Quaid-I-Azam University

Department of Chemistry

PhD Admission Test (Organic Chemistry)

Semester Dated:

Time Allowed: 90 min Max Marks: 50

SAMPLE PAPER for PhD ADMISSION PREPARATION

Q. 1: Encircle the most appropriate option in the following set of questions:

1. Which of the following statements is incorrect regarding mass spectrometry?
a) Isotopic distribution patterns are observed in mass spectra.
b) Parent ions are not always observed in the mass spectra of compounds.
c) Mass spectrometry provides direct structural data.
d) Mass spectrometry gives information about fragmentation patterns.

2. The base peak in a mass spectrum is:
a) the lowest mass peak
b) the peak set to 100% relative intensity
c) the peak corresponding to the parent ion
d) the highest mass peak

3. Triethylamine has the formula $(CH_3CH_2)_3N$. In the mass spectrum of triethylamine, the base peak is at $m/z = 86$. This is consistent with:
a) cleavage of a C–C bond in the parent molecule
b) cleavage of a C–N bond in the parent molecule
c) loss of an ethyl group (CH_2CH_3) from the parent molecule
d) observation of the parent ion

4. The mass spectrum of acetone (CH_3COCH_3) shows major peaks at $m/z = 58$, 43 and 15. What can be deduced from these data?
a) The parent ion is observed, and fragmentation involves loss of CO.
b) The parent ion is observed, and fragmentation involves cleavage of two C–C bonds.
c) The parent ion is observed, and fragmentation involves cleavage of a C–C bond.
d) The parent ion is not observed.

5. The mass spectrum of nitromethane, CH_3NO_2, shows major peaks at $m/z = 61$, 46, 30 (base peak) and 15. Which statement is inconsistent with these data?
a) C–N bond cleavage occurs.
b) $[NO_2]^+$ is not formed as a fragment.
c) The parent ion is observed.
d) $[NO]^+$ is a fragment ion.

6. The intensity of macroscopic magnetization in an NMR experiment is not dependent on:
a) the natural abundance of the nucleus
b) the spin number of the nucleus
c) the gyromagnetic ratio (γ) of the nucleus

d) the magnetic field strength (B_o)

7. Which one of the following is correct regarding the condition of phase coherence:

a) The populations N_α and N_β are equal

b) No signal is observed

c) The magnetization along *z*-axis is zero

d) The absorption and emission processes cancel each other

8. The compound *iso*-propylbenzene has two groups of protons belonging to spin systems:

a) A_3B_3C and A_2B_2C

b) A_6X and $AA'BB'C$

c) A_3B_3C and $AA'BB'C$

d) A_3B_3M and $AA'BB'C$

9. Which one of the following is incorrect regarding the NOE developed while recording BB ^{13}C NMR spectra:

a) The NOE changes the intensities of the signal

b) The NOE and the dipole-dipole relaxation mechanism are intimately connected

c) It results in population ratios which correspond to the equilibrium situation

d) The integration in such an experiment is not adequate

10. Which one of the following is incorrect regarding a COSY spectrum:

a) If the diagonal peaks are plotted as dispersion-signals, the cross-peaks appear as absorption signals

b) The diagonal and cross peaks of a pair of mutually coupled nuclei form the corners of a square

c) The cross-peaks always occur when the nuclei interact through a scalar coupling

d) The absorption signals above the diagonal have positive amplitudes while those below the diagonal have negative

Q. 2: Choose the correct option for the following questions.

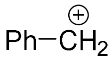
1) $LiBH_4$ can reduce esters as it is stronger reducing agent than $NaBH_4$ because;

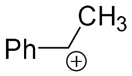
   a) Li is bigger in size,
   b) Li is stronger Lewis acid
   c) Li is more electronegative
   d) Sodium is less electropositive

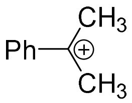
2) Which of the following cannot undergo S_N2 substitution reaction;

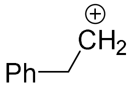
   a) Methyl iodide
   b) Ethyl bromide
   c) *tert*-Butyl bromide
   d) isopentyl bromide

3) Which of the following carbocation is more stable;

a) 
$Ph-\overset{\oplus}{C}H_2$

b) 

c) 

d) 

4) Based on Saytzeff's rule, select the most stable alkene;

   a) 1-methylcyclohexene
   b) 3-methylcyclohexene
   c) 4-methylcyclohexene
   d) They are all of equal stability

5) Select the major product for the following reaction;

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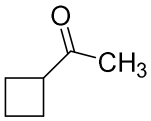
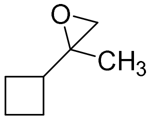
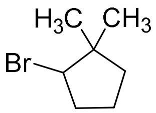
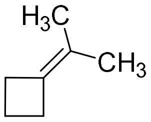
a) 

b) 

c) 

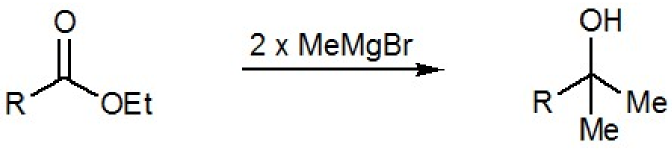
d) 

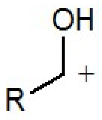
Q.3

a) Secondary aliphatic nitro compounds can be converted to ketones by:

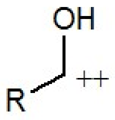
i) Collins reagent
ii) TiCl$_3$
iii) LiAlH$_4$
iv) Moffat reagent

b) Which synthon (A-D) corresponds to the following reaction?

