a) Sketch a suitable mechanistic scheme for each of the following trans-formations : 2×2=4

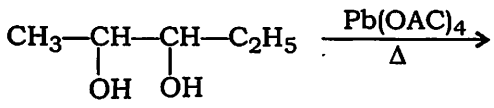
(i) 

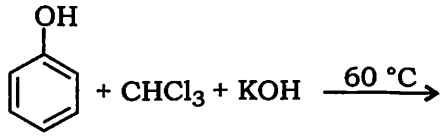
(ii) 

(b) Predict the effect that increasing solvent polarity will have on the rate of an S_N1 reaction. 2

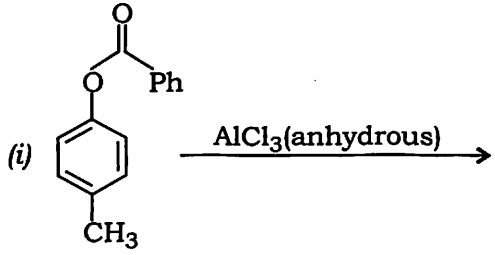
4. Predict the major products of the following reactions and suggest mechanism : 2×3=6

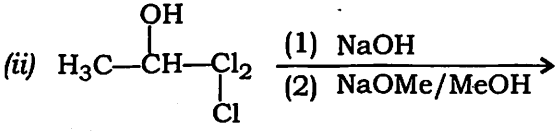
(i) 

(ii) 

(iii) 

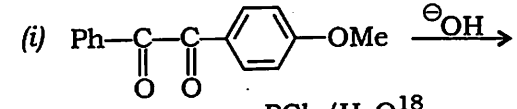
5. *(a)* Predict the major products of the following reactions and suggest mechanism : 2×2=4

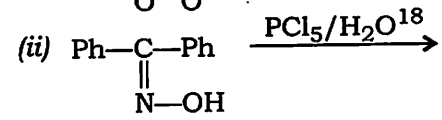
(i) 

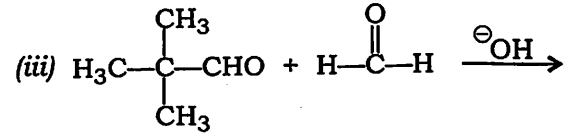
(ii) 

(b) How can salicylic acid be prepared from phenol by only one step reaction and suggest the mechanism of the reaction. 2

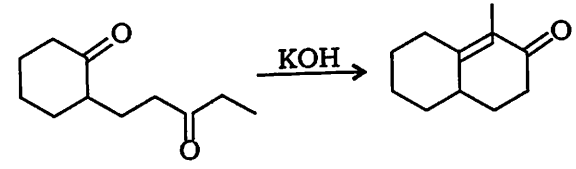
6. Give the product along with the mechanism of each of the following reactions : 2×3=6

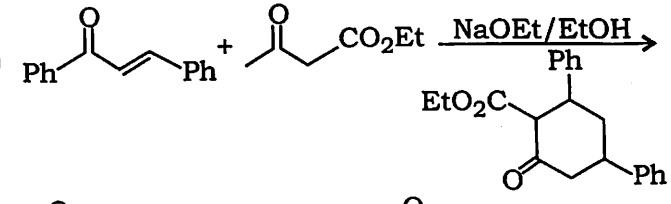
(i) 

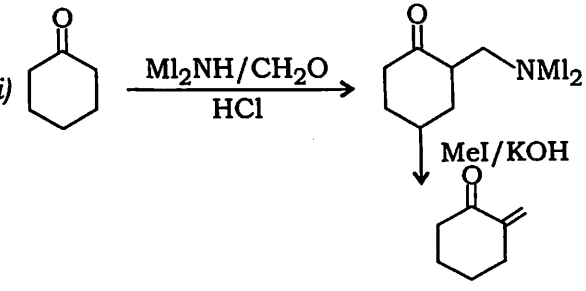
(ii) 

(iii) 

7. Provide the mechanism of the following reactions : 2×3=6

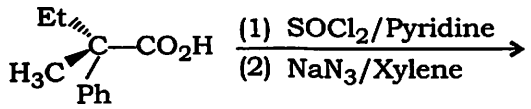
(i) 

(ii) 

(iii) 

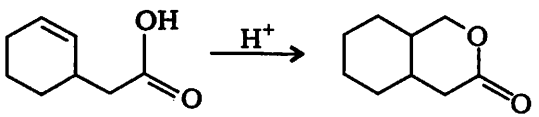
8. *(a)* A dicarboxylic acid (*A*), $C_4H_6O_4$ gave a compound *B*, $C_6H_{10}O_4$ upon treatment with excess of methanol and trace of H_2SO_4. Subsequent treatment *B* with LAH followed by usual work-up afforded *C* ($C_4H_{10}O_2$). Pyrolysis of *A* yielded *D* ($C_4H_4O_2$). Assign structures to *A*, *B*, *C* and *D*. 2

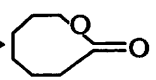
(b) Provide the major products of the following reactions and suggest mechanism : 2×2=4

(i) 

(ii) $N{\equiv}C(CH_2)_4CONH_2 \xrightarrow[NaOCH_3]{Br_2}$

9. *(a)* Sketch a suitable mechanistic pathway for each of the following reactions : 2×2=4

(i) 

(ii) $BrCH_2(CH_2)_4CH_2COOH \xrightarrow[(2)\ H^+/\Delta]{(1)\ OH^{\ominus}}$ 

(b) Identify *A*, *B*, *C* and *E* for the following reactions sequence : 2

$$ClCH_2CO_2H \xrightarrow[(ii)\ NaCN]{(i)\ Na_2CO_3} A \xrightarrow[OH^{\ominus}]{C_6H_5CHO} B$$

$$\xrightarrow[(ii)\ H_3O^{\ominus}]{(i)\ NaCN} C \xrightarrow{H_3O^+} [D] \longrightarrow E$$

10. *(a)* Sketch the synthesis of 3-ethylpentane-2-one from ethyl acetoacetate. Discuss the mechanism of all steps involved in the transformation. 3

(b) Explain with the help of the following equations, what happens when : 1½×2=3

(i) Phenyl lithium is treated with pyridine

(ii) A Grignard reagent is treated with a carboxyl compound having an α-hydrogen atom

11. *(a)* Sketch a plausible mechanistic scheme for each of the following : 1½×2=3

(i) $2RSH \xrightarrow{air/\overset{\ominus}{O}H} R{-}S{-}S{-}R$

(ii) $(CH_3)_2S \xrightarrow{(i)\ Br_2/H_2O} (CH_3)_2S{=}O$

(b) Outline the synthesis of the following from malonic ester : 1½×2=3

(i) Succinic acid

(ii) Cyclobutane carboxylic acid

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