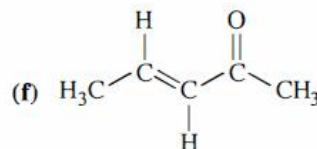
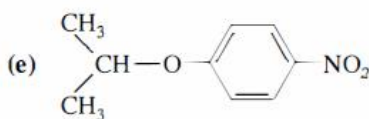
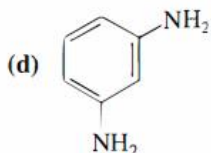
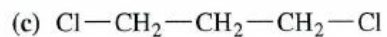
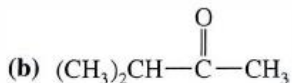
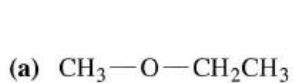
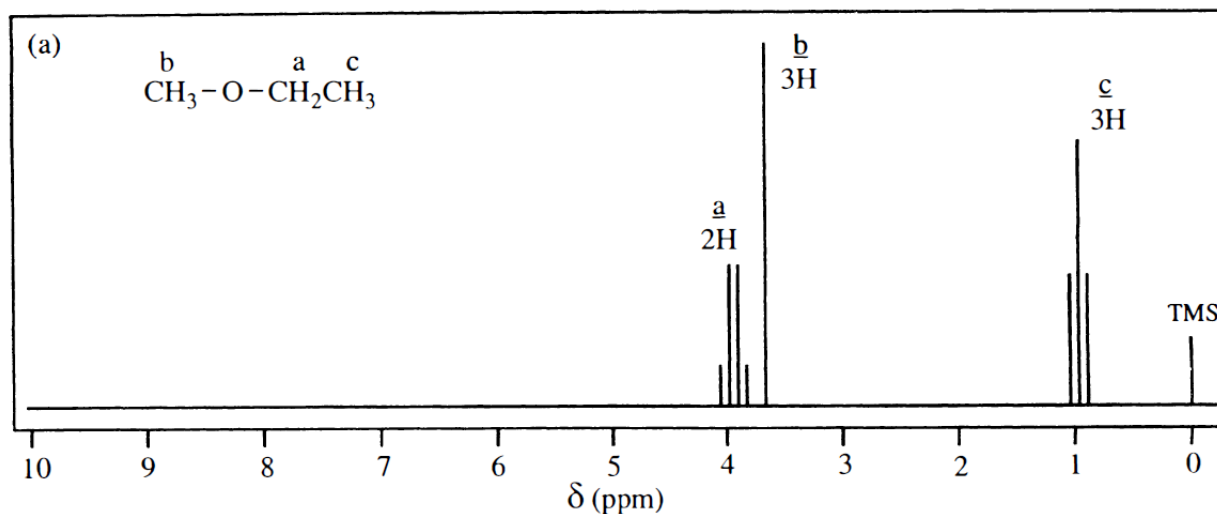


NMR Exercise

QI. Sketch your predictions of the proton NMR spectra of the following compounds.



SOLUTION FOR PROBLEM (a)



QII. An unknown compound has the molecular formula $\text{C}_9\text{H}_{11}\text{Br}$. Its proton NMR spectrum shows the following absorptions:

singlet, δ 7.1, integral 4.4 cm

singlet, δ 2.3, integral 13.0 cm

singlet, δ 2.2, integral 6.7 cm

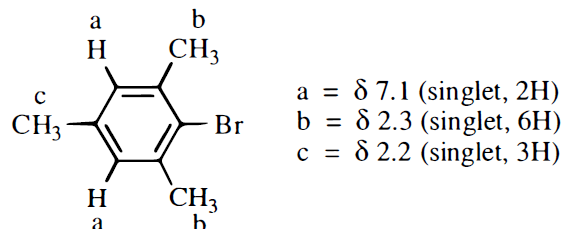
Propose a structure for this compound.

