Total No. of printed pages = 10

3 (Sem 1) CHM M2

2015

CHEMISTRY

(Major)

Paper : 1.2

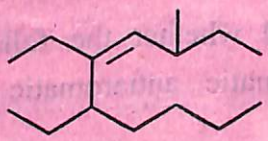
Full Marks – 60

Time – Three 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) Draw the structural formula of bicycle [4·2·0] octan –3–01.

[Turn over

$HC\equiv\bar{C} < \bar{O}H < \bar{N}H_2 < CH_3\bar{C}H_2$

15

(c) Arrange the following species in increasing order of basic strength :

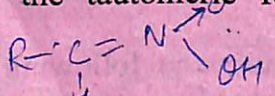
$\bar{O}H$, $\bar{N}H_2$, $HC\equiv\bar{C}$, $CH_3\ \bar{C}H_2$

(d) Suggest an explanation for the difference in dipole moments for the following pairs :

CH_3CH_2CHO	$CH_3CH = CH–CHO$
$\mu = 2.73$ D	$\mu = 3.67$ D

(e) The C–N bond length in H_2NCONH_2 is 0.137 nm instead of normal C–N bond length (0.147 nm). Explain.

(f) Draw and name the tautomeric forms of $RCH_2–NO_2$.



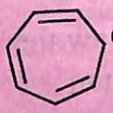
(g) Arrange the following compounds in increasing order of nucleophilicity.

Ammonia, pyridine, aniline, potassium amide

(h) Find whether the following molecules are aromatic, antiaromatic or non-aromatic.

(i) 

anti

(ii) 

non

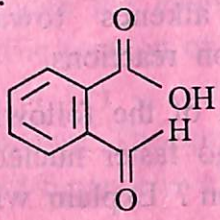
$NH_3 <$ aniline $<$ py $< KNH_2$

15

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

(a) What is the nature of CH_3CN ? Illustrate with a reaction. 1+1=2

(b) Show the tautomeric forms of the following compound : 1+1=2



Give an example of valence tautomerism.

(c) What are pseudoaromatic compounds ? Give an example. 1+1=2

(d) Arrange the following intermolecular forces in increasing order of strength Dipole-dipole interaction, H-bonding force, London forces.

HCl boils at a much higher temperature than Argon. Which forces acting on it ? Explain. 1+1=2

V < D-D < H-bond

(e) Draw the following molecule :

(i) (E)–2–(But–2–enyl) benzene–1, 3–dicarboxylic acid

(ii) 9–Oxa–6–aza spiro [4, 5] decane 1+1=2

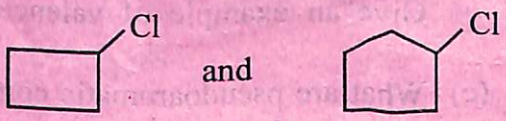
15

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

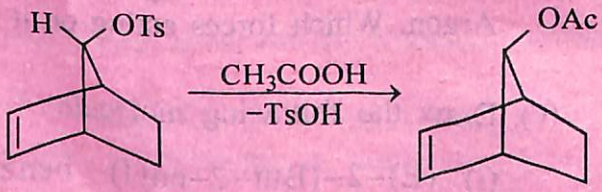
(a) (i) Between Furan and thiophene which one has higher resonance energy and why ? 2

(ii) Explain why alkynes are less reactive than alkenes towards electrophilic addition reactions. 3

(b) (i) Which of the following molecules will undergo faster nucleophilic substitution reaction ? Explain with reason. 3



(ii) What is neighbouring group participation ? Following molecule gives 100% retention of configuration. Explain. 2



(c) (i) Although in ethyl methyl amine N is asymmetric still it is optically inactive. Explain. 2½

(ii) What is atropisomerism ? Give an example. 1+1½=2½

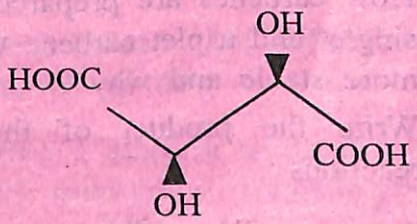
(d) (i) What do you mean by optical purity ? Illustrate. 2

(ii) Calculate the enantiomeric excess and specific rotation of a mixture containing 10g of (+) -2 -butanol and 6g of (–) -2-butanol. The specific rotation of pure (+) -2-butanol is $+13.5^{o}$.

4. Answer the following questions :

[Either (i) or (ii) and (iii) or (iv) from (A), (B) and (C). 10×3=30

(A) (i) Assign R, S-notation to the following chiral molecule : 2

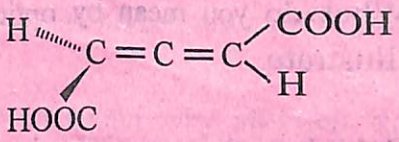


Give an example each of enantiotopic atoms and diastereotopic faces.

