

Příklad 9

Exercise 001 (001)

Preliminary Observation

The mass spectrum can be used to get the molecular mass of the compound, to detect the presence of chlorine, bromine or other heteroatoms, and to obtain structural information from the fragmentation pattern. The IR spectrum provides evidence of functional groups and other structural features. The ^{13}C NMR spectrum gives the number of different carbon in the molecule, as well as their degree of substitution and functionality. The ^1H NMR spectrum can provide a count of the number of protons and information on their environment. The ^1H coupling patterns give indications of the connectivity of the components of the molecule.

Mass Spectrum

The isotope patterns give no indication of the presence of chlorine or bromine. The molecular ion (M^+) is usually the highest mass ion (with its associated isotope peaks). An odd-mass molecular ion usually indicates the presence of an odd number of nitrogen atoms. In this spectrum, the highest mass ion 74 (44%) has a ^{13}C isotope peak at 75 (2%). The natural abundance of ^{13}C is 1.1%; therefore, each carbon contributes 1.1% to the intensity of the isotope peak. The relative intensity of the $\text{M}+1$ peak in this compound is 4.5% ($100 \times 2/44$), indicating the presence of four carbons. The most intense peak is known as the base peak and is assigned an intensity of 100%. The ion at 31 (100%) indicates the presence of oxygen in the molecule. The highest mass hydrocarbon in that region is 29 (CH_3CH_2^+), but if oxygen is present a peak at 31 (CH_2OH^+) is possible. The peak at 59 corresponds to $\text{M}-15$, suggesting the presence of a CH_3 group.

^{13}C NMR

The simplest spectrum, the broad band (BB) decoupled spectrum in which all of the C–H coupling is removed, shows signals from only two types of carbon. In the off-resonance (OR) spectrum, the size of the direct C–H coupling is reduced to make the coupled spectrum more easily readable. In this exercise, the direct C–H coupling gives a quartet for a methyl group (CH_3), and a triplet for a methylene group (CH_2). The DEPT spectrum shows inverted signals for CH_2 carbons, and in this example has one such signal. Carbons bearing an odd

number of protons show upright signals, and here it shows one such signal, that of the CH_3 group. Quaternary carbons (bearing no H) give no signal in the DEPT spectrum. The chemical shift of the lower field carbon, (66 ppm) is in the range of a methylene carbon bonded to oxygen. The molecule must have an element of symmetry, because the mass spectrum indicates that it has four carbons.

^1H NMR

The ^1H NMR spectrum shows only two types of proton, a triplet and a quartet. The small peak at 0.0 ppm is that of the tetramethylsilane reference standard. This simple coupling pattern is easily recognized as that of an ethyl group ($-\text{CH}_2\text{CH}_3$), with the methyl protons split by the neighbouring CH_2 protons into a triplet, and the methylene protons being split by the neighbouring CH_3 protons into a quartet. The integration of the spectrum indicates that the two signals have a relative intensity of 2 to 3. A molecule that has no nitrogen or halogen or other odd-valent atom, must have an even number of protons. Thus, there must be an even number of ethyl groups. The low field chemical shift (3.5 ppm) of the CH_2 group indicates that it is attached to an electron-withdrawing group, the oxygen atom in this case.

Infrared

The band at 1140 cm^{-1} is a clear indication of C–O stretching, most likely that of an ether function. Other than the bands due to the alkyl groups, there are no bands that can be assigned to other functional groups. The IR spectrum can be used very effectively to show that certain functional groups are absent. For instance, in this case one can say with certainty that there is neither a carbonyl group, nor hydroxyl present in the molecule.

Summary

The ^1H and ^{13}C NMR evidence indicates the presence of an ethyl group bonded to oxygen (ethoxy group). The mass spectrum gives a molecular mass of 74, and since an ethoxy group has a mass of 45, another ethyl group (mass 29) is required to complete the structure. The compound is diethyl ether, $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$.

Příklad 10

Exercise 002 (003)

Preliminary Observation

In a preliminary scan of the spectra there are several points that stand out. In the IR spectrum, there is a very strong peak in the carbonyl region near 1740 cm^{-1} . The mass spectrum appears to have a peak for the molecular ion, since the highest mass ion has an even mass. The ^{13}C NMR spectrum can be used to determine the number and type of carbons, and the ^1H NMR spectrum to get the connections between the carbons. The chemical shifts and the IR spectrum will identify the functional group. The mass spectrum can be used to get the molecular weight of the compound.

^{13}C NMR

The broad band spectrum shows that there are four types of carbon in the molecule. The off-resonance spectrum indicates that two of the carbons are methyl groups (quartets, CH_3), one is a methylene group (triplet, CH_2) and one a quaternary carbon (singlet, no attached hydrogen). The DEPT spectrum shows one inverted signal corresponding to the CH_2 carbon, and the disappearance of a peak at 171 ppm corresponding to the quaternary carbon. There are two different CH_3 groups, one CH_2 group, and a strongly deshielded carbon bearing no hydrogens (quaternary carbon). This spectrum shows that the compound has four carbons and eight protons or a multiple of these.

^1H NMR

The ^1H NMR spectrum shows the signals from three different types of proton. The integration of the spectrum shows a relative intensity of 2:3:3 (4.2, 2.0 and 1.3 ppm), for a total of eight protons, which agrees with the ^{13}C NMR spectrum that indicated a total of eight protons. One CH_3 group is not coupled to any other hydrogen (singlet at 2 ppm), and the other CH_3 (triplet at 1.3 ppm) is coupled to the CH_2 group. Thus, we have an ethyl group and an isolated methyl group. The singlet at 2 ppm is in the chemical shift region of a methyl group attached to an sp^2 carbon, while the CH_2 (4.1 ppm) is in the region of a methylene group attached to an oxygen. As the CH_2 group is coupled to a methyl group, we have a $\text{CH}_3\text{CH}_2\text{O}$ group.

Infrared

This infrared spectrum has two very significant bands of the functional group of the compound. The band at 1740 cm^{-1} clearly shows the presence of a carbonyl group ($\text{C}=\text{O}$), and the band at 1250 cm^{-1} indicates the presence of a $\text{C}-\text{O}$ single bond. The frequencies of both of these bands are compatible with an ester group ($\text{C}-\text{O}-\text{C}=\text{O}$).

