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Solutions manual to accompany ORGANIC CHEMISTRY SECOND EDITION

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Organic Chemistry

Second Edition

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OXFORD

UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP, United Kingdom

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First edition published 2001

Impression: 1

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> > British Library Cataloguing in Publication Data

Data available

978-0-19-966334-7

Printed in Great Britain by

Ashford Colour Press Ltd, Gosport, Hampshire

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Suggested solutions for Chapter 2

2

PROBLEM 1

Draw good diagrams of saturated hydrocarbons with seven carbon atoms having (a) linear, (b) branched, and (c) cyclic structures. Draw molecules based on each framework having both ketone and carboxylic acid functional groups in the same molecule.

Purpose of the problem

To get you drawing simple structures realistically and to steer you away from rules and names towards more creative and helpful ways of representing molecules.

Suggested solution

There is only one linear hydrocarbon but there are many branched and cyclic options. We offer some possibilities, but you may have thought of others.

linear saturated hydrocarbon (*n*-heptane) some branched hydrocarbons





We give you a few examples of keto-carboxylic acids based on these structures. A ketone has to have a carbonyl group not at the end of a chain; a carboxylic acid functional group by contrast *has* to be at the end of a chain. You will notice that no carboxylic acid based on the first three cyclic structures is possible without adding another carbon atom.



Draw for yourself the structures of amoxicillin and Tamiflu shown on page 10 of the textbook. Identify on your diagrams the functional groups present in each molecule and the ring sizes. Study the carbon framework: is there a single carbon chain or more than one? Are they linear, branched, or cyclic?



Purpose of the problem

To persuade you that functional groups are easy to identify even in complicated structures: an ester is an ester no matter what company it keeps and it can be helpful to look at the nature of the carbon framework too.

Suggested solution

The functional groups shouldn't have given you any problem except perhaps for the sulfide (or thioether) and the phenol (or alcohol). You should have seen that both molecules have an amide as well as an amine.



The ring sizes are easy and we hope you noticed that one bond between the four- and the five-membered ring in the penicillin is shared by both rings.



The carbon chains are quite varied in length and style and are broken up by N, O, and S atoms.





Purpose of the problem

Identifying functional groups is not just a sterile exercise in classification: spotting the difference between an ester, an ether, an acetal and a hemiacetal is the first stage in understanding their chemistry.

Suggested solution

The functional groups are marked on the structures below. Particularly important is to identify an acetal and a hemiacetal, in which both 'ether-like' oxygens are bonded to a single carbon, as a single functional group.



What is wrong with these structures? Suggest better ways to represent these molecules



Purpose of the problem

To shock you with two dreadful structures and to try to convince you that well drawn realistic structures are more attractive to the eye as well as easier to understand and quicker to draw.

Suggested solution

The bond angles are grotesque with square planar saturated carbon atoms, bent alkynes with 120° bonds, linear alkenes with bonds at 90° or 180°, bonds coming off a benzene ring at the wrong angles and so on. If properly drawn, the left hand structure will be clearer without the hydrogen atoms. Here are better structures for each compound but you can think of many other possibilities.



PROBLEM 5

Draw structures for the compounds named systematically here. In each case suggest alternative names that might convey the structure more clearly if you were speaking to someone rather than writing.

- (a) 1,4-di-(1,1-dimethylethyl)benzene
- (b) 1-(prop-2-enyloxy)prop-2-ene
- (c) cyclohexa-1,3,5-triene

Purpose of the problem

To help you appreciate the limitations of systematic names, the usefulness of part structures and, in the case of (c), to amuse.

Suggested solution

(a) A more helpful name would be *para*-di-*t*-butyl benzene. It is sold as 1,4-di-*tert*-butyl benzene, an equally helpful name. There are two separate numerical relationships.



(b) This name conveys neither the simple symmetrical structure nor the fact that it contains two allyl groups. Most chemists would call it 'diallyl ether' though it is sold as 'allyl ether'.



(c) This is of course simply benzene!

PROBLEM 6

Translate these very poor structural descriptions into something more realistic. Try to get the angles about right and, whatever you do, don't include any square planar carbon atoms or any other bond angles of 90°.

- (a) $C_6H_5CH(OH)(CH_2)_4COC_2H_5$
- (b) $O(CH_2CH_2)_2O$
- (c) (CH₃O)₂CH=CHCH(OCH₃)₂

Purpose of the problem

An exercise in interpretation and composition. This sort of 'structure' is sometimes used in printed text. It gives no clue to the shape of the molecule.

