TDC (CBCS) Even Semester Exam., 2023

CHEMISTRY

(Honours)

(2nd Semester)

Course No. : CHMHCC–201T

(Organic Chemistry—I)

Full Marks : 50

Pass Marks : 20

Time : 3 hours

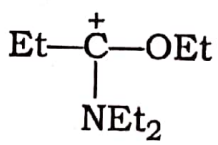
The figures in the margin indicate full marks for the questions

SECTION—A

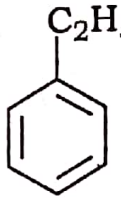
Answer any *ten* questions : 2×10=20

1. Draw the orbital picture of $CH_3CH=C=O$.

2. Write the canonical forms of the following carbocation and indicate with reason, the most contributing canonical form :

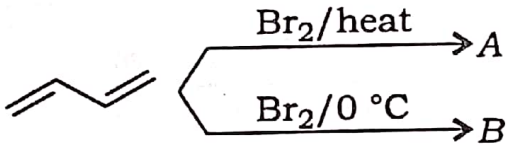


3. Between sodium chloride and sodium bromide in dimethyl sulfoxide (DMSO) solution, Cl^- ion behaves as a better nucleophile than Br^- ion. Explain.

4. Carry out the synthesis of 

using Wurtz-Fittig reaction. Comment on the choice of the starting materials.

5. Identify *A* and *B* for the following reactions :



6. Give the major products of the reaction of 1-methylcyclohexene with the following reagents separately : 1+1=2

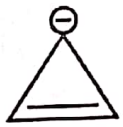
   (a) HBr

   (b) HBr/Peroxide

7. Arrange the following species according to their stability. Give reason of your choice : 1+1=2

   (a) 

   (b) 

   (c) 

8. Although all C—C bonds are equal length, C_1—C_2 bond length in naphthalene is 1·365 Å. While for C_2—C_3, it is 1·404 Å. How do you account for this?

9. What would be the product composition if an equimolar mixture of toluene and chlorobenzene is treated with 1 molar proportion of bromine in presence of iron powder? Predict with plausible reaction mechanism involved.

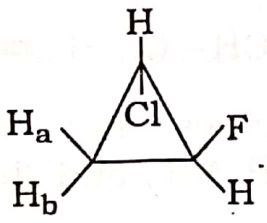
10. Give examples which corroborate the following facts : 1+1=2

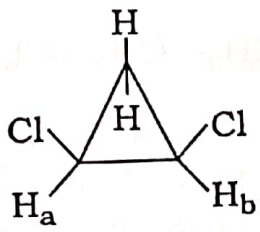
    (a) A meso compound having three chiral centres

    (b) A chiral molecule that cannot be resolved

11. Draw the Fischer projection formula of (2S, 3R)-3-chloro-butan-2-ol and convert it into Newman projection formula (any conformer). 1+1=2

12. Mention whether ligands H_a and H_b in each of the following compounds are homotopic/ enantiotopic or diastereotopic : 1+1=2





13. Indicate the preferred conformation of *trans*-1,3-di-tert-butyl cyclohexane with proper reasons.

14. Discuss the symmetry and optical activities of *cis*- as well as *trans*-1,2-dimethylcyclohexane

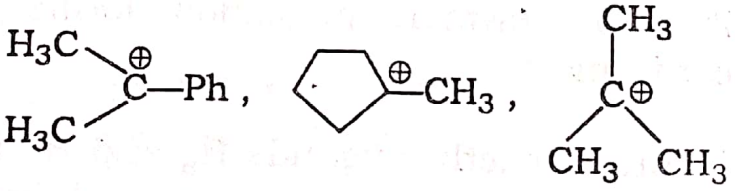
15. Equal amounts of (a, a) and (e, e) conformers of *trans*-1,2-dibromocyclohexane exist in non-polar solvents but the (e, e) conformation prevails in polar solvent. Explain.

