OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
CHM 407- Fundamentals of Physical Organic Chemistry

2024/2025 Mid-semester Exam **Time: 40 minutes**

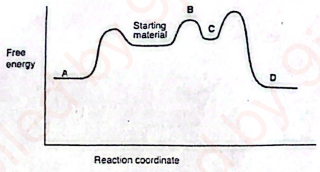
ATTEMPT ALL QUESTIONS

1. a. Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

i. $CH_3CH(OEt)_2 + H^+ \xrightleftharpoons{\text{fast}} H_3CHC(\overset{\oplus}{O}HOEt)H \xrightarrow{\text{slow}} H_3CHC{=}\overset{\oplus}{O}Et \xrightarrow{\text{fast}} CH_3CHO + EtOH$

ii. $CH_3COCH_3 + HA \xrightarrow{\text{slow}} CH_3\overset{\oplus}{C}OHCH_3 + A^- \xrightarrow{\text{fast}} CH_3C(OH){=}CH_2$

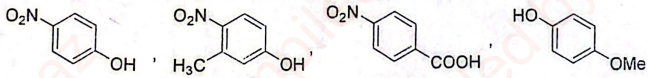
b.



In the reaction profile above, what do letters **A-D** represent?

2. a. In water, phenol has a pK_a of 10 while acetic acid has a pKa of 4. In the gas phase, phenol and acetic acid have comparable acidities. Explain this observation.

b. Arrange the following in order of increasing acidity,



4 < 2 < 1 < 3

3. a. Write the rate law that would be expected to describe the kinetic behavior for the following system, where k_1, k_{-1}, $k_3 >> k_2$:

$$C_2H_2Br_2 + R_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2HBr_2^- + R_3\overset{+}{N}H$$

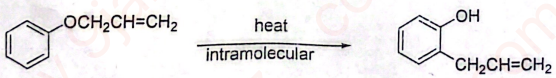
$$C_2HBr_2^- \xrightarrow{k_2} C_2HBr + Br^-$$

$$C_2HBr + R_3N \xrightarrow{k_3} C_2H\overset{+}{N}R_3 + Br^-$$

b. Predict the sign of the entropy of activation for each of the following reactions:

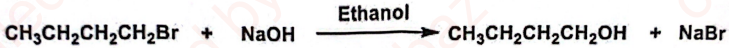
i. $C_2H_4NO_2^- + H^+ \rightarrow C_2H_5NO_2$ in solution

ii.



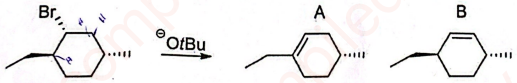
DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UNIVERSITY ILE-IFE
CHM 407 (PART B) MID-SEMESTER TEST
2024/2025 SESSION

1(a). Which mechanism is involved in the reaction shown below

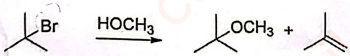


(b) What is the rate expression for the reaction?
(c) Draw the enrgy diagram for the reaction. Label all parts. You may assume that the products are lower in energy than the reactants
(d) What will be the effect on the rate of the reaction of doubling the concentration of n-butyl bromide?
(e) What will be the effect on the rate of the reaction of halving the concentration of sodium hydroxide?
(f) Will the rate of the reaction change significatly if the solvent is cahnged to 80% ethanol, 20% water?

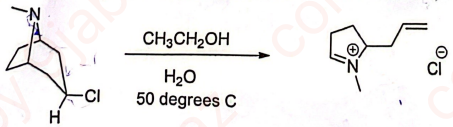
2(a). In the reaction below, B is the major product. Explain.



(b). The molecule below reacts through an SN1/E1 pathway in methanol. Draw the mechanism for each pathway.



3(a). Write a generally acceptable mechanism for the reaction shown below



(b) The alkaloid coniine has been isolated from hemlock and purified. Its molecular formula is $C_8H_{17}N$. Treatment of coniine with excess methyl iodide, followed by silver oxide and heating, gives the pure (S)-enantiomer of N,N-dimethyloct-7-ene-4-amine. Propose two possible structures for coniine, and show how this reaction (write a generally acceptable mechanism) gives the observed product starting with any of the proposed structures for coniine.

A Kinyele Oluwaferanmi

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. (Chemistry) Degree Examination Part IV
CHM 407 – FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY
Harmattan Semester Examination (2024/2025 Session)

Date: 5th March 2026

Time Allowed: $2\frac{1}{2}$ hours

INSTRUCTION:
(i) Answer "ALL" Questions from SECTION A
(ii) Answer ANY TWO Questions from SECTION B.

Constants: $R = 8.314\ Jmol^{-1}K^{-1}$; $h = 6.626 \times 10^{-34}\ Js$; $k = 1.38 \times 10^{-23}\ JK^{-1}$

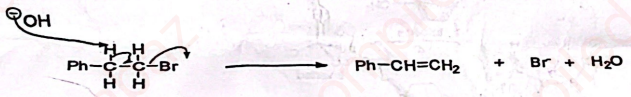
SECTION A

1(a). Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of *m*-chlorobenzyl *p*-toluenesulphonate from the data below:

Temperature (°C)	$k_r \times 10^5\ (s^{-1})$
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

(b). The base-catalysed elimination of 1-bromo-2-phenylethane to 2-phenylethene could proceed by either of the following mechanisms:

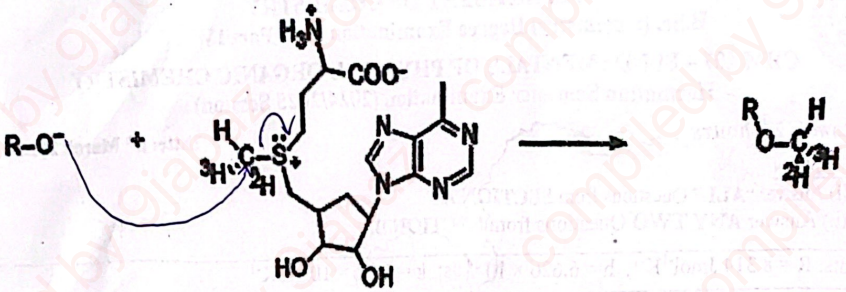
i. $PhCH_2CH_2Br \xrightarrow{\text{slow}} PhCH_2\overset{+}{C}H_2 + Br^- \xrightarrow{OH^-} PhCH{=}CH_2$

ii. 

Outline 2 different experiments to decide which mechanism is actually operating, stating clearly what results you expect.

(c). Maleic anhydride reacts with furan to give two possible tricyclic products: a sterically crowded endo product **P** and/or a less crowded exo product **Q**. Under some specific laboratory conditions, **P** is obtained exclusively as the product of this reaction. Using a simple energy profile diagram, illustrate the reaction paths and explain what type of control is in effect. [20 marks]

2(a). The reaction shown below was used to help clarify the S_N2 nature of the alkylation reactions of S-adenosylmethionine. Explain what the results tell us about the mechanism. And write a generally acceptable mechanism (using arrows to show the movement of electrons) for the reaction.



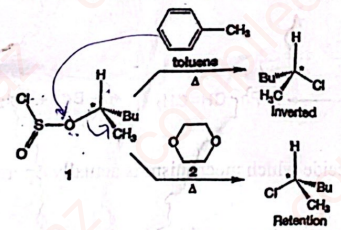
(b). Explain the experimental observations in the reactions presented below (why is the second reaction faster?).

Reaction 1 $CH_3CH_2CH_2CH_2CH_2Br + NaCN \xrightarrow[CH_3OH,\ \Delta,\ 20\ h]{S_N2} CH_3CH_2CH_2CH_2CH_2CN + NaBr$ (71%)

Reaction 2 $CH_3CH_2CH_2CH_2CH_2Cl + NaCN \xrightarrow[DMSO,\ 20\ min]{S_N2} CH_3CH_2CH_2CH_2CH_2CN + NaCl$ (91%)

(c). Rationalize the following curious experimental results. When the optically active chlorosulfite (1) is heated in toluene, the chloride with inverted configuration is obtained along with SO_2. However, when (1) is decomposed in 1,4-dioxane (2), retention of configuration in the resulting chloride is observed.

Hint: One route involves an S_Ni mechanism, and also think about the differences between toluene and 1,4-dioxane as solvents. A good Lewis structure for 1,4-dioxane may also be helpful.



(i) Which method involves S_N2 and which is S_Ni?
(ii) Write a generally acceptable mechanism for each method
(iii) How did the solvent facilitate each mechanism? [20 marks]

SECTION B

3(a). Ethyl vinyl ether is hydrolysed in dilute acid according to the following equation:

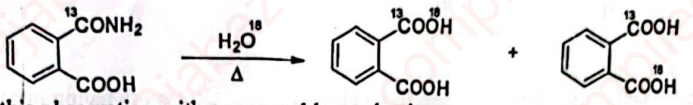
$$CH_3CH_2OCH{=}CH_2 + H_2O \rightarrow CH_3CH_2OH + CH_3CHO$$

Given that:

(i) The reaction is subject to general acid catalysis
(ii) The reaction is faster in H_2O than in D_2O by a factor of 2.93
(iii) The ethanol obtained by hydrolysis in isotopically labelled water contains no ^{18}O.

With reasons, suggest a mechanism for the hydrolysis which is consistent with these observations. State clearly which step is rate limiting.

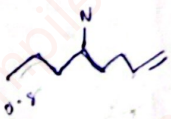
(b). Hydrolysis of ^{13}C labeled *o*-phthalamic acid in water enriched in ^{18}O gives phthalic acid with the ^{18}O label equally located on each carboxyl group as shown below.



Explain this observation with a reasonable mechanism.

(c). Match the following $\frac{k_H}{k_D}$ values with the appropriate reactions below:

$\frac{k_H}{k_D}$: 6.1, 0.8, 1.3



i. $CH_3CH^*O + H_2O \longrightarrow H_3C-\underset{OH}{\overset{OH}{C}}-H^*$

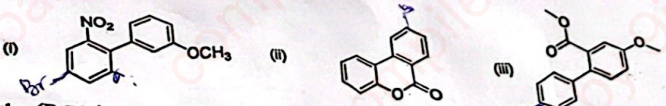
ii. $H_3C-\underset{H^*}{CH}-Cl + H_2O \longrightarrow H_3C-\underset{H^*}{CH}-OH + HCl$ S_N1 mechanism

iii. $(CH_3)_2CH^*-\overset{O}{\overset{\|}{C}}-CH_3 + OH^- \xrightarrow{\text{slow}} (CH_3)_2C=\overset{O^-}{\overset{|}{C}}-CH_3 + H^*-OH$

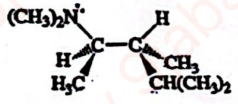
[15 marks]

4(a). Using equations with reaction conditions, show how toluene can be converted to 3,5-dibromotoluene in good yield. Explain your rationale for every reaction step you decide to use, taking into account energetics and reaction rates

(b). Predict the major products of bromination of the following compounds, using Br_2 and $FeBr_3$ in the dark.

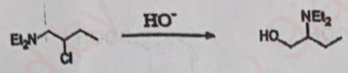


(c). When the (R,R) isomer of the amine shown below is treated with an excess of methyl iodide, then silver oxide, then heated, a major product is observed in the elimination reaction. Draw the structure of the major product and a generally acceptable mechanism for the formation of the product.

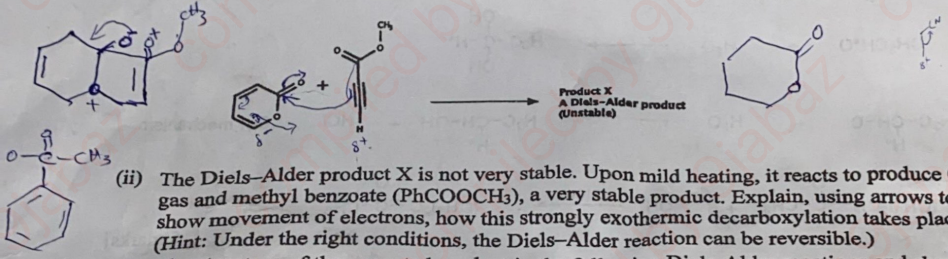


[15 marks]

5(a). The following reaction takes place under second-order conditions (strong nucleophile), yet the structure of the product shows rearrangement. Also, the rate of this reaction is several thousand times faster than the rate of substitution of hydroxide ion on 2-chlorobutane under similar conditions. Propose a mechanism to explain the enhanced rate and rearrangement observed in this unusual reaction.

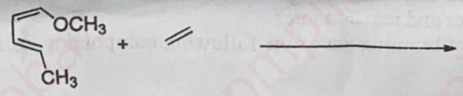


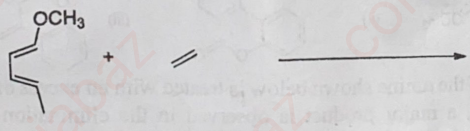
(b). (i) The diene lactone shown in the equation below has one electron-donating group (-OR) and one electron-withdrawing group (C=O). This diene lactone is sufficiently electron-rich to serve as the diene in a Diels–Alder reaction. What product would you expect to form when this diene reacts with methyl acetylenecarboxylate, a strong dienophile? Write a generally acceptable mechanism for the formation of the product

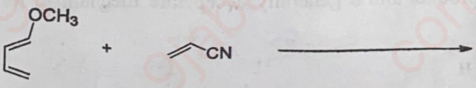


(ii) The Diels–Alder product X is not very stable. Upon mild heating, it reacts to produce CO_2 gas and methyl benzoate ($PhCOOCH_3$), a very stable product. Explain, using arrows to show movement of electrons, how this strongly exothermic decarboxylation takes place. (*Hint:* Under the right conditions, the Diels–Alder reaction can be reversible.)

(c). Draw the structure of the expected product in the following Diels-Alder reactions and show the stereochemistry where it is applicable.

i 

ii 

iii 

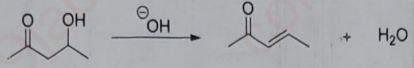
[15 marks]

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

CHM 407- Fundamentals of Physical Organic Chemistry

Tutorial Set 1 (2014)

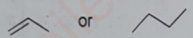
1. Propose two possible mechanistic hypothesis for the following transformation, showing the rate law for each:



2. Given the reaction below,

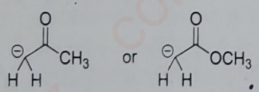
If the K_{eq} is 10^{-5}, predict which direction the equilibrium lies and hence suggest which of the acid species is stronger.

3. Which of the following is more acidic and why?

a. 

b. $R_2SH^{\oplus}$ or $R_2OH^{\oplus}$

4. Which of the following is more basic and why?



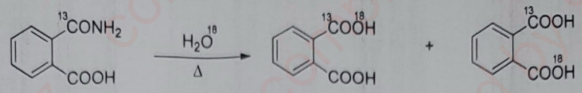
5. The elimination reaction of 2-bromopropane could proceed by either of the following mechanisms:

i) $(CH_3)_2CHBr + C_2H_5O^-Na^+ \longrightarrow CH_3CH{=}CH_2 + C_2H_5OH + NaBr$ 1 step

ii) $(CH_3)_2CHBr \xrightarrow{slow} (CH_3)_2\overset{\oplus}{C}H \xrightarrow{C_2H_5O^-Na^+} CH_3CH{=}CH_2 + C_2H_5OH + NaBr$

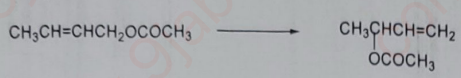
Outline two different experiments to decide which mechanism is actually operating, stating clearly what results you expect.

6. Hydrolysis of ^{13}C labeled o-phthalamic acid in water enriched in ^{18}O gives phthalic acid with the ^{18}O label equally located on each carboxyl group as shown below.



