TUTORIAL PROBLEMS IN ORGANIC CHEMISTRY

D. C. NONHEBEL

and

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FOREWORD

It is usual to picture the student of organic chemistry of a past generation as exposed to a desert of damned poets, irrigated grudgingly by sketchy theory; whereas those of our time are furnished with theory, deficient in facts as points of calibration—theory which they can recite forwards but cannot apply backwards. The settings of problems can provide a disheartening diagnosis, and, skilfully applied over a period of time, offer hopes of a cure.

Drs. Nonhebel and Watts present a collection of such problems, classified as to topics of which they cover a wide range and graded in difficulty; they are directed in the main towards students near the middle of an undergraduate course. About two-thirds of the book consists of solutions to the problems, with succinct but sufficient explanation, from time to time pointing a matter of general principle.

The book is so signposted that a responsible student can use it to effect without constant direction. Much of the material has been in use in this Department during the past few years, and I have had the opportunity of observing its salutary effect on, and appreciation by, the students concerned.

The teachers will receive the book with gratitude, for the construction of suitable watertight problems is a more difficult and time-consuming job than it looks. The examiner, seeking to devise testing material good and new, may have more mixed feelings—*pereant illi qui ante nos nostra dixerunt*! For the serious student there is a stimulus to intelligent thinking and a useful means of self-assessment.

I wish success to the book and much advantage to its many readers.

10 September 1970 T. S. Stevens

PREFACE

Over the past few years, the teaching of organic chemistry has moved in emphasis towards an ordered presentation of basic principles rather than a collage of experimental facts and observations. Comparison of the better modern textbooks with the older variety clearly underlines this change in approach. To those involved in teaching the subject, it is obvious that, if these basic concepts are grasped and understood by the student, the foundation has been firmly laid upon which an understanding of the more advanced aspects can be built. We are convinced from experience that this end can be best served by providing the student with a broad range of carefully chosen problems through which he can test his comprehension of the subject. We have attempted to provide such a selection in this book which has developed from a set of tutorial problems which we have been using successfully over the past few years at the University of Strathclyde.

The book is principally directed towards students taking their first university course in organic chemistry. It is hoped that it will also be of considerable use to students in the Open University and to those enrolled in H.N.C., C.N.A.A. and G.R.I.C. courses. The majority of students in these categories do not have the advantage of the tutorial system enjoyed by most university students. The scope of the book has been dictated by a desire to limit the size and hence the price to a modest level without a sacrifice in thoroughness. Consequently, we have omitted almost completely spectroscopic problems, which are well covered in a number of other books, and have not treated some of the more specialized areas of the subject such as carbohydrate and natural product chemistry.

The problems presented cover a broad variety including those of the conventional deductive type found in many other texts. A large number are concerned with the interpretation of physical and chemical data and with the relationship between reactivity and molecular stereochemistry. The latter type are best tackled with the use of molecular models which help in the appreciation of the three-dimensional nature of molecules. In Chapter 4, the longest in the book, we have attempted to provide problems which illustrate how the properties of a functional group are influenced by its neighbours and by its location in the molecule. Thus, in this chapter we have deliberately included questions on reaction mechanisms based on the chemistry of a particular functional group. In this way, we wish to emphasize that an understanding of mechanism forms an integral part of organic chemistry. Reaction mechanisms are dealt with more fully in Chapter 5 where the emphasis is on the reaction type rather than on a particular group. We have included a chapter on synthesis, a subject which is troublesome to students and which is only sketchily treated in most other problem books.

The level of difficulty of the problems range from elementary to fairly advanced. Those of the latter grade have been indicated by an asterisk and could well be omitted on a first use of the book. Inevitably, this choice is a somewhat subjective one. An answer has been provided for all of the problems; we feel this is mandatory in a book of this nature. The answers to some of the questions are very comprehensive whilst others are only given in outline. This has been done to keep the book to a reasonable length, and hence price, without sacrificing a detailed consideration of all of the fundamental concepts underlying the questions.