Suggested solution

You probably need a few 'trial and error' drawings first but simply drawing out the carbon chain gives you a good start. The first is straightforward—the (OH) group is a substituent joined to the chain and not part of it. The second compound must be cyclic—it is the ether solvent commonly known as dioxane. The third gives no hint as to the shape of the alkene and we have chosen *trans*. It also has two ways of representing a methyl group. Either is fine, but it is better not to mix the two in one structure.



Identify the oxidation level of all the carbon atoms of the compounds in problem 6.

Purpose of the problem

This important exercise is one you will get used to very quickly and, before long, do without thinking. If you do it will save you from many trivial errors. Remember that the oxidation *state* of all the carbon atoms is +4 or C(IV). The oxidation *level* of a carbon atom tells you to which oxygen-based functional group it can be converted without oxidation or reduction.

Suggested solution

Just count the number of bonds between the carbon atom and heteroatoms (atoms which are not H or C). If none, the atom is at the hydrocarbon level (\Box) , if one, the alcohol level (\bigcirc) , if two the aldehyde or ketone level, if three the carboxylic acid level (\bigcirc) and, if four, the carbon dioxide level.





Draw full structures for these compounds, displaying the hydrocarbon framework clearly and showing all the bonds in the functional groups. Name the functional groups.

(a) AcO(CH₂)₃NO₂

(b) MeO₂CCH₂OCOEt

(c) CH₂=CHCONH(CH₂)₂CN

Purpose of the problem

This problem extends the purpose of problem 6 as more thought is needed and you need to check your knowledge of the 'organic elements' such as Ac.

Suggested solution

For once the solution can be simply stated as no variation is possible. In the first structure 'AcO' represents an acetate ester and that the nitro group can have only four bonds (not five) to N. The second has two ester groups on the central carbon, but one is joined to it by a C–O and the other by a C–C bond. The last is straightforward.



PROBLEM 9

Draw structures for the following molecules, and then show them again using at least one 'organic element' symbol in each.

(a) ethyl acetate

- (b) chloromethyl methyl ether
- (c) pentanenitrile
- (d) N-acetyl p-aminophenol
- (e) 2,4,6,-tri-(1,1-dimethylethyl)phenylamine

Purpose of the problem

Compound names mean nothing unless you can visualize their structures. More practice using 'organic elements'.

Suggested solution

The structures are shown below—things to look out for are the difference between acetyl and acetate, the fact that the carbon atom of the nitrile group is included in the name, and the way that a *tert*-butyl group can be named as '1,1-dimethylethyl'.

■ There is a list of the abbreviations known as 'organic elements' on page 42 of the textbook.



PROBLEM 10

Suggest at least six different structures that would fit the formula C_4H_7NO . Make good realistic diagrams of each one and say which functional groups are present.

Purpose of the problem

The identification and naming of functional groups is more important than the naming of compounds, because the names of functional groups tell you about their chemistry. This was your chance to experiment with different groups and different carbon skeletons and to experience the large number of compounds you could make from a formula with few atoms.

Suggested solution

We give twelve possible structures – there are of course many more. You need not have used the names in brackets as they are ones more experienced chemists might use.



10

Suggested solutions for Chapter 3

PROBLEM 1

Assuming that the molecular ion is the base peak (100% abundance) what peaks would appear in the mass spectrum of each of these molecules:

(a) C₂H₅BrO

(b) C₆₀

(c) C₆H₄BrCl

In cases (a) and (c) suggest a possible structure of the molecule. What is (b)?

Purpose of the problem

To give you some practice with mass spectra and, in particular, at interpreting isotopic peaks. The molecular ion is the most important ion in the spectrum and often the only one that interests us.

Suggested solution

Bromine has two isotopes, ⁷⁹Br and ⁸¹Br in about a 1:1 ratio. Chlorine has two isotopes ³⁵Cl and ³⁷Cl in about a 3:1 ratio. There is about 1.1% ¹³C in normal compounds.

(a) C_2H_5BrO will have two main molecular ions at 124 and 126. There will be very small (2.2%) peaks at 125 and 126 from the 1.1% of ¹³C at each carbon atom.

(b) C_{60} has a molecular ion at 720 with a strong peak at 721 of 60 x 1.1 = 66%, more than half as strong as the ¹²C peak at 720. This compound is buckminsterfullerene.