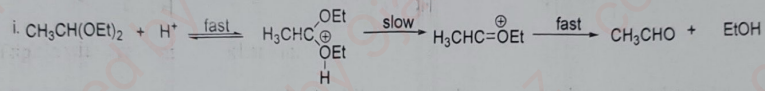
Explain with a reasonable mechanism.

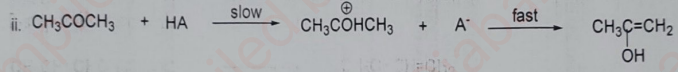
7. .i. Suggest two possible mechanisms for the following reaction – a 1-step intramolecular and a 2-step ionic mechanism.



ii. How would you differentiate between the two mechanisms?

8. Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

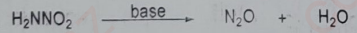




9. a. Maleic anhydride react with furan to give two possible tricyclic products: a sterically crowded endo product **A** and/or a less crowded exo product **B**. Under some specific laboratory conditions, **A** is obtained exclusively as the product of this reaction. Using a simple energy profile diagram, explain what type of control is in effect.

b. Is it possible to convert **A** to **B**? If yes, suggest how.

10. The decomposition of nitramide is base catalysed:



The following rates were obtained for a number of bases.

i) Show that they obey the Bronsted catalysis law and determine the value of β for this reaction.

ii) Comment on the magnitude of β for this reaction.

Base	pK_a	k_r ($Lmol^{-1}min^{-1}$)
p-toluidine	5.12	1.16
m-toluidine	4.69	0.64
aniline	4.58	0.54
o-toluidine	4.39	0.38
p-chloroaniline	3.98	0.21
m-chloroaniline	3.34	0.081
o- chloroaniline	2.64	0.018

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

CHM 407- Fundamentals of Physical Organic Chemistry

Mid-semester Exam **Time: 1 hour**

ATTEMPT ALL QUESTIONS

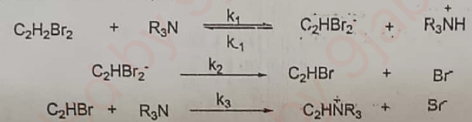
1. a. Given the reaction below,

If the K_{eq} is 10^{-5}, predict which direction the equilibrium lies and hence suggest which of the acid species is stronger.

b. Arrange the following in order of increasing acidity
$Cl_2CHCOOH$, CH_3CH_2OH, $BrCH_2COOH$, CH_3COOH, $ClCH_2COOH$, C_6H_5OH.

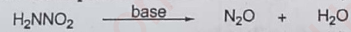
2. a. Explain why the dissociation of benzoic acid exhibits a positive entropy of activation in the gas phase but a negative entropy of activation in aqueous medium.

b. Write the rate law that would be expected to describe the kinetic behavior for the following system, where $k_1, k_{-1}, k_3 >> k_2$:



3. a. Assuming the following reaction is general acid catalysed, propose a mechanism for it, indicating the rate limiting step and the fast step.

b. The decomposition of nitramide is base catalysed:



The following rates were obtained for a number of bases.

i) Show that they obey the Bronsted catalysis law and determine the value of β for this reaction.

ii) Comment on the magnitude of β for this reaction.

Base	pK_a	k_r ($Lmol^{-1}min^{-1}$)
p-toluidine	5.12	1.16
m-toluidine	4.69	0.64
aniline	4.58	0.54
o-toluidine	4.39	0.38
p-chloroaniline	3.98	0.21
m-chloroaniline	3.34	0.081
o- chloroaniline	2.64	0.018

β is closer to 1

$\frac{-0.68-(-1.09)}{3.98-3.34}$

≈ 0.64.

CHM/2018/002

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. (Chemistry) Degree Examination Part IV
CHM 407 – Fundamentals of Physical Organic Chemistry
Harmattan Semester Examination (2023/2024 Session)

Time Allowed: $2\frac{1}{2}$ hours **Date: 24th February 2025**

INSTRUCTION:
(i) ***SECTION A***: Answer **"ANY TWO" Questions** from Section A
(ii) ***SECTION B***: Answer **TWO Question (Question 4** and **ANY** other **Question** from **5 & 6).**

IF YOU MAKE USE OF A GRAPH OR AN EXTRA SHEET, ENSURE YOUR REGISTRATION NUMBER IS CLEARLY INDICATED AS APPROPRIATE.

Constants: $R = 8.314\ Jmol^{-1}K^{-1}$; $h = 6.626 \times 10^{-34}\ Js$; $k = 1.38 \times 10^{-23}\ JK^{-1}$

SECTION A

1(a). Which mechanism is involved in the reaction shown below:

$$CH_3CH_2CH_2CH_2Br + NaOH \xrightarrow{\text{Ethanol}} CH_3CH_2CH_2CH_2OH + NaBr$$

SN2

(b) What is the rate expression for the reaction?

(c) Draw the energy diagram for the reaction and label all the parts. You may assume that the products are lower in energy than the reactants

$R = k[CH_3CH_2CH_2CH_2Br][NaOH]$

(d) What will be the effect of doubling the concentration of n-butyl bromide on the rate of the reaction?

(e) What will be the effect of halving the concentration of sodium hydroxide on the rate of the reaction?

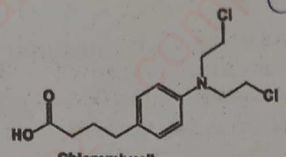
DNF (f) Will the rate of the reaction change significantly if the solvent is changed to 80% ethanol, 20% water?

2. Many compounds that are toxic to cells act by alkylating DNA. One such compound is chlorambucil, which is used in the chemotherapy of cancer, especially for leukaemia. The compound reacts with the nitrogen on position 7 of guanine, one of the four bases that are part of the genetic code of DNA. The reaction is helped by the participation of the non-bonding electrons on the nitrogen at position 9 in guanine.

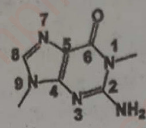
(a) Draw a mechanism for the reaction of guanine with chlorambucil. Only one of the leaving group is lost in the reaction.

(b) In DNA, chlorambucil can react twice, linking different parts of the DNA helix together, thus stopping reproduction of the cell. Draw the structure of the product formed when chlorambucil reacts with two guanine units.

CHM/2018/022

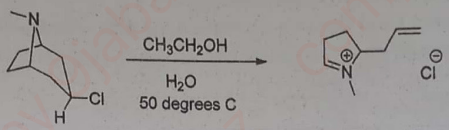


Chlorambucil



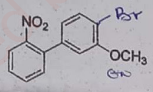
Guanine

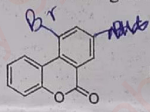
(c) Write a generally acceptable mechanism for the reaction shown below

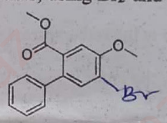


3(a). Using equations with reaction conditions, show how toluene can be converted to 3,5-dibromotoluene in good yield. Explain your rationale for every reaction step you decide to use taking into account energetics and reaction rates

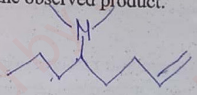
(b) Predict the major products of bromination of the following compounds, using Br_2 and $FeBr_3$ in the dark.

(i) 

(ii) 

(iii) 

(c) The alkaloid coniine has been isolated from hemlock and purified. Its molecular formula is $C_8H_{17}N$. Treatment of coniine with excess methyl iodide, followed by silver oxide and heating, gives the pure (S)-enantiomer of N,N-dimethyloct-7-ene-4-amine. Propose a complete structure for coniine and show how this reaction (write a generally acceptable mechanism) gives the observed product.



SECTION B

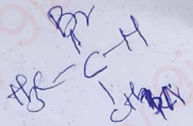
4(a). The elimination reaction of 2-bromopropane could proceed by either of the following mechanisms:

i) $(CH_3)_2CHBr + C_2H_5O^-Na^+ \longrightarrow CH_3CH{=}CH_2 + C_2H_5OH + NaBr$ 1 step

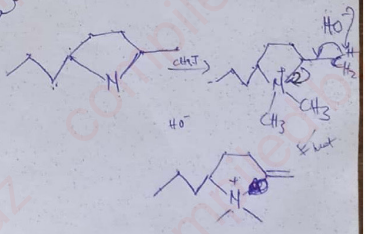
Correct

ii) $(CH_3)_2CHBr \xrightarrow{\text{slow}} (CH_3)_2\overset{\oplus}{C}H \xrightarrow{C_2H_5O^-Na^+} CH_3CH{=}CH_2 + C_2H_5OH + NaBr$

Experimentally, the primary deuterium isotope effect $\frac{k_H}{k_D}$ for the reaction is 6.9 at 25 °C, which of the 2 mechanisms is correct and why?



Endo product are faster because



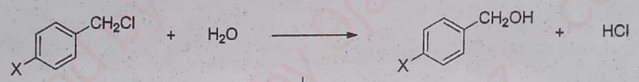
(b). Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

i. $CH_3CH(OEt)_2 + H^+ \xrightleftharpoons{\text{fast}} H_3CHC(\overset{\oplus}{O}HEt)(OEt) \xrightarrow{\text{slow}} H_3CHC{=}\overset{\oplus}{O}Et \xrightarrow{\text{fast}} CH_3CHO + EtOH$

ii. $CH_3COCH_3 + HA \xrightarrow{\text{slow}} CH_3\overset{\oplus}{C}OHCH_3 + A^- \xrightarrow{\text{fast}} CH_3C(OH){=}CH_2$

(c). Maleic anhydride reacts with furan to give two possible tricyclic products: a sterically crowded endo product **P** and/or a less crowded exo product **Q**. Under some specific laboratory conditions, **P** is obtained exclusively as the product of this reaction. Using a simple energy profile diagram illustrate the reaction paths and explain what type of control is in effect.

5(a). Given that the Hammet reaction constant, ρ, for the reaction shown below is -1.31. Calculate how much faster *p*-bromobenzyl chloride will solvolyze in water than *p*-nitrobenzyl chloride from the data given.



X	σ
H	0.00
Br	0.23
NO_2	0.78

(b). The mechanism of semicarbazone formation from substituted benzaldehyde is shown below:

$$ArCHO + NH_2NHCONH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar{-}\overset{OH}{\underset{H}{C}}{-}NHNHCONH_2 \xrightarrow{k_2} ArHC{=}N{-}NHCONH_2 + H_2O$$

The Hammet plot is acid dependent. At pH = 7.00, ρ = +0.07, but at pH = 1.75, ρ = +0.91. Explain the difference in ρ values.

(c). Explain the wide difference in the values of the substituent constants σ_m and σ_p, which are +0.337 and +0.062 respectively for the F substituent of fluorobenzene.

6(a). Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of *m*-chlorobenzyl *p*-toluenesulphonate from the data below:

$k_r = \frac{k_b T}{h} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta H^{\ddagger}}{RT}}$

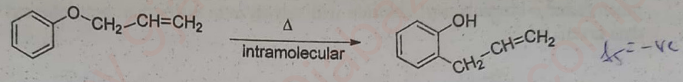
$\frac{k_r}{T} = \frac{k_b}{h} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta H^{\ddagger}}{RT}}$

$\ln\left(\frac{k_r}{T}\right) = \ln\frac{k_b}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$

Temperature (°C)	k_r (s^{-1})
25.0	1360
40.0	8600
50.1	27200
58.8	72600

(b). Predict with reason the $\Delta S^{\ddagger}$ for each of the following reactions:

(i) $C_2H_4NO_2^- + H^+ \rightarrow C_2H_5NO_2$ in solution ΔS = -ve + ΔS

(ii) 

ΔS = -ve

(c). Match the following $\frac{k_H}{k_D}$ values with the appropriate reactions below: $\frac{k_H}{k_D}$: 6.1, 0.8, 1.3

i. $CH_3CH^*O + H_2O \longrightarrow H_3C-\underset{OH}{\overset{OH}{C}}-H^*$ 0.8

ii. $H_3C-\underset{H^*}{CH}-Cl + H_2O \longrightarrow H_3C-\underset{H^*}{CH}-OH + HCl$ S_N1 mechanism 1.3

iii. $(CH_3)_2CH^*-\overset{O}{\overset{\|}{C}}-CH_3 + OH^- \xrightarrow{\text{slow}} (CH_3)_2C=\overset{O^-}{\overset{|}{C}}-CH_3 + H^*-OH$ 6.1

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

CHM 407- Fundamentals of Physical Organic Chemistry

Mid-semester Exam **Time: 1 hour**

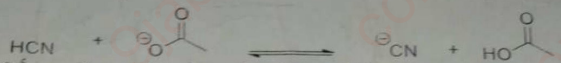
ATTEMPT ALL QUESTIONS

Constants: $R = 8.314\ Jmol^{-1}K^{-1}$; $h = 6.626 \times 10^{-34}\ Js$; $k = 1.38 \times 10^{-23}\ JK^{-1}$

1. a. Arrange the following in the order of increasing acidity

$Cl_2CHCOOH$, CH_3CH_2OH, $BrCH_2COOH$, CH_3COOH, $ClCH_2COOH$, C_6H_5OH

b. Given the reaction below,

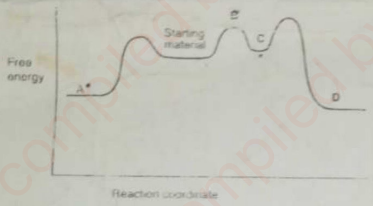


If the K_{eq} is 10^{-5}, predict which direction the equilibrium lies and hence suggest which of the acid species is stronger.

2. a. Assuming the following reaction is general acid catalysed, propose a mechanism for it, indicating the rate limiting step and the fast step.

$$CH_3CH_2OCH{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH + CH_3CHO$$

b.



In the reaction profile above, what do letters A-D represent?

3. a. Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

i. $CH_3CH(OEt)_2 + H^+ \overset{fast}{\rightleftharpoons} H_3CHC(\overset{\oplus}{O}HOEt)OEt \overset{slow}{\longrightarrow} H_3CHC{=}\overset{\oplus}{O}Et \overset{fast}{\longrightarrow} CH_3CHO + EtOH$

ii. $CH_3COCH_3 + HA \overset{slow}{\longrightarrow} CH_3\overset{\ominus}{C}OHCH_3 + A^- \overset{fast}{\longrightarrow} CH_3C(OH){=}CH_2$

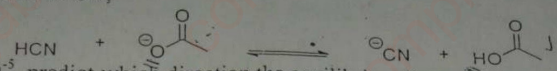
b. Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of *m*-chlorobenzyl *p*-toluenesulphonate from the data below:

Temperature (°C)	$k_r \times 10^5\ (s^{-1})$
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

ATTEMPT ALL QUESTIONS

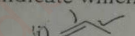
Time: 1 hour

1. a. Given the reaction below,

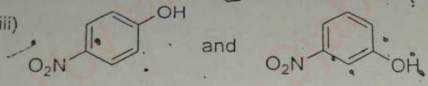


If the K_{eq} is 10^{-5}, predict which direction the equilibrium lies and hence suggest which of the acid species is stronger.

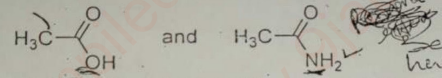
b. Indicate which of each pair of compounds is likely to be more acidic and why?

i)  or 

ii) $R_2\overset{\oplus}{S}H$ or $R_2\overset{\oplus}{O}H$

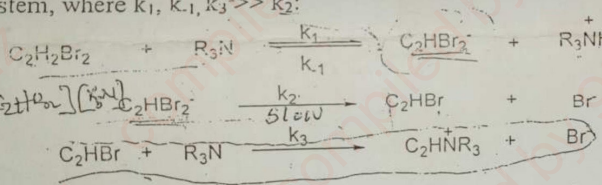
iii) 

iv) $PhC{\equiv}CH$ and $PhC{\equiv}CCH_3$

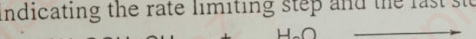
v) 

a. Explain why the dissociation of benzoic acid exhibits a positive entropy of activation in the gas phase but a negative entropy of activation in aqueous medium.

