GX301

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SEMESTER II, 2000

THIRD UNIVERSITY B.Sc. EXAMINATION IN SCIENCE (INCLUDING DENOMINATED DEGREES)

Paper III: Organic Chemistry (CH311)

Professor R.C.F. Jones
Professor R.N. Butler
and Internal Examiners

Time Allowed: Two Hours
Answer four questions

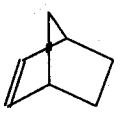
All questions carry equal marks. For a question with a choice between parts, all parts of that question carry equal marks.
Leave the first page of the answer book blank and list on it clearly the numbers of the questions attempted.

1. **Answer each of the following:**

(i) Explain the influence of the nitrogen atom in pyridine and pyrrole on the electrophilic substitution reactions of these molecules.

(ii) Briefly describe how the Diels-Alder reaction could be used to determine the relative aromaticities of pyrrole and furan using the Robinson chemical criterion of aromatic behaviour.

(iii) Name the molecule **1** and show how it could be made in low yield from a Diels-Alder reaction.



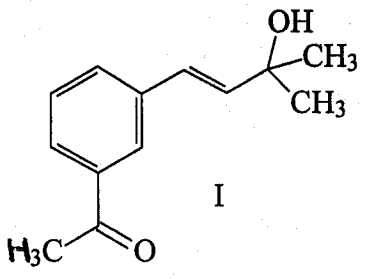
2. **Answer <u>each</u> of the following:**

(i) Explain the terms "5-*exo*-trig" and "6-*exo*-tet" as applied to cyclisation reactions for the synthesis of heterocyclic rings. Give one example in each case and comment on why these types of cyclisations are favoured.

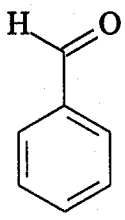
(ii) Explain the terms "chiral recognition", "agonist", "antagonist" in connection with the biological activity of molecules.

(iii) Show the structure of nicotine and outline the main degradation steps of this compound which lead to DNA damage in humans.

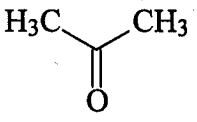
3. Discuss the importance of chemical yield in the context of a multistep synthesis. Describe the retrosynthetic analysis of any molecule of your choice, using it to provide examples of a disconnection, a synthon, a synthetic equivalent, and a functional group interconversion.
Carry out a retrosynthetic analysis on the molecule I back to benzaldehyde and acetone:



I

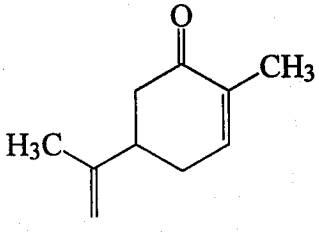


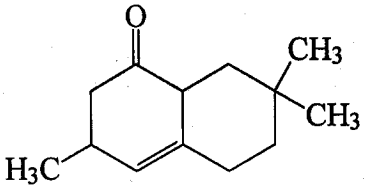
Benzaldehyde

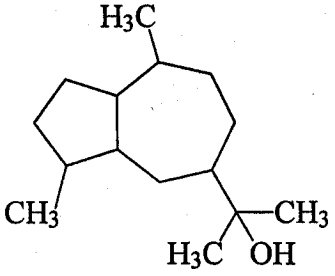


Acetone

4. **(i)** Explain what is meant by the isoprene rule and, giving your reasoning, use it to decide which of the following are terpenes:







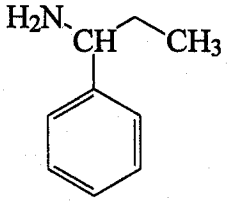
(ii) What is the biosynthetic equivalent of isoprene? Explain in detail how sesquiterpenes are biosynthesised from it.

(iii) Draw a diagram showing the conformation of a basic steroid with all rings *trans* fused, an angular methyl group on C10, and an equatorial OH group on C3. Label the rings in the standard way and identify the α and β faces of the steroid.

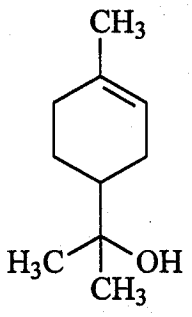
contd.

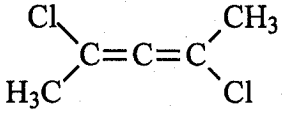
5. **(i)** Explain what is meant by **resolution** of a racemic mixture and describe the methods by which it can be carried out.

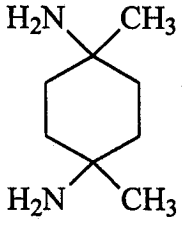
(ii) Explain in detail how the following amine might be resolved on a large scale:

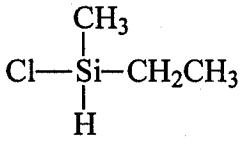


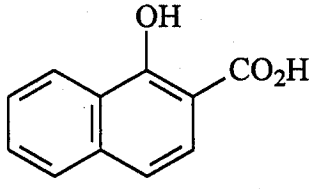
(iii) Which of the following can, at least in principle, be resolved:









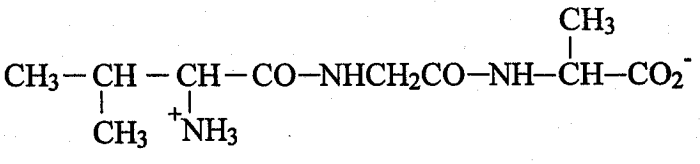


Justify your answer in each case.

6. **(i)** Outline the strategy involved in peptide syntheses under the headings:

(a) Protection
(b) Peptide bond formation
(c) Removal of the protecting group.

(ii) How would you synthesise the tripeptide shown? Name the compound.



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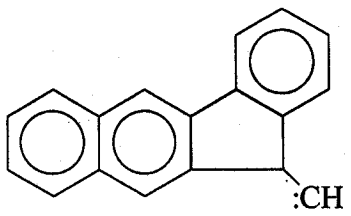
7. **(i)** Give a general synthesis of carbenes and describe some typical "traps" that are used to divert them.

(ii) Distinguish between insertion and addition trapping.

(iii) Mention the names of two reactions in which carbenes are implicated.

(iv) In the automerization of the 5- and the 6-carbons of benz[A]anthracene under nitrogen the carbene shown below has been suggested as an intermediate. Can you propose a suitable trap for this transient intermediate?



8. In the study of aromatic rearrangements the molecularity of the reaction (i.e. is an INTER or INTRA molecular mechanism operating) is normally the key mechanistic question to answer.
With the aid of a few examples show how
(a) 'crossover' experiments
(b) product analysis
(c) isotope experiments
can provide an answer to this question.
In the Fries Rearrangement of phenolic esters to hydroxyphenones shown, the reaction was found to be INTERmolecular. Draw two different phenolic esters which could be rearranged side by side to establish this.