Suggested solutions for Chapter 2

2

Problem 1

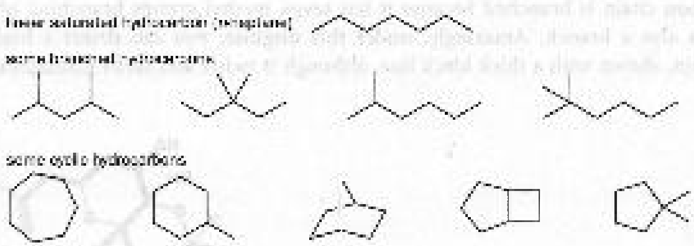
Draw good diagrams of saturated hydrocarbons with seven carbon atoms having (a) linear, (b) branched, and (c) cyclic frameworks. Draw molecules based on each framework having both ketone and carboxylic acid functional groups.

Purpose of the problem

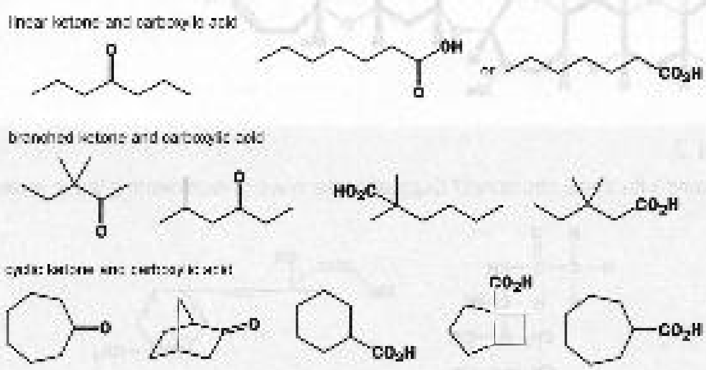
To get you drawing simple structures well and to steer you away from rules and names towards creative structural ideas.

Suggested solution

There is only one linear saturated hydrocarbon with seven carbon atoms but there is a wide choice for the rest. We offer some possibilities but you may well have thought of others.



We give just a few examples for the ketones and carboxylic acids. You will notice that no C_7 carbocyclic acid is possible based on, say, cycloheptane without adding an extra carbon atom.



Problem 2

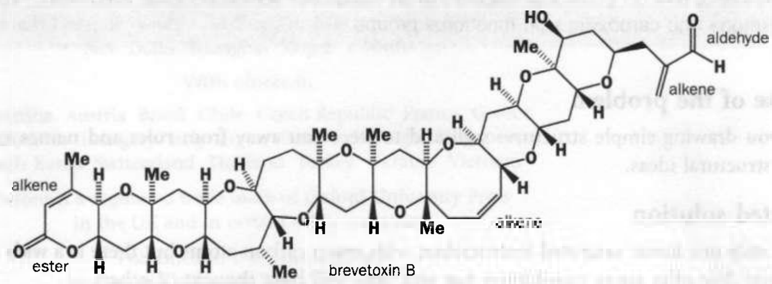
Study the structure of brevetoxin on p. 33. Make a list of the different types of functional group (you already know that there are many ethers) and of the numbers of rings of different sizes. Finally, study the carbon framework – is it linear, cyclic, or branched?

Purpose of the problem

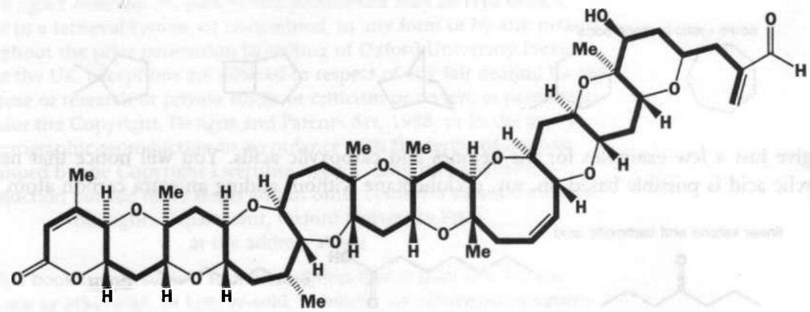
To persuade you that functional groups are easily recognized even in complicated molecules and that, say, an ester is an ester whatever company it may keep. You were not expected to see the full implications of the carbon framework part of the question. That was to amuse and surprise you.