We should like to thank Professor P. L. Pauson and his staff of the University of Strathclyde for help and encouragement during the preparation of this book and particularly Professor T. S. Stevens for constructive and instructive comment. We are greatly indebted to students in the University of Strathclyde, Glasgow, on whom much of the material in this book has been tested. Their reactions to earlier drafts have shown us many ways in which the original material could be improved. We are also indebted to Miss G. Forrest and Miss B. Martin who cheerfully and painstakingly typed the manuscript.

Glasgow, 1970

D. C. Nonhebel
W. E. Watts

GUIDE TO USE OF BOOK

The maximum benefit can be derived from this book by first tackling Chapters 1 to 5 in the order in which they appear. Mastery of the material covered in Chapters 2 and 3 should ensure a sound understanding of the more important basic principles which control the physical and chemical behaviour of organic molecules. This knowledge can then be applied to the problems in Chapter 4 which are concerned with the chemistry of particular functional groups. This chapter contains a variety of problem types ranging from synthesis to reaction mechanisms. Chapter 5 is specifically concerned with reaction mechanisms and treats this topic from the viewpoint of reaction type rather than functional group.

The last four chapters can be tackled in any order and require application of the principles covered in the preceding chapters. The problems on synthesis (Chapter 8) and the deductive questions (Chapter 9), in general, involve the chemistry of compounds containing more than one functional group and can be logically considered after Chapter 4.

The more difficult problems have been indicated by an asterisk. These should not be attempted until the topics covered in the simpler problems have been thoroughly understood. The nature of the subject is such that the most challenging problems are to be found in the chapter on reaction mechanisms. Many of the problems on stereochemistry can only be satisfactorily solved with the use of molecular models.

Some of the answers, particularly those relating to problems on differentiation and synthesis, are not unique solutions.

CONTENTS

1

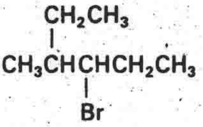
Nomenclature

1. Write structural formulae for each of the following compounds:

- (a) *trans*-1-Phenylpent-3-en-1-ol.
- (b) But-1-en-3-yne.
- (c) *trans*-1-(3,5-Dichlorophenyl)-3-phenylpropenone.
- (d) *cis*-1,4-Dibromocyclohexane.
- (e) *cis*-Hexa-1,4-diene.
- (f) 3,5-Dimethylphenol.
- (g) 4-Methylhexyl 3-chloro-3-methylheptanoate.

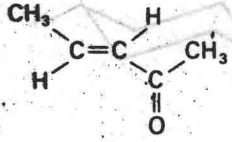
2. Name each of the following compounds by the I.U.P.A.C. nomenclature system:

(a)



$\mathrm{CH_3\overset{CH_2CH_3}{\overset{|}{C}}H\underset{Br}{\underset{|}{C}}HCH_2CH_3}$

(b)



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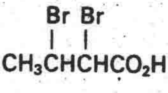
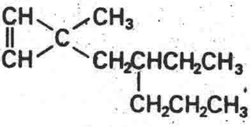


$\mathrm{CH_3\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}HCO_2H}$

(d) $\mathrm{CH_2{=}CHOCH_2CH_2Br}$

(e)



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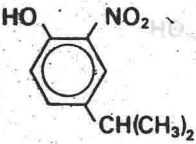

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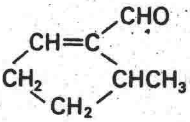
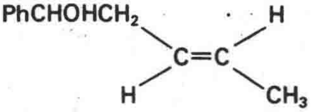
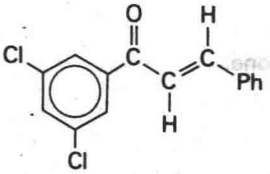
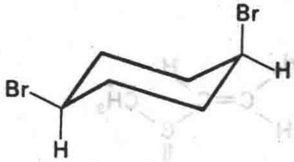


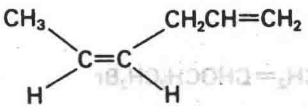
SOLUTIONS TO CHAPTER 1

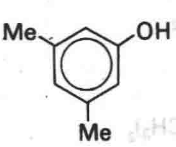
1. (a)  (-ol takes precedence over -ene)