(c) This compound is more complicated. It will have a 1:1 ratio of ⁷⁹Br and ⁸¹Br and a 3:1 ratio of ³⁵Cl and ³⁷Cl in the molecular ion. There are four peaks from these isotopes (ratios in brackets) $C_6H_4^{79}Br^{35}Cl$ (3), $C_6H_4^{81}Br^{35}Cl$ (3), $C_6H_4^{81}Br^{37}Cl$ (1), and $C_6H_4^{81}Br^{37}Cl$ (1), the masses of these peaks being 190, 192, 192, and 194. So the complete molecular ion will have three main peaks at 190, 192, and 194 in a ratio of 3:4:1 with peaks at 191, 193, and 194 at 6.6% of the peak before it.

Compounds (a) and (c) might be isomers of compounds such as these:



Buckminsterfullerene is on page 25 of the textbook.

Ethyl benzoate $PhCO_2Et$ has these peaks in its ¹³C NMR spectrum: 17.3, 61.1, 100–150 (four peaks) and 166.8 ppm. Which peak belongs to which carbon atom? You are advised to make a good drawing of the molecule before you answer.

Purpose of the problem

To familiarize you with the four regions of the spectrum.

Suggested solution

It isn't possible to say which aromatic carbon is which and it doesn't matter. The rest are straightforward.



PROBLEM 3

Methoxatin was mentioned on page 44 of the textbook where we said 'it proved exceptionally difficult to solve the structure by NMR.' Why is it so difficult? Could anything be gained from the ¹³C or ¹H NMR? What information could be gained from the mass spectrum and the infra red?

Purpose of the problem

To convince you that this structure really needs an X-ray solution but also to get you to think about what information is available by the other methods. Certainly mass spectroscopy, NMR, and IR would have been tried first.

Suggested solution

There are only two hydrogens on carbon atoms and they are both on aromatic rings. There are only two types of carbon atom: carbonyl groups and unsaturated ring atoms. This information is mildly interesting but is essentially negative—it tells us what is not there but gives us no information on the basic skeleton, where the carboxylic acids are, nor does it reveal the 1,2-diketone in the middle ring.

■ These regions are described on page 56 of the textbook.

The mass spectrum would at least give the molecular formula $C_{14}H_6N_2O_8$ and the infra-red would reveal an N–H group, carboxylic acids, and perhaps the 1,2-diketone. The X-ray was utterly convincing and the molecule has now been synthesized, confirming the structure.



■ The synthesis of methoxatin is described in J. A. Gainor and S. M. Weinreb, *J. Org. Chem.*, 1982, **47**, 2833.

PROBLEM 4

The solvent formerly used in some correcting fluids is a single compound $C_2H_3Cl_3$, having ^{13}C NMR peaks at 45.1 and 95.0 ppm. What is its structure? How would you confirm it spectroscopically? A commercial paint thinner gives two spots on chromatography and has ^{13}C NMR peaks at 7.0, 27.5, 35.2, 45.3, 95.6, and 206.3 ppm. Suggest what compounds might be used in this thinner.

Purpose of the problem

To start you on the road to structure identification with one very simple problem and some deductive reasoning. It is necessary to think about the size of the chemical shifts to solve this problem.

Suggested solution

With the very small molecule $C_2H_3Cl_3$ it is best to start by drawing all the possible structures. In fact there are only two.



The first would have a peak for the methyl group in the 0-50 region and one for the CCl₃ group at a very large chemical shift because of the three chlorine atoms. The second isomer would have two peaks in the 50–100 region, not that far apart. The second structure looks better but it would be easily confirmed by proton NMR as the first structure would have one peak only but the second would have two peaks for different CHs. The solvent is indeed the second structure 1,1,2-trichloroethane.

Two of the peaks (45.3 and 95.6) in the paint thinner are much the same as those for this compound (chemical shifts change slightly in a mixture as the two compounds dissolve each other). The other compound has a carbonyl group at 206.3 and three saturated carbon atoms, two close to the carbonyl group (larger shifts) and one further away. Butanone fits the bill perfectly. You were not expected to decide which CH_2 group belongs to which molecule—that can be found out by running a spectrum of pure butanone.



PROBLEM 5

The 'normal' O–H stretch in the infrared (i.e. without hydrogen bonding) comes at about 3600 cm⁻¹. What is the reduced mass (μ) for O–H? What happens to the reduced mass when you double the mass of each atom in turn, i.e. what is μ for O–D and what is μ for S–H? In fact, both O–D and S–H stretches come at about 2,500 cm⁻¹. Why?

Purpose of the problem

To get you thinking about the positions of IR bands in terms of the two main influences: reduced mass and bond strength.