Suggested solution

The ethers are all the unmarked oxygen atoms in the rings: all are cyclic, seven in six-membered rings, two in seven-membered rings, and one in an eight-membered ring. There are two carbonyl groups, one an ester and one an aldehyde, and three alkenes.

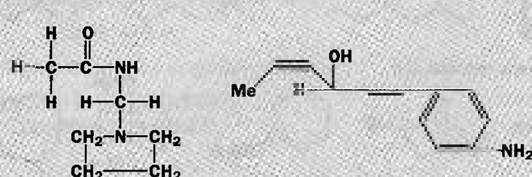


The carbon chain is branched because it has seven methyl groups branching off it and the aldehyde is also a branch. Amazingly, under this disguise, you can detect a basically linear carbon chain, shown with a thick black line, although it twists and turns throughout the entire molecule!



Problem 3

What is wrong with these structures? Suggest better ways of representing these molecules.

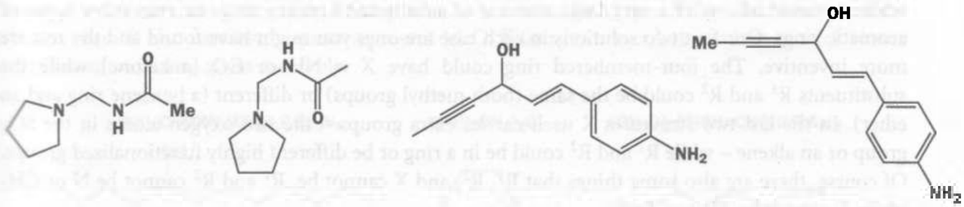


Purpose of the problem

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

Suggested solution

The bond angles are grotesque with square planar saturated carbon, alkynes at 120°, alkenes at 180°, bonds coming off benzene rings at the wrong angle, and so on. The left-hand structure would be clearer if most of the hydrogens were omitted. Here are two possible better structures for each molecule. There are many other correct possibilities.



Problem 4

Draw structures corresponding to these names. In each case suggest alternative names that might convey the structure more clearly to someone who is listening to you speak.

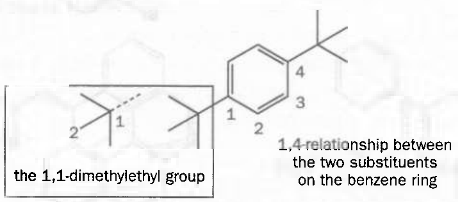
(a) 1,4-di-(1,1-dimethylethyl)benzene
(b) 3-(prop-2-enyloxy)prop-1-ene
(c) cyclohexa-1,3,5-triene

Purpose of the problem

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

Suggested solution

(a) 1,4-di-(1,1-dimethylethyl)benzene. More helpful name *para*-di-*t*-butyl benzene. It is sold as 1,4-di-*tert*-butyl benzene, an equally helpful name.

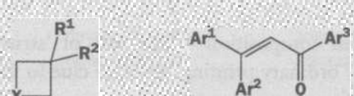


(b) 3-(prop-2-enyloxy)prop-1-ene. This name does not convey the simple symmetrical structure nor that it contains two allyl groups. Most chemists would call this 'diallyl ether' though it is sold as 'allyl ether'.

(c) cyclohexa-1,3,5-triene. This is, of course, benzene, but even IUPAC has not tried to impose this 'correct' name for such an important compound.

Problem 5

Draw one possible structure for each of these molecules, selecting any group of your choice for the 'wild card' substituents.