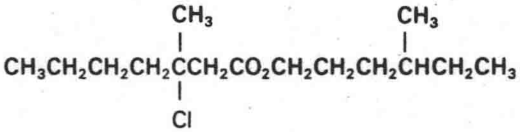
(b) $CH_2{=}CHC{\equiv}CH$ (-ene takes precedence over -yne)

(c)  (-one take precedence over -ene)

(d) 

(e) 

(f) 

(g) 

$CH_3CH_2CH_2CH_2\overset{CH_3}{\underset{Cl}{C}}CH_2CO_2CH_2CH_2CH_2\overset{CH_3}{C}HCH_2CH_3$

2. (a) 3-Bromo-4-methylhexane (bromo takes precedence over methyl).
(b) *trans*-Pent-3-en-2-one (-one takes precedence over -ene).
(c) 2,3-Dibromobutanoic acid (this may also be called $\alpha\beta$-dibromobutyric acid).
(d) 2-Bromoethyl vinyl ether.
(e) 3-(2-ethylpentyl)-3-methylcyclopropene.
(f) 4-Isopropyl-2-nitrophenol.
(g) 1-Formyl-5-methylcyclopentene.

2

Physical Properties of Organic Molecules

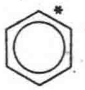
(a) BONDING

3. Sketch the orbitals involved in the bonding and electronic structure of the following compounds. Ignore anti-bonding orbitals. Indicate the expected bond angles.

(a) $CH_2{=}O$. (b) *trans*-$PhN{=}NPh$.
(c) $CH_3C{\equiv}N$. (d) $CH_2{=}C{=}CH_2$.

4. List the compounds of the following groups in order of increasing bond length for the carbon–carbon bonds indicated:

(a) $CH_3C\overset{*}{\equiv}CH$; $CH_3CH_2\overset{*}{-}CH_3$; $CH_3CH\overset{*}{=}CH_2$.
(b)* $CH_3\overset{*}{-}C{\equiv}CH$; $CH_3\overset{*}{-}CH_2CH_3$; $CH_3\overset{*}{-}CH{=}CH_2$.
(c)*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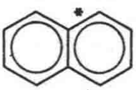
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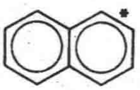


5. List the compounds of the following groups in order of increasing stretching frequency for the bonds indicated:

(a) $PhC{\equiv}CH$; $PhCH_2{-}CH_3$; $PhCH{=}CH_2$ (carbon–carbon).
(b) $CH_3C{\equiv}N$; $CH_3CH{=}NCH_3$; CH_3NH_2 (carbon–nitrogen).
(c) CH_3OCH_3; CO; $CH_2{=}O$ (carbon–oxygen).

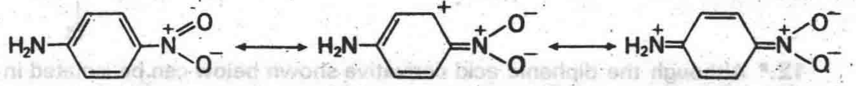
6. Comment upon the importance of the various canonical forms in the following resonance hybrid structures:

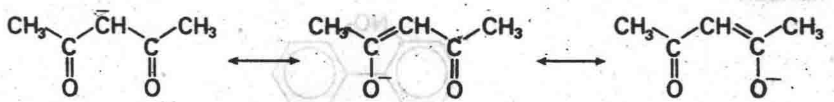
(a) $CH_3{-}C{\equiv}N \longleftrightarrow CH_3{-}\overset{+}{C}{=}\overset{/-}{N} \longleftrightarrow CH_3{-}\overset{-}{C}{=}\overset{+}{N}$

(b)


$$CH_3{-}C\begin{matrix}\diagup O^- \\ \diagdown\!\!\diagdown O\end{matrix} \longleftrightarrow CH_3{-}C\begin{matrix}\diagup\!\!\diagup O \\ \diagdown O^-\end{matrix}$$

(c) $CH_2{=}CH{-}CH{=}O \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{O} \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH{-}\overset{+}{O}$

(d) 

(e) 

7. The heats of combustion of cyclobutane, cyclopentane and cyclohexane are 2743, 3317 and 3949 kJ/mole respectively. Discuss.