SECTION—B

Answer any *five* questions : 6×5=30

16. *(a)* Tertiary butyl alcohol is miscible in water in all proportions but 1-butanol is partially miscible. Account for the observation. 1½

(b) Comment on the relative stabilities of the following carbocations : 1½

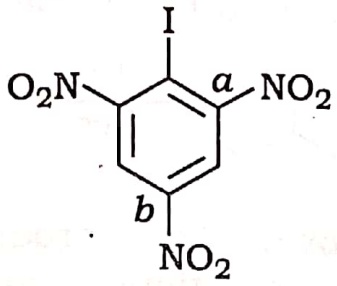


(c) Compare and explain the dipole moments of the following compounds : 3

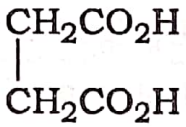
$CH_3—CH_2—Cl$, $H_2C=CH—Cl$, $HC\equiv C—Cl$

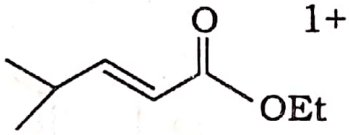
17. *(a)* Compare the basicities and nucleophilicities of NH_3, NH_2NH_2 and NH_2OH. Give reasons. 2½

(b) Explain which C—N bond, *a* or *b* has a shorter bond length in the following compound : 1½

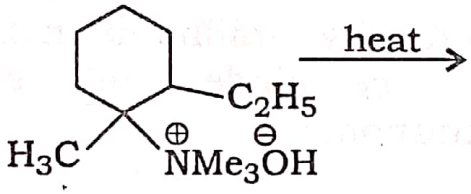


(c) Write IUPAC names of the following compounds : 1+1=2

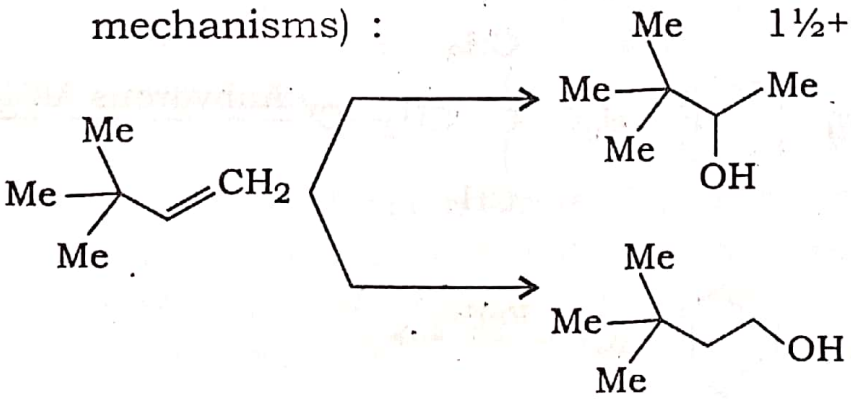
(i) 

(ii) 

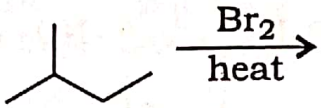
18. (a) Give the structures of all possible alkenes that could form in the following reaction. Indicate the major product and explain its formation : 3



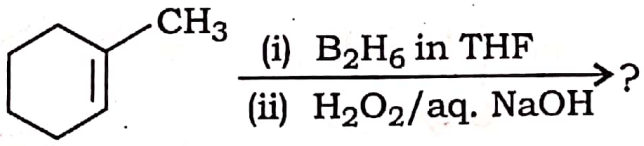
(b) Indicate suitable reagents to carry out the following conversions (show the intermediate compounds and mechanisms) : 1½+1½=3



19. *(a)* Write the structure of product(s) of the following reaction and comment on the relative amount (%) of the product(s). 1+1=2