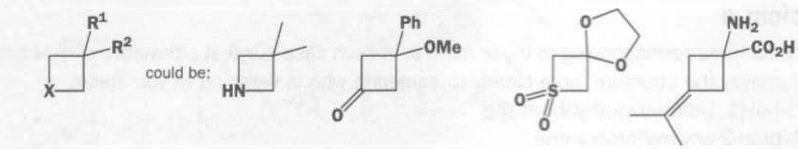


Purpose of the problem

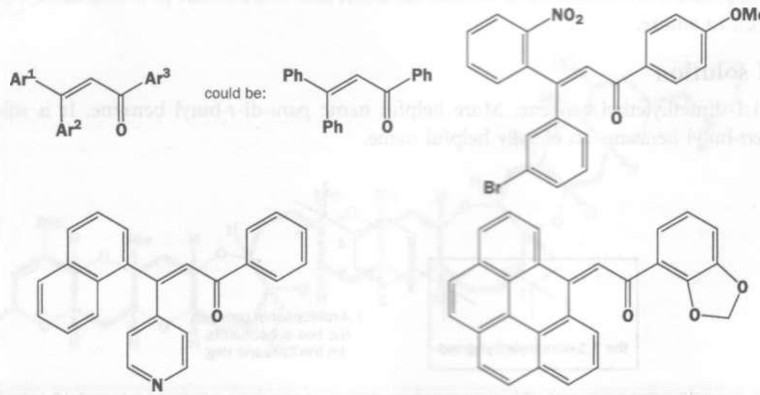
To help you appreciate the wide range and versatility of general structures with X, R^1, Ar^1, etc. These become more important when you start a database search for a part structure.

Suggested solution

There are, of course, many possible solutions. X could be a heteroatom or a structural fragment while Ar could be any of a very large number of substituted benzene rings or even other types of aromatic rings. Our first two solutions in each case are ones you might have found and the rest are more inventive. The four-membered ring could have X = NH or CO (a ketone) while the substituents R^1 and R^2 could be the same (both methyl groups) or different (a benzene ring and an ether). In the last two structures X itself carries extra groups – the two oxygen atoms in the SO_2 group or an alkene – while R^1 and R^2 could be in a ring or be different highly functionalized groups. Of course, there are also some things that R^1, R^2, and X cannot be. R^1 and R^2 cannot be N or CH_2 while X cannot be Ph or Cl.



The three aryl groups in the second example might all be different or some might be the same. In the last two structures we show some unusual aromatic rings including some linked together and one with a nitrogen atom in the ring.



Problem 6

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

$C_6H_5CH(OH).(CH_2)_4COC_2H_5$ **$O(CH_2CH_2)_2O$** **$(CH_3O)_2CHCH{=}CHCH(OMe)_2$**

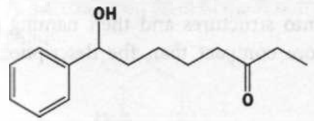
Purpose of the problem

An exercise in interpretation and composition – this sort of 'structure', which is used when structures must be represented by ordinary printing, gives no clue to the shape of the molecule and you must decide that for yourself.

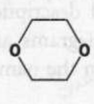
Suggested solution

You probably needed a few trial and error drawings first, but simply drawing out the carbon chains gives you the answers. The first is straightforward though you may not previously have seen the dot on the middle of the formula. This does not represent any atom but simply shows that the atom immediately before the dot is not joined to that immediately after it. The (OH) group is a substituent off the chain, not part of the chain itself. The second has no ends (Me groups, etc.) and so must be an unbroken ring. The third gives no clue as to the shape of the alkene and we have chosen *trans*. It also uses two ways to represent MeO. Either is correct but it is best to stick to one representation in any given molecule.

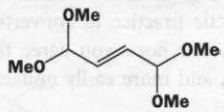
$C_6H_5CH(OH).(CH_2)_4COC_2H_5$



$O(CH_2CH_2)_2O$



$(CH_3O)_2CHCH{=}CHCH(OMe)_2$



Problem 7

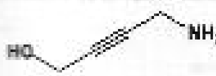
Suggest at least six different structures that would fit the formula C_4H_7NO. Make good realistic diagrams of each one and say which functional group(s) are present.

Purpose of the problem

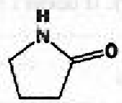
The identification and naming of functional groups is more important than the naming of compounds. This was your chance to experiment with different functional groups as well as different carbon skeletons.

Suggested solution

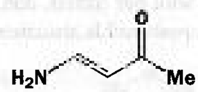
You will have found the carbonyl and amino groups very useful, but did you also use alkenes and alkynes, rings, ethers, alcohols, and cyanides? Here are twelve possibilities but there are many more. The functional group names in brackets are alternatives: some you will not have known. You need not have classified the alcohols and amines.



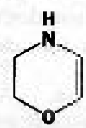
alkyne, primary alcohol, primary amine



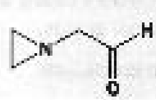
cyclic amide



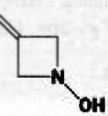
ketone, alkene, primary amine (enamine)



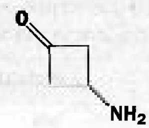
ether, alkene, secondary amine



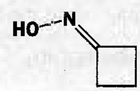
cyclic tertiary amide, aldehyde



alkene, amine, alcohol (cyclic hydroxylamine)



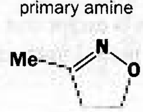
cyclic ketone, primary amine



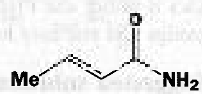
oxime, imine + alcohol

ether, nitrile (cyanide)

primary alcohol, nitrile (cyanide)



imine, ether (isoxazoline)



alkene, primary amide

Problem 8

Draw and name a structure corresponding to each of these descriptions.