8. Arrange the following compounds in order of increasing heat of hydrogenation:

(a) But-I-ene; *cis*-but-2-ene; *trans*-but-2-ene.
(b) Cyclohexene; cyclopentene.
(c)* *cis*- and *trans*-Cyclooctene.

9. Rationalize the following observations:

(a) Although ethanol and dimethyl ether are isomeric, the boiling point of the latter compound is lower by 101°.

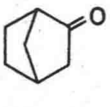
(b) Of the three nitrophenols, only the *ortho*-isomer is steam-volatile.

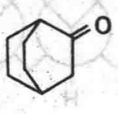
(b) STEREOCHEMISTRY

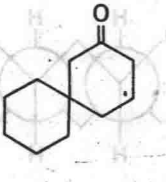
10. Sketch all possible structures for the following compounds. Indicate the type of isomerism involved in each case.

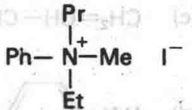
(a) 1-Phenylethanol.
(b) Cyclobutane-1,2-dicarboxylic acid.
(c) Hexa-2,4-diene.
(d) 2,3-Dibromobutane.
(e)* Cyclooctene.
(f) Benzaldoxime.

11.* Which of the following compounds can exist in optically active forms? Draw the structures of the enantiomeric forms in these examples.

(a) 

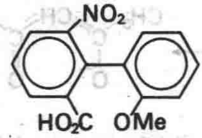
(b) 

(c) 

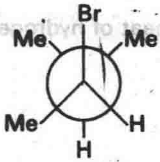
(d) PhCH=C=CHPh (e) MeNHPh (f) 

$Ph-\overset{Pr}{\underset{Et}{N^{+}}}-Me\ I^{-}$

12.* Although the diphenic acid derivative shown below can be isolated in optically active forms, these slowly lose their optical activity on standing. Explain this behaviour.



13. Which of the following pairs of structural formulae represent different compounds?

(a) 

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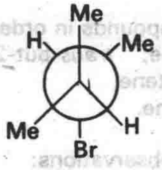
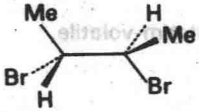


(b) 

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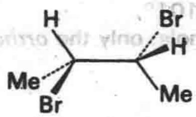
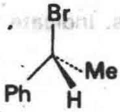


(c) 

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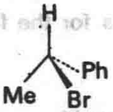
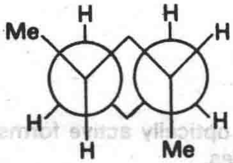


(d) 

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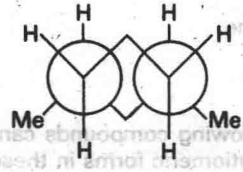
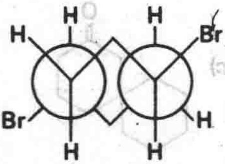


(e) 

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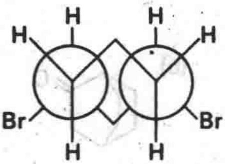


14. 2,5-Dimethylcyclopentane-1,1-dicarboxylic acid can be obtained in more than one stereoisomeric form. Draw structures for each of these forms and indicate which, if any, would be optically active. On gentle heating, each stereoisomer undergoes decarboxylation to give a 2,5-dimethylcyclopentanecarboxylic acid. Draw structures for all possible stereoisomers of the latter indicating from which isomer they are derived and whether or not they show optical activity.

15. Draw structural formulae for the most stable conformation of each of the following compounds:

(a) *cis*-1,3-Di-t-butylcyclohexane.
(b) *trans*-1,3-Di-t-butylcyclohexane.
(c) *cis*-4-t-Butylmethylcyclohexane.
(d) *cis*-Cyclohexane-1,3-diol.