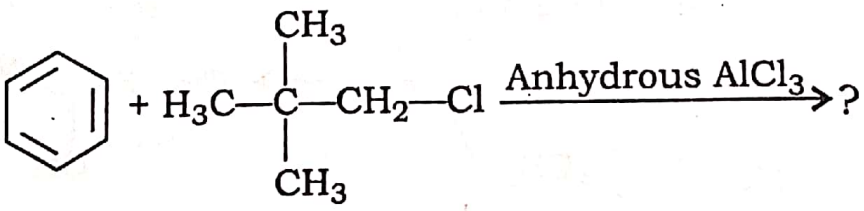
(b) Write down the products of the following reactions with plausible mechanisms : 2+2=4

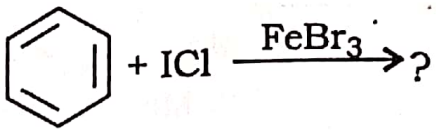
(i) 

(ii) $H_3C—CH_2—C\equiv CH \xrightarrow{H_2SO_4/Hg^{2+}} ?$

20. *(a)* Explain why aniline is more reactive than acetanilide in electrophilic substitution. 2

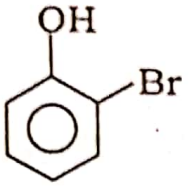
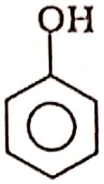
(b) Predict the products and outline the mechanisms for each of the following reactions : 2+2=4

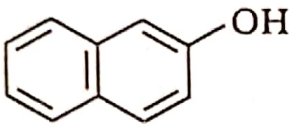
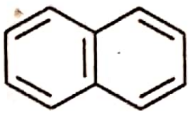
(i) 

(ii) 

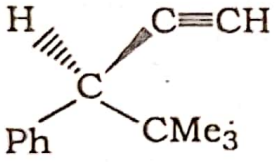
21. *(a)* Provide Haworth synthesis of anthracene. 3

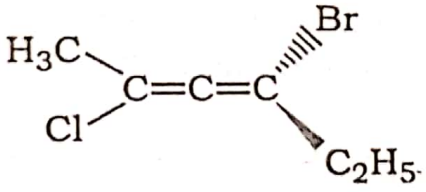
(b) Provide the synthesis of the following compounds. You can use any reagent and solvent for the purpose : 1½+1½=3

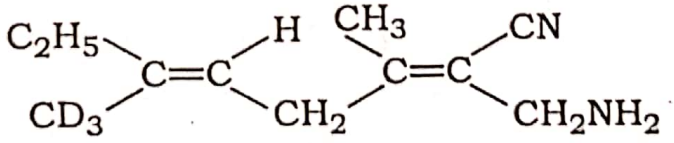
(i)  from 

(ii)  from 

22. *(a)* Assign R/S and E/Z configurations of the following compounds : 1×3=3

(i) 

(ii) 

(iii) 

(b) Draw the Fischer projection of a meso-isomer of $H_3C(CHOH)_3CH_3$ and point out the stereogenic and achirotopic centre(s), if any, in it. Explain. 3

23. *(a)* What is meant by enantiomeric excess (ee)? The pure (+) enantiomer of a compound shows a specific rotation of +80°. Calculate the percentage of the (–) enantiomer of the same compound in a partially resolved sample showing a specific rotation of –20°. 1+2=3

(b) Write all possible stereoisomers of the following compound and comment on their optical activity : 3

$H_3C—CH=CH—CH(CH_3)—CH=CH—CH_3$

24. *(a)* With appropriate conformations, delineate the preferred pathway for chair⇌twist boat interconversion of cyclohexane. Which symmetry element is retained along the pathway? Discuss. 3

(b) Draw all possible conformations of 1,3-dihydroxy cyclohexanes. Which conformation is most stable one? Which one is optically active? 3

25. *(a)* What is Sachse-Mohr theory? Explain. 2½

(b) Applying conformational analysis, explain the observation that one of the diastereomers of 4-hydroxycyclohexane-carboxylic acid undergoes facile lactonization on brief heating. 2½

(c) Draw boat conformation of cyclohexane in Newman Projection. 1

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