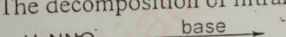
b. Write the rate law that would be expected to describe the kinetic behavior for the following system, where k_1, k_{-1}, $k_3 >> k_2$:



a. Assuming the following reaction is general acid catalysed, propose a mechanism for it, indicating the rate limiting step and the fast step.



b. The decomposition of nitramide is base catalysed:



The following rates were obtained for a number of bases.

i) Show that they obey the Bronsted catalysis law and determine the value of β for this reaction.

ii) Comment on the magnitude of β for this reaction.

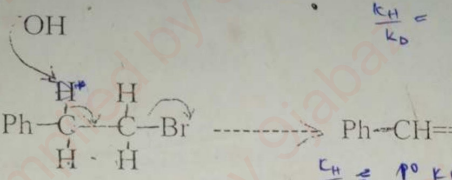
Base	pK_a	k_r ($Lmol^{-1}min^{-1}$)
p-toluidine	5.12	1.16
m-toluidine	4.69	0.64
aniline	4.58	0.54
o-toluidine	4.39	0.38
p-chloroaniline	3.98	0.21
m-chloroaniline	3.34	0.081
o- chloroaniline	2.64	0.018

Tutorial Set 1

1. The base-catalyzed elimination of 1-bromo-2-phenylethane to 2-phenylethene could proceed by either of the following mechanisms viz:

a. $PhCH_2CH_2Br \xrightarrow{slow} PhCH_2CH_2^{+} \xrightarrow{OH^-} PhCH{=}CH_2$

b.



$Ph{-}CH{=}CH_2 + Br^- + H_2O$ 1 step

Outline 2 different experiments to decide which mechanism is actually operating, stating clearly what results you expect.

2. Match the following k_H/k_D values with the appropriate reactions below:

K_H/k_D : 1.3, 0.8, 4.66, 1.1

i. $CH_3CHO + HCN \longrightarrow CH_3{-}C(H)(OH){-}CN$

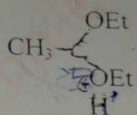
ii. $PhCH_3 + Br_2 \longrightarrow PhCH_2Br + HBr$

iii. $PhCH_2Cl \xrightarrow[H_2O]{CH_3CH_2OH} PhCH_2OH$ S_N1 mechanism

iv. $CH_3CH(NO_2)CH_3 + OH^- \longrightarrow CH_2{=}C(NO_2)CH_3 + H_2O$

[Note -: H* indicates the Hydrogen being substituted]

3. Classify the following reactions as either specific or general acid catalyzed:

i. $CH_3CH(OEt)_2 + H^+$ (fast) $\xrightarrow[H_2O]{}$ 

$CH_3CH{=}\overset{+}{O}Et \xrightarrow{H_2O} CH_3CHO + EtOH$

ii

$CH_3COCH_3 + HA \xrightarrow{slow} CH_3\overset{\oplus}{C}(OH)CH_3 + A^-$

$CH_3\overset{OH}{C}{=}CH_2 + HA$

4. Predict either an increase or decrease in the rate of each of the following reactions with increase in solvent polarity.

a. $I^- + CH_3Cl \longrightarrow Cl^- + CH_3I$

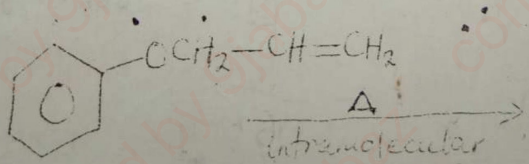
b. $Br^- + CH_3CH_2\overset{\oplus}{N}(CH_3)_3 \longrightarrow (CH_3)_3N + CH_3CH_2Br$

c. $(CH_3)_3N + CH_3CH_2I \longrightarrow I^- + CH_3CH_2\overset{\oplus}{N}(CH_3)_3$

d. $NH_3 + CH_3{-}S(CH_3)_2 \longrightarrow S(CH_3)_2 + CH_3NH_3$

5. Predict the sign of ΔS for each of the following reactions:

a. $C_2H_4NO_2^- + H^+ \longrightarrow C_2H_5NO_2$ in solution

b. 

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Chemistry Degree Examination
CHM 407: FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY
2018/2019 Harmattan Semester Examination

Time Allowed: 3 Hours **Date: 26th July, 2019**

Instructions: Answer Section A in a separate booklet and Section B & C in another booklet.

SECTION A: Answer all questions in this section (in a separate booklet)

QUESTION 1

a. Calculate the enthalpy and entropy of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) for the acetolysis of m-chlorobenzyl and p-toluenesulphonate from the data below.

Temp (^{0}C)	k X 10^5, s^{-1}
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

b. Explain the difference in values of σ_m and σ_p for each of the following groups in terms of the electronic character of each group.

Substituent	σ_m	σ_p
$NHCOCH_3$	+0.21	0.00
F	+0.337	+0.062
Cl	+0.373	+0.227

c. Match ρ values with the appropriate reaction:

ρ = -3.3, -8.06, +1.00, +2.61

i. $ArCH_2CO_2Et + OH^- \longrightarrow ArCH_2CO_2^- + EtOH$

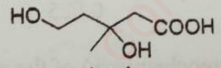
ii. $ArNMe_2 + MeI \longrightarrow ArNMe_3^+I^-$

iii. $ArCO_2Et + OH^- \longrightarrow ArCO_2^- + EtOH$

iv. $ArH + Cl_2 \longrightarrow ArCl + HCl$

QUESTION 2

a. Mevalonic acid (shown below) can potentially form two possible lactones, however in nature just one these lactones is formed.



i. Show, with mechanism, how lactonization can occur to give both products

ii. Indicate which product if not formed and suggest why.

b. Ethyl vinyl ether is hydrolysed in dilute acid according to the following equation:

$CH_3CH_2OCH{=}CH_2 + H_2O \rightarrow CH_3CH_2\overset{18}{O}H + CH_3CHO$

Given that:

i. The reaction is subject to general acid catalysis

ii. The reaction is faster in H_2O than in D_2O by a factor of 2.93

iii. The ethanol obtained by hydrolysis in isotopically labelled water contains no ^{18}O.

With reasons suggest a mechanism for the hydrolysis which is consistent with these observations. State clearly which step is rate limiting.

c. Match the following K_H/K_D values with the appropriate reactions below:
6.1, 0.7, 1.2

i. $Ph_2C{=}C{=}O + PhHC{=}CH_2^{\bullet} \longrightarrow Ph_2C(\overset{O}{\diagdown})-CH(Ph)-CH_2^{\bullet}$

ii. $H_3C-CH(H^{\bullet})-Cl + H_2O \longrightarrow H_3C-CH(H^{\bullet})-OH + HCl$ S_N1 mechanism

iii. $(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-CH_3 + OH^- \xrightarrow{\text{slow}} (CH_3)_2C{=}\overset{O^-}{\overset{|}{C}}-CH_3 + {}^{\bullet}H-OH$

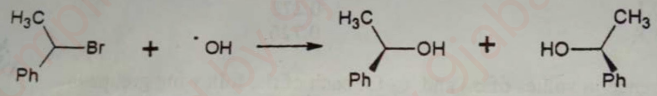
SECTION B: Answer ALL Questions in this Section

QUESTION 3

(a). Give three factors that determine whether an alkyl halide will undergo an S_N1 or an S_N2 reaction.

(b). Are S_N1 reactions faster in polar solvents?

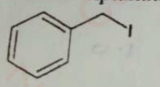
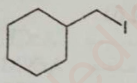
©. Draw the complete mechanism (showing the structures of the reactants, intermediate and products) of the following S_N1 reaction:



(d). Draw the Free Energy versus Reaction Progress diagram for the S_N1 reaction in ©, showing the activation energy, transition states, ionic intermediate, starting materials and products.

QUESTION 4

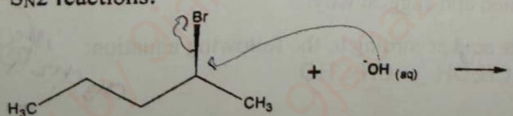
Give a brief explanation for each of the following experimental observations:

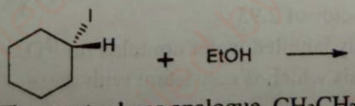
(a)  is more reactive than 

(b) Average relative S_N2 reaction rates for some alkyl halides:

R	relative rate
CH_3	30
CH_3-CH_2	1
CH_3-CH_2-CH_2	0.4
Iso-propyl	0.025

(c) Predict the structure (specifying stereochemistry) of the product in each of the following S_N2 reactions:

(i) 

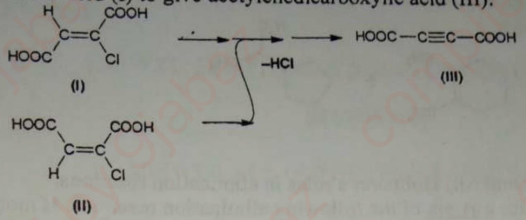
(ii) 

(d) The mustard gas analogue, $CH_3CH_2SCH_2CH_2Cl$, is hydrolyzed to $CH_3CH_2SCH_2CH_2OH$

more rapidly than $CH_3CH_2CH_2CH_2CH_2$-Cl.

(e) In the S_N1 reaction $CH_3CH_2CH_2$-Br + EtOH ⟶ increase in solvent polarity enhances rate of reaction.

(e). The elimination reaction of cis-chloromaleic acid (II) occurs 50 times slower than trans-chloromaleic acid (I) to give acetylenedicarboxylic acid (III):



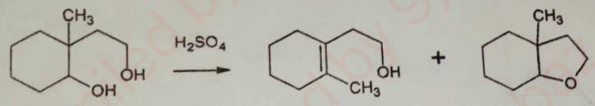
SECTION C: Answer any of Question 5 or 6

QUESTION 5

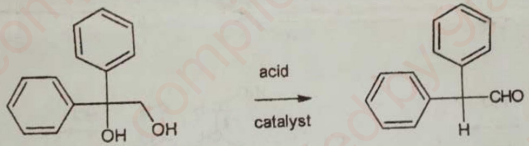
(Answer any five)

Provide detailed mechanisms for the following reactions:

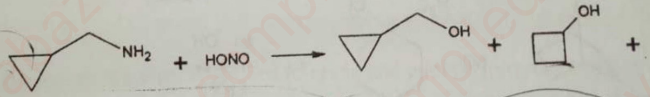
(i)



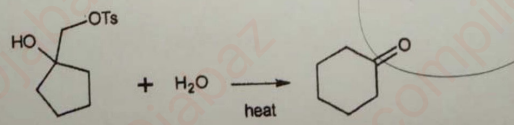
(ii)



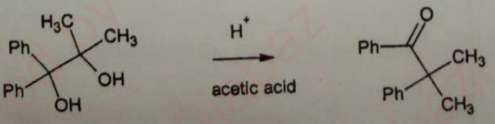
(iii)



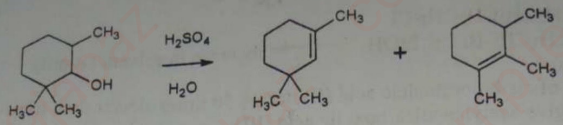
(iv)



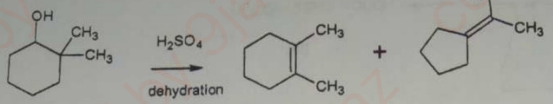
(v)



(vi)



(vii)

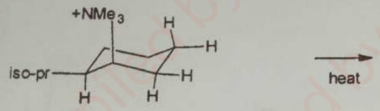


QUESTION 6

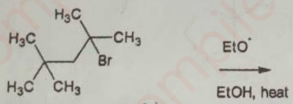
(a). State (i) Bredt's (ii) Zaitsev's and (iii) Hofmann's rules in elimination reactions.

(b). Give the product or products for **any six** of the following elimination reactions. If more than one product is formed, indicate with brief explanation, which is the major product:

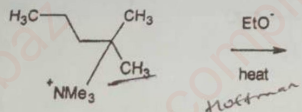
(i)



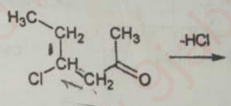
(ii)



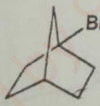
(iii)



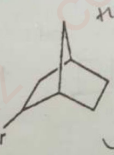
(iv)



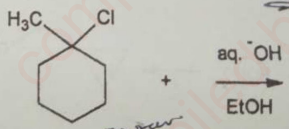
(v)



(vi)

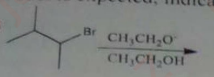


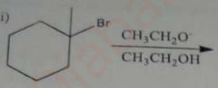
(vii)

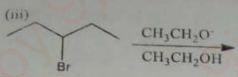


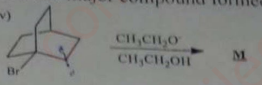
QUESTION 1

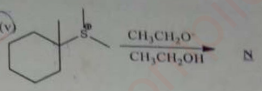
a. Predict the products of the following bimolecular elimination reactions. If more than one product is expected, indicate which will be the major compound formed

(i) 

(ii) 

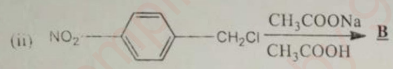
(iii) 

(iv) 

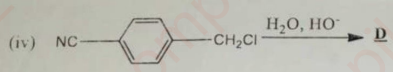
(v) 

b. Each of the following nucleophilic substitution reactions has been reported in the chemical literature, Predict the product of each reaction.

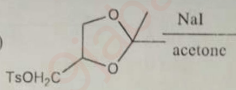
(i) $BrCH_2COOCH_2CH_3 \xrightarrow[\text{acetone}]{NaI} \underline{A}$

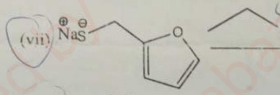
(ii) 

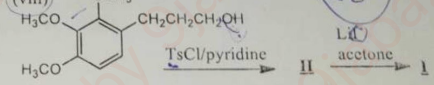
(iii) $CH_3CH_2OCH_2CH_2Br \xrightarrow[\text{ethanol-water}]{NaCN} \underline{C}$

(iv) 

(v) $ClCH_2COOCH_2CH_3 \xrightarrow[\text{acetone-water}]{NaN_3} \underline{E}$

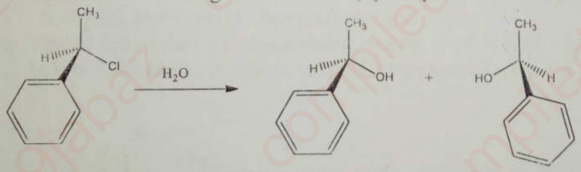
(vi) 

(vii) 

(viii) 

QUESTION 2

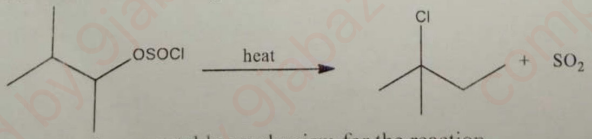
a. Consider the following SN1 reaction (hydrolysis of 1-chloro-1-phenylethane)



(41 % retention) (59 % inversion)

Explain why there is a slight excess of inversion instead of the expected racemeization

b. Consider the following reaction:



Propose a generally acceptable mechanism for the reaction

c. Predict the effect on rate of the change indicated in each of the following and give the basis for your prediction

i. Change to a more polar solvent in an SN2 reaction between HO^- amd ethyl iodide

Change of R from CH_3- to $CH_3C{=}O$ in an SN1 reaction of $R(CH_3)CHCl$

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part IV
CHM 407: Fundamentals of Physical Organic Chemistry
Harmattan Semester Examination 2017/2018 Session

TIME ALLOWED: 3 HOURS **DATE: AUGUST, 2018**

Instructions:
(i) Answer Each Section in a Separate Booklet
(ii) Answer ALL Questions in Section A and ANY THREE (3) Questions in Section B.

SECTION A

QUESTION 1

a. Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of m-chlorobenzyl and p-toluenesulphonate from the data below.