Suggested solution

Using the equation on page 64 of the textbook we find that the reduced mass of OH is 16/17 or about 0.94. When you double the mass of H, the reduced mass of OD becomes 32/18 or about 1.78—nearly double that of OH. But when you double the mass of O, the reduced mass of SH is 32/33 or about 0.97 – hardly changed from OH! The change in the reduced mass from OH to OD is enough to account for the change in stretching frequency—a change of about $\sqrt{2}$. But the change in reduced mass from OH to SH cannot account for the change in frequency. The explanation is that the S–H bond is weaker than the O–H bond by a factor of about 2. So both both O–D and S–H absorb at about the same frequency.

There is an important principle to be deduced from this problem. Very roughly, all the reduced masses of all bonds involving the heavier elements (C, N, O, S etc.) differ by relatively small amounts and the differences in stretching frequency are mainly due to changes in bond strength, though it can be significant in comparing, say, C–O with C–Cl. With bonds involving hydrogen the reduced mass becomes by far the most important factor.

Three compounds, each having the formula C_3H_5NO , have the IR data summarized here. What are their structures? Without ¹³C NMR data it might be easier to draw some or all possible structures before trying to decide which is which. In what ways would ¹³C NMR data help?

(a) One sharp band above 3000 cm⁻¹ and one strong band at about 1700 cm⁻¹

- (b) Two sharp bands above 3000 cm⁻¹ and two bands between 1600 and 1700 cm⁻¹
- (c) One strong broad band above 3000 cm^{-1} and a band at about 2200 cm^{-1}

Purpose of the problem

To show that IR alone does have some use but that NMR data are usually essential as well. In answers to exam questions of this type it is important to show how you interpret the data as well as to give a structure. If you get the structure right, this doesn't matter, but if you get it wrong, you may still get credit for your interpretation.

Suggested solution

(a) One sharp band above 3000 cm⁻¹ must be an N–H and one strong band at about 1700 cm⁻¹ must be a carbonyl group. That leaves C_2H_4 , so we might have one of the structures shown below, though other less likely structures are possible too. ¹³C NMR data would help as it would definitely show two types of saturated carbon (along with the carbonyl group) for the first compound, but only one for the second.



(b) Two sharp bands above 3000 cm^{-1} must be an NH₂ group and two bands between 1600 and 1700 cm⁻¹ suggest a carbonyl group and an alkene. This leaves us with three hydrogen atoms so we must have something like the molecules below. ¹³C NMR data would help as it would show an alkene carbon shifted downfield by being joined to electronegative nitrogen in the second case.



■ You will meet other ways of distinguishing these compounds in chapters 13 and 18.

(c) One strong broad band above 3000 cm⁻¹ must be an OH group and a band at about 2200 cm⁻¹ must be a triple bond, presumably CN as otherwise

we have nowhere to put the nitrogen atom. This means structures of this sort.



PROBLEM 7

Four compounds having the formula $C_4H_6O_2$ have the IR and NMR data given below. How many DBEs (double bond equivalents—see p. 75 in the textbook) are there in $C_4H_6O_2$? What are the structures of the four compounds? You might again find it useful to draw a few structures to start with.

- (a) IR: 1745 cm⁻¹; ¹³C NMR 214, 82, 58, and 41 ppm
- (b) IR: 3300 cm⁻¹ (broad); $^{\rm 13}C$ NMR 62 and 79 ppm.
- (c) IR: 1770 cm⁻¹; ¹³C NMR 178, 86, 40, and 27 ppm.
- (d) IR: 1720 and 1650 cm⁻¹ (strong); ¹³C NMR 165, 133, 131, and 54 ppm.

Purpose of the problem

First steps in identifying a compound from two sets of data. Because the molecules are so small (only four carbon atoms) drawing out a few trial structures is a good way to start.

Suggested solution

Here are some possible structures for $C_4H_6O_2$. It is clear that there are two double bond equivalents and that double bonds and rings are likely to feature. Functional groups are likely to include alcohol, aldehyde, ketone and carboxylic acid.



(a) IR: 1745 cm⁻¹ must be a carbonyl group; ¹³C NMR 214 must be an aldehyde or ketone, 82 and 58 look like two carbons next to oxygen and 41 is a carbon not next to oxygen but not far away. As the second oxygen doesn't show up in the IR, it must be an ether. As there is only one double bond, the compound must be cyclic. This suggests just one structure.

(b) IR: 3300 cm⁻¹ (broad) must be an OH; ¹³C NMR 62 and 79 show a symmetrical molecule and no C=O so it must have a triple bond and a saturated carbon next to oxygen. This again gives only one structure.

