

THE NATIONAL UNIVERSITY OF IRELAND, GALWAY

SUMMER EXAMINATION 1999

SECOND SCIENCE EXAMINATION

CHEMISTRY
THIRD PAPER

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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 equal marks. 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

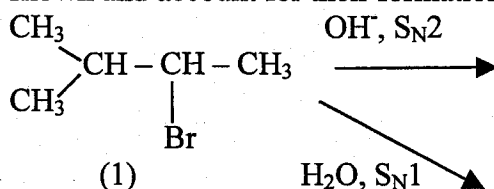
1. Answer any three of the following:

- Briefly discuss the industrial importance of the alkanes and comment on fuel performance.
- Perform a conformational analysis of the 2,3-bond of n-butane.
- Briefly explain how single C-C bonds can be made in organic synthesis and comment on the Wurtz and Corey-House reactions.
- Draw structures for the products of the following reaction and account for their formation.

$$\text{CH}_3\text{-CH}_2\text{-CH}_3 \xrightarrow[\text{h}\nu]{\text{Cl}_2}$$
- Briefly explain the use of potential energy diagrams to represent reaction mechanisms.

2. Answer two of the following:

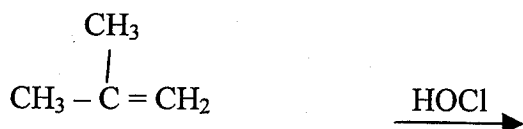
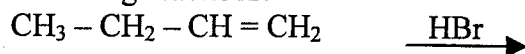
- Compare and contrast the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reaction mechanisms of alkyl halides.
- Draw the R-form of compound (1), write structures for the products of the reactions shown and account for their formation.



- Assess the importance of S_{N} reactions in organic synthesis
- Explain the influence of solvent polarity in S_{N}^1 and S_{N}^2 reactions.

3. Answer any two of the following:

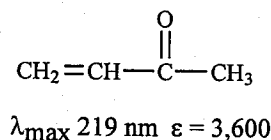
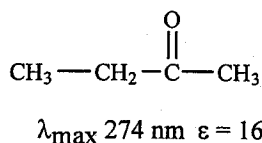
- (a) Explain the term "Markovnikov addition to an alkene". Complete and explain the following reactions:



- (b) Comment on the synthetic importance of the addition reactions of the alkenes.
- (c) Briefly discuss and explain the influence of the C=C bond on the chemical reactivity of nearby bonds in a molecule. Write the following molecules in the order of their reactivity in an S_N1 reaction giving reasons for your choice.
 $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$; $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br}$; $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{Br}$
 (A) (B) (C)
- (d) Compare and contrast the chemical bonding and the molecular structure and dimensions of the molecules, ethane, ethene and ethyne and briefly comment on the main type of reaction undergone by each molecule.

4. Answer all parts

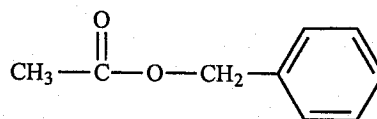
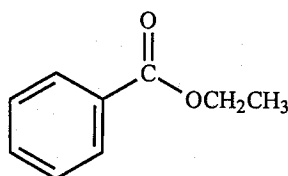
- (i) Explain the effect of introducing conjugation into a molecule on the wavelength of maximum UV absorption, discuss the following molecules in your answer



- (ii) Discuss briefly the value of infrared spectral analysis for the structural determination of organic molecules
- (iii) The significant spectroscopic data for two isomeric esters A and B are given, assign the structures shown to A and B and interpret the data in so far as you can

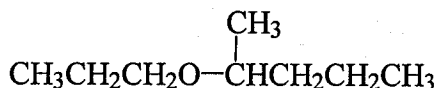
A IR; 1720, 1560, 1480, 750, 700 cm⁻¹:
 UV 264 nm ($\epsilon = 158$):
 MS 150, 108, 91, 65, 51, 43

B IR; 1725, 1608, 1590, 1455, 750, 680 cm⁻¹:
 UV 228 nm ($\epsilon = 10,000$) and 272 nm ($\epsilon = 630$):
 MS 150, 135, 122, 105 (base), 91, 77, 51, 45, 29



Section B

5. Ethers are normally synthesised by either the Williamson synthesis (alkoxide and alkyl halide or sulphonate) or by alkoxymercuration-demercuration (of alkenes). Outline the two methods of syntheses. Using the latter method how would you synthesise the ether?



Name this ether.

6. Write briefly on Grignard reagents under the headings:

- (i) Preparation
- (ii) Structure
- (iii) Reactions where the Grignard reagent functions as a base (e.g. with H_2O , ROH , $\text{R}-\text{C}\equiv\text{C}-\text{H}$) and as a nucleophile (e.g. with carbonyl compounds). How would you prepare triphenylcarbinol, Ph_3COH , using a suitable Grignard reagent and carbonyl compound.

7. In electrophilic aromatic substitution nitrobenzene is meta-activating while phenol is ortho-/para activating. Explain this finding.

Write a brief note on cationic σ -complexes (arenium ions or Wheland intermediates) in electrophilic aromatic substitution.

Show how you would convert benzene into:

- (i) aniline
- (ii) phenol
- (iii) toluene.

8. Answer two of the following:

- (a) Show how a mixture of glycine and alanine can form four different dipeptides.
- (b) Discuss the stereochemistry of the tartaric acids, $\text{HO}_2\text{C}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CO}_2\text{H}$
- (c) Discuss the stereochemistry of the cyclohexane molecule and of monosubstituted cyclohexane derivatives.