Temp (°C)	$k \times 10^5$, s^{-1}
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

b. Explain the difference in values of σ_m and σ_p for each of the following groups in terms of the electronic character of each group.

Substituent	σ_m	σ_p
$NHCOCH_3$	+0.21	0.00
F	+0.337	+0.062
Cl	+0.373	+0.227

c. Match ρ values with the appropriate reaction:

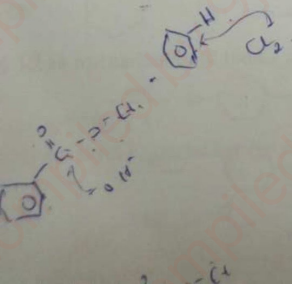
ρ = -3.3, -8.06, +1.00, +2.61

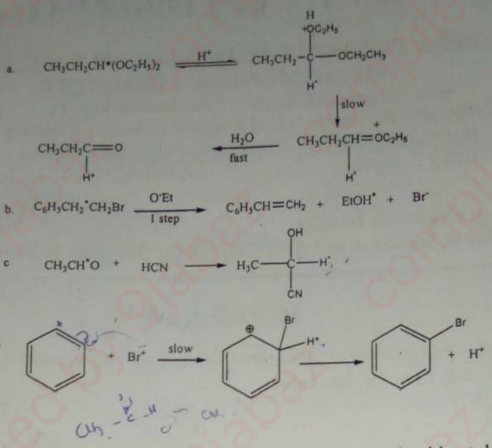
i. $ArCH_2CO_2Et + OH^- \rightarrow ArCH_2CO_2^- + EtOH$
ii. $ArNMe_2 + MeI \rightarrow ArNMe_3^+I^-$
iii. $ArCO_2Et + OH^- \rightarrow ArCO_2^- + EtOH$
iv. $ArH + Cl_2 \rightarrow ArCl + HCl$

QUESTION 2

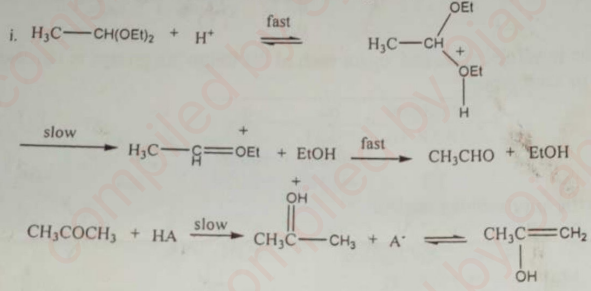
a. i. What are the two main modes of studying reaction kinetics? Explain how each of these is carried out.
ii. Which of the two is often preferred and why?

b. Predict and explain whether normal, inverse, or no isotope effects will be observed for each reaction below. Indicate any reactions in which you expect $K_H/K_D > 2$





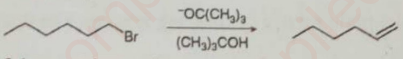
c. Classify the following reactions as either specific or general acid catalysis



SECTION B

QUESTION 3

a. Consider the following E2 reaction:



i. Draw the by-products of the reaction and use curved arrows to show the movement of electrons

ii. What happens to the reaction rate with each of the following changes?

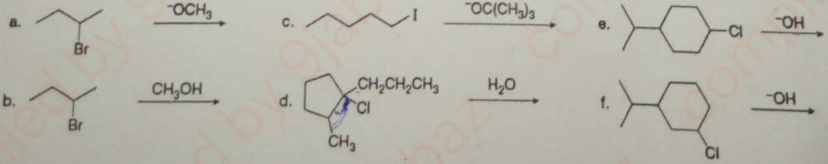
(a) The solvent is changed to DMF (dimethylformamide)

(b) The concentration of $(CH_3)_3CO^-$ is decreased

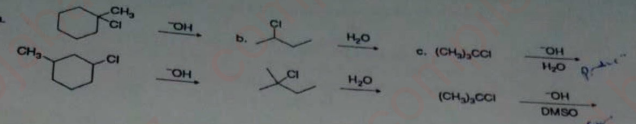
(c) The base is changed to HO^-

(d) The halide is changed to $CH_3CH_2CH_2CH_2CH(Br)CH_3$

b. Draw all constitutional isomers formed in each elimination reaction. Label the mechanism as E1 or E2



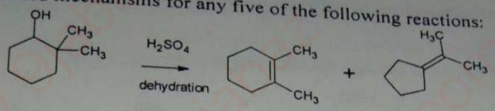
c. Which elimination reaction in each pair is faster?



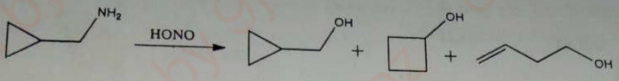
QUESTION 4

Provide detailed mechanisms for any five of the following reactions:

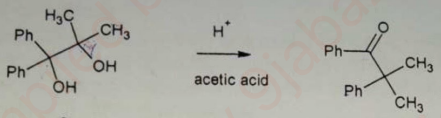
(i)



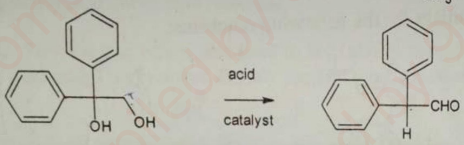
(ii)



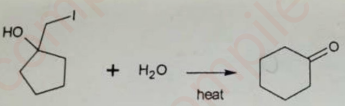
(iii)



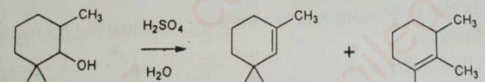
(iv)



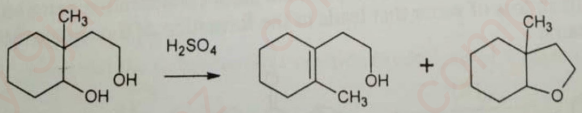
(v)



(vi)

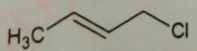
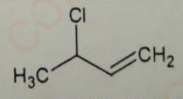


(vii)



QUESTION 5

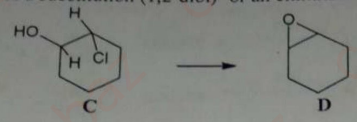
Give a brief explanation for each of the following experimental observations:

(a)  affords the same products as  with aqueous NaOH

(b) Mustard gas, $ClCH_2CH_2SCH_2CH_2Cl$, is hydrolyzed to $ClCH_2CH_2SCH_2CH_2OH$ much more rapid than that expected for a primary alkyl halide.

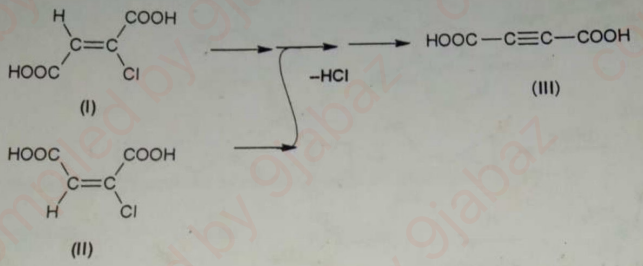
(c) In the reaction $CH_3CH_2CH_2\text{-}Br + H_2O \longrightarrow$: , increase in solvent polarity enhances rate o reaction.

(d) The reaction of the chloro-alcohol **C** with base ($^-$**OH**) gave the epoxide **D** as the organic product, instead of a substitution (1,2-diol)- or an elimination (alkene)- product:



C **D**

(e). The elimination reaction of trans-chloromaleic acid (I) occurs 50 times faster than cis- chloromaleic acid (II) to give acetylenedicarboxylic acid (III):

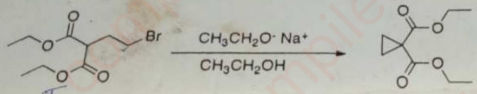


(I) (II) (III)

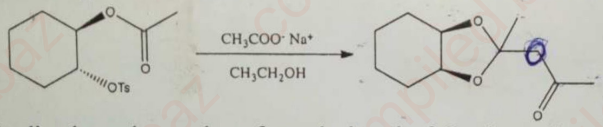
QUESTION 6

a. *Propose a generally acceptable mechanism for the following reactions:*

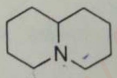
i.



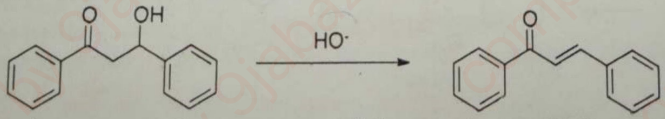
ii.



b. Predict the major products formed when the following amines undergo exhaustive methylation, followed by treatment with Ag_2O and heating.

i. 2-methylpiperidine ii. *N*-ethylpiperidine iii.  iv.  v. 

c. The E1cB mechanism is involved in one of the key steps in the aldol condensation reaction, specifically the step that results in loss of water that leads to the formation of the alkene from the ald as shown in the following scheme



Describe, using arrows to show movement of electrons, how an E1cB mechanism will lead to the elimination of water in the scheme presented above.

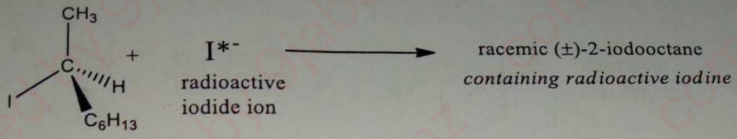
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
BSc (CHEMISTRY) DEGREE EXAMINATION, 2016/2017
CHM 407: FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY
AUGUST 2017
TIME ALLOWED: 3 HOURS

INSTRUCTIONS: ANSWER SECTION A & B IN SEPARATE BOOKLETS

SECTION A: Answer question 1 and 2 and any one between question 3 or 4

QUESTION 1

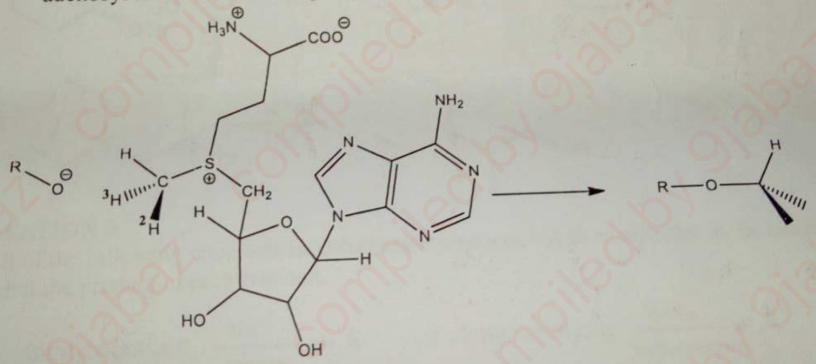
a. In one of the classic experiments used to explore the stereochemistry of the SN2 reactions, two different rates were measured for the reaction shown below.



(s)-(+)-2-iodooctane

Radioactive iodide ion was used to measure the rate at which iodine was substituted in (s)-(+)-2-iodooctane. The rate at which the starting alkyl halide lost its optical activity, the rate of racemization, was also measured. The rate of racemization is twice the rate of the substitution reaction. Explain these observations.

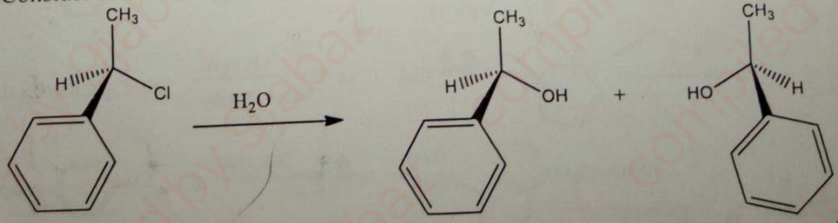
b. The reaction below was used to help clarify the SN2 nature of the alkylation reactions of S-adenosyl methionine. Briefly explain what the results tell us about the mechanism.



^3H = Titrium (T)

^2H = Deuterium (D)

c. Consider the following SN1 reaction (hydrolysis of 1-chloro-1-phenylethane)



(41 % retention) (59 % inversion)

Explain why there is a slight excess of inversion instead of the expected racemeization

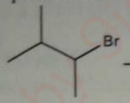
d. Predict the effect on rate of the change indicated in each of the following and give the basis for your prediction

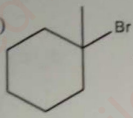
i. Change to a more polar solvent in an SN2 reaction between HO^- amd ethyl iodide

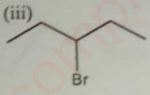
ii. Change of R from CH_3- to $CH_3C{=}O$ in an SN1 reaction of $R(CH_3)CHCl$

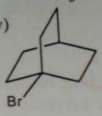
QUESTION 2

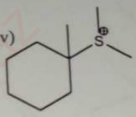
a. Predict the products of the following bimolecular elimination reactions. If more than one product is expected, indicate which will be the major compound formed

(i)  $\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$ J

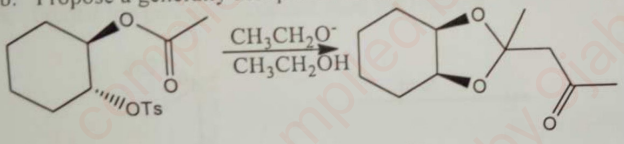
(ii)  $\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$ K

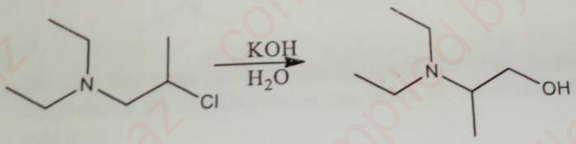
(iii)  $\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$ L

(iv)  $\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$ M

(v)  $\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$ N

b. Propose a generally acceptable mechanism for the following reactions

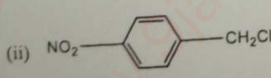




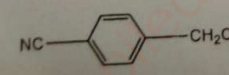
QUESTION 3

Each of the following nucleophilic substitution reactions has been reported in the chemical literature, Predict the product of each reaction.

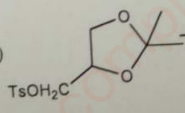
(i) $BrCH_2COOCH_2CH_3 \xrightarrow[\text{acetone}]{NaI}$ A

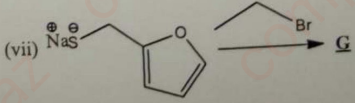
(ii)  $\xrightarrow[CH_3COOH]{CH_3COONa}$ B

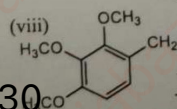
(iii) $CH_3CH_2OCH_2CH_2Br \xrightarrow[\text{ethanol-water}]{NaCN}$ C

(iv)  $\xrightarrow{H_2O,\ HO^-}$ D

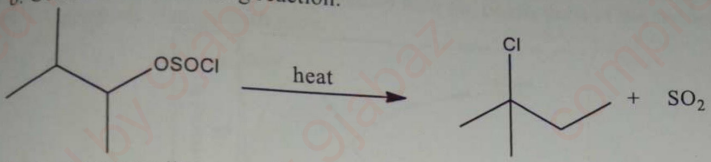
(v) $ClCH_2COOCH_2CH_3 \xrightarrow[\text{acetone-water}]{NaN_3}$ E

(vi)  $\xrightarrow[\text{acetone}]{NaI}$ F

(vii)  G

(viii)  $\xrightarrow{TsCl/pyridine}$ H $\xrightarrow[\text{acetone}]{LiI}$ I

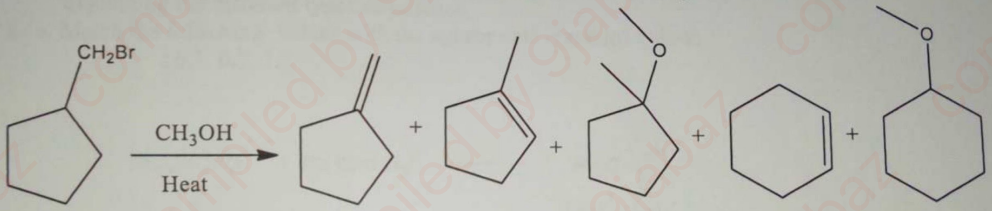
b. Consider the following reaction:



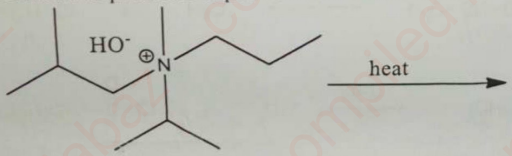
Propose a generally acceptable mechanism for the reaction

QUESTION 4

a. Solvolysis of bromo methylcyclopentane in methanol gives a complex product mixture of the following five compounds. Propose mechanisms to account for these products.

