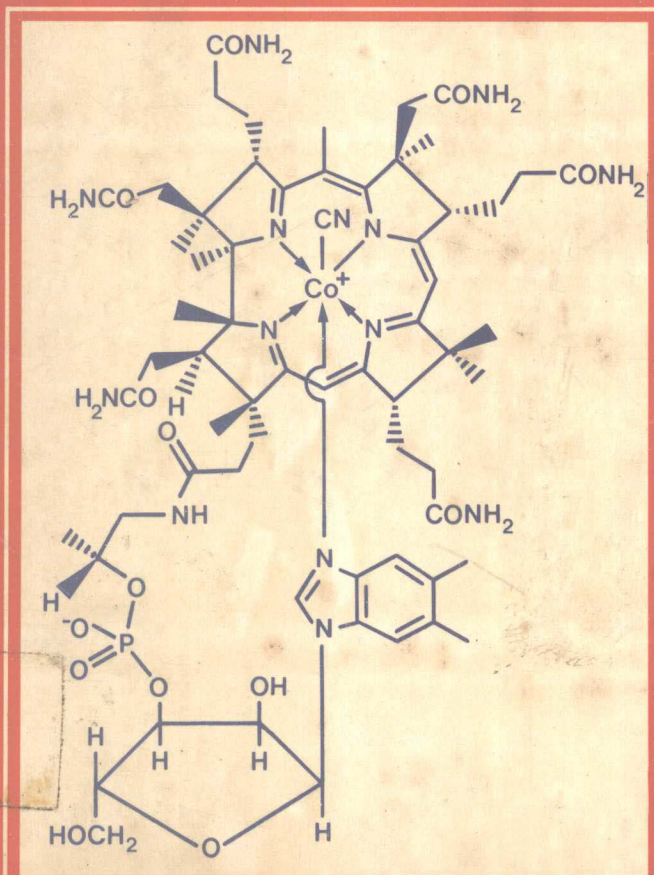
Worked Examples in Essential Organic Chemistry



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WORKED EXAMPLES IN ESSENTIAL ORGANIC CHEMISTRY

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Preface

This book has been written primarily as a companion text to *Essential Organic Chemistry for Students of the Life Sciences*. It consists of questions designed to reinforce the basic principles of organic chemistry and to allow self assessment by the student.

Answers to the problems are at the end of the book, and are given with fully developed arguments where appropriate. The book contains definitions and explanations of many of the terms used by organic and biological chemists, in addition to questions of the traditional type.

The book is structured in chapters which correspond to those in *Essential Organic Chemistry for Students of the Life Sciences*, but it has been written so as to be self-contained. Thus, it can be used as a study aid in conjunction with any other textbook of organic chemistry intended for first-year university students. It is especially useful for students of medicine, biology, or other life sciences who are studying organic chemistry as an ancillary subject, and as a source of problems for teachers and lecturers of organic chemistry.

We thank Mrs L. E. Smith for typing the manuscript.

A. P. R. K. S. R. S. W.

Abbreviations Used

Organic or other groups

R	an alkyl or aryl group
Ar	an aryl group
Me	a methyl group, CH_3—
Et	an ethyl group, C_2H_5—
Pr	a propyl group, C_3H_7—
Bu	a butyl group, C_4H_9—
Ac	an acetyl group, CH_3CO—
P	a phosphate group, H_2O_3P—

Important biochemical compounds

NAD^+	nicotinamide adenine dinucleotide
NADH	reduced NAD^+
$NADP^+$	nicotinamide adenine dinucleotide phosphate
NADPH	reduced $NADP^+$
ADP	adenosine diphosphate
ATP	adenosine triphosphate

Prefixes of names

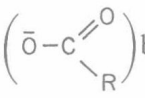
R **S** D L	indicate stereochemistry of compounds
Z **E** *cis* *trans*	

Contents

Questions

CHAPTER 1

Introduction

1. There are more compounds known which contain carbon than the total of all known compounds which do not. What factors do you think are primarily responsible for the great number and diversity of carbon compounds?
2. Define the term *structural isomer*, and draw all of the possible structures corresponding to the formula C_3H_9N.
3. Explain the significance of the words in italics: 'the carbon atom of methane is *tetrahedrally substituted*; in methane all H—C—H *bond angles* are 109.5° and all C—H *bond lengths* are 154 pm (1.54 Å)'.
4. Draw the shape of a 1s(or 2s) orbital, and the shapes and orientation of a set of 2p orbitals.
5. Define the terms *molecular orbital*, *bonding orbital*, and *antibonding orbital*, and illustrate your answer by reference to the hydrogen (H_2) molecule.
6. Explain what is meant by the terms *hybrid orbital*, *σ bond*, and *π bond* and illustrate your answer with respect to the orbital picture for ethene.
7. Represent the stabilization of a carboxylate anion  both by the concept of resonance (two canonical forms) and by the concept of extended overlap of atomic orbitals.
8. Use the curly arrow notation to represent the mechanisms of the reactions shown below, and in each case state which of the reactants is behaving as an *electrophile* and which as a *nucleophile*.