Mass Spectrum

The highest even-mass ion in the spectrum is at 88, and is probably that of the molecular ion. The most intense peak (the base peak) is found at 43, which is a fragment most commonly associated with an acylium ion ($\text{CH}_3\text{C}\equiv\text{O}^+$). This would arise from the loss of the ethoxy radical by α cleavage at the carbonyl group. The ion at 73 comes from the loss of one of the methyl groups. The ion at 70 arises from the loss of a molecule of water, a common rearrangement fragmentation in esters. The majority of the fragment ions have odd masses, which is typical of compounds without nitrogen. These odd-mass ions have an even number of electrons, and are generally more stable than the even-mass fragments, as they consist of the less stable odd-electron radical ions. Even-mass ions are generally formed when a rearrangement creates a stable small molecule, such as, in this case, the loss of water yields the ion at 70.

Summary

The structural components that have been identified are: an ethyl group, a methyl group and a quaternary carbon, the mass of these adding to 56, which is 32 less than the molar mass of 88 that was found from the mass spectrum. The missing mass is equivalent to two oxygen atoms (2×16), exactly the number required for the ester group that was identified in the IR spectrum. The NMR chemical shifts of the CH_2 group indicate that it is attached directly to the oxygen of the ester. The chemical shifts of the uncoupled methyl group indicate that it is attached to a polarized sp^2 carbon, which would place it on the carbonyl ($\text{C}=\text{O}$) carbon. This gives us the complete structure $\text{CH}_3(\text{C}=\text{O})\text{OCH}_2\text{CH}_3$, ethyl acetate.

Příklad 11

Exercise 005 (094)

Preliminary Observation

After a preliminary scan of the spectra to check for the presence of functional groups, one can try to determine the molecular formula from the mass spectrum. The alkyl groups can be identified by the ^{13}C and ^1H NMR spectra. From the molecular formula and the types of carbon, one can combine the groups to create a structure for the compound.

Infrared

The infrared spectrum shows no evidence of the presence of a functional group. All the peaks may be assigned to alkyl groups. The band at 1380 cm^{-1} may be assigned to a deformation band of a CH_3 group. If this peak appears as a doublet, it could be taken as evidence of *gem*-dimethyl group (isopropyl $-\text{CH}(\text{CH}_3)_2$, *tert*-butyl $-\text{C}(\text{CH}_3)_3$ or $>\text{C}(\text{CH}_3)_2$).

Mass Spectrum

The highest mass ion in the spectrum (142) has an even mass, and the majority of the fragments are odd mass ions of the alkane family, 29, 43, 57, 71 and 113. This suggests that the compound has a molecular mass of 142, and is probably a hydrocarbon. Dividing the mass of 142 by 14 indicates that the molecule has a mass equivalent of 10 CH_2 units, plus a remainder of 2. This is an exact match for the saturated hydrocarbon ($\text{C}_{10}\text{H}_{22}$). The first fragment ion in the spectrum is found at 113, due to the loss of 29, CH_3CH_2 ; the lack of an $\text{M}-15$ peak suggests that there is no CH_3 at a branch carbon. Note that there is no peak at 31, which would have been an indication of the presence of oxygen.

^1H NMR

The proton NMR shows signals that are so close together that a precise integration is difficult. In a higher field spectrometer, the peaks would be better separated and a better integration could be obtained. The triplet near 0.9 ppm is due to methyl groups and shows the distortion typical of a methyl group split by protons with a similar chemical shift. This supports the mass spectral evidence for the presence of a CH_3CH_2 group in the molecule. The only other signals are at a slightly lower field, where one would expect to see the signals for CH_2 and CH protons.

^{13}C NMR

Although the molecular formula is $\text{C}_{10}\text{H}_{22}$, only three types of carbon are observed. There are obviously some isochronous carbons present. All the signals are found in the range

for sp^3 -hybridized carbons, unaffected by functional groups. The DEPT spectrum shows the absence of quaternary carbons (no signals disappear), but does show the presence of one type of secondary carbon (CH_2 signal inverted). The doublet at 43.1 ppm in the off-resonance spectrum represents CH carbons, the triplet at 22.9 ppm represents CH_2 carbons and the quartet at 12.6 ppm, the CH_3 carbons.

Structure

The accumulated evidence indicates that the molecule has ethyl groups (CH_3CH_2-) and methine carbons ($>\text{CH}-$), but no quaternary carbons. For each new branch in the chain, a methyl group is needed to terminate the new chain. A straight chain alkane has two methyl groups but no $>\text{CH}$ carbons. Insertion of a $>\text{CH}-$ adds a branch, thus requiring another CH_3 . In this example the methyl groups are part of ethyl groups. Starting with a straight chain of two ethyl groups, adding a $>\text{CH}-$ requires another ethyl group giving seven carbons. Adding another $>\text{CH}-$ requires another ethyl group which gives the required 10 carbons. Thus there are four ethyl groups and two methine carbons in the molecule. The only way to arrange these to make the ethyl groups equivalent and the methines equivalent is in the molecule of 3,4-diethylhexane, $(\text{CH}_3\text{CH}_2)_2\text{CHCH}(\text{CH}_2\text{CH}_3)_2$.

Notes

The peaks at 71 and 70 arise from cleavage of the bond at the centre of the molecule, resulting in two peaks, one at 71 from the loss of a pentyl radical, and the other at 70 from the loss of a pentane molecule by a rearrangement reaction. In the 90-MHz ^1H NMR spectrum, the $>\text{CH}-$ and $>\text{CH}_2$ protons appear in an unresolved cluster below the peaks of the methyl protons. In a 400-MHz ^1H NMR spectrum, the signal would be better resolved and it may be possible to analyse the pattern. Note that the two protons of each CH_2 group are not equivalent. They are diastereotopic, being adjacent to a carbon atom bearing three different substituents. They form an AB pair ($^2J = 13\text{ Hz}$), further coupled to the protons of the CH_3 group ($^3J = 7.2\text{ Hz}$). In addition, they are not equally coupled to the neighbouring methine proton, having different coupling constants ($^3J = 2$ and $^3J = 6.5\text{ Hz}$).