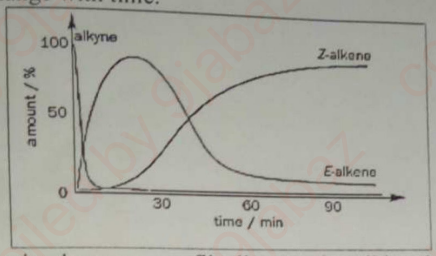


b. Predict the products expected from the reaction



Identify the major product, give the reason for your choice and write a generally acceptable mechanism for the elimination that led to the formation of the major product from the substrate.

b. On addition of HCl to an alkyne (1-phenylpropyne) two geometrical alkene isomers are produced. The graph below shows how the proportions of the starting material and the two products change with time.



Generate a simple energy profile diagram describing the change taking place in this reaction, explaining the different types of product.

8. a. Match the following values with the appropriate reactions below:
: 6.1, 0.7, 1.2

i. $Ph_2C{=}C{=}O + PhHC{=}CH_2^* \longrightarrow Ph_2C(-C(=O)-)-PhHC-CH_2^*$

ii. $H_3C-\underset{H^*}{CH}-Cl + H_2O \longrightarrow H_3C-\underset{H^*}{CH}-OH + HCl$ S_N1 mechanism

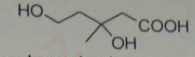
iii. $(CH_3)_2CH^*-C(=O)-CH_3 + OH^- \xrightarrow{\text{slow}} (CH_3)_2C{=}C(O^-)-CH_3 + {}^*H-OH$

b. Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of *m*-chlorobenzyl *p*-toluenesulphonate from the data below:

Temperature (°C)	$k_r \times 10^5$ (s^{-1})
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

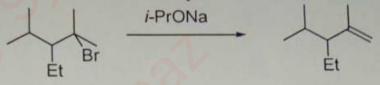
SECTION B: ANSWER QUESTION 5 AND ANY 2 OTHERS

5. a. Mevalonic acid (shown below) can potentially form two possible lactones, however in nature just one these lactones is formed.



i. Show, with mechanism, how lactonization can occur to give both products
ii. Indicate which product if not formed and suggest why.

b. The elimination reaction shown below gives predominantly the terminal olefin. Is this reaction under kinetic or thermodynamic control? Why?



c. Ethyl vinyl ether is hydrolysed in dilute acid according to the following equation:

$CH_3CH_2OCH{=}CH_2 + H_2O \rightarrow CH_3CH_2OH + CH_3CHO$

Given that:
i. The reaction is subject to general acid catalysis
ii. The reaction is faster in H_2O than in D_2O by a factor of 2.93
iii. The ethanol obtained by hydrolysis in isotopically labelled water contains no ^{18}O.

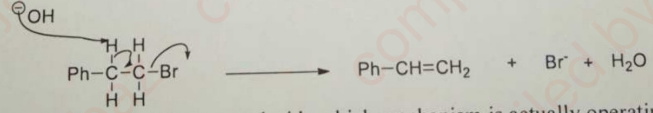
With reasons suggest a mechanism for the hydrolysis which is consistent with these observations. State clearly which step is rate limiting.

d. Match the ρ values with the appropriate reactions. Explain your reasoning.
Reaction constants: **+2.45, +0.75, -2.39, -7.29**.
Reactions:
i) nitration of substituted benzenes
ii) ionization of substituted benzenethiols
iii) ionization of substituted benzenephosphonic acids
iv) reaction of substituted N,N-dimethylanilines with methyl iodide.

6. a. The base-catalysed elimination of 1-bromo-2-phenylethane to 2-phenylethene could proceed by either of the following mechanisms:

i. $PhCH_2CH_2Br \xrightarrow{\text{slow}} PhCH_2\overset{+}{C}H_2 + Br^- \xrightarrow{OH^-} PhCH{=}CH_2$

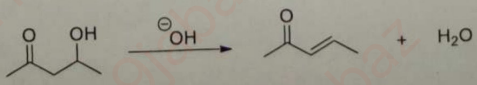
ii.



Outline 2 different experiments to decide which mechanism is actually operating, stating clearly what results you expect.

b. Predict with reason the $\Delta S^{\ddagger}$ for each of the following reactions:
i. in solution
ii.

7. a. Propose two possible mechanistic hypothesis for the following transformation, showing the rate law for each:



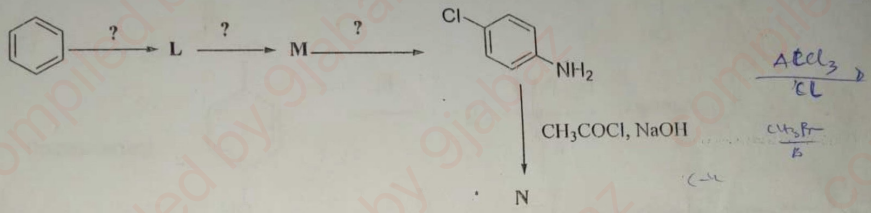
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. (CHEMISTRY) DEGREE EXAMINATION
2016/2017 RAIN SEMESTER EXAMINATION
FERBRUARY 2018
TIME ALLOWED: 3 HOURS

INSTRUCTION: ANSWER SECTIONS A & B IN SEPARATE BOOKLETS

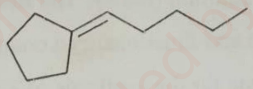
SECTION A

(ANSWER ALL QUESTIONS IN THIS SECTION)

1a. In the scheme below, indicate the missing reagents, intermediates and the product.

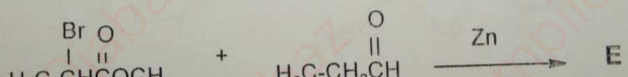


1b. Using the disconnection approach, design a synthesis for the compound below from alcohols with not more than 5 carbons.



2a. Enamines are closely related to enols and enolate ions. Give specific structural example in each case in support of this statement. Comment briefly on the nucleophilic character of the alpha carbon atoms of these nucleophilic reagents. 5 mks

2b. Consider this Reformatsky reaction



(i) Give the structure and the name of the product (**E**),

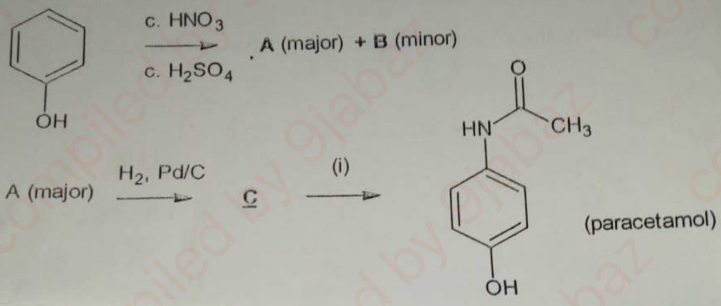
write the structures of compounds **F** - **H** in the following reactions of compound **E**

(ii) E + H_2SO_4/Δ → F

(iii) F + H_2/Pd → G

(iv) G + $LiAlH_4$ → H 5 mks

3a. Write the structures of the lettered compounds and reagent (i) in the following sequence of reactions:

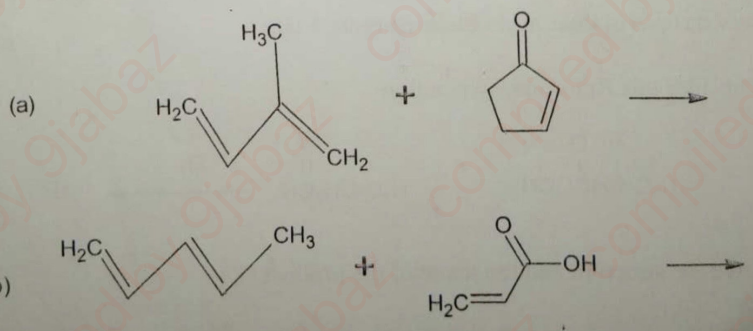


{5 marks}

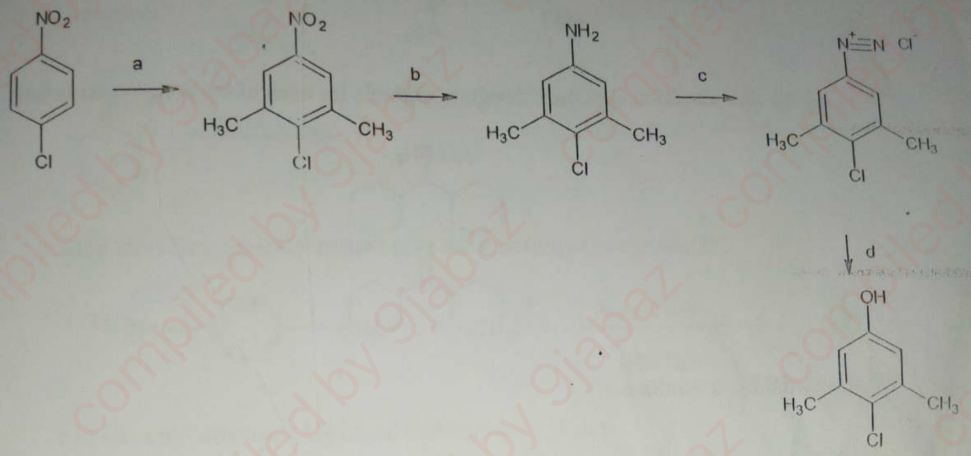
Give a suitable name (as a derivative of phenol) for paracetamol.

3b. What is functional group addition (FGA)? The strategy of FGA is often applied to the synthesis of hydrocarbons and functionalized compounds. Using the disconnection approach, propose a scheme for the synthesis of 2-methylhexane. {5 marks}

4. Draw the product of each of the following Diels-Alder reactions: {2 1/2 marks each}.



4c. Suggest reaction conditions, a-d, (solvents and/or inorganic reagents or other) necessary to carry out the following sequence of reactions:

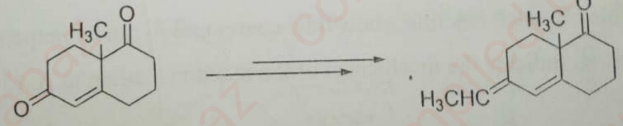


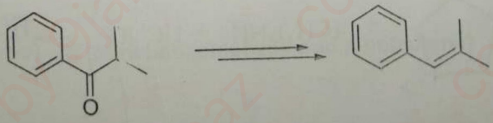
SECTION B

(ANSWER ANY TWO QUESTIONS FOR 30 MARKS)

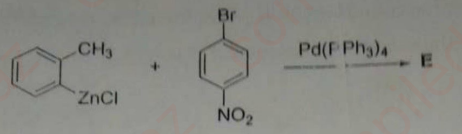
Question 5 (15 Mks)

a. Using equation(s) only, show how you will effect the following transformations indicating the appropriate reagents and intermediates.

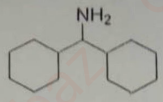
i. 

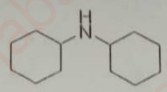
ii. 

b. Predict the product of the reaction below and state the name of this reaction.

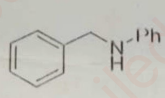


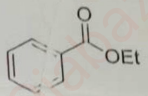
c. Using the disconnection approach, design a synthesis for each of the compounds below:

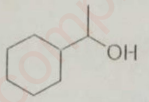
i. 

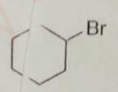
ii. 

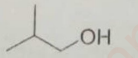
d. How would you synthesize

i. 

from 

ii. 

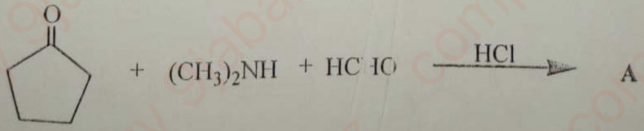
from 

iii. 

from 

Question 6 (15 Mks)

(a) In this Mannich reaction, show how compound **A** can be prepared from the given starting. Indicate the mechanism of the reaction leading to **A**. (5 mks)

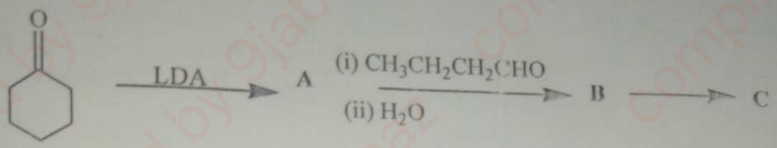


(b) Using malonic ester as a starting reagent, prepare a named aliphatic alpha branched chain monocarboxylic acid? (5 mks)

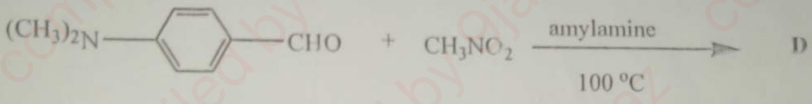
Mbaike Sylvester chm/2017/005

(c) Consider the following condensation reactions:

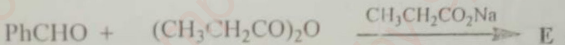
(i) Give the structures of the compounds represented by letters **A - C** in this crossed Aldol reaction.



(ii) In this Knoevenagel reaction; give the structure of compound **D**



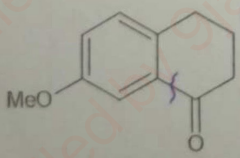
(iii) Give the structure of **E** in the Perkin reaction below



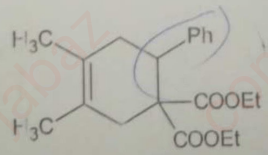
5 mks

Question 7 (15 Mks)

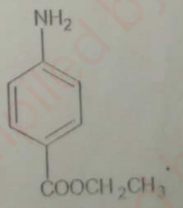
(a) Using the disconnection approach, write out a synthetic route to any one of the following compounds (A, B, C):



A (from methoxybenzene)

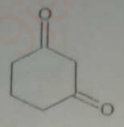


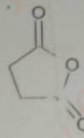
B (from benzaldehyde and a butadiene)



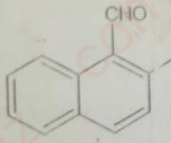
C (from toluene)

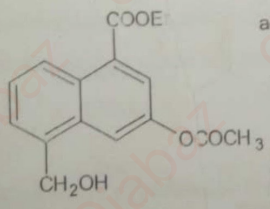
(b) Write the structures of the lettered compounds and reagent (i) in each of the following reactions:

(i)  + CH_3I (1 equiv.) $\xrightarrow{CH^-}$ A $\xrightarrow[\text{(ii) KOH /glycol}]{\text{(i) } 2\ NH_2NH_2}$ B

(ii)  +  $\xrightarrow{AlCl_3}$ C $\xrightarrow{NaBH_4}$ D $\xrightarrow[\text{heat}]{}$ E

(iii)  $\xrightarrow[AlCl_3]{CH_3COCl}$ F $\xrightarrow[AlCl_3]{}$ G

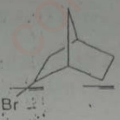
(iv)  + acetic anhydride $\xrightarrow[\text{heat}]{}$ H

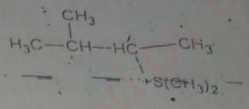
(v)  $\xrightarrow[\text{prolonged heating}]{\text{aq. NaOH}}$ 

$\xrightarrow{NaBH_4}$ J

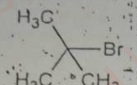
$\xrightarrow[r.t]{H^+ \text{ aq. } Na_2Cr_2O_7}$ K

(f) 

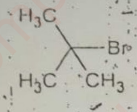
(g) 

(h) 

3. (a) Give short explanations for the following experimental observations:

(i) 

97 % elimination
3 % substitution

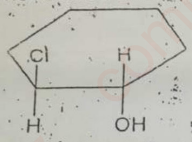
(ii) 

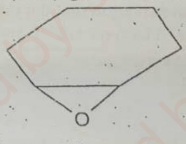
19 % elimination
81 % substitution

(iii) $ClCH_2CH_2SCH_2CH2Cl$ is hydrolyzed much faster than CH_3CH_2Cl

(iv) $CH_3CH{=}CHCl$ is very unreactive toward nucleophiles

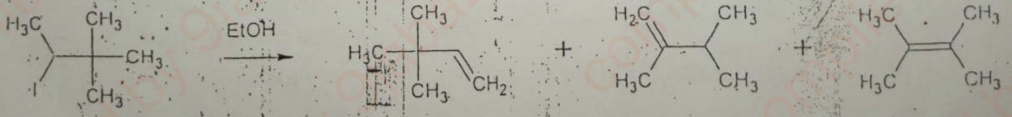
(v) The reaction of compound I with base (EtO^-) gave II as the organic product


(I)


(II)

(b) Use the reaction of an alcohol with thionyl chloride to discuss S_Ni reaction.