(a) 

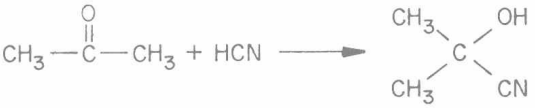
(b) 

(c) 

9. The reaction between acetone (propanone) and bromine, shown below, is found to occur at a rate which is independent of the concentration of bromine, i.e. Rate $= k$[acetone]. What does this tell you about the reaction?

10. Classify the following reactions as *addition*, *elimination*, *substitution*, or *rearrangement* reactions.

(a) 

(b) 

(c) $CH_3S^- + CH_3{-}Cl \longrightarrow CH_3{-}S{-}CH_3 + Cl^-$

(d) $H_2C{=}CH_2 + BH_3 \longrightarrow H_3C{-}CH_2BH_2$

(e) $2Br_2 + HC{\equiv}CH \longrightarrow HCBr_2CHBr_2$

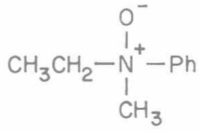
(f) $CH_3{-}CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$

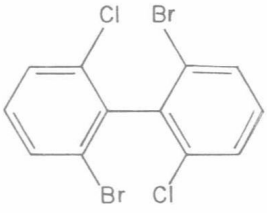
11. Propane ($CH_3CH_2CH_3$) boils at $-42\ ^\circ C$ at 1 atmosphere pressure, whereas ethanol (CH_3CH_2OH), with about the same molecular mass, boils at $78\ ^\circ C$ at 1 atmosphere pressure. Rationalize this observation.

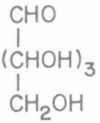
CHAPTER 2

Stereochemistry

1. With the aid of suitable examples, explain clearly the difference between each of the following pairs of terms:
   (a) *geometrical isomer; optical isomer*
   (b) *cis-; trans-*
   (c) *chiral; achiral.*
2. Draw out all of the possible stereoisomers of each of the following compounds, and indicate which, if any, are optically active:
   (a) 3-chlorobut-1-ene
   (b) 4-chloropent-2-ene
   (c) 2,4-diphenylpenta-2,3-diene
   (d) dimethyl cyclopropane-1,2-dicarboxylate
   (e) 2-bromocyclohexanol.
3. Give an example of each of the following:
   (a) a pair of *enantiomers*
   (b) a pair of *diastereoisomers*
   (c) a *meso* compound
   (d) a *racemic* mixture.
4. Briefly discuss any points of stereochemical interest associated with each of the following compounds:

(a) 

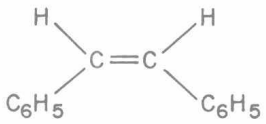
(b) 

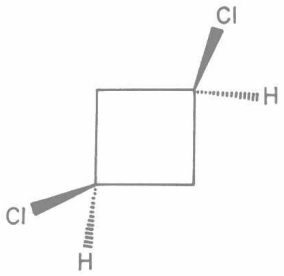
(c) 

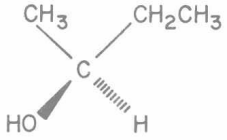
(d) 

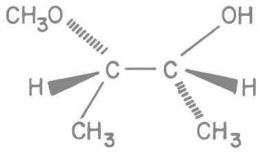
(e) Br_2CHCHF_2

5. Draw clear structural formulae for each of the following compounds:
   (a) *cis*, *trans*-1,4-diphenylbuta-1,3-diene
   (b) (*E*)-2-chlorobut-2-enoic acid
   (c) (*S*)-2-bromobutane
   (d) *trans*-4-*tert*-butylcyclohexanol
   (e) (2*R*:3*S*)-3-chloropentan-2-ol
6. Write systematic names for each of the following compounds:

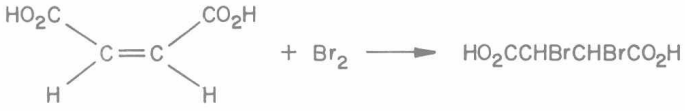
(a) 

(b) 

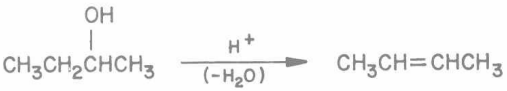
(c) 

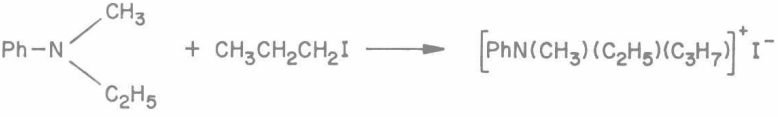
(d) 

7. In each of the following reactions two stereoisomers of the products are possible. Draw out the structures of both possible products.