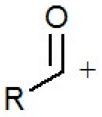




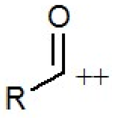
A



B

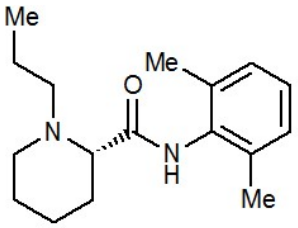


C

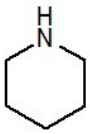


D

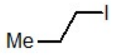
c) Carry out a retrosynthetic analysis of ropivacaine and identify which of the reagents (A-D) is least likely to be useful.



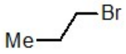
Ropivacaine



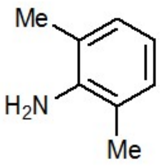
A



B



C

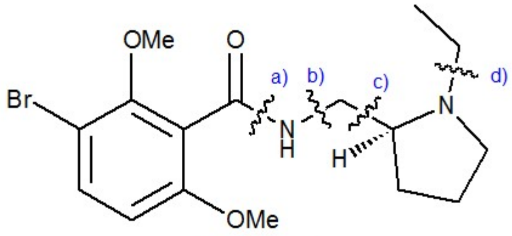


D

d) In Wittig reaction, the more stable YLIDE will react with aldehydes to yield mainly

  i) E-alkene
  ii) Z-alkene
  iii) E-alkenol
  iv) Z-alkenol

e) For the following structure, which of the disconnections (A-D) is likely to be the best option?

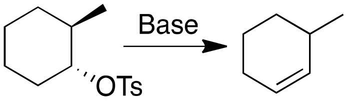


Remoxipride

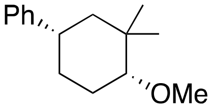
1. a)
2. b)
3. c)
4. d)

Q. 4. Answer following five parts; (10 marks)

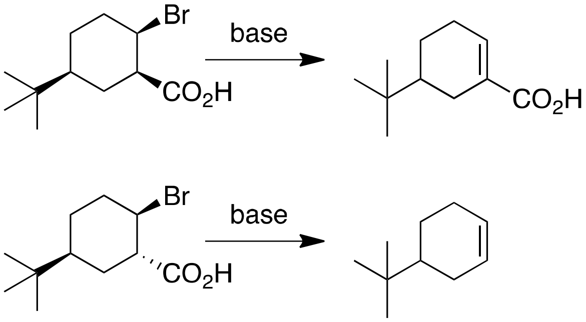
1. Comment on the position taken up by the alkene in following elimination reaction. Although Zaitsev's rule predicts the contrary. (Hint: Cyclohexane chair) 2



2. Draw most stable chair conformation corresponding to following structure. 1



3. Account for the contrasting results in these two reactions. (4)

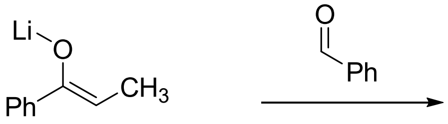


4. Conformational energies of substituents at 1,4 positions are additive but this additivity for 1,2 substituents o cyclohexane chair breaks down due to ---------------- (1)

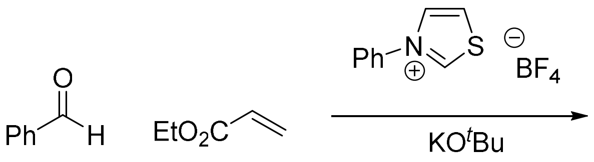
5. Out of cyclobutene and methylenecyclobutane which one has higher strain? Why (2)

Q.5 Answer the following questions.

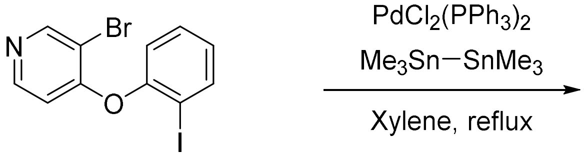
1) Complete the following aldol reaction showing the relative stereochemistry of the product.



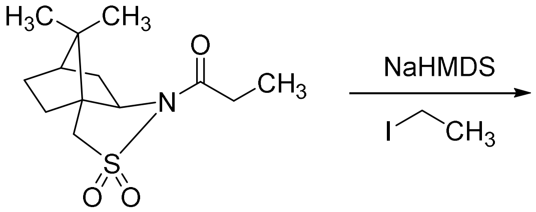
2) Write the product for the following Stetter reaction.



3) Write the product for the following Stille Kelly coupling reaction.



4) Oppolzer have discovered camphor sultam chiral auxiliary. It has been applied for the following enolate alkylation reaction. Write the product structure with absolute stereochemistry.



5) Reagent control asymmetric carbonyl allylation can directly result in the allylation product with excellent enantioselectivity. Write the product for the following reaction showing stereochemical outcome.