Příklad 12

Exercise 008 (011)

Preliminary Observation

Looking for evidence of functional groups in the IR spectrum seems somewhat unproductive in this spectrum. One might have better luck in the mass spectrum and the NMR spectra. Note that the molecular ion appears to be odd-mass, and that many of the fragment ions are even-mass.

Mass Spectrum

The molecular ion is found at 101 (18%), and has an $M+1$ isotope peak intensity of 1%, too weak to provide a reliable relative intensity calculation. The odd mass of the compound suggests that it contains nitrogen (or an odd number of N) and an odd number of monovalent atoms. In addition, the principal fragments have even masses, 30, 58 and 86, as might be expected for a compound containing nitrogen (normally a majority of odd fragments for non-nitrogen compounds, and even fragments for nitrogen-containing compounds). The predominant cleavage occurs by loss of a radical from the carbon bonded to the nitrogen (α cleavage), in this case yielding an ion at 86 (100%) from the loss of CH_3 , and an ion at 100 (7%) from the loss of H. The greater loss of the more complex radical is a general phenomenon. The ion at 30 is due to the $\text{H}_2\text{C}=\text{NH}_2^+$ ion, which is a common fragment of amines.

^{13}C NMR

The DEPT spectrum indicates the presence of a CH_2 group (inverted peak), and the chemical shift (42 ppm) suggests that it is attached to a nitrogen atom. The quartet in the off-resonance spectrum indicates the presence of a methyl group (CH_3). Thus we have a CH_2 group deshielded by a heteroatom, and a CH_3 group, for a total of five protons on the two carbons. To get the required mass one needs more carbons; doubling the carbons would give 10H (an even number of monovalent atoms, and secondary amine), but still of inadequate mass. By taking three of these groups, one gets 6C and 15H (an odd number of protons atoms, and tertiary amine).

^1H NMR

The ^1H NMR spectrum shows the presence of two signals with an integration ratio of 2:3. The splitting pattern (triplet and quartet) shows that the CH_2 and CH_3 groups are coupled.

This coupling pattern and the chemical shift of the quartet suggest that the $\text{CH}_3\text{--CH}_2\text{--N}$ chain is present in the molecule. Knowing that the molecule has some symmetry, one could consider triethylamine, as there is no indication of the presence of an NH or an NH_2 in any of the spectra. The ^1H NMR spectrum essentially confirms that the CH_2 and CH_3 groups that are observed in the ^{13}C NMR, are present as an ethyl group (as established by the observed proton–proton coupling pattern).

Infrared

The infrared spectrum does not show bands that clearly identify the functionality of the molecule. The medium intensity bands between 1000 and 1400cm^{-1} suggest the presence of an amine, although they might be overlooked because of their proximity to the C–C stretching bands. Tertiary amines are generally difficult to detect by infrared spectroscopy because there is no N–H stretching band near 3100cm^{-1} , and the C–N band is less intense than the C–O band (which is easier to detect). In fact, knowing the saturated nature of the compound from the molecular formula, and that the absence of bands is characteristic of primary or secondary amines, one is led by default to a tertiary amine.

Summary

The mass spectrum gives us a molecular ion peak at 101; the compound contains nitrogen and an odd number of protons atoms. The presence of nitrogen is confirmed by the principal fragments, which are at even masses 30, 58 and 86. The ^{13}C NMR spectrum shows that there are only two types of carbon, CH_2 and CH_3 . The proton–proton couplings seen in the ^1H NMR spectrum establishes that there is a bond between these two carbons. The $\text{CH}_3\text{CH}_2\text{N}$ is confirmed by the chemical shifts of the CH_2 . The presence of nitrogen is difficult to determine from the infrared spectrum. Knowing the molecular mass of the compound, it is certain that the molecule is symmetric, as three ethyl groups ($\text{CH}_3\text{--CH}_2$) and one nitrogen atom are needed to yield the required molecular mass.

Příklad 13

Exercise 010 (005)

¹H NMR

This ¹H NMR spectrum is very simple: it has only two signals, both of which are sharp single peaks. The integration gives a relative intensity of 9 to 1, for a total of 10 protons. The signal at 1.1 ppm (9 H) is probably due to three equivalent CH₃ groups, most likely in a *tert*-butyl group. The signal at 9.5 (1 H) is strongly deshielded by an electron-withdrawing group such as a carbonyl; it is in the appropriate range for the proton of an aldehyde.

¹³C NMR

Three types of carbon can be seen in the broadband and off-resonance spectra. The DEPT spectrum shows only two signals. The missing peak (43 ppm) corresponds to a quaternary carbon (bearing no hydrogen). The two other signals are attributed to CH (doublet in off-resonance) and CH₃ groups (quartet in off-resonance). The strongly deshielded peak at 205 ppm corresponds to the CH carbon of an aldehyde.

Infrared

The infrared spectrum has many bands, but the most significant bands are those characteristic of the functional group of the molecule. The strong band at 1720 cm⁻¹ represents the stretching vibration of a carbonyl group. The two bands at 2700 and 2800 cm⁻¹ are characteristic of an aldehyde group. The double peaks of different intensities near 1380 cm⁻¹ are typical of the *tert*-butyl group.

Mass Spectrum

The peak at 86 is probably the molecular ion. Its even-mass suggests that there is no nitrogen in the molecule. A mass of 86 could correspond to a C₆ alkane (C₆H₁₄) or to a compound with

one oxygen and one unsaturation, or with two oxygens and two unsaturations. An accurate mass measurement of the 86 ion gave a value of 86.0732, which fits with a molecular formula of C₅H₁₀O (mass 86.073165), but not with C₆H₁₄ (mass 86.1096). The loss of 15 (ion at 71) is often an indication of CH₃ in the molecule. The peak at 57 is either the C₄H₉ (*tert*-butyl) or C₃H₅O ion.