■ The alkyne does not show up in the IR as it is symmetrical: see p. 71 of the textbook. (c) IR: 1770 cm⁻¹ must be some sort of carbonyl group; ¹³C NMR 178 suggests an acid derivative, 86 is a saturated carbon next to oxygen, 40 and 27 are saturated carbons not next to oxygen. There is only one double bond so it must be a ring. Looks like a close relative of (a).

(d) IR 1720 and 1650 cm⁻¹ (strong) must be C=C and C=O; ¹³C NMR 165 is an acid derivative, 131 and 133 must be an alkene, and 54 is a saturated carbon next to oxygen. That defines all the carbon atoms. It is not significant that we cannot say which alkene carbon is which.



PROBLEM 8

You have dissolved *tert*-butanol in MeCN with an acid catalyst, left the solution overnight, and found crystals in the morning with the following characteristics. What are the crystals?



IR: 3435 and 1686 cm⁻¹; ¹³C NMR: 169, 50, 29, and 25 ppm; ¹H NMR: 8.0, 1.8, and 1.4 ppm; Mass spectrum (%): 115 (7), 100 (10), 64 (5), 60 (21), 59 (17), 58 (100), and 56 (7). Don't try to assign all the peaks in the mass spectrum.

Purpose of the problem

This is a common situation: you carry out a reaction and find a product that is not starting material, but what is it? You'll need to use all the information and some logic. What you must *not* do is to decide in advance what the product is from your (limited) knowledge of chemistry and make the data fit.

Suggested solution

The molecular ion in the mass spectrum is 115 and is presumably $C_6H_{13}NO$ —the sum of the two reagents *t*-BuOH and MeCN. It appears that they have added together but the IR shows that neither OH nor CN has survived. So what do we know?

- The IR tells us we have an N-H and a C=O group, accounting for both heteroatoms.
- The ¹³C NMR shows a carbonyl group (169) and three types of saturated carbon.

• There must be a lot of symmetry, suggesting that the *t*-Bu group has survived.

This leaves four fragments: NH, C=O, Me, and *t*-Bu, confirmed also by the ¹H NMR spectrum, which tells us that we have three types of H atoms. We can join these fragments up in two ways:



We might prefer the second as it retains the skeleton of MeCN, but a better reason is the base (100%) peak in the mass spectrum at 58. This is $Me_2C=NH_2^+$ which could easily come from the second structure but only by extensive reorganization of the first structure.

The second structure is in fact correct but we need further analysis of the proton NMR (chapter 13) to be sure.

PROBLEM 9

How many signals would you expect in the ¹³C NMR spectrum of these compounds?



Purpose of the problem

To get you thinking about symmetry.

Suggested solution

Compound **A** has tetrahedral symmetry and there are only two types of carbon: every CH_2 is the same, as is every CH, so it has two signals. This is the famous compound adamantane—a crystalline solid in spite of its being a hydrocarbon with only ten carbon atoms. If you do not see the symmetry, make a model—it is a beautiful structure.

■ If you are solving this problem after having already studied the more detailed description of ¹H NMR spectroscopy in chapter 13, it will help you to know that all three signals in the ¹H spectrum are singlets: no two types of H atom can be adjacent to each other. Compound **B** is symmetrical too: the two C=O groups are the same and so are all the other carbon atoms in the ring. It is an orange crystalline solid called quinone. Two signals.

Compound C is naphthalene and has high symmetry: the two benzene rings are the same and there are only three types of carbon atom. Three signals.

Compound \mathbf{D} is 'triethanolamine' used a lot by biochemists. It has threefold symmetry and only two types of carbon atom. Two signals.

Compound E is 'EDTA' (ethylenediaminetetraacetic acid) an important chelating agent for metals. This time there are three types of carbon atom. Three signals.



When benzene is treated with *tert*-butyl chloride and aluminium trichloride, a crystalline product **A** is formed that contains only C and H. Mass spectrometry tells us the molecular mass is 190. The ¹H NMR spectrum looks like this:



If crystals of **A** are treated again with more *tert*-butyl chloride and aluminium chloride, a new oily compound **B** may be isolated, this time with a molecular mass of 246. Its ¹H NMR spectrum is similar to that of **A**, but not quite the same:



What are the two compounds? How many signals do you expect in the ¹³C NMR spectrum of each compound?



Purpose of the problem

Identifying compounds from spectroscopic data, whether you know the reaction or not, is a key skill you must develop.