SOLUTION:

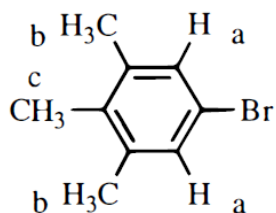
The formula $\text{C}_9\text{H}_{11}\text{Br}$ indicates four elements of unsaturation, just enough for a benzene ring. Here is the most accurate method for determining the number of protons per signal from integration values when the total number of protons is known. Add the integration heights : 4.4

cm + 13.0 cm + 6.7 cm = 24.1 cm. Divide by the total number of hydrogens: 24.1 cm./ 11 H = 2.2 cm/H. Each 2.2 cm of integration height = 1 H, so the ratio of hydrogens is 2 : 6 : 3.

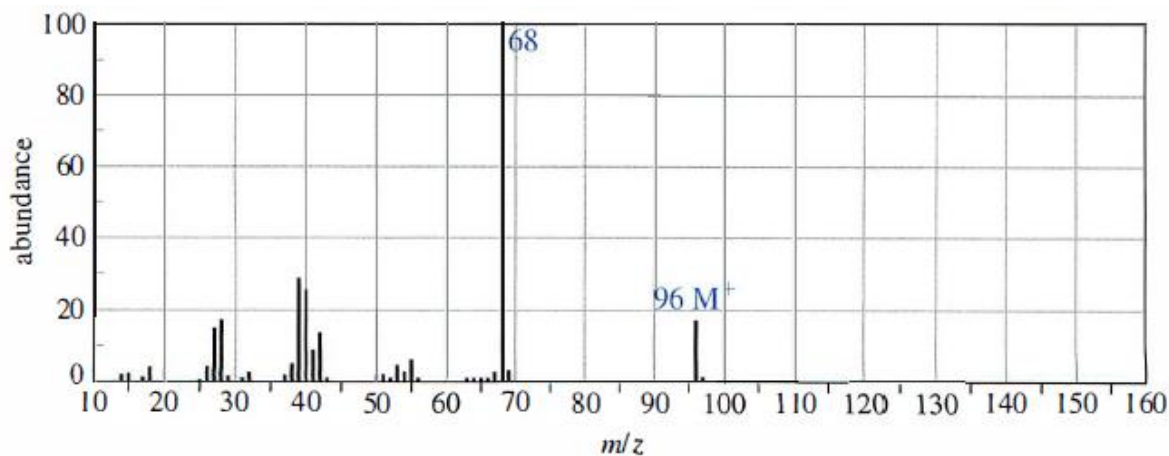
The 2H singlet at $\delta 7.1$ means that only two hydrogens remain on the benzene ring, that is, it has 4 substituents. The 6H singlet at $\delta 2.3$ must be two CH_3 's on the benzene ring in identical environments. The 3H singlet at $\delta 2.2$ is another CH_3 in a slightly different environment from the first two. Substitution of the three CH_3 's and the Br in the most symmetric way leads to the next structures .