Summary

Information for deriving the molecular formula (C₅H₁₀O) can be obtained from various spectra, such as the mass spectrum (molecular ion at 86), the ¹H NMR (10H, integration), the IR (oxygen of the carbonyl group), and the ¹³C NMR (5C). The ¹³C NMR spectra do not have integrations like proton NMR, but in some cases the information may be obtained from comparisons of peak intensities of the same types of carbon. In this case the large peak for methyl carbons represents three of them, as indicated by the 9H peak in the ¹H NMR. The functional group is shown to be an aldehyde by the IR carbonyl stretching band at 1720 cm⁻¹, and the characteristic two bands near 2700 and 2800 cm⁻¹. Confirmation is obtained from the chemical shift of the aldehyde H in the ¹H NMR, and the chemical shift and splitting of the aldehyde C in the ¹³C NMR. The presence of a *tert*-butyl group, as indicated by the ¹H and ¹³C NMR spectra, is supported by the observation of a pair of peaks of different intensities at about 1380 cm⁻¹ in the IR spectrum. The base peak in the mass spectrum at 57 corresponds to the *tert*-butyl cation. Adding the *tert*-butyl group to the aldehyde function gives (CH₃)₃CCHO, pivalaldehyde or trimethylacetaldehyde.

Příklad 14

Exercise 011 (066)

Preliminary Observation

The pair of peaks in the IR spectrum at 3300 and 3400 cm^{-1} should give a clue as to the functional group. The mass spectrum provides another hint as to the nature of the functional group. Note that the molecular ion appears to be odd-mass, and that many of the fragment ions are even-mass. The ^{13}C NMR spectrum can give the number of different carbons in the molecule, and the ^1H NMR spectrum can give the number of different types of proton.

Mass Spectrum

The spectrum has a small peak for the molecular ion at m/z 101. The weakness of the molecular ion, M , and its isotope peak, $M+1$, make it impractical to use the isotope ratios to determine the number of carbons in the molecule. The presence of nitrogen in the molecule is indicated by the odd-mass molecular ion, and by the presence of several even-mass fragment ions obtained by the loss of alkyl groups (86 for $M-15$, 72 for $M-29$ and 58 for $M-43$). The very stable base peak at 30 ($\text{CH}_2 = \text{NH}_2^+$) is a typical fragment ion observed in alkyl amines, arising from α cleavage at the nitrogen. The molecular formula of an alkyl amine with a mass of 101 is $\text{C}_6\text{H}_{15}\text{N}$.

Infrared

The broad bands between 3300 and 3400 cm^{-1} are characteristic of the symmetric and asymmetric N–H stretching bands of a primary amine. That is confirmed by the band at 1620 cm^{-1} corresponding to the NH_2 scissoring movement, and the broad band at 800 cm^{-1} associated with the out-of-plane bending of the NH_2 . The alkyl chain bands are seen between 2980 and 2860 cm^{-1} (C–H stretching), at 1470 (CH_2 scissoring) and 1370 cm^{-1} (CH_3 deformation).

^1H NMR

In the ^1H NMR spectrum there are four groups of signals with some overlapping peaks. The observed integrations are 2:8:2:3 for a total of 15H, an odd number of hydrogens, as expected

for an amine. The peak at 0.9 ppm (3H) corresponds to a CH_3 group of an alkyl chain, which appears as a triplet, distorted in the shape typical of linear alkyl chains (coupling to a CH_2 having a similar chemical shift). The broad peak between 1.1 and 1.4 ppm includes the CH_2 groups of the alkyl chain, all having nearly the same chemical shift. The CH_2 attached to the nitrogen is the only one that has a distinctly different chemical shift. It appears as a triplet (coupled to its neighbouring CH_2) at 2.7 ppm, (deshielded by the nitrogen). The peak at 1.2 ppm corresponds to the two hydrogens of the amino group (NH_2); note the high chemical shift of this type of proton.

^{13}C NMR

The DEPT spectrum shows the presence of five different CH_2 carbons (inverted signals). This is confirmed in the off-resonance spectrum by the presence of five triplets. One quartet in the off-resonance indicates the presence of a methyl group. The doublet at 42 ppm in the off-resonance spectrum corresponds to a CH_2 bonded to an amine nitrogen.

Summary

The presence of a nitrogen atom is confirmed by the pair of bands at $3300\text{--}3400\text{ cm}^{-1}$ in the infrared spectrum. The ^1H NMR spectrum shows 15H (originating from the odd molecular mass). The ^{13}C NMR spectrum shows the presence of at least six carbons. The mass spectrum shows the presence of an odd number of nitrogen atoms (the odd mass of M). The only possible structure that could be constructed from the combination of five CH_2 groups, a CH_3 group and an NH_2 is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, hexylamine.

Příklad 15

Exercise 017 (018)

Preliminary Observation

Close inspection of the C–H stretching region in the IR spectrum reveals that there are peaks for both sp^3 C–H and sp^2 C–H vibrations. There are also peaks in the ^1H and ^{13}C spectra that indicate the presence of an alkene or aromatic group.

Mass Spectrum

It appears that the peak for the molecular ion is at 82 (43%) with an isotope peak 83 (3%) for a relative intensity (3/43) of 6.9%, indicating the presence of six carbons, $6 \times 1.1\% = 6.6\%$. The molecular formula of a compound with six carbons and a molecular mass of 82, is C_6H_{10} . The ions at 27, 41, 55, indicate the presence of an unsaturation (fragments typical of alkenes). The base peak at $M-15$ suggests the presence of a methyl group, but you must be careful as many cyclic compounds give a peak for the loss of a methyl group. Even the simplest cyclic compounds, such as cyclohexane and cyclopentane, give a strong peak for $M-15$. Rearrangement of radical ions by hydrogen transfer is common in cyclic hydrocarbons. The even-mass ion at 54 is due to the loss of a molecule of ethylene, a retro Diels–Alder reaction.

^{13}C NMR

The broadband spectrum shows signals for only three types of carbon, a CH (doublet in OR), and two different CH_2 carbons (triplets in OR, and inverted signals in DEPT). The chemical shift of the signal at 127 ppm corresponds to that of an olefinic carbon. Since we see only one peak for sp^2 carbons, and we need two carbons to make the double bond ($>\text{C}=\text{C}<$), the peak must represent two equivalent carbons, and thus we have a symmetric molecule. The carbon multiplicities (two CH_2 and one CH) indicate the presence of a total of five protons, only half that in the molecular mass determination, again showing that each signal represents two carbon atoms.