4 (a) The solvolysis of 3-iodo-2,2-dimethylbutane with ethanol gives three elimination products in addition to two substitution products as shown below:



(i) Show all the steps involved in the formation of the elimination products.

(ii) Show the structures of the substitution products.

(b) Propose a mechanism for the following reaction:

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

BSc (CHEMISTRY) DEGREE EXAMINATION, 2015/2016

CHM 407: FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY

NOVEMBER 2016 TIME ALLOWED: 3 HOURS

INSTRUCTION: ANSWER SECTIONS A & B IN SEPARATE BOOKLETS

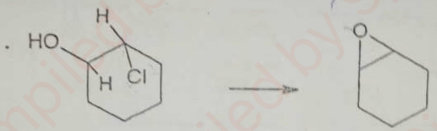
SECTION A

ATTEMPT ALL QUESTIONS IN THIS SECTION

QUESTION 1.

Give short explanations for the following experimental observations:

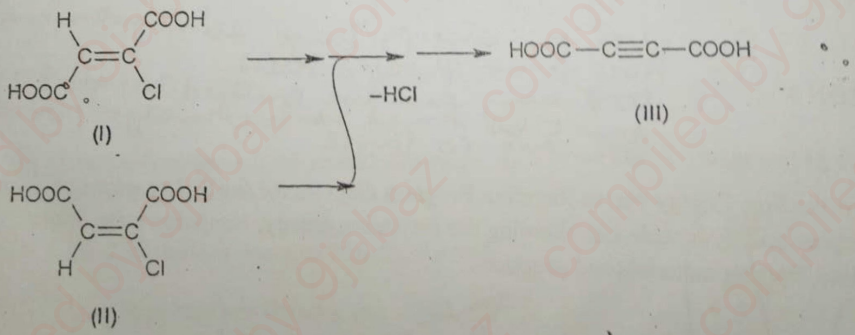
(a) The reaction of the chloro-alcohol **C** with base ($^-$OH) gave the epoxide **D** as the organic product, instead of a substitution 1,2-diol- or an elimination alkene- product:



C D

(b) 2-(Ethylthio)ethyl chloride, $CH_3CH_2SCH_2CH_2Cl$, is hydrolyzed much faster than n-butyl chloride in aqueous ethanol.

(c) The elimination reaction of trans-chloromaleic acid (I) occurs 50 times faster than cis-chloromaleic acid (II) to give acetylenedicarboxylic acid (III):

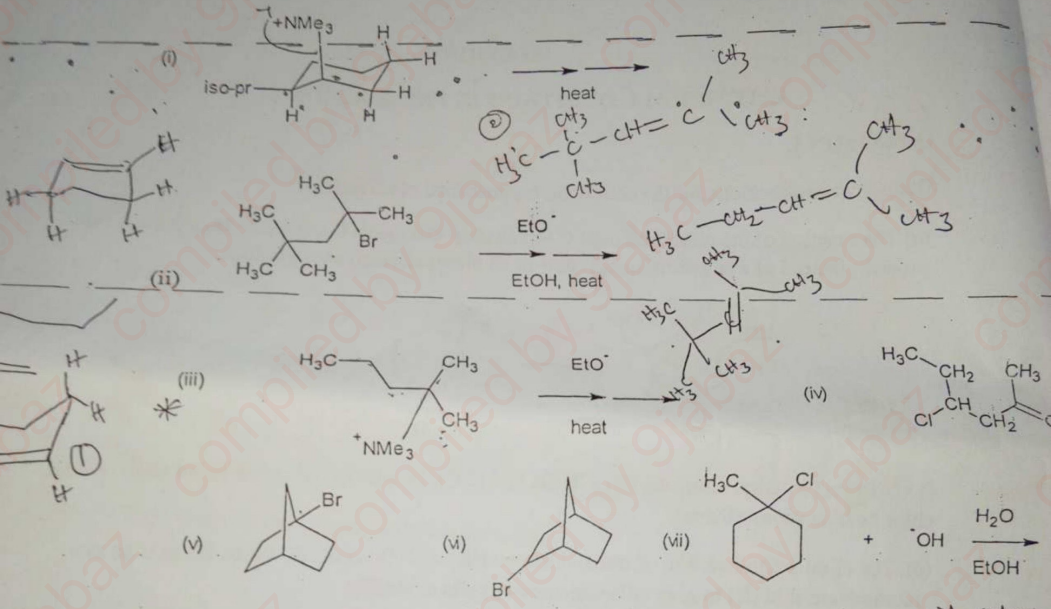


(d) $CH_3CH{=}CHCl$ is very unreactive toward nucleophiles under either S_N1 or S_N2 conditions.

QUESTION 2

(a). State (i) Bredt's rule (ii) Zaitsev's rule (iii) Hofmann's rule; in elimination reactions.

(b). Give the product or products for <u>any six</u> of the following elimination reactions. If more than one product is formed, indicate with brief explanation, which is the major product:



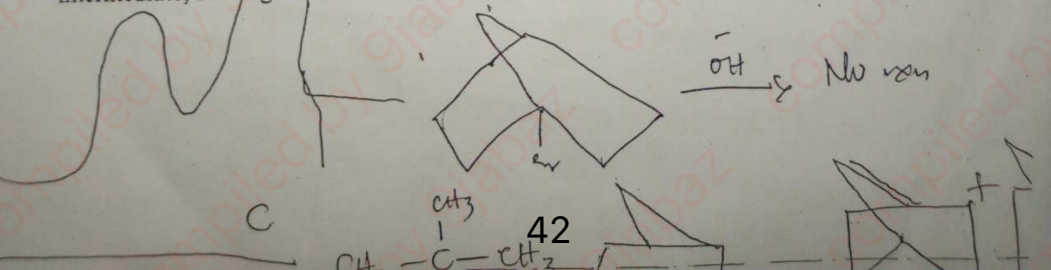
Unless the ring is large elimination cannot take place at the bridged head

will also

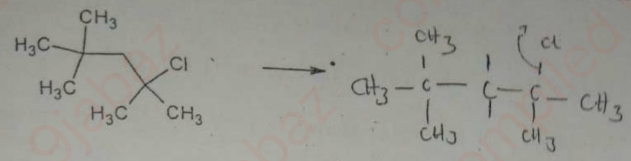
cannot be formed at the bridge position unless the ring is large.

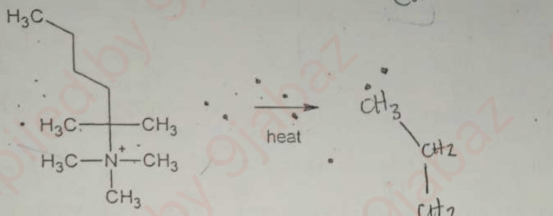
QUESTION 3

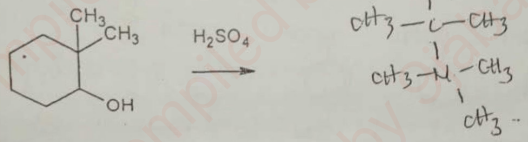
(a). Draw the Free Energy versus Reaction Progress diagram for the S_N1 reaction of 2-bromo-2-methylpropane and hydroxide ion, showing the activation energy, transition state, ionic intermediate, starting materials and products.

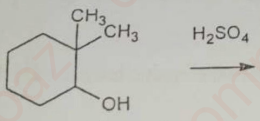


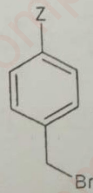
4a. Show the products of the following elimination reactions and indicate which is major:

(i) 

(ii) 

(iii) 

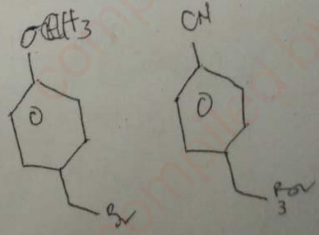
(iii) 



(b) Consider compounds of general structure Z What will be the effect on S_N1 reaction rates when

(i) Z is electron donating (e.g. OCH_3)

(ii) Z is electro withdrawing (e.g. CN)?



SECTION B

Answer question 5 and any 2 others (three questions in all) in this section.

Constants: $R = 8.314\ Jmol^{-1}K^{-1}$; $h = 6.626 \times 10^{-34}\ Js$; $k = 1.38 \times 10^{-23}\ JK^{-1}$

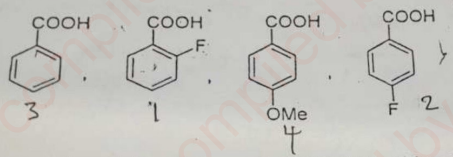
5. a. Calculate the enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the acetolysis of *m*-chlorobenzyl *p*-toluenesulphonate from the data below:

Temperature (°C)	$k_r \times 10^5\ (s^{-1})$
25.0	0.0136
40.0	0.086
50.1	0.272
58.8	0.726

b. Arrange the following in order of decreasing acid strength:

i. $Cl_2CHCOOH$, CH_3CH_2OH, $BrCH_2COOH$, CH_3COOH, $ClCH_2COOH$, C_6H_5OH

ii.



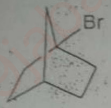
c. Explain why methanol is much more acidic than chloroform in aqueous medium while their acidities are almost identical in the gas phase.

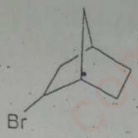
d. Write the rate law that would be expected to describe the kinetic behavior for the following system, where $k_1, k_{-1}, k_3 >> k_2$:

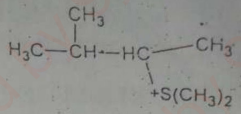
$$C_2H_2Br_2 + R_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2HBr_2^- + R_3NH$$

$$C_2HBr_2^- \xrightarrow{k_2} C_2HBr + Br^-$$

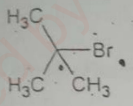
$$C_2HBr + R_3N \xrightarrow{k_3} C_2H\overset{+}{N}R_3 + Br^-$$

(f) 

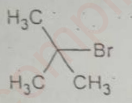
(g) 

(h) 

(a) Give short explanations for the following experimental observations:

(i) 

2nd order conditions → 97 % elimination, 3 % substitution

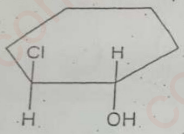
(ii) 

1st order conditions → 19 % elimination, 81 % substitution

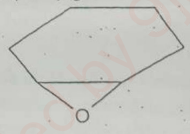
(iii) $ClCH_2CH_2SCH_2CH_2Cl$ is hydrolyzed much faster than CH_3CH_2Cl

(iv) $CH_3CH{=}CHCl$ is very unreactive toward nucleophiles

(v) The reaction of compound I with base (EtO^-) gave II as the organic product



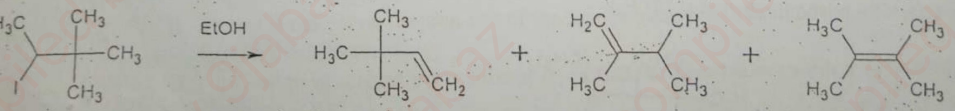
(I)



(II)

(b) Use the reaction of an alcohol with thionyl chloride to discuss S_Ni reaction.

4 (a) The solvolysis of 3-iodo-2,2-dimethylbutane with ethanol gives three elimination products in addition to two substitution products as shown below:



(i) Show all the steps involved in the formation of the elimination products.

(ii) Show the structures of the substitution products.

(b) Propose a mechanism for the following reaction:

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE; NIGERIA

B.Sc (CHEMISTRY) DEGREE EXAMINATIONS, 2013/2014 HARMATTAN SEMESTER, CHM 407-Fundamentals of Physical Organic Chemistry

NOVEMBER 2014 TIME ALLOWED: 3 HOURS

INSTRUCTION: ANSWER ALL QUESTIONS.

ANSWER SECTIONS A & B IN SEPARATE BOOKLETS

SECTION A

1. Assume that the reaction of benzyldiazonium chloride with water to yield benzyl alcohol proceeds by an S_N1 mechanism:

$$PhCH_2N_2^+ \xrightarrow{\text{slow}} PhCH_2^+ + N_2$$

$$PhCH_2^+ \xrightarrow[\text{fast}]{H_2O} PhCH_2OH_2^+$$

(a) Draw an appropriate energy diagram for the process, showing the activation energy, transition states, ionic intermediate, starting materials and product.

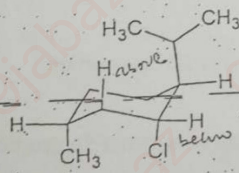
(b) Rationalize the observation that the rate of benzyl alcohol formation is

(i) Decreased by a para-nitro group

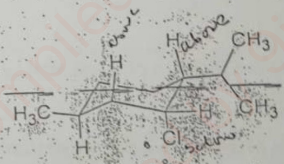
(ii) Increased by a para-methoxy group

2. State (i) Bredt's rule (ii) Zaitsev's rule (iii) Hofmann's rule, in elimination reactions. Predict, with explanations, the elimination products expected in each of the reactions of the following compounds with base (e.g. aq ^-OH), indicating the minor and major ones:

(a)

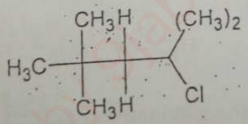


(b)

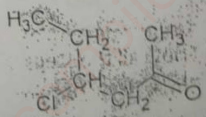


(c) $CH_3CH_2CBr(CH_3)CH(CH_3)_2$

(d)



(e)



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
BSc (CHEMISTRY) DEGREE EXAMINATION
2014/2015 Harmattan Semester

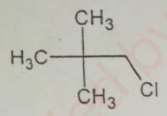
CHM 407: FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY
Time allowed: 3 Hours Date: Oct. 2015
INSTRUCTIONS: Answer each section in a separate booklet.

SECTION A

Answer any three questions in this section.

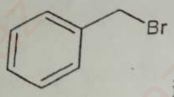
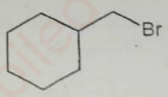
1. Give a brief explanation for the following experimental observations:

(a) Neopentyl chloride (NP) does not react with hot NaOH in ethanol, but reacts with aqueous silver oxide.



NP

(b) Neopentyl alcohol [$(CH_3)_3C\text{-}CH_2\text{-}OH$] reacts with aqueous HCl to give rearrangement products with only a low yield of neopentyl chloride. However, with thionyl chloride ($SOCl_2$), it gives a good yield of neopentyl chloride.

(c)  is more reactive than  toward aqueous NaOH.

