B.Sc. 3rd Semester (Honours) Examination, 2018 (CBCS)

Subject : Chemistry

(Organic Chemistry-III)

Paper : CC-7

Time: 2 Hours **Full Marks: 40**

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: 2×5=10

(a) Triple bonds are less reactive to electrophilic attack than double bonds in spite of their higher electron density. Explain.

(b) The keto tautomers are usually more stable than their enol forms. Justify.

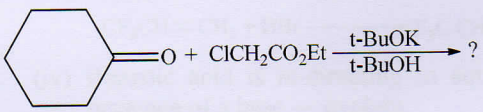
(c) Nitrobenzene is used as a good solvent for Friedel-Crafts reaction than benzene. Why?

(d) The boiling points of 2-propanol, propanone and 2-methyl propene (approx. same molecular weight) are 82°C, 57°C and –7°C respectively. Justify.

(e) Convert PhCHO to PhCDO.

(f) Reaction of 1 mole each of Br_2 and $PhCOCH_2CH_3$ in basic solution yields 0·5 mol of $PhCOCBr_2CH_3$ and 0·5 mol of unreacted $PhCOCH_2CH_3$. Explain.

(g) Predict the product with mechanism.



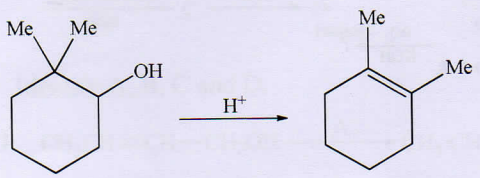
(h) The acid chloride of formic acid (HCOCl) is not used to introduce formyl group. (— CHO) into the benzene ring by Friedel-Crafts acylation–why?

2. Answer *any two* from the following: 5×2=10

(a) (i) *trans*–3–hexene $\xrightarrow{Br_2/CCl_4}$ 'A'

Identify 'A'. Show the mechanism and comment on the optical activity of 'A'. 1+2+½=3½

(ii)



Propose a mechanism. 1½

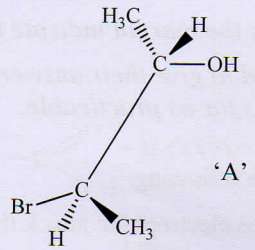
(b) (i) Comment on the optical activity of the following reaction and identify the product. 2+1=3

$CH_3CH_2CH(CH_3)CHO \xrightleftharpoons{NaOD/D_2O} ?$

Optically active

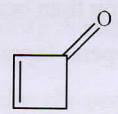
(ii) 3-bromo-2-butanol with the stereochemical structure 'A', on treatment with concentrated HBr yields *meso*–2, 3–dibromo butane. 2

Justify with proper mechanism.

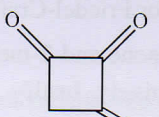


(c) (i) The enol content of biacetyl $CH_3COCOCH_3$ is somewhat higher than that of butanone, but much less than that of 1, 2-cyclohexadione. —Explain. 3

(ii)



Cyclo – butenone

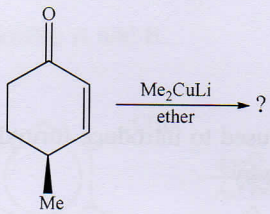


tri-Keto Cyclobutane

Which one will enolise at a faster rate? Why? 1+1=2

(d) (i) How does a benzyne intermediate accounts for the formation of *m*–OMe $C_6H_4NH_2$ from either *o*–OMe C_6H_4Br and *m*–OMe C_6H_4Br. 2+2=4

(ii)

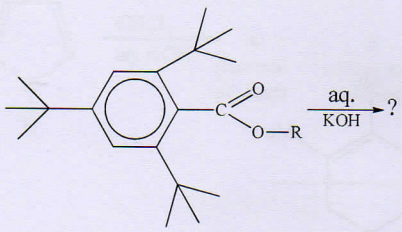


Identify the product with stereochemistry. ½+½=1

3. Answer *any two* from the following: 10×2=20

(a)

(i)