(a) 

(*Note*: addition of Br_2 occurs in a *trans* manner)

(b) 

(c) 

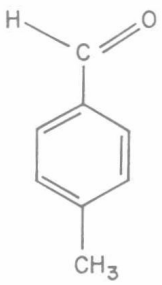
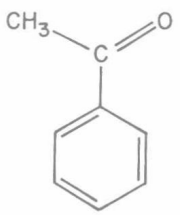
8. With the aid of suitable examples, explain clearly the difference between the following pairs of terms:
   (a) *conformation; configuration*
   (b) *stereoisomer; conformer*
   (c) *staggered* conformation; *eclipsed* conformation
   (d) *gauche; anti.*
9. Draw two conformations of each of the following compounds, and indicate in each case which (if any) will be the more stable:
   (a) *cis*-4-*tert*-butyl-1-methylcyclohexane
   (b) 2-methylbutane
   (c) *trans*-cyclohexane-1,2-dicarboxylic acid
   (d) 1,1-dimethylcyclohexane
   (e) *cis*-1,2-dichlorocyclohexane.
10. Draw clear diagrams of each of the following:
   (a) an *eclipsed conformation of ethane*-1,2-*diol*
   (b) a *gauche* conformation of 1,2-dibromoethane
   (c) a *chair* conformation of cyclohexanol
   (d) a *boat* conformation of cyclohexanone
   (e) a *Fischer projection formula* of (*R*)-butan-2-ol.

CHAPTER 3

Techniques of Organic Chemistry

1. Suggest the most appropriate non-chromatographic method for obtaining a pure sample of the first compound from a sample contaminated by the second, in each of the following cases:
   (a) hexane; octane
   (b) common sugar (sucrose); candle wax
   (c) benzamide; benzoic acid
   (d) ethanol (ethyl alcohol); benzamide.
2. 'Extraction of a compound from an aqueous solution with diethyl ether or other water-immiscible solvent is more efficient when carried out several times with relatively small quantities of solvent than when carried out once with a large quantity of solvent.' Justify this statement by choosing a hypothetical example and working out the quantities of compound extracted under the two sets of conditions.
3. Explain the meaning of the following terms which refer to aspects of chromatography:
   (a) mobile phase
   (b) stationary phase
   (c) R_f value
   (d) eluate.
4. Give the nature of the stationary and mobile phases in each of the following types of chromatography:
   (a) thin-layer chromatography
   (b) column chromatography
   (c) ion-exchange chromatography
   (d) gas chromatography.
5. Suggest the most appropriate chromatographic technique for analysis (*not* quantitative separation) of each of the following mixtures:
   (a) a petroleum (gasoline) sample
   (b) a sample of blood containing ethanol (alcohol)
   (c) a mixture of amino acids (involatile solids with ionic character).
6. An unknown compound analyses for 37.5% (by mass) carbon, 12.5% hydrogen, and 50.0% oxygen, and mass spectrometry shows a molecular mass of 32. Deduce the molecular formula of the compound and draw out a structure which corresponds to that formula. (Relative atomic masses: C = 12, H = 1, O = 16.)

7. Explain carefully how each of the following techniques could be used to differentiate butanone ($CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$) from butenone ($CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_3$):
   (a) mass spectrometry
   (b) u.v. spectroscopy
   (c) i.r. spectroscopy
   (d) n.m.r. spectroscopy.
8. Define the following terms:
   (a) molecular ion
   (b) electronic transition
   (c) carbonyl group frequency
   (d) chemical shift
   (e) spin–spin coupling
9. Choose a technique for differentiating between each of the following pairs of isomers, explaining the basis of your choice in each case:

   (a)  and 

   (b) $CH_3CH_2CH_2OH$ and $CH_3CH_2OCH_3$

   (c) $CH_2{=}CHCH_2CH{=}CH_2$ and $CH_2{=}CH{-}CH{=}CH{-}CH_3$

10. Predict the approximate appearance of the ^1H n.m.r. spectrum of 2,4-dimethylpentan-3-one.

$$(CH_3)_2CH\overset{\overset{O}{\|}}{C}CH(CH_3)_2$$