(a) An aromatic compound containing one benzene ring with the following substituents: two chlorine atoms having a *para* relationship, a nitro group having an ortho relationship to one of the chlorine atoms, and an acetyl group having a meta relationship to the nitro group.

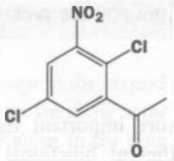
(b) An alkyne having a trifluoromethyl substituent at one end and a chain of three carbon atoms at the other with a hydroxyl group on the first atom, an amino group on the second, and the third being a carboxyl group.

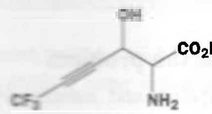
Purpose of the problem

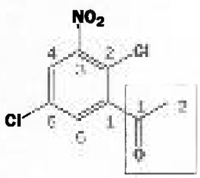
Just a little practice in converting verbal descriptions into structures and then naming them is justified. We hope you agree that the diagrams are more compact than the description in the question and more easily understood than the name.

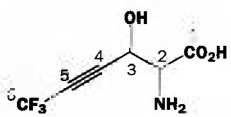
Suggested solution

The structures are uniquely described by the rather verbose descriptions.









Naming the compounds requires (1) identifying the boss functional group, (2) numbering the skeleton, and (3) locating the functional group by name and number. The aromatic compound is a ketone with two carbon atoms – an ethanone (even though there cannot be a two-carbon ketone!). The carbonyl group is C1. The aromatic ring is joined on by its C1 at C1 and is numbered so as to give the smallest possible numbers to the substituents. It is (2,5-dichloro-3-nitrophenyl)ethanone.

The aliphatic compound is a carboxylic acid which becomes C1. The rest is straightforward. Groups are usually named in alphabetical order. It is 2-amino-3-hydroxy-6,6,6-trifluorohex-4-ynoic acid. If you don't agree with our names, don't worry. It doesn't really matter. What does matter is: did you draw clear comprehensible structures?

Problem 9

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

$AcO(CH_2)_3NO_2$ $MeO_2C.CH_2.OCOEt$ $CH_2{=}CH.CO.NH(CH_2)_2CN$

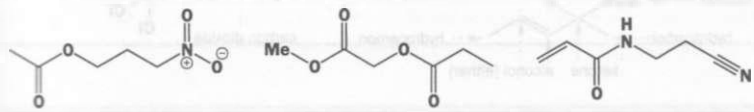
Purpose of the problem

This is rather like Problem 6 except that more thought is needed for the details of the functional groups and you may have needed to check the 'organic elements' Ac, Et, and so on in the chapter.

Suggested solution

For once the solution can be simply stated as no variation is really possible The tricks for the first one are to see that 'AcO' represents an ester and to have only four bonds to nitrogen in NO_2. The second has two ester groups on the central CH_2 group but one is joined to it by a CO bond and the other by a CC bond. The last is straightforward except for the dots used to separate the substituents explained in the answer to Problem 6).

$AcO(CH_2)_3NO_2$ $MeO_2C.CH_2.OCOEt$ $CH_2{=}CH.CO.NH(CH_2)_2CN$



Problem 10

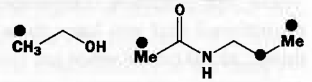
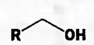
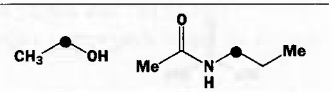
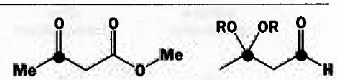
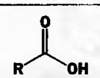
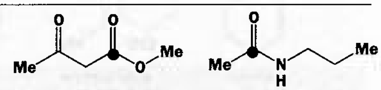
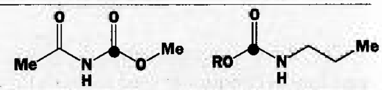
Identify the oxidation level of each of the carbon atoms in these structures with some sort of justification.