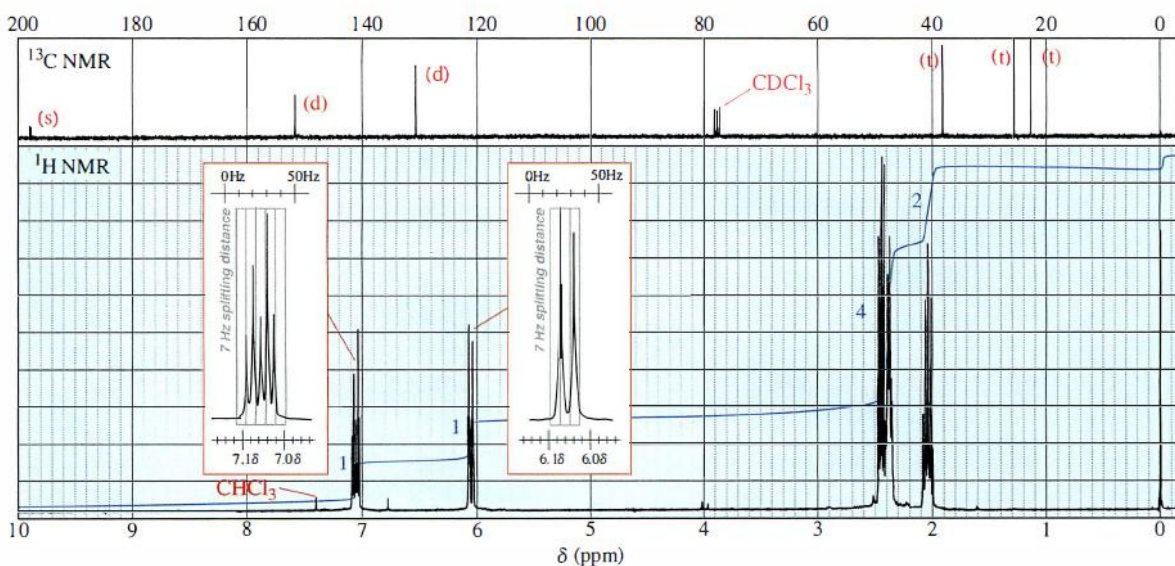
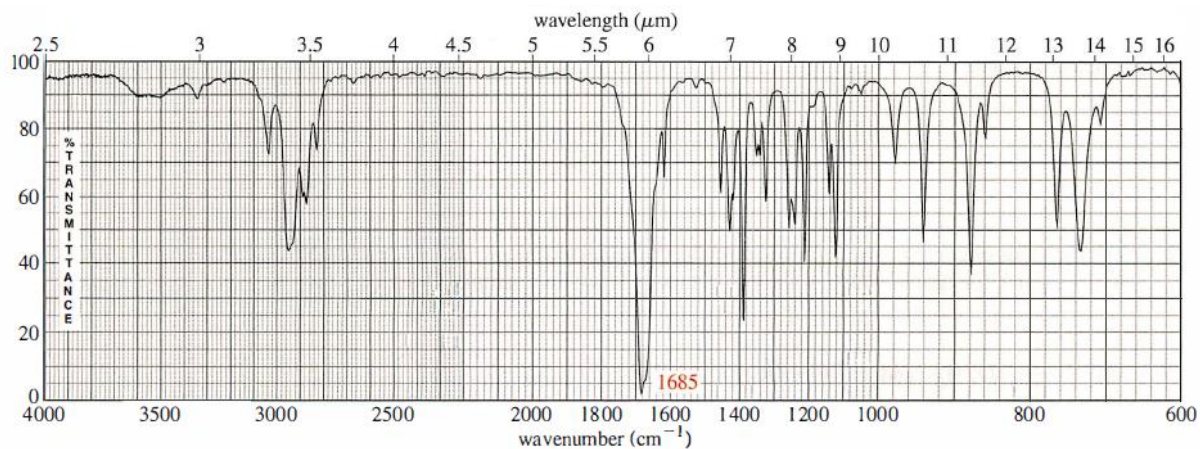


a second structure is also possible although it is less likely because the Br would probably deshield the Hs labeled "a" to about 7.3-7.4



QIII. The following spectra are taken from a compound that is an important starting material for organic synthesis. Determine the structure, first by considering each spectrum individually, then by considering all the spectra together. Assign peaks to show that your proposed structure accounts for all the major features of each spectrum:





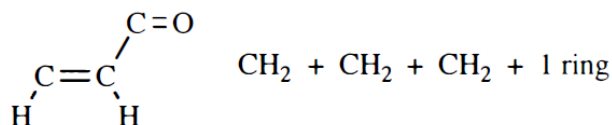
SOLUTION:

This is a challenging problem, despite the molecule being relatively small.

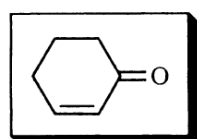
Mass spectrum: The molecular ion at 96 suggests no Cl, Br, or N. The molecule must have seven carbons or fewer.