^1H NMR

The ^1H NMR spectrum shows the presence of three signals, with integrations of 1:2:2 for a total of five protons. As the integration gives ratios only, the actual number of protons in the molecule is 10. The peak at 5.65 ppm represents olefinic protons, the peak 1.98 ppm represents allylic protons ($-\text{CH}_2\text{C}=\text{C}$) and the peak at 1.60 ppm represents the CH_2 β to the double bond. The coupling pattern is complex and the individual splitting cannot be discerned in this spectrum.

Infrared

The band above 3000cm^{-1} is characteristic of olefinic $=\text{C}-\text{H}$ stretching, confirming the presence of an alkene group. The band for the $>\text{C}=\text{C}<$ stretching vibration is seen at 1660cm^{-1} , and the out-of-plane bending band is seen at 720cm^{-1} , in the range of the typical position for *cis*-disubstituted (Z) alkenes.

Summary

The mass spectrum gives a peak for the molecular at 82 and the $M+1$ indicates six carbons for a molecular formula of C_6H_{10} , two sites of unsaturation. The ^{13}C NMR shows three types of carbon, of which there are two CH_2 and one olefinic CH, for a total of three carbons and five hydrogens; clearly there is a symmetry element in the molecule. The infrared shows bands for alkene C–H stretching, the $\text{C}=\text{C}$ stretching, as well as a band typical of the out-of-plane bending of two *cis* hydrogens. The two centres of unsaturation consist of a double bond and a ring. The compound is cyclohexene. The mass spectrum shows a peak for the loss of a methyl group, but this is due to a rearrangement reaction, common in cyclic hydrocarbons.

Příklad 16

Exercise 020 (012)

Preliminary Observations

Scanning the IR spectrum for evidence of a functional group gives a clear indication of an aromatic ring. There are bands in all four regions that one would search for signs of an aromatic ring: CH stretching bands between 3000 and 3100 cm^{-1} , small overtone-combination bands between 2000 and 1600 cm^{-1} , strong peaks near 1600 and 500 cm^{-1} , and finally out-of-plane bending bands in the region of $700\text{--}900\text{ cm}^{-1}$.

Mass Spectrum

This spectrum appears to have a particularly strong peak for the molecular ion at 92 (77%) and a strong $M-1$ peak at 91 (100%). The peak at 91 cannot be the molecular ion because the $M+1$ isotope peak would be too high. The principal peaks of the fragments ions have odd masses at 39, 63 and 65, which are the typical ions of a phenyl ring.

^{13}C NMR

There are five signals in the spectrum, one methyl (quartet in OR), one quaternary carbon in the aromatic region (disappears in DEPT) and three aromatic CH carbons (inverted in DEPT, doublets in OR). The three signals of the CH carbons are not of the same intensity. Two of them are about twice the intensity of the third, suggesting that they each represent two carbons. This is a peak pattern that is typical of a monosubstituted benzene ring.

^1H NMR

The ^1H NMR spectrum shows two types of protons with an intensity ratio of 5:3. The peak at 2.4 ppm represents a CH_3 bonded to an sp^2 carbon, and the signal at 7.2 ppm is due

to the five aromatic protons (monosubstitution). Although there are three different types of aromatic proton (*o*, *m*, *p*), the chemical shifts are very close and are not seen as separate peaks in this low-resolution spectrum (60 MHz). The differences in the three positions are seen clearly in the ^{13}C spectrum, which shows three types of tertiary sp^2 carbons (H-C=), one para to the CH_3 group and, because of the symmetry of the molecule, two equivalent ortho carbons and two equivalent meta carbons.

Infrared

The bands between 3000 and 3100 cm^{-1} show the presence of hydrogen on an sp^2 carbon (C-H stretching), either the C-H of an alkene or an aromatic ring. The presence of bands at 1500 and 1600 cm^{-1} for the ring $>\text{C}=\text{C}<$ stretching, and the bands at 700 and 750 cm^{-1} for the out-of-plane C-H bending, are typical of a monosubstituted benzene ring.

Summary

The mass spectrum gives us a peak for the molecular ion at 92, and a large $M-1$ ion at 91, the tropylium ion, which is commonly observed for alkyl benzenes. The ^{13}C NMR indicates the presence of five types of carbon, one quaternary, three types of CH and one CH_3 . The ^1H NMR confirms the presence of a CH_3 group, and five aromatic five protons. Therefore there is a benzene ring with a CH_3 group on the ring, $\text{C}_6\text{H}_5\text{CH}_3$, toluene.

Příklad 17

Exercise 021 (013)

Preliminary Observation

There are no indications of a functional group other than an aromatic ring in the IR spectrum. The simplicity of the NMR spectra indicates that the molecule has a great deal of symmetry.

Mass Spectrum

The mass spectrum indicates that the molecular mass of the compound is 120. The relative intensity of the M+1 peak, 9.56% ($100 \times 6.7/70.1$) indicates that there are nine carbons in the molecule. The expected value of the M+1 isotope peak for nine carbons is actually 9.9%. In fact, a more accurate calculation of the relative ratio of M+1/M would give 9.8% ($100 \times 6.7/68.4$) if one reduced the size of M by taking out the contribution of the isotope peak of the M-1 ion. The peaks at 77 (C_6H_5^+), at 91 (C_7H_7^+) and at 105 (C_8H_9^+) suggest the presence of alkyl groups on a benzene ring.

^{13}C NMR

There are three peaks in the broad band spectrum: a quaternary carbon (signal disappears in DEPT) in the aromatic region (137.7 ppm); a CH carbon (doublet in OR spectrum), also in the aromatic region (127.7 ppm); and a methyl carbon (quartet in OR spectrum) in the aliphatic region (21.8 ppm). The compound has only three types of carbon although the molecular formula has nine, therefore there must be some three-fold symmetry element within the compound.

