

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

Semester 1 Examinations 2001

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.

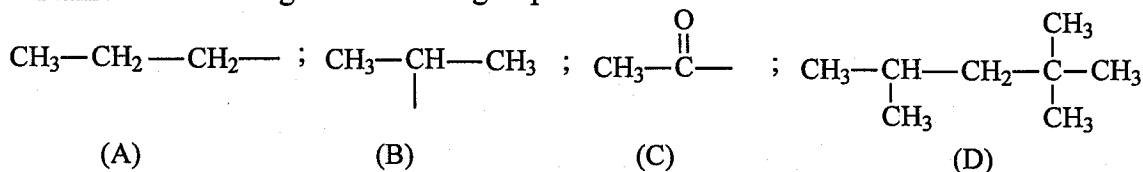
Leave the front page of the Answer Book blank and clearly list on it the numbers of the questions attempted.

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Section A

1. Answer each of the following:

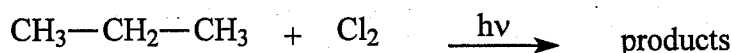
- (i) Name the following molecules or groups:



[5 marks]

- (ii) Explain the importance of the molecule (D) in the fuel industry and comment on fuel performance. [6 marks]

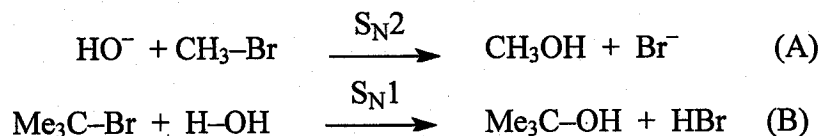
- (iii) Show the main products and explain the mechanism and regiochemistry of the following reaction: [14 marks]



2. Answer (i) and (ii):

- (i) Compare and contrast the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms in the substitution reactions of alkyl halides and summarize the main evidence for each. [15 marks]

- (ii) Comment on the influence of solvent polarity on reaction rates. Suggest how increasing solvent polarity would affect the rates of the reactions (A) and (B).



[10 marks]

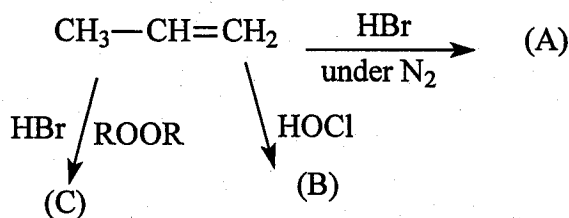
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3. Answer any three of the following: [8.3 marks each]

- (i) Compare and contrast the hybridization of the carbon atoms and the structures of the molecules ethane, ethene and ethyne and comment on the relative acidity of these molecules.
- (ii) Briefly discuss the structures and stabilities of carbocations and carbon free radicals. In your discussion give the preferred structures for the radicals CH_3^\bullet and CF_3^\bullet and give the order of stability of the carbocations CH_3CH_2^+ ; $\text{CH}_3\text{-CH}^+\text{-CH}_3$ and $\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{|}{\text{C}^+}}\text{-CH}_3$
- (iii) Carry out a conformational analysis of the 2,3-bond of n-butane.
- (iv) Draw a portion of the following polymer which contains at least four monomer units and explain the regiochemistry of the monomer links. Describe the possible stereoisomers of the polymer and comment on their physical properties:
- $$\text{CH}_3\text{-CH=CH}_2 \xrightarrow{\text{RO-OR}} \text{Polymer}$$
- (v) Devise a viable synthetic scheme to elongate the chain of n-butane to convert it to n-pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

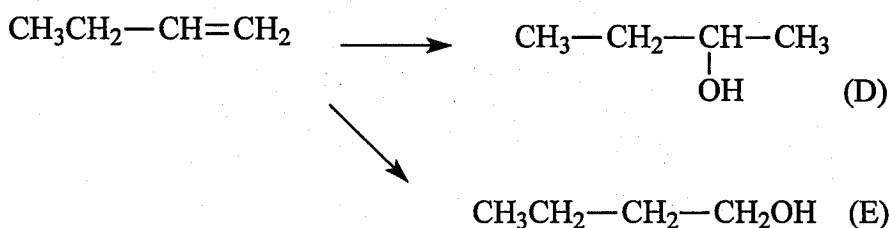
4. Answer each of the following:

- (i) Briefly discuss the synthetic importance of the addition reactions of the alkenes. [8 marks]
- (ii) Draw the products (A), (B) and (C) from the following reactions. Explain the mechanisms and regiochemistry of these reactions.



[10 marks]

- (iii) Suggest any viable routes by which the following conversions could be achieved:



[7 marks]

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Section B

5. One of the most common reactions of aromatic compounds is electrophilic aromatic substitution. For the reaction of toluene ($\text{C}_6\text{H}_5\text{-CH}_3$) with NO_2^+ show the following:

- (i) The three possible *mono*-nitration products of the reaction [5 Marks]
- (ii) The relative distribution of these three possible products [5 Marks]
- (iii) The detailed mechanism by which the transformation occurs [5 Marks]
- (iv) The reason for the observed product distribution [5 Marks]

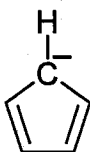
What would be the single major product from reaction of nitrobenzene ($\text{C}_6\text{H}_5\text{-NO}_2$) with NO_2^+ ? [5 Marks]

6. Answer any two of the following:

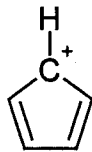
- (i) Draw the two possible isomers of 2-chlorobutane [5 Marks]
Assign each isomer as (R) or (S) configuration [5 Marks]
What interaction with plane polarised light would you expect for each isomer? [2.5 Marks]
- (ii) Show how phenylmagnesium bromide ($\text{C}_6\text{H}_5\text{MgBr}$) may be prepared in the laboratory including all experimental precautions. [8 Marks]
Show the product of reaction of this Grignard reagent with benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$). [4.5 Marks]
- (iii) Define the Huckel rule of aromaticity [4.5 Marks]
Use this rule to predict which of the following four compounds are aromatic. [8 Marks]



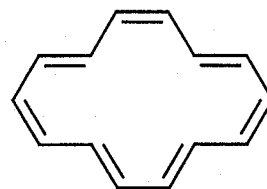
Cyclobutadiene



Cyclopentadienyl anion



Cyclopentadienyl cation



[14] Annulene

7. In the organic laboratory the methods used to synthesise alcohols fall into two categories:

- (i) Reduction and [10 Marks]
- (ii) Addition to alkenes. [10 Marks]

Discuss these methods briefly and give some examples of each type.

Give a method for converting an alcohol to a carboxylic acid.

[5 Marks]

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