(c) SPECTROSCOPY

16.* Comment upon the following spectroscopic information:

(a) The carbonyl stretching frequency of but-2-enal is lower than that of butanal.
(b) The infrared spectrum of *cis*-1,2-diphenylethylene contains a C$=$C stretching absorption but this is absent in the spectrum of the *trans*-isomer.

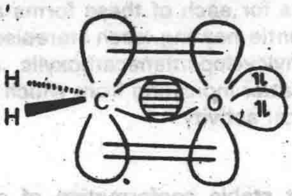
17. 2,2,5,5-Tetramethylhexane-3,4-diol exists in *dl*- and *meso*-forms. The infrared spectrum of one form contains two hydroxyl stretching absorptions whereas the other gives only one absorption. Explain these observations.

18. From the spectroscopic information given, identify the following compounds:

(a) C_3H_6O: UV 275 nm ($\epsilon = 17$); IR 1715 cm^{-1}; NMR δ2·15 (singlet).
(b) C_3H_6O: UV no max. > 210 nm; IR 1080 cm^{-1}; NMR δ4·75 (triplet, 4H), 2·75 (quintet, 2H); $J = 7{\cdot}1$ Hz.
(c) C_4H_7N: UV no max. > 200 nm; IR 2273 cm^{-1}; NMR δ2·82 (septet, 1H), 1·33 (doublet, 6H); $J = 6{\cdot}7$ Hz.
(d) C_3H_7NO: UV 219 nm ($\epsilon = 60$); IR 3413, 3236, 1667 cm^{-1}; NMR δ6·50 (broad singlet, 2H), 2·25 (quartet, 2H), 1·10 (triplet, 3H); $J = 7{\cdot}5$ Hz.
(e) $C_9H_{10}O$: UV 260 ($\epsilon = 365$), 285 nm ($\epsilon = 80$); IR 1720 cm^{-1}; NMR δ7·2 (multiplet, 5H), 3·6 (singlet, 2H), 2·1 (singlet, 3H).
(f) C_3H_7NO: UV 222 nm ($\epsilon = 80$); IR 1660 cm^{-1}; NMR δ8·06 (singlet, 1H), 2·94 (singlet, 3H), 2·80 (singlet, 3H). At 111°, the δ2·94 and 2·80 singlets coalesce to give a new six-proton singlet at δ2·87.
(g) $C_8H_8O_2$: UV 270 nm ($\epsilon = 420$); IR 1725 cm^{-1}; NMR δ11·95 (singlet, 1H), 7·21 (singlet, 5H), 3·53 (singlet, 2H). The singlet at δ11·95 disappears when D_2O is added to the solution.

SOLUTIONS TO CHAPTER 2

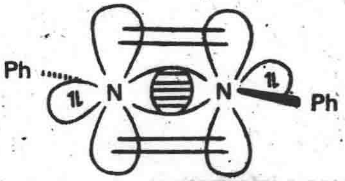
3. (a)



$\hat{HCH} = \hat{HCO} \approx 120°$

C atom sp^2-hybridized (only one hybrid orbital shown). O atom sp^2-hybridized (two non-bonding electron pairs located in these hybrid orbitals).

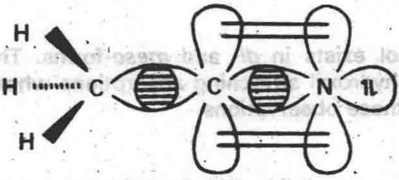
(b)



$\hat{CNN} \approx 120°$

N atoms sp^2-hybridized (only two hybrid orbitals shown for each; one non-bonding electron pair located on each N in one of these hybrid orbitals). Benzene ring orbitals are omitted for clarity.