Infrared

The peak at 3017 cm^{-1} is due to C-H stretching of hydrogen on an sp^2 carbon. It could be the C-H on either an alkene or an aromatic ring. The bands at 1500 and 1600 cm^{-1} represent the

ring >C=C< stretching, and the band at 835 cm^{-1} , an out-of-plane C-H bending typical of an isolated hydrogen on an aromatic ring. This indicates that we have a trisubstituted benzene ring, the substituents being meta to one another.

^1H NMR

The ^1H NMR spectrum shows two signals, with no perceptible coupling and an integration of 1:3. The peak at 2.3 ppm corresponds to a CH_3 group on an sp^2 carbon, and the peak at 6.7 ppm to protons on an aromatic ring. The chemical shift of the aromatic protons is upfield from the benzene position by 0.5 ppm, which agrees with the effect calculated for two ortho and one para methyl groups.

Summary

The mass spectrum has a molecular peak at 120 (C_9H_{12}), and the ^{13}C NMR shows three types of carbon – sp^2 quaternary, sp^2 tertiary (CH) and primary (CH_3). The ^1H NMR has only signals for the methyl group and an aromatic proton. The IR spectrum shows =C-H and >C=C< stretching bands, and an out-of-plane bending band for an isolated H (between two substituents) on a benzene ring. Therefore the compound has three methyl groups on a benzene ring. The ^{13}C NMR confirms the substitution pattern, as there are only three signals for the nine carbons, therefore there is a three-fold element of symmetry in the compound, a 1,3,5 trisubstituted benzene ring. The compound is mesitylene, or 1,3,5-trimethylbenzene.

Příklad 18

Exercise 022 (025)

Preliminary Observation

A scan of the spectra tells one that there is an aromatic system, and that a substituent has a shielding effect on some of the protons in the ^1H NMR. The compound has a significant peak for the molecular ion, probably because of the aromatic π system.

Infrared

The typical peaks of an aromatic ring stand out in this spectrum. The C–H stretching bands are seen between 3000 and 3100 cm^{-1} , small bands are obvious in the fingerprint region (2000 – 1600 cm^{-1}), C=C stretching bands are seen at 1600 and 1500 cm^{-1} , and there are bands in the out-of-plane region of 675 – 870 cm^{-1} . The fingerprint pattern and the out-of-plane bending bands at 700 and 750 cm^{-1} are typical of five adjacent protons on an aromatic ring (monosubstituted benzene ring). The band at 2836 cm^{-1} corresponds to C–H stretching in a methoxy group, and the band at 1250 cm^{-1} is characteristic of =C–OC stretching.

^{13}C NMR

There are five signals in the BB spectrum, two of them being much more intense, indicating that they each may represent more than one carbon. The DEPT spectrum indicates the presence of one quaternary carbon (loss of signal at 160), quite deshielded by being directly bonded to an oxygen (ipso carbon). The off-resonance spectrum indicates the presence of three sp^2 carbons as doublets (CH) and one quartet (CH_3), and confirms the presence of a quaternary carbon. Of the four types of aromatic carbon, the two more intense peaks belong to the ortho and meta isochronous pairs, with the higher field signal belonging to the more highly shielded ortho carbons. The lower intensity CH signal belongs to the para carbon. The chemical shifts are explained by the resonance donor effect shielding the ortho and para carbons but having little effect on the meta carbons. The carbons directly bonded to the oxygen are strongly deshielded; OCH_3 carbon at 55 ppm, and ipso carbon of the ring at 160 ppm.

^1H NMR

The proton NMR shows the presence of three groups of signals, with integration ratios of 2:3:3 at 7.3, 6.9 and 3.7 ppm respectively. The singlet at 3.7 ppm is at the characteristic

shift of a methoxy group on a benzene ring. The signals situated between 6.9 and 7.3 ppm represent five aromatic protons. The triplet at 7.3 ppm represents the meta protons coupled to an ortho and para proton. Unlike the para and ortho protons, the meta protons are not significantly shielded by the resonance-donating effect of the oxygen substituent. The signals for the para and ortho protons are found near 6.9 ppm, which is upfield from the normal benzene position of 7.3 ppm. They are shielded by the resonance effect of the oxygen at the ortho and para positions. The signals consist of a triplet for the para proton and a doublet for the ortho protons.

Mass Spectrum

The mass spectrum has a peak for the molecular ion at 108 (100%), and the M+1 isotope peak of 7.9%, indicating that the compound has seven carbons. The ion at 93 corresponds to the loss of a methyl group, the ion at 78 to the loss of formaldehyde, and the ion at 77 is the phenyl ion (C_6H_5^+) corresponding to the loss of CH_3O . In this case, the mass spectrum alone gives strong evidence that the compound is anisole: $\text{C}_6\text{H}_5\text{OCH}_3$.

Summary

In each spectrum there are strong indications of the presence of a phenyl ring. The ^1H NMR spectrum has two signals in the aromatic region, one near the chemical shift of benzene and the second at a higher field, which indicates that it is shielded by an electron-donating substituent. Shielding of aromatic protons occurs by resonance donation from a substituent with non-bonding electrons, usually oxygen or nitrogen, and is most effective at the ortho and para positions. The methoxy group is an example of such a group. The methoxy group is found as a singlet at the expected chemical shift (3.8 ppm). The compound is clearly anisole, $\text{C}_6\text{H}_5\text{OCH}_3$.

Příklad 19

Exercise 029 (027)

Preliminary Observation

In looking for evidence of a functional group, the infrared spectrum gives a strong indication of a functional group, as does the mass spectrum.

Infrared

The very sharp band at 2260cm^{-1} stands out in a fairly exclusive region of the spectrum – the triple bond stretching region. Alkyne triple bonds usually have very weak bands unless they are terminal bonds, in which case they would also show a band at 3300cm^{-1} for the $\equiv\text{C-H}$ stretch, which is absent in this case. The most likely possibility is that this band belongs to a nitrile group, $-\text{C}\equiv\text{N}$. An aromatic ring is indicated by the sp^2 C-H stretching bands between 3000 and 3100cm^{-1} , the weak overtone-combination bands between 2000 and 1600cm^{-1} , the ring bond stretching at 1600 and 1500cm^{-1} and the out-of-plane bending bands at 700 and 750cm^{-1} .