Infrared spectrum: The dominant functional group peak is at 1685 cm⁻¹, a carbonyl that is conjugated with C=C (lower wavenumber than normal, very intense peak). The presence of an oxygen and a molecular ion of 96 lead to a formula of C₆H₈O, with three elements of unsaturation, a c=O and one or two c=c.

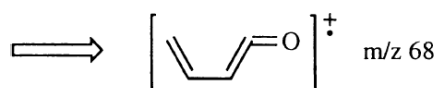
Carbon NMR spectrum: The six peaks show, by chemical shift, one carbonyl carbon (196), two alkene carbons (129, 151), and three aliphatic carbons (23, 26, 36). By off-resonance decoupling multiplicity, the groups are: three CH₂ groups, two alkene CH groups, and carbonyl. Since the structure has one carbonyl and only two alkene carbons, the third element of unsaturation must be a ring.



Since the structure has no methyl group, and no $\text{H}_2\text{C}=\text{}$, all of the carbons must be included in the ring. The only way these pieces can fit together is in cyclohex-2-enone. Notice that the proton NMR was unnecessary to determine the structure, fortunately, since the ^1H NMR was not easily interpreted except for the two alkene hydrogens; the hydrogen on carbon-2 appears as the doublet at 6.0.

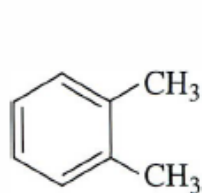


cyclohex-2-enone



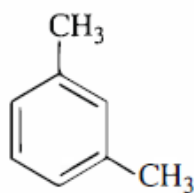
The mystery mass spec peak at m/z 68 comes from a fragmentation that will be discussed later; it is called a retro-Diels-Alder fragmentation.

QIV. The three isomers of dimethyl benzene are commonly named *ortho*-xylene, *meta*-xylene, and *para*-xylene. These three isomers are difficult to distinguish using proton NMR, but they are instantly identifiable using ^{13}C NMR.



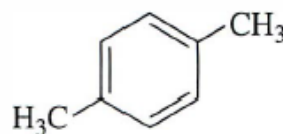
ortho-xylene

1,2-dimethylbenzene



meta-xylene

1,3-dimethylbenzene

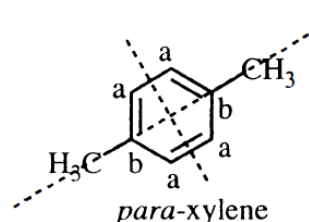
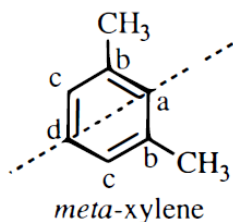
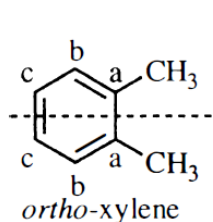


para-xylene

1,4-dimethylbenzene

- (a) Describe how carbon NMR distinguishes these three isomers.
 (b) Explain why they are difficult to distinguish using proton NMR.

SOLUTION: The key to the carbon NMR lies in the symmetry of these structures.



- (a) In each molecule, the methyl carbons are equivalent, giving one signal in the ^{13}C NMR. Considering the ring carbons, the symmetry of the structures shows that *ortho*-xylene would have 3 carbon signals from the ring (*total of 4 peaks*), *meta*-xylene would have 4 carbon signals from the ring (*total of 5 peaks*), and *para*-xylene would have only 2 carbon signals from the ring (total of 3 peaks). These compounds would be instantly identifiable simply by the number of peaks in the carbon NMR.
- (b) The proton NMR would be a completely different problem. Unless the substituent on the benzene ring is moderately electron-withdrawing or donating, the ring protons absorb at roughly the same position. A methyl group has essentially no electronic effect on the ring hydrogens, so while the *para* isomer would give a clean singlet because all its ring protons are equivalent, the *ortho* and *meta* isomers would have only slightly broadened singlets for their proton signals. (Only a very high field NMR, 500 MHz or higher, would be able to distinguish these isomers in the proton NMR.)