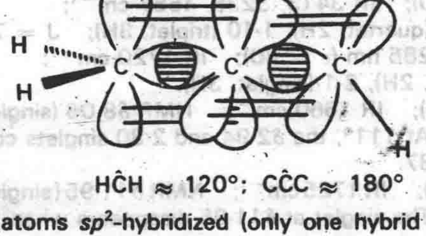
(c)



$\hat{HCH} \approx 109°$; $\hat{CCN} \approx 180°$

C_{CH_3} atom sp^3-hybridized (only one hybrid orbital shown). C_{CN} atom sp-hybridized. N atom sp-hybridized (non-bonding electron pair located in one of these hybrid orbitals). Only one π-bond is shown above. Another is located in the plane at right angles to the plane of the first (cf. acetylene).

(d)



$\hat{HCH} \approx 120°$; $\hat{CCC} \approx 180°$

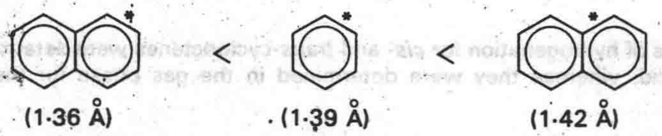
C_{CH_2} atoms sp^2-hybridized (only one hybrid orbital shown for each). $C_{central}$ atom sp-hybridized. The planes of the CH_2 groups are at right angles to each other.

4. (a) $CH_3C\overset{*}{\equiv}CH$ (1·20 Å) < $CH_3CH\overset{*}{=}CH_2$ (1·34 Å) < $CH_3CH_2\overset{*}{-}CH_3$ (1·54 Å).

(b) $CH_3\overset{*}{-}C\equiv CH$ (1·46 Å) < $CH_3\overset{*}{-}CH=CH_2$ (1·50 Å) < $CH_3\overset{*}{-}CH_2CH_3$ (1·54 Å).

sp^3-sp sp^3-sp^2 sp^3-sp^3

(c)



Consider the Kekulé forms for naphthalene.

5. (a) $PhCH_2-CH_3$ (~1030 cm^{-1}) < $PhCH=CH_2$ (1640 cm^{-1}) < $PhC\equiv CH$ (2230 cm^{-1}).

(b) CH_3-NH_2 (~1080 cm^{-1}) < $CH_3CH=NCH_3$ (1670 cm^{-1}) < $CH_3C\equiv N$ (2250 cm^{-1}).

(c) CH_3-OCH_3 (~1100 cm^{-1}) < $CH_2=O$(1720 cm^{-1}) < CO (2143 cm^{-1}).

N.B. $\nu_{max.} = \frac{1}{2\pi c}\left[\frac{f}{u}\right]^{\frac{1}{2}}$

where f = force constant and u = reduced mass of the vibrating atoms.
The force constant is proportional to the bond order.

6. (a) $CH_3-\bar{C}=\overset{+}{N}$ does not contribute significantly since nitrogen is more electronegative than carbon, whereas $CH_3-\overset{+}{C}=\bar{N}$ makes a contribution to the hybrid structure.

(b) Both forms are of equal energy and hence of equal importance.

(c) $\bar{C}H_2-CH=CH-O^+$ is not a contributing form. See (a).

(d) All forms contribute significantly to the resonance hybrid.

(e) All forms contribute significantly. The second and third forms are of equal energy.

7. The heats of combustion per CH_2 for cyclobutane, cyclopentane, and cyclohexane are 686, 663 and 658 kJ/mol respectively. Higher values reflect strain in the cycloalkane which is released on combustion. The value per CH_2 for cyclohexane is identical with that for a long chain alkane, consistent with a strainless structure. Cyclobutane is considerably strained (chiefly angle strain) and cyclopentane is somewhat strained (mainly eclipsing strain).

8. (a) *trans*-But-2-ene (115 kJ/mol) < *cis*-but-2-ene (119·5 kJ/mol) < but-1-ene (127 kJ/mole). Lower values indicate that the alkene is relatively more stable. The but-2-enes are more stable than but-1-ene because of hyperconjugative effects (cf. the degree of substitution of the double bond). *cis*-But-2-ene is less stable than the *trans*-isomer because of steric interaction between the methyl groups.

(b) Cyclopentene (113 kJ/mol) < cyclohexene (119·5 kJ/mol). The value for cyclopentene is *less* than that for cyclohexene because cyclopentane (formed by hydro-