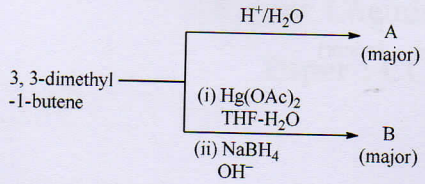


(I) Predict the product with proper mechanism and explanation. 1+1+2=4

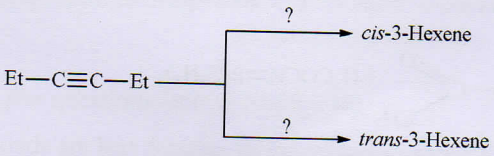
(II) What will be the symbolic representation of the mechanism? 1

(III) If the –R group is chiral, what will be the fate of the chiral centre after the reaction? 1

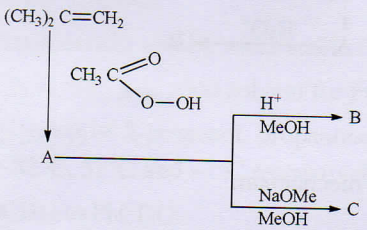
(ii) Complete the reactions with proper explanations. 2+2=4



(b) (i) Complete the reactions: 1+1=2



(ii) 1+1+1=3



Identify A, B and C.

(iii) Account for the slow rate of addition and the *anti*-Markonikov's product of the following: 1+1=2

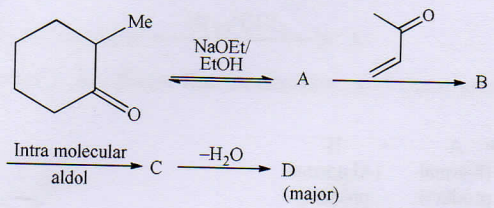
$$CF_3CH{=}CH_2 + HBr \longrightarrow F_3C\,CH_2 - CH_2Br$$

(iv) Benzoic acid is *m*-directing in aqueous or acidic solutions but *o*–, *p*–directing in presence of a base — explain. 3

(c) (i) Benzoin condensation reaction fails when strong electron donating or withdrawing groups are present ortho/para to the aldehyde group. Why? 1½+1½=3

(ii) Benzoin condensation reaction is an example of Umpolung phenomenon. Justify. 2

(iii)

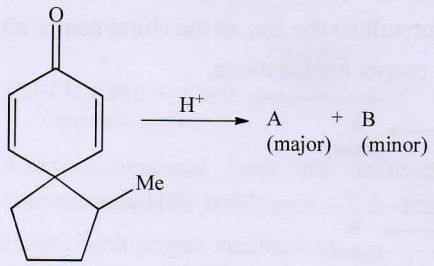


Identify A, B, C and D. 4

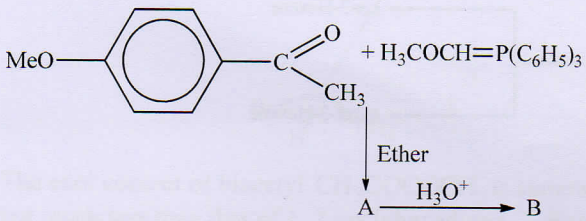
(iv) $CH_3CH{=}CH{-}CH_2OH \xrightarrow{A} CH_3\,CH{=}CH - CHO$

What is the reagent A? 1

(d)

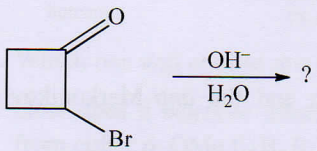
(i) 

Identify A and B. 1+1=2

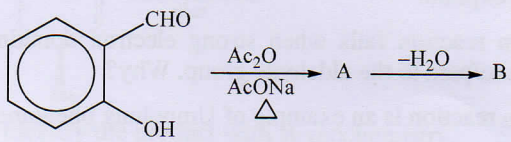
(ii) 

Identify A and B. 1+1=2

(iii) Predict the product with suitable mechanism: 1+1=2

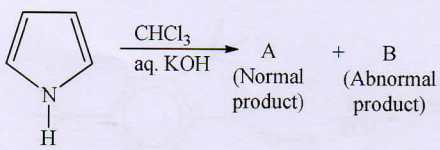


(iv) Identify A and B.



1+1=2

(v) Identify A and B.



1+1=2