^{13}C NMR

There are six peaks in the BB spectrum, with only one being in the sp^3 region, a methylene group at 25 ppm (peak inverted in DEPT, and triplet in OR). The lower field peaks are close together and have to be examined carefully. Two of them (120 and 131 ppm) are identified as quaternary carbons by the disappearance of their signals in the DEPT spectrum. The other three peaks are tertiary carbons ($>\text{CH}$), and are unchanged in the DEPT spectrum. Only CH and CH_3 carbons are unchanged in DEPT spectra, and no methyl group would occur in this region. Also, if you look carefully in the OR spectrum, you will see that each is split into a doublet ($>\text{CH}$). In summary, we have the quaternary carbon of the nitrile at 120 ppm , the quaternary ring carbon at 131 ppm , and peaks for three types of ring CH carbon (two ortho, two meta, and a para carbon). The carbon of a $\text{C}\equiv\text{N}$ is frequently missed in the ^{13}C NMR, as it is in the same region as sp^2 carbons, but can be easily detected in the IR spectrum. Finally, the signal at 25 ppm represents a CH_2 substituted with two deshielding groups, an aromatic ring and a nitrile group.

Mass Spectrum

This mass spectrum is not difficult to interpret. The strong $\text{M}-1$ at 116 arises from the loss of a hydrogen from the position α to both the benzene ring and the nitrile. The molecular ion is the base peak, thus the intensity of the $\text{M}+1$ at 118 is known with some precision, allowing one to make a reliable determination of the number of carbons. The $\text{M}+1$ at 118 of intensity 8.9% indicates the presence of eight carbons (1.1% for each carbon). The ion at 90 results from the loss of a molecule of $\text{HC}\equiv\text{N}$ (27), often observed in nitriles. The lower intensity ions (77 , 51 and 65) are the typical fragment ions of a benzene ring.

^1H NMR

The proton NMR shows only two signals, one for five protons at 7.3 ppm and one for two protons at 3.7 ppm . The peak at 3.7 ppm represents the CH_2 and is substituted with two deshielding substituents, an aromatic ring and a nitrile group. The signal at 7.3 ppm for 5 H shows the presence of five aromatic H in one unresolved peak, a situation commonly found in benzene rings substituted with a CH_2 group, ($\text{C}_6\text{H}_5\text{CH}_2-$).

Summary

The nitrile group can be recognized readily in the IR spectrum, but it does not stand out in the ^{13}C NMR because it occurs in the same region as the aromatic carbons. However, the presence of the nitrile can be confirmed by the signal for the quaternary carbon near 120 ppm . In the mass spectrum, one frequently observes peaks for the loss of $\text{HC}\equiv\text{N}$. The aromatic ring is easily detected in the IR spectrum, the ^1H NMR and ^{13}C NMR spectra. The only sp^3 carbon in the molecule is identified by the singlet in the aliphatic region of the ^1H NMR and the triplet in the off-resonance ^{13}C spectrum. Joining the components gives the complete structure, $\text{C}_6\text{H}_5\text{CH}_2\text{C}\equiv\text{N}$, benzylnitrile.

Příklad 21

Exercise 035 (082)

Preliminary Observation

Be careful in the interpretation of the weak bands near 2700 and 2800 cm^{-1} ; they are possibly overtone bands.

Infrared

The very broad band centred near 3350 cm^{-1} represents the O–H stretching of strongly hydrogen bonded OH. Only a small peak on its shoulder at about 3650 cm^{-1} can be seen for the free OH stretching vibration. The associated intense band at 1220 cm^{-1} , suggests an enol or a phenol. Note that the intensity of the stretching band of the O–H of phenols is medium to strong, somewhat weaker than that of alcohols. The bands near 1580 and 1480 cm^{-1} are representative of >C=C< stretching vibrations of the aromatic ring, the strength of the band at 1580 cm^{-1} indicating strong polarization. The band near 780 cm^{-1} is characteristic of three adjacent hydrogens on an aromatic ring, while the band at 850 cm^{-1} is characteristic of a single hydrogen between two substituents.

Mass Spectrum

There is a strong peak for the molecular ion at m/z 128 (100%). The $M+1$ isotope peak 129 (6.9%) indicates that the compound has six carbons ($6 \times 1.1\%$). The $M+2$ isotope peak 130 (32.1%) indicates that the compound contains one chlorine atom. The IR spectrum has clear evidence of an OH group. The six carbons, one oxygen and one chlorine atom have a mass of 123 ($6 \times 12 + 6 + 35$). As the molecular mass of the compound is 128, five hydrogens are needed to complete the molecular formula, $\text{C}_6\text{H}_5\text{ClO}$. The molecular ion is very stable, having a large electron source in the ring π system, and the non-bonding electrons of the oxygen and chlorine. The loss of a chlorine atom provides the fragment ion at 93 (6.4%), and loss of HCl yields the peak at 92 (6/3%). The peak at 100 (16.5%), and its associated isotope peak at 102 (5.4%) are due to the loss of $\text{C}\equiv\text{O}$. The fragment at 65 (53%) for C_5H_5^+ , and its fragmentation product at 39 (30%) for C_3H_3^+ (from the loss of acetylene), are classic fragments of benzene rings.

^{13}C NMR

Signals are seen for the six carbons of the benzene ring, two quaternary carbons (signals disappear in DEPT), and four methine carbons (doublets in OR). The lack of symmetry

in the ring indicates that it is not para substituted. The quaternary carbon at 156 ppm is furthest downfield, being attached to the strongly electronegative oxygen atom. The other quaternary carbon at 135 ppm corresponds to the one having the chlorine substituent. The methine carbons (four CH doublets in OR) at 114, 116, 121 and 131 ppm represent the four unsubstituted carbons.

