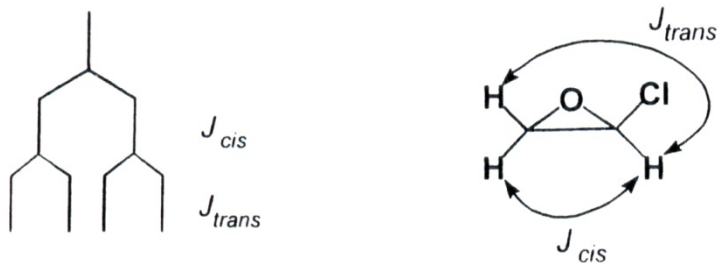


Chapter 2

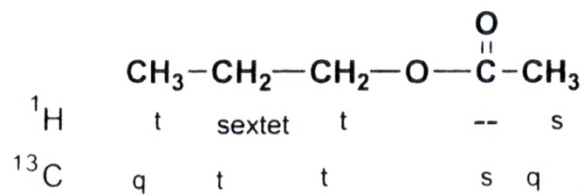
Introduction

- 2-1 (a) All seven carbons are distinct. There are four groups of hydrogens: one methyl, four different methylenes, and one proton attached to an alkene carbon.
- (b) The molecule has a plane of symmetry that is perpendicular to the apparent plane of the ring (in its flat depiction on the page) and runs through the double bond and the carbon opposite the double bond. Thus there are five different types of carbon in the ratio 1/2/2/1/1: the three carbons on the plane of symmetry and the two pairs off the plane. There are four groups of hydrogens in the ratio 2/4/4/2: the exomethylene (=CH₂) group, two pairs of methylene protons off the plane, and the saturated methylene on the plane. This analysis assumes rapid ring flipping.
- (c) First, draw out the phenyl ring in order to see its structure. There are seven types of carbons in the ratio 1/2/2/1/1/1/1: the para carbon, the two meta carbons, the two ortho carbons, the ipso carbon, the methylene carbon, the carbonyl carbon, and the methyl carbon. The protons fall into five groups in the ratio 1/2/2/2/3: the para hydrogen, the two meta hydrogens, the two ortho hydrogens, the methylene hydrogens, and the methyl hydrogens.
- (d) There is a plane of symmetry that runs through the oxygen, the bridge CH, the middle of the double bond, and the middle of the C—C single bond of the bismethylene bridge. The carbons occur in four groups in the ratio 2/2/1/2: the alkene carbons, the bridgehead carbons, the bridge methine, and the bismethylene carbons. The hydrogens occur in six groups in the ratio 2/2/1/1/2/2: the alkenic protons, the bridgehead protons, the methine proton, the hydroxy proton, the pair of exo protons, and the pair of endo protons.
- 2-2 (a) Each pair of terminal methylene protons is split into a 1/3/1 triplet by the two internal methylene protons, and the internal methylene protons are split into a 1/4/6/4/1 quintet by the four terminal methylene protons.
- (b) The methine proton is split into a 1/6/15/20/15/6/1 septet by the two methyl groups, and the methyl protons are split into a doublet by the methine proton.
- (c) The methyl protons are split into a 1/2/1 triplet by the methylene group, and the methylene protons are split into a 1/3/3/1 quartet by the methyl group. The para proton is split into a 1/2/1 triplet by the two meta protons, the meta proton into a 1/2/1 triplet by the para and ortho protons (if the couplings are equal), and the ortho proton into a 1/1 doublet by the adjacent meta proton.
- (d) Each proton is split into a doublet by one proton and into another doublet by the other proton, so all resonances are doublets of doublets (dd). The diagram on the next page illustrates this result for the proton geminal to chlorine.

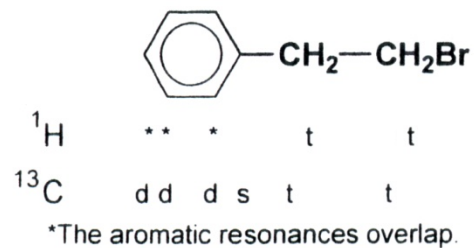


2-3 [s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet]

(a)

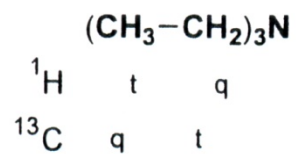


(b)

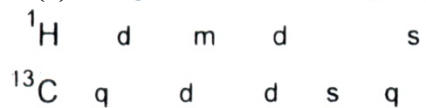


(c)

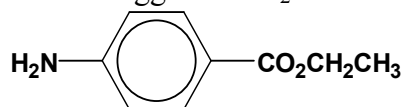
(d)



(e) $\text{CH}_3\text{-CH=CH-CO}_2\text{CH}_3$



- 2-4 (a) The molecule is saturated ($U = 0$). The triplet at highest frequency must be from a CH_2Br group, and the triplet at lowest frequency from a methyl group. A CH_2 between two other methylene groups gives the quintet, and the CH_2 between one methylene and one methyl group gives the sextet: $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 1-bromobutane.
- (b) The molecule is saturated and has no rings ($U = 0$). The triplet and quartet indicate an ethyl group, and the integral requires that the ethyl group is present three times in the molecule. The high frequency of the methylene resonance (δ 3.6) indicates that CH_2 is bonded to O, leaving only the CH portion. The only way to assemble these fragments is as $\text{HC}(\text{OCH}_2\text{CH}_3)_3$, triethyl orthoformate, an unusual functional group.
- (c) There are two unsaturations, two methyl groups, and two alkenic CH pieces coupled to each other. The methyl chemical shifts suggest that the two oxygens are present as carbonyl and ether linkages. The entire structure then is *trans*- $\text{CH}_3\text{OCH}=\text{CH}(\text{C}=\text{O})\text{CH}_3$, *trans*-4-methoxy-3-buten-2-one. Methods for determining the stereochemistry of the double bond are discussed in Chapter 4.
- (d) The unsaturation number of 4 indicates a benzene ring. The protons on a *para*-disubstituted benzene ring produce the pair of doublets. The triplet and quartet indicate an ethyl group. The broad peak at δ 4.1 has an integral of 2, which suggests NH_2 . The entire molecule then may be assembled as



, ethyl 4-aminobenzoate.

- (e) The molecule has an unsaturation number of 2. The triplet at lowest frequency (integral of 3) is associated with the quartet and hence indicates an ethyl group (5 of the 9 protons). The remaining pair of triplets indicate mutually adjacent methylene groups (CH_2CH_2), accounting for the remaining 4 protons and 4 of the 5 carbons. The unsaturations must be associated with the remaining single C, O, and N atoms and are best explained by a nitrile group and an ether linkage: $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CN}$, 3-ethoxypropionitrile. An alternative structure, *N*-ethylpropiolactone would give a similar ^1H spectrum but could be distinguished easily by ^{13}C NMR spectroscopy (Chapter 3).

