2016

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

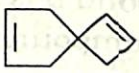
Full Marks : 60

Time : 3 hours

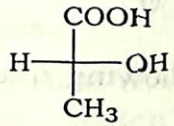
The figures in the margin indicate full marks for the questions

1. Answer the following questions (any *seven*) : 1×7=7

(a) Write the IUPAC name of the following compound :



(b) Convert the following Fischer formula into flying-wedge formula :



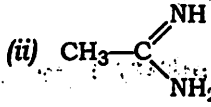
(c) Arrange the following molecules in order of decreasing dipole moment :

$CH_2=CH-Cl$, $HC\equiv CCl$, CH_3CH_2Cl

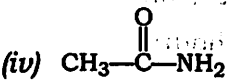
(d) Acetyl acetone is highly stable in enol form. Explain.

(e) Arrange the following compounds in order of their correct basicities :

(i) $CH_3CH_2NH_2$

(ii) 

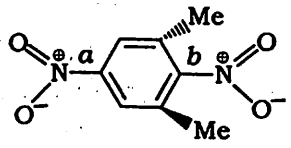
(iii) $(CH_3)_2NH$

(iv) 

(f) The molecule  does not exist. Explain.

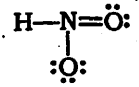
(g) Between salicylic acid and *p*-hydroxy benzoic acid which is stronger? Explain in terms of H-bonding.

(h) The C—N bond *a* is shorter than *b* in the following compound. Explain :



2. Answer the following questions (any *four*) : 2×4=8

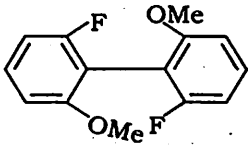
(a) Calculate the formal charge on each of the constituent atoms of



(b) Between toluene and *tert*-butyl benzene, which one is more susceptible to electrophilic substitution reaction? Explain.

(c) Explain whether [10] annulene is aromatic or not.

(d) State and explain whether the following molecule will be optically active or not :



(e) What product do you get when *trans*-butenedioic acid is treated with Br_2? Write equation as well.

3. Answer the following questions (any *three*) : 5×3=15

(a) Draw the number of possible stereo-isomers of the following molecule :

HOOC—CH(OH)—CH(OH)—CH(OH)—COOH

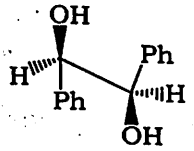
Also find the number of optical isomers and *meso* forms. 3+2=5

(b) Account for the fact that guanidine is a strong base. Which nitrogen of guanidine is more likely to be protonated? Explain. What are alternant and non-alternant hydro-carbons? Give example of each. 3+2=5

(c) What is resolution of a racemic mixture? What are different methods of resolution of racemic mixture? How will you separate a racemic mixture of an alcohol? 1+1+3=5

(d) Explain the cause of optical activity of biphenyls giving suitable substituents. Are their any compounds to show atropisomerism? Give example. 4+1=5

(e) Designate the following flying-wedge formula with *R,S*-notations and convert into Fischer projection. What do you understand by stereomutation? 3+2=5



4. Answer the following questions [*either (i)* and *(ii) or (iii)* and *(iv)* from *(a), (b)* and *(c)*] : 10×3=30

(a) *(i)* Draw the orbital picture of different states of nitrene. How can nitrenes be trapped for detection? Give one important reaction of nitrene as intermediate. 2+2+1=5

(ii) Explain with example, what you mean by kinetically controlled and thermodynamically controlled reactions. Draw the energy profile diagram. 3+2=5

Or

(iii) The *cis*-isomer of 4-*t*-butyl cyclohexyl bromide reacts with $PhS^{\ominus}Na^{\oplus}$ in aqueous ethanol at a much faster rate than the *trans*-isomer. Explain. 2½+2½=5

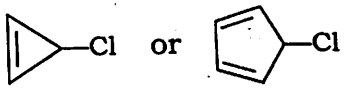
(iv) Write the mechanism of the following reaction and obtain the products :

$$CH_3—CH_2—OH \xrightarrow{CS_2,\ NaOH} X \xrightarrow{CH_3I} Y \xrightarrow{200\ ^\circ C} Z$$

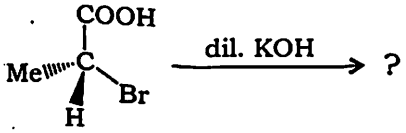
Also name the intermediate products. 3½+1½=5

(b) *(i)* The rate of bromine addition to styrene is greater than that to propene. Place a suitable explanation along with the reaction intermediate formed. 2½+2½=5

(ii) (1) Which of the following would undergo solvolysis in methanol more readily? Explain : 3

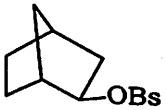


(2) Find the stereochemistry of the product for the following reaction along with the mechanism : 2



Or

(iii) What are classical and non-classical carbocations? Give example. The rate of acetolysis of exo-norbornyl brosylate is many times faster than endoisomer. Explain : 3+2=5



exo-norbornyl brosylate

(iv) Define carbon-free radicals. How are these detected? How can carbon-free radical be generated? 1+2+2=5

(c) *(i)* How are the nucleophilic substitution reactions affected by the nature of leaving group and nucleophiles? Explain with examples. 2½+2½=5

(ii) Explain the criteria for showing optical activity. Draw an allene which displays chirality. 4+1=5

Or

(iii) Define syn- and anti-elimination reactions. Why is anti-elimination preferred over syn-elimination? Give an example. 2+2+1=5

(iv) Draw the chair-conformations of *cis*- and *trans*-1-methyl-4-*t*-butyl cyclohexane and comment on their optical activities. 3+2=5

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