2×1½=3

Or

(ii) Following allene is chiral although it has no chiral centre. Explain. 2



Draw the more stable cis-orientation of 1, 3-cyclohexanediol. Which conformer of cis-1, 3-cyclohexanediol is more stable ? Explain with due reason.

1+2=3

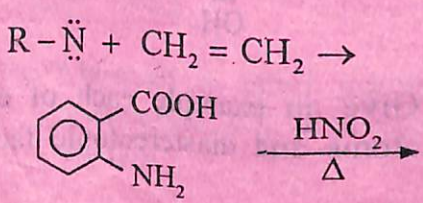
(iii) What do you mean by kinetically controlled and thermodynamically controlled reaction ? Draw the energy profile diagram for these two reactions.

2+3=5

Or

(iv) How carbenes are prepared ? Between singlet and triplet carbene which one is more stable and why ? 1+2=3

Write the product of the following reactions :



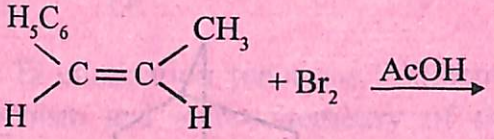
1

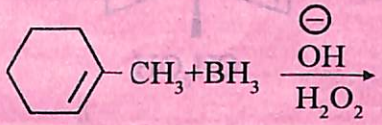
1

(B) (i) What product will you obtain when trans but-2- ene is treated with $O_5\ O_4$ and the product is hydrolysed ? Find the stereochemistry of the reaction. 5

Or

(ii) Find the major product of the following reactions : $2\times1\frac{1}{2}=3$

(a) 

(b) 

Which one of the following alkenes will give optically active product with Br_2/CCl_4

(a) 1-butene (b) propene (c) cis-2-butene (d) trans-2-butene. 2

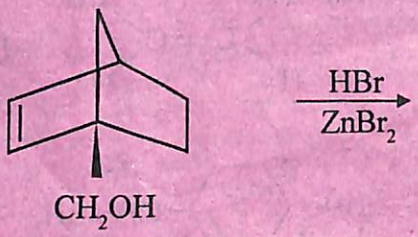
(iii) Give a reaction to show evidence that SN^1 mechanism involves carbocation as intermediate. $2\frac{1}{2}$

How does solvent polarity influence the rate of SN^1 and SN^2 reactions ? $1\frac{1}{2}+1=2\frac{1}{2}$

Or 15

(iv) (R)-2-Butanol is found to have lost its optical activity after standing in acidic solution. Account for this observation. 3

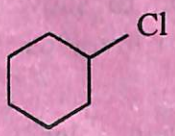
Find the product of the following reaction : 1

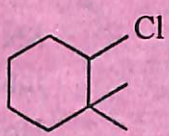


Which one of the following will be most reactive in SN^2 reaction ? 1

(a) 

(b) 

(c) 

(d) 

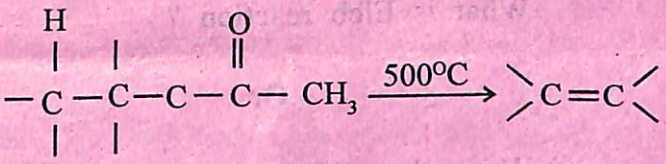
(C) (i) Write the product and find a probable mechanism of the following reaction :

$$CH_3CH=CH_2 \xrightarrow[h\nu/CCl_4]{NBS}$$ 3

Give an example of nucleophilic addition reaction. 2

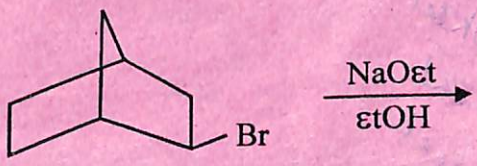
Or

(ii) What are Ei elimination reactions ? Discuss the mechanism and stereochemistry of the following reaction : 1½+2½=4



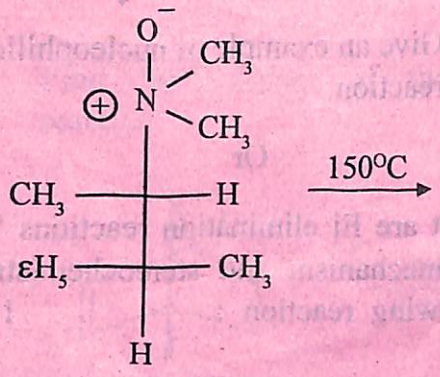
$+ CH_2COOH$

Predict the product of the following reaction. 1



1

(iii) What is Cope reaction ? Find the product of the following reaction showing favourable conformation for elimination in Newmann projection. 1½+2½=4



What is Elcb reaction ? 1

Or

(iv) Write the different factors on which E1 reactions complete with SN^1 reaction. Illustrate your answer with examples. 5

H-bond 5-10 kJ/mol
D-D - 2 kJ/mol
Van - 1 kcal