

Ollscoil *na* hÉireann, Gaillimh
National University of Ireland, Galway

Autumn Examinations 2002

SECOND YEAR CHEMISTRY

ORGANIC CHEMISTRY (CH202)

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Time Allowed: Two Hours

Answer Four questions: Two from Section A and Two from Section B.

Use separate Answer Books for Section A and Section B.

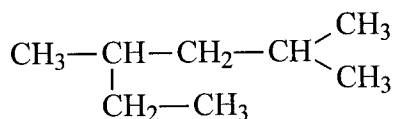
All questions carry 25 marks distributed as shown. For a question with a choice between parts all parts of that question carry equal marks.

Leave the front page of the Answer Book blank and clearly list on it the numbers of the questions attempted.

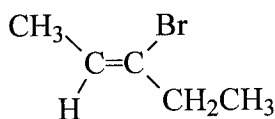
Section A

1. Answer each of the following:

- (i) Name the molecules (A) and (B) and explain how you determined the names:



(A)

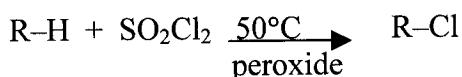
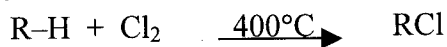


(B)

[6 marks]

- (ii) Discuss the industrial importance of the alkanes and comment on the performance of alkanes as combustion fuels. [7 marks]

- (iii) Explain why alkanes were once called “paraffins”. Describe the main features of a chain reaction and show how an alkane can be converted to an alkyl chloride by treatment with Cl_2 at high temperatures ($\sim 400^\circ\text{C}$) (or under UV irradiation) or by treatment with sulfuryl chloride (SO_2Cl_2) at low temperatures ($\sim 50^\circ\text{C}$) in the presence of benzoylperoxide.

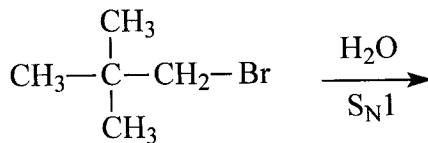


[12marks]

2. Answer each of the following:

- (i) Explain the $\text{S}_\text{N}2$ mechanism in the substitution reactions of alkyl halides and evaluate the experimental evidence on which it is based. [11 marks]

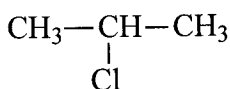
- (ii) Name compound (A) and write and explain the product from an $\text{S}_\text{N}1$ reaction of (A) with water.



(A)

[7 marks]

- (ii) Compound (B) could react with a nucleophile by either an $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ pathway. Propose and explain experimental conditions which would favour each pathway.

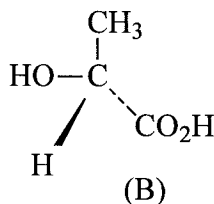
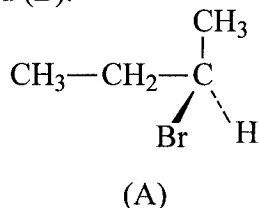


(B)

[7 marks]

3. Answer any three of the following [8.3 marks each]

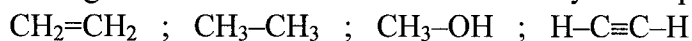
- (i) Explain the terms “enantiomer”, “racemic mixture” and “specific rotation”. Explain the R and S naming system and assign R or S designations to the molecules (A) and (B).



- (ii) Explain the influence of the alkene double bond on the chemical reactivity of bonds α and β to it and comment on the relative reactivity of the molecules vinyl chloride and allyl chloride in S_N reactions.



- (iii) Place the following molecules in the order of their acidity and explain your choice:



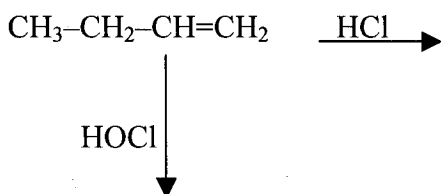
- (iv) Write a brief explanatory note on the hydroboration of alkenes.

- (v) Explain the terms “transition state”, “intermediate” and briefly discuss the use of potential energy diagrams to represent reaction mechanisms.

4. Answer each of the following:

- (i) Explain the mechanism of the addition reaction of Br_2 with the alkene double bond and discuss the evidence for it. [8 marks]

- (ii) Briefly discuss and explain the “Markovnikov rule” for the addition reactions of alkenes. Illustrate your discussion by showing of the products the following reactions and commenting on the intermediates involved.



[8 marks]

- (iii) An alkene of formula C_6H_{10} when treated with hydrogen gas over palladium gave an alkane of formula C_6H_{14} . Ozonolysis of one mole of the alkene followed by oxidation of the ozonide gave one mole each of methanoic acid (formic acid, HCO_2H), ethanoic acid (acetic acid, $\text{CH}_3\text{CO}_2\text{H}$) and 1,3-propanedioic acid (malonic acid, $\text{CO}_2\text{H}-\text{CH}_2-\text{CO}_2\text{H}$). Identify the alkene C_6H_{10} and explain your answer.

[9 marks]

Section B

5. Draw and name the products of the reaction of benzene (C_6H_6) with the following reagents:

- (i) Bromine and iron (III) bromide ($Br_2/FeBr_3$) [5 Marks]
- (ii) Sulfuric acid and sulfur trioxide (H_2SO_4/SO_3) [5 Marks]
- (iii) Acetyl chloride and aluminium (III) chloride ($CH_3COCl/AlCl_3$) [5 Marks]
- (iv) Nitric acid and sulfuric acid (HNO_3/H_2SO_4) [5 Marks]

Show the mechanism for the transformation in part (iv) [5 Marks]

6. Answer any two of the following:

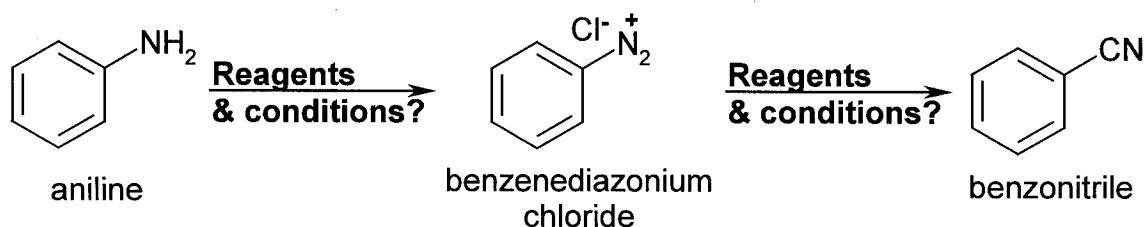
- (i) Explain with examples each of the following types of isomerism:
 - (a) Structural [4 Marks]
 - (b) Geometrical [4 Marks]
 - (c) Optical [4.5 Marks]

- (ii) Show how methylmagnesium iodide (CH_3MgI) may be prepared in the laboratory. [2.5 Marks]

Show the product formed by reaction of excess of this Grignard reagent with

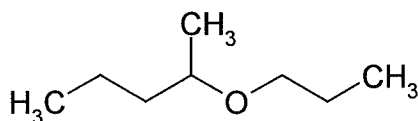
- (a) Carbon dioxide (CO_2) [5 Marks]
- (b) Methyl benzoate ($C_6H_5CO_2CH_3$) [5 Marks]

- (iii) Show how the following transformations may be accomplished [5 Marks each]
How might aniline be prepared from benzene? [2.5 Marks]



7. Describe briefly the Williamson and alkoxymercuration–demercuration syntheses of ethers. [16 Marks]

Using the former method how would you synthesise the ether shown below. [5 Marks]



What is the name of the above ether? [4 Marks]