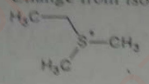
(d) Ethanol does not react with NaBr, but addition of small amount of H_2SO_4 leads to formation of ethyl bromide.

2. a. Draw a well-labeled free energy versus reaction progress diagram for S_N1 reaction of 2-bromo-2-methylpropane and hydroxide anion.

b. Predict the effect on reaction rate of the change indicated in each of the following and give the basis for your prediction:

(i) Change to a more polar solvent in an S_N2 reaction between ethyl iodide and hydroxide anion (OH^-).

(ii) Change from iso-propanol to water in an S_N2 reaction between



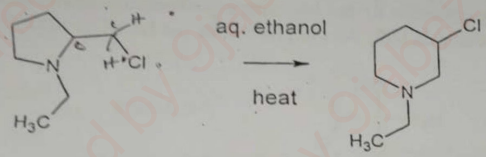
and hydroxide ion

(iii) Change of R from CH_3- to $CH_3C{=}O$ in an S_N1 reaction of

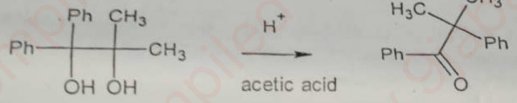
(iv) Change from 2-propanol to propanone as the solvent in S_N1 reaction of 2-chloro-2-methylpropane.

3a. Propose mechanisms for the following reactions:

(i)

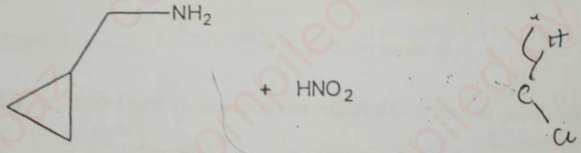


(ii)

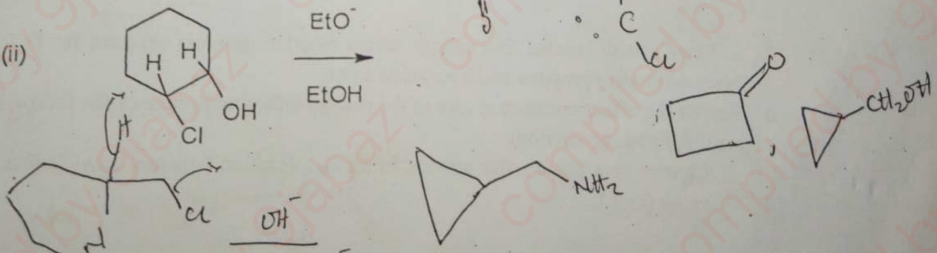


b. Predict all possible products for each of the following reactions:

(i)



(ii)



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE; NIGERIA

B.Sc (CHEMISTRY) DEGREE EXAMINATIONS, 2013/2014 HARMATTAN SEMESTER, CHM 407-Fundamentals of Physical Organic Chemistry

TIME ALLOWED: 3 HOURS

NOVEMBER 2014

INSTRUCTION: ANSWER ALL QUESTIONS.

ANSWER SECTIONS A & B IN SEPARATE BOOKLETS

SECTION A

1. Assume that the reaction of benzyldiazonium chloride with water to yield benzyl alcohol proceeds by an S_N1 mechanism:

$$PhCH_2N_2^+ \xrightarrow{\text{slow}} PhCH_2^+ + N_2$$

$$PhCH_2^+ \xrightarrow[\text{fast}]{H_2O} PhCH_2OH_2^+$$

(a) Draw an appropriate energy diagram for the process, showing the activation energy, transition states, ionic intermediate, starting materials and product.

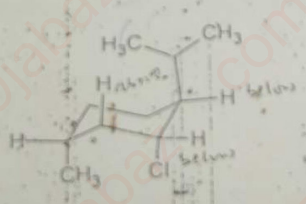
(b) Rationalize the observation that the rate of benzyl alcohol formation is

(i) Decreased by a para-nitro group

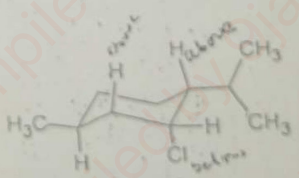
(ii) Increased by a para-methoxy group

2. State (i) Bredt's rule (ii) Zaitsev's rule (iii) Hofmann's rule, in elimination reactions. Predict, with explanations, the elimination products expected in each of the reactions of the following compounds with base (e.g. aq. ^-OH), indicating the minor and major ones:

(a)

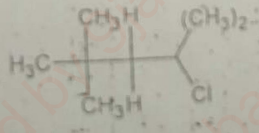


(b)

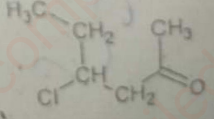


(c) $CH_3CH_2CBr(CH_3)CH(CH_3)_2$

(d)



(e)



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

B.Sc (CHEMISTRY) DEGREE EXAMINATIONS, 2013/2014 HARMATTAN SEMESTER, CHM 407-Fundamentals of Physical Organic Chemistry

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$$PhCH_2N_2^+ \xrightarrow{\text{slow}} PhCH_2^+ + N_2$$

$$PhCH_2^+ \xrightarrow[\text{fast}]{H_2O} PhCH_2OH_2^+$$

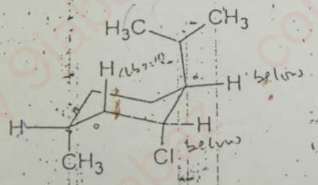
(a) Draw an appropriate energy diagram for the process, showing the activation energy, transition states, ionic intermediate, starting materials and product.

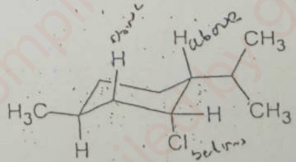
(b) Rationalize the observation that the rate of benzyl alcohol formation is

(i) Decreased by a para-nitro group

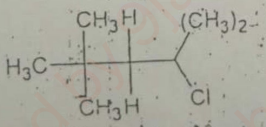
(ii) Increased by a para-methoxy group

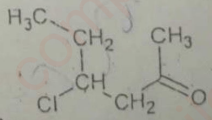
2. State (i) Bredt's rule (ii) Zaitsev's rule (iii) Hofmann's rule, in elimination reactions. Predict, with explanations, the elimination products expected in each of the reactions of the following compounds with base (e.g. aq. ^-OH), indicating the minor and major ones:

(a) 

(b) 

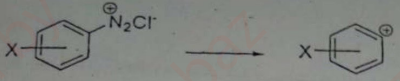
(c) $CH_3CH_2CBr(CH_3)CH(CH_3)_2$

(d) 

(e) 

QUESTION 8

a. The decomposition of aryldiazonium chloride in aqueous HCl, a first order reaction shown below was studied and gave the tabulated data:



Substituent	σ	$k \times 10^7$ (s^{-1})
m-CH_3	-0.07	3400
H	0	740
m-Cl	+0.37	31
m-NO_2	+0.71	0.69
p-OCH_3	-0.27	–

i. Calculate the Hammet reaction constant

ii. compute the rate constant for *p*-OCH_3

b. a. Match the following $\frac{k_H}{k_D}$ values with the appropriate reactions below:

$\frac{k_H}{k_D}$: 6.1, 0.8, 1.3

i. $CH_3CH^*O + H_2O \xrightarrow{0.8} H_3C-\overset{OH}{\underset{OH}{C}}-H^*$

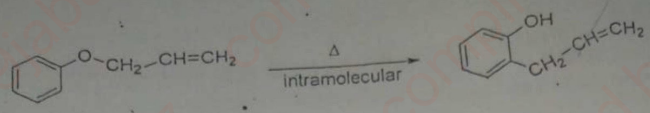
ii. $H_3C-\underset{H^*}{CH}-Cl + H_2O \xrightarrow{6.1} H_3C-\underset{H^*}{CH}-OH + HCl$ S_N1 mechanism

iii. $(CH_3)_2CH^*-\overset{O}{C}-CH_3 + OH^- \xrightarrow{\text{slow}} (CH_3)_2C=\overset{O^-}{C}-CH_3 + H^*-OH$

$\log\left(\frac{k_{CH_3}}{k_H}\right) = \rho\sigma$ 6.66 =

$\log \frac{k_{NO_2}}{k_H} = \rho\sigma$

$\log 0.69 = \rho \times 0.71$

ii. 

five

QUESTION 6

a. The elimination reaction of 2-bromopropane could proceed by either of the following mechanisms:

i) $(CH_3)_2CHBr + C_2H_5O^-Na^+ \longrightarrow CH_3CH=CH_2 + C_2H_5OH + NaBr$ ✓ 1 step

ii) $(CH_3)_2CHBr \xrightarrow{slow} (CH_3)_2\overset{\oplus}{C}H \xrightarrow{C_2H_5O^-Na^+} CH_3CH=CH_2 + C_2H_5OH + NaBr$

Experimentally, the primary deuterium isotope effect, $\frac{k_H}{k_D}$, for the reaction is 6.9 at 25 °C, which of the 2 mechanisms is correct and why?

b. Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

Specific — does not depend on the pH of undissociated acid.

i. $CH_3CH(OEt)_2 + H^+ \overset{fast}{\rightleftharpoons} H_3CHC(\overset{\oplus}{O}HOEt)OEt \xrightarrow{slow} H_3CHC=\overset{\oplus}{O}Et \xrightarrow{fast} CH_3CHO + EtOH$

General.

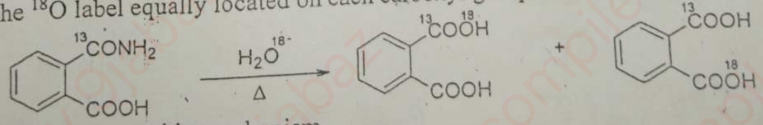
ii. $CH_3COCH_3 + HA \xrightarrow{slow} CH_3\overset{\oplus}{C}OHCH_3 + A^- \xrightarrow{fast} CH_3C=CH_2$ (OH)

depends on the conc and undissociated acid.

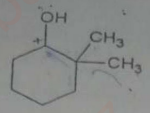
QUESTION 7

a. Maleic anhydride reacts with furan to give two possible tricyclic products: a sterically crowded endo product **P** and/or a less crowded exo product **Q**. Under some specific laboratory conditions, **P** is obtained exclusively as the product of this reaction. Using a simple energy profile diagram, illustrate the reaction paths and explain what type of control is in effect.

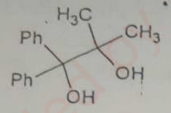
b. Hydrolysis of ^{13}C labeled *o*-phthalamic acid in water enriched in ^{18}O gives phthalic acid with the ^{18}O label equally located on each carboxyl group as shown below.

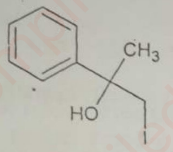


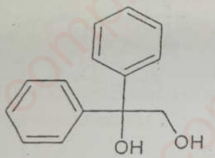
Explain with a reasonable mechanism.

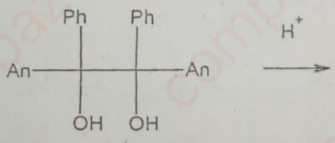
(i)  H_2SO_4, dehydration → two **major** and four **minor** alkenes

(ii)  + HONO → two alkenes + two alcohols

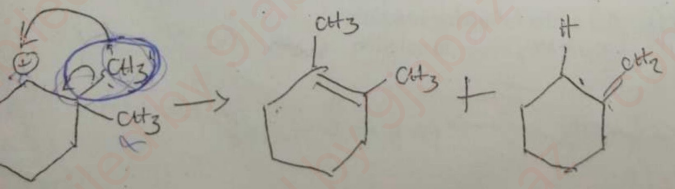
(iii)  H^+, acetic acid → ketone

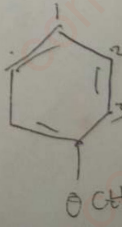
(iv)  + aq $AgNO_3$ → ketone

(v)  acid catalyst → aldehyde

(vi)  H^+ →

(An = 4-methoxyphenyl)





SECTION B: Answer question 5 and any 2 others (3 questions in all)

QUESTION 5

a. Write the rate law that would be expected to describe the kinetic behavior for the following system, where $k_1, k_{-1}, k_3 >> k_2$:

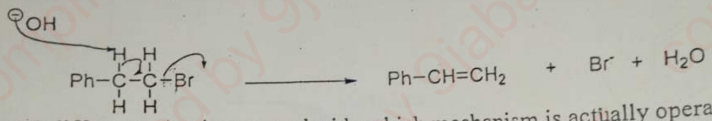
$$C_2H_2Br_2 + R_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2HBr_2^- + R_3NH^+$$

$$C_2HBr_2^- \xrightarrow{k_2} C_2HBr + Br^-$$

$$C_2HBr + R_3N \xrightarrow{k_3} C_2HNR_3^+ + Br^-$$

b. The base-catalysed elimination of 1-bromo-2-phenylethane to 2-phenylethene could proceed by either of the following mechanisms:

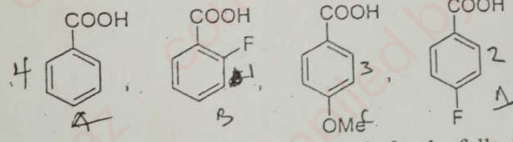
i. $PhCH_2CH_2Br \xrightarrow{slow} PhCH_2\overset{+}{C}H_2 + Br^- \xrightarrow{OH^-} PhCH=CH_2$

ii. 

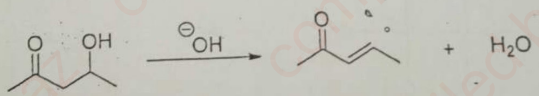
Outline 2 different experiments to decide which mechanism is actually operating, stating clearly what results you expect.

c. Arrange the following in order of increasing acid strength:

i. $CH_3CH_2CH_2OH$, $CH_3CHClCOOH$, CH_3CH_2COOH, C_6H_5OH

ii. 

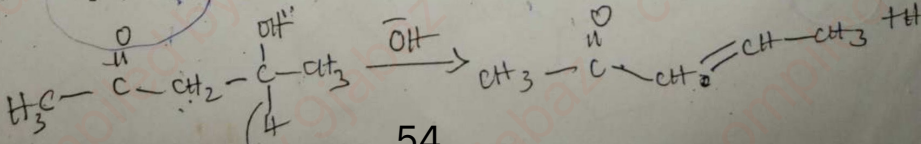
d. Propose two possible mechanistic hypothesis for the following transformation, showing the rate law for each:



e. Explain why methanol is much more acidic than chloroform in aqueous medium while their acidities are almost identical in the gas phase.

f. Predict with reason the $\Delta S^{\ddagger}$ for each of the following reactions:

i. $C_2H_4NO_2^- + H^+ \rightarrow C_2H_5NO_2$ in solution



6. a. The elimination reaction of 2-bromopropane could proceed by either of the following mechanisms:

i) $(CH_3)_2CHBr + C_2H_5O^-Na^+ \longrightarrow CH_3CH{=}CH_2 + C_2H_5OH + NaBr$ 1 step

ii) $(CH_3)_2CHBr \xrightarrow{\text{slow}} (CH_3)_2\overset{\oplus}{C}H \xrightarrow{C_2H_5O^-Na^+} CH_3CH{=}CH_2 + C_2H_5OH + NaBr$

Experimentally, the primary deuterium isotope effect $\frac{k_H}{k_D}$ for the reaction is 6.9 at 25 °C, which of the 2 mechanisms is correct and why?