Purpose of the problem

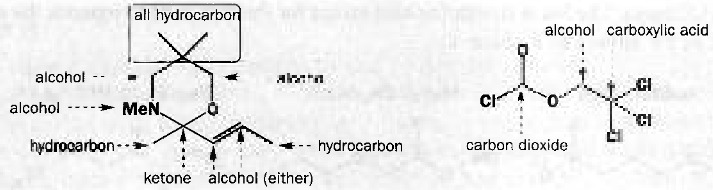
This important exercise is one you will get used to very quickly and, before long, do without thinking. If you do, it will save you from many trivial errors. Remember that the oxidation *state* of carbon is +4, or C(IV), in all these compounds. The oxidation *level* of a functional group tells you with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

Suggested solution

Just count the number of bonds to heteroatoms. These can range from none to four. The only tricky ones are alkenes and alkynes, which have no heteroatoms but are formed by dehydration of alcohols, aldehydes, or ketones. There is a summary chart on p. 36 of the textbook, but briefly:

Bonds to heteroatoms	Oxidation level	Type structure	Examples
0	hydrocarbon	$R{-}CH_3$	
1	alcohol		
2	aldehyde or ketone		
3	carboxylic acid		
4	carbon dioxide	$O{=}C{=}O$	

In these cases we have examples of all oxidation levels. Check the answer against yours and the table. In the case of the alkene, formally a dehydration product from an alcohol, either but not both of the C atoms is at the alcohol oxidation level.



Problem 11

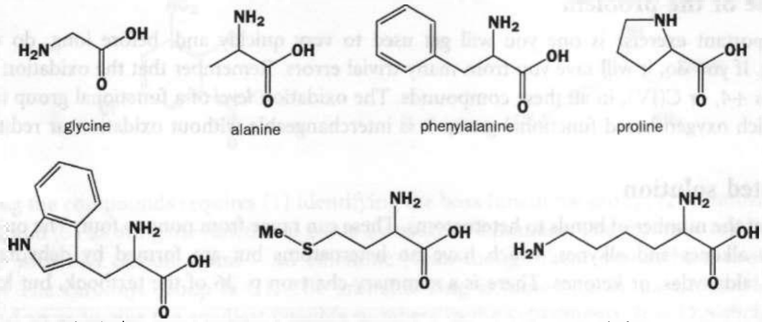
If you have not already done so, complete the exercises on pp. 23 (drawing amino acids) and 44 (giving structures for the 10 common compounds and three common solvents).

Purpose of the problem

These compounds are important so drawing them again is not just a useful exercise; it also helps reinforce your knowledge of these structures.

Suggested solution

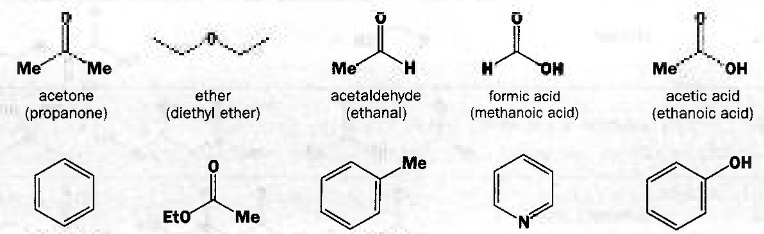
Here are the drawings we suggested for the amino acids on p. 23. There are other ways.



glycine alanine phenylalanine proline

tryptophan methionine lysine

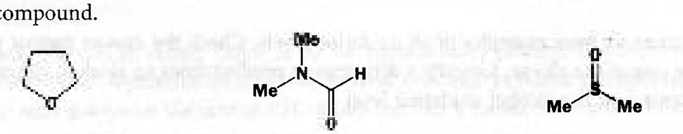
The 'ten common compounds' and 'three common solvents' are specially important and we recommend that you learn these structures. We generally pour scorn on the idea of memorizing things, so take note when we recommend it!



acetone (propanone) | ether (diethyl ether) | acetaldehyde (ethanal) | formic acid (methanoic acid) | acetic acid (ethanoic acid)

benzene | ethyl acetate (ethyl ethanoate) | toluene | pyridine | phenol

The three common solvents below join ether, acetone, ethyl acetate (EtOAc), toluene, and pyridine as commonly used solvents for organic reactions. One or other of these will dissolve almost any organic compound.



tetrahydrofuran (THF) | dimethylformamide (DMF) | dimethylsulfoxide (DMSO)