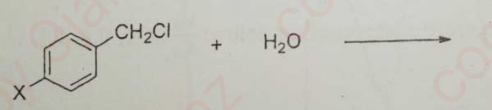
b. Classify the following as either specific or general acid-catalysed. Provide a brief explanation for your choice in each case.

i. $CH_3CH(OEt)_2 + H^+ \overset{\text{fast}}{\rightleftharpoons} H_3CHC(\overset{\oplus}{O}HOEt)OEt \xrightarrow{\text{slow}} H_3CHC{=}\overset{\oplus}{O}Et \xrightarrow{\text{fast}} CH_3CHO + EtOH$

ii. $CH_3COCH_3 + HA \xrightarrow{\text{slow}} CH_3\overset{\oplus}{C}OHCH_3 + A^- \xrightarrow{\text{fast}} CH_3C(OH){=}CH_2$

c. Maleic anhydride reacts with furan to give two possible tricyclic products: a sterically crowded endo product **P** and/or a less crowded exo product **Q**. Under some specific laboratory conditions, **P** is obtained exclusively as the product of this reaction. Using a simple energy profile diagram illustrate the reaction paths and explain what type of control is in effect.

7. a. Given that the Hammet reaction constant, ρ, for the reaction shown below is -1.31. Calculate how much faster *p*-bromobenzyl chloride will solvolyze in water than *p*-nitrobenzyl chloride from the data given.



X	σ
H	0.00
Br	0.23
NO_2	0.78

b. The mechanism of semicarbazone formation from substituted benzaldehyde is shown below:

$$ArCHO + NH_2NHCONH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar-\underset{H}{\overset{OH}{C}}-NHNHCONH_2 \xrightarrow{k_2} ArHC=N-NHCONH_2 + H_2O$$

The Hammet plot is acid dependent. At pH = 7.00, ρ = +0.07, but at pH = 1.75, ρ = +0.91. Explain the difference in ρ values.

c. Explain the wide difference in the values of the substituent constants σ_m and σ_p, which are +0.337 and +0.062 respectively for the F substituent of fluorobenzene.

8. a. Ethyl vinyl ether is hydrolysed in dilute acid according to the following equation:

$$CH_3CH_2OCH=CH_2 + H_2O \rightarrow CH_3CH_2OH + CH_3CHO$$

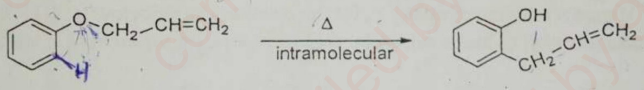
Given that:

i. The reaction is subject to general acid catalysis
ii. The reaction is faster in H_2O than in D_2O by a factor of 2.93
iii. The ethanol obtained by hydrolysis in isotopically labelled water contains no ^{18}O.

With reasons suggest a mechanism for the hydrolysis which is consistent with these observations. State clearly which step is rate limiting.

b. Predict with reason the $\Delta S^{\ddagger}$ for each of the following reactions:

i. $C_2H_4NO_2^- + H^+ \rightarrow C_2H_5NO_2$ in solution

ii. 

c. Match the following $\frac{k_H}{k_D}$ values with the appropriate reactions below: $\frac{k_H}{k_D}$: 6.1, 0.8, 1.3

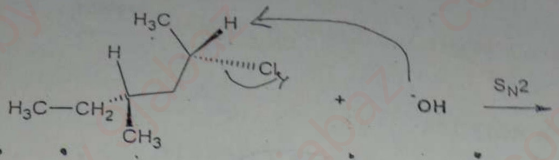
i. $CH_3\overset{H^+}{C}HO + H_2O \xrightarrow{0.8} H_3C-\underset{OH}{\overset{OH}{C}}-H^+$

ii. $H_3C-\underset{H^+}{CH}-Cl + H_2O \xrightarrow{6.1} H_3C-\underset{H^+}{CH}-OH + HCl$ S_N1 mechanism 1·3

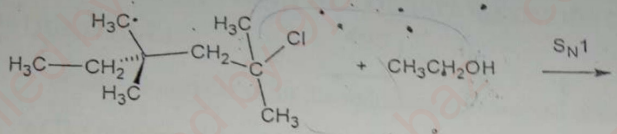
iii. $(CH_3)_2\overset{H^+}{C}-\overset{O}{\overset{\|}{C}}-CH_3 + OH^- \xrightarrow[1.3]{\text{slow}} (CH_3)_2C=\overset{O^-}{\overset{|}{C}}-CH_3 + H^+-OH$

(b). Show the product, including stereochemistry, of any one of the following substitution reactions:

(i)



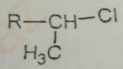
(ii)



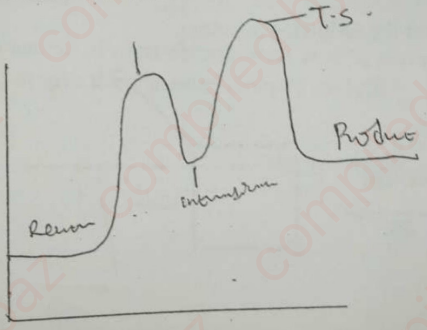
©. Predict the effect on rate of the change indicated in each of the following and give the basis for your prediction:

(i). Change to a more polar solvent in an S_N2 reaction between ^-OH and ethyl iodide.

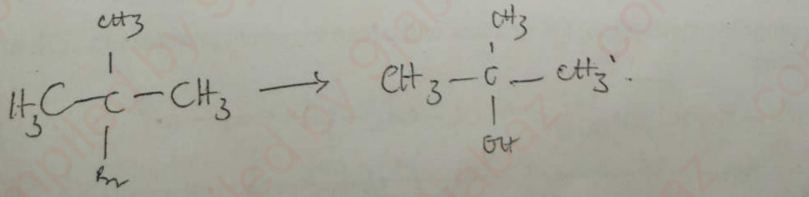
(ii). Change of R from CH_3- to $CH_3C{=}O$ in an S_N1 reaction of



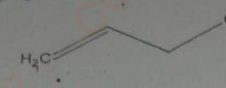
(d). Explain whether the following reactions follow the S_N1 or S_N2 mechanism: **(Answer any three)**.

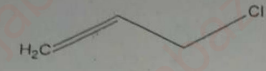


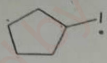
C

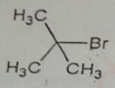


Predict the Product

(i)  + $CH_3\ddot{O}H$ ⟶

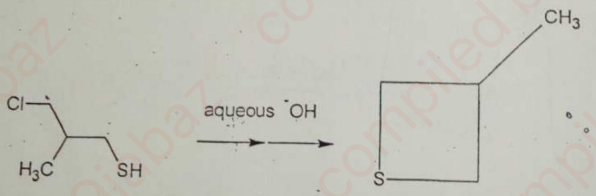
(ii)  + CH_3COO^- ⟶ (acetone)

(iii)  + ^-SH ⟶ (DMF)

(iv)  + CH_3COO^- ⟶ (acetic acid)

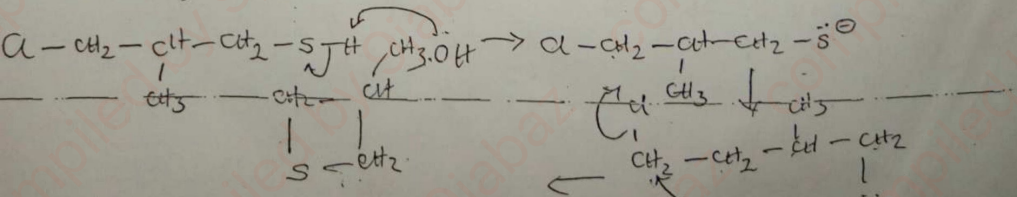
QUESTION 4

(a) Propose a mechanism for the following reaction:



(Answer (i) & (ii) and any other two)

b) Predict (with appropriate mechanism) the structure of the rearrangement product/s in each of the following reactions:



Tutorial Set 2

1. The pK_a of phenol is 10.0 while that of meta-nitrophenol is 8.50. Given that the value for ionization of phenol is + 2.11, calculate the value of σ for the nitro group in the meta position.

Which will have a higher ρ value:

i) ionization of substituted benzenephosphonic acids or ionization of substituted benzenethols.

ii) dissociation of benzoic acids in water or the same reaction inbenzene.

2. For the reaction in acetone solution at 75°C;

$$p\text{-}XC_6H_4CH_2CH_2Cl + I^- \longrightarrow p\text{-}XC_6H_4CH_2CH_2I + Cl^-$$

the following data were obtained:

X	K ($M^{-1}.s^{-1}$)	σ
H	1.00	0.00
NO_2	2.62	0.78
CH_3	?	-0.17

a) Calculate the reaction constant ρ.

b) Calculate the rate constant for the reaction with $X \equiv CH_3$

3. Match the ρ values with the appropriate reactions.

a) $ArH + HNO_3 \longrightarrow ArNO_2 + H_2O$ −2.39

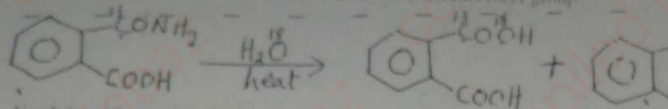
b) $ArSH \longrightarrow ArS^{\ominus} + H^{\oplus}$ 0.75

c) $Ar-P(=O)(OH)-OH \longrightarrow Ar-P(=O)(OH)-O^{\ominus} + H^{\oplus}$ 2.45

d) $Ar-NMe_2 + MeI \longrightarrow ArN^{\oplus}Me_3I^-$ −7.29

ρ: +2.45, +0.75, −2.39, −7.29

1. Hydrolysis of [^{13}C] o-phthalamic acid in water enriched in ^{18}O gives phthalic acid with the ^{18}O label equally located on each carboxyl group



Explain with a reasonable mechanism.

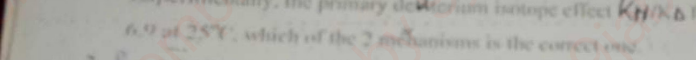
2. The elimination reaction of isopropyl bromide could proceed by either of the following two (2) mechanisms:

(a) $(CH_3)_2CHBr + Na^+\bar{O}C_2H_5 \xrightarrow{1\ step} (CH_3)_2CH^+ + CH_2 + NaBr + C_2H_5OH$

(b) $(CH_3)_2CHBr \xrightarrow{slow} (CH_3)_2\dot{C}H \xrightarrow{Na^+\bar{O}C_2H_5} CH_3 + CHCH_2 + EtOH + NaBr$

Experimentally, the primary deuterium isotope effect k_H/k_D for the reaction is 6.9 at 25°C, which of the 2 mechanisms is the correct one.

3. (a) Arrange the following in order of decreasing acid strength and explain your arrangement briefly.



(b) Arrange in order of decreasing base strength

4. (A) The decomposition of nitramide is catalyzed by bases

$$H_2NNO_2 \xrightarrow{base} N_2O + H_2O$$

The following rates were obtained for a number of bases. Show that they obey the Bronsted catalysis law and determine the value of β for this reaction.

Base	pKa	K_r l.mol-1. min-1
p-toluidine	5.12	1.16
m-toluidine	4.69	0.64
aniline	4.58	0.54
0-toluidine	4.39	0.38
p-chloroaniline	3.98	0.21
m-chloroaniline	3.34	0.081
0-chloroaniline	2.64	0.018

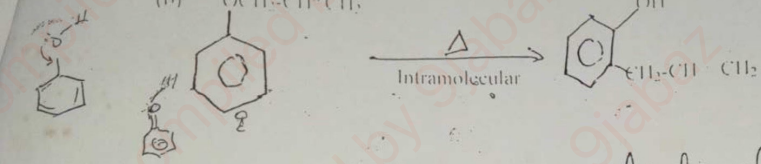
(b) Comment on the magnitude of β for this reaction.

5. Explain why primary heavy atom isotope effects (^{13}C and ^{14}C) are large in SN2 reactions and small in SN1, whereas deuterium isotope effects are small in SN2 and large in SN1 reactions.

Bcos of the crowding in the transition state w.r.t alternate the bending freq. relief.

6. Predict the sign of $\Delta S^{\ddagger}$ for each of the following reactions.

(a) $C_2H_4NO_2^- + H^+ \longrightarrow C_2H_5NO_2$ in solution

(b) 

* Isotope effects are greatest when, in the transition state, the hydrogen is symmetrically bonded to the atoms blw which it is being transferred.

* Isotope effects are at a max when the hydr ~~is symmetrically bonded to the atoms b~~ in the transition state is on the straig line connecting the two atoms blw wc d Hydrogen is being transferred & that for sufficiently non linear Conf gurations they decrease to $k_H/k_D = 1$

* The cause of β isotope effect has been a mat of much controversy, but they are most lik due to hyperconjugation effects in the tra ion state.

$-\log k_a = pK_a$

Table 3.1 lists pK_a values for a selection of acids relative to water as the solvent. The values in the middle pK_a range of the table are the most accurate because they can be measured strength.

TABLE 3.1 Relative Strength of Selected Acids and Their Conjugate Bases

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	$HSbF_6$	< -12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	-3.8	$(CH_3)_2O$	
	$(CH_3)_2C{=}\overset{+}{O}H$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF_3CO_2^-$	
	HF	3.2	F^-	
	CH_3CO_2H	4.75	$CH_3CO_2^-$	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3C\bar{O}CHCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	C_6H_5O-	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3CCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest base

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA.
B.Sc (CHEMISTRY) DEGREE EXAMINATION.
HARMATTAN SEMESTER, 1999/2000 SESSION.

CHM 407: FUNDAMENTALS OF PHYSICAL ORGANIC CHEMISTRY.

OCTOBER, 2000. TIME ALLOWED: 3 HOURS.

INSTRUCTIONS: Answer ALL Questions. Answer each section in a separate booklet.

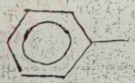
SECTION A

1. Rationalize the following experimental observations:

(a) An alcohol, R-OH, does not react with NaBr, but addition of small amount of H_2SO_4 leads to the formation of R-Br (a bromoalkane).

(b) $CH_2=CH^*CH_2Cl$ (*C represents radioactive carbon) reacts with a nucleophile, under S_N1 conditions, to afford a product P, which upon ozonolysis gave methanal which contains both C and *C.

(c) $CH_3CH=CHCl$ is very unreactive toward nucleophiles under either S_N1 or S_N2 conditions.

(d)  is more reactive than  toward aqueous NaOH.

2. Write brief discussions on the following topics:

(a) Neighboring group participation

(b) Ion-pairs in S_N1 mechanism

(c) Zaitsev's rule for elimination

(d) Effect of solvent polarity in S_N2 reactions.

3. (a) When $ClCH_2CH(CH_3)CH_2SH$ is warmed in dilute alkali, a cyclic sulfur-containing compound, C_4H_8S, is formed.
Suggest a structure and mechanism for its formation.

(b) Predict all possible products for the reaction between  and HNO_3.

4 (a) Suggest mechanistic explanation, with equations if necessary, for each of the following experimental observations:

(i) $ClCH_2CH_2SCH_2CH_2Cl$ is hydrolyzed to $ClCH_2CH_2SCH_2CH_2OH$ much more rapidly than that expected for a primary alkyl halide.

(ii) $(CH_3)_3C\text{-}CCl(CH_3)_2$ hydrolyzes much faster than t-butyl chloride.

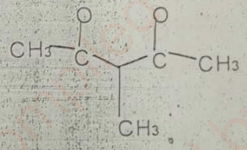
(iii) Hydrolysis of R-2-bromopropanoic acid in aqueous NaOH solution (S_N2) leads to a product with the same configuration as the starting material.

(b) With a β-halo acid such as $BrCH_2CH_2COOH$ is warmed with base, elimination occurs involving loss of both the carboxyl group (COOH) and the halide ion, to give an alkene (in this case, ethene). Suggest a mechanism for this process on the basis of a stereospecific trans-elimination.

5 (a) List 5 different methods of investigating organic reaction mechanisms, and briefly discuss one of them.

(b) Predict the sign of ΔS° for each of the following reactions.

(i) $C_2H_4NO_2^- + H^+ \longrightarrow C_2H_5NO_2$ (in solution).

(ii) $CH_3COCHCH_3$ (with CH_3) $+ H_2O \longrightarrow$  (in solution)

(iii)