^1H NMR

The ^1H NMR spectrum has signals for five different protons, four of them in the aromatic region and one at a chemical shift (5.4 ppm) typical of a phenol in a CDCl_3 solution. The ring protons that are shifted significantly upfield compared to benzene (7.27 ppm), would be in positions ortho and para to the oxygen, a strong resonance donor to the ortho position (-0.50 ppm) and para position (-0.40 ppm). The protons meta to the oxygen are much less strongly shielded (-0.14 ppm). The effect of the chlorine is insignificant compared to the effect of oxygen (ortho, $+0.03$; meta, -0.06 ; para, -0.04). One of the upfield protons (6.84 ppm) shows no ortho coupling; it appears as a very narrowly split triplet (meta coupling). This proton must have the two substituents on either side of it, resulting in a meta-substituted ring. The proton with an ortho Cl and ortho OH has a calculated chemical shift of 6.80 ppm ($7.27 - 0.50 + 0.03$), very close to the observed value of 6.84 ppm. The triplet with the larger splitting would be between two ortho protons. The calculated shift of this proton is 7.07 ppm ($7.27 - 0.14 - 0.06$), very close to the observed value of 7.11 ppm. The doublet at 6.70 ppm corresponds to the proton para to the Cl ($7.27 - 0.50 - 0.04 = 6.73$), and the doublet at 6.91 ppm corresponds to the proton para to the OH ($7.27 - 0.40 + 0.03 = 6.90$). Each doublet also shows fine meta coupling.

Conclusion

The compound is *m*-chlorophenol, $\text{ClC}_6\text{H}_4\text{OH}$.

Příklad 22

Exercise 036 (091)

Preliminary Observation

The IR spectrum has a peak above 3000 cm^{-1} for aromatic protons, but none below 3000 cm^{-1} for aliphatic protons. The isotope peaks in the mass spectrum are interesting.

Mass Spectrum

The mass spectrum has a molecular ion at 206 (99.2%), with an isotope peak at 208 (96.7%). The natural abundance isotope ratio of ^{79}Br to ^{81}Br is 100 to 97.2. The observed isotope ratio in this spectrum is 97.5% ($100 \times 96.7/99.2$), indicating that the molecule contains a bromine atom. The base peak at 127 (100%) represents the fragment derived from the loss of the bromine atom. The ^{13}C isotope peaks at 207 (11.7%) and 209 (10.7%) indicate the presence of 10 carbons. Ten carbons and one bromine have a mass of 199 ($10 \times 12 + 79$); seven hydrogens are needed to make up the rest of the mass of 206 ($\text{C}_{10}\text{H}_7\text{Br}$). The other weak fragments are those of the 'aromatic family'; for example, the peak at 101 is $127 - 26$ (loss of acetylene), typical of aromatic rings. Note also the typical ions of phenyl ring fragmentation at 77, 51 and 39.

^{13}C NMR

There are peaks for 10 types of carbon, all aromatic. The DEPT spectrum has three peaks disappear, thus there are three types of quaternary carbon. The 10-carbon aromatic system formed from two benzene rings (naphthalene) has two quaternary carbons at the ring junction; a substituent would account for a third quaternary carbon. The α and β carbons of naphthalene have chemical shifts of 127.8 and 125.6 ppm respectively, and the ring junction carbons 134.5 ppm. Bromine has a shielding effect on the ipso carbon (-5.5 , heavy atom effect) and para carbon (-1.3), and a deshielding effect on the ortho ($+3.4$) and meta carbons ($+1.7$). The substituent effect on the junction carbons of naphthalene is less than that of unsubstituted carbons. In this spectrum, the junction carbons are found at 131.9 and 134.5 ppm, and the quaternary carbon bearing the bromine at 122.8 ppm. The other carbons are found between 129.8 and 126.0 ppm.

^1H NMR

The spectrum has a doublet at 8.19, three overlapping doublets between 7.73 and 7.70, two triplets between 7.51 and 7.44 and a triplet at 7.21 ppm. Naphthalene itself has only

two different protons, the α and β protons, seen at 7.84 (α) and 7.47 (β). The effect of bromine on the chemical shifts in a benzene ring are: ortho ($+0.22$), meta (-0.13) and para (-0.03). The other significant effect in a naphthalene ring is the peri effect ($\alpha - \alpha$ on adjacent rings), which is about $+0.30$ for bromine. The major couplings in naphthalene are the ortho couplings (7–8 Hz). The meta couplings (about 1 Hz) and para couplings (<1 Hz) are significantly smaller. The α and β protons can be easily distinguished by their splitting pattern. The α protons are doublets, and the β protons are triplets (each with the additional small meta coupling). The doublet ($^3J = 8\text{ Hz}$) at 8.19 ppm is an α proton shifted downfield by the peri effect of the bromine in the α position of the other ring. The two other α protons are found in the group of three doublets near 7.7 ppm which also includes the doublet of the β proton ortho to the bromine. The triplet at 7.21 ppm is the β proton meta to the bromine. The two β protons on the unsubstituted ring are seen as triplets at 7.51 and 7.44 ppm.

Infrared

The spectrum has peaks in the aromatic regions: between 3000 and 3100 cm^{-1} for sp^2 CH stretching, between 2000 and 1600 for weak overtone-combination bands, at 1505 and 1600 cm^{-1} for aromatic >C=C< stretching, at 760 cm^{-1} for out-of-plane deformation of four adjacent ring hydrogens, and at 800 cm^{-1} for three adjacent hydrogens. The infrared spectrum supports substitution at the α position. The frequency of the C–Br stretching is below 500 cm^{-1} , thus it is not observed.

Summary

The compound is 1-bromonaphthalene $\text{C}_{10}\text{H}_7\text{Br}$. The mass spectrum is critical for the detection of bromine. The molecular mass and the doublet from the isotope pattern indicate the presence of bromine. The evidence from the ^{13}C NMR, ^1H NMR and IR spectra supports the assignment of substitution at the α position. In the ^1H NMR, the major couplings produce three triplets and four doublets as expected for an α -substituted naphthalene. The bands at 760 cm^{-1} and 800 cm^{-1} represent out-of-plane deformations of four adjacent hydrogens and of three adjacent hydrogens on the ring.

Příklad 23

Exercise 039 (087)

Infrared

The bands just above 3000 cm^{-1} correspond to the $=\text{C}-\text{H}$ stretching vibrations of an aromatic ring. The band near 1600 cm^{-1} confirms the presence of an aromatic ring (stretching $>\text{C}=\text{C}<$). The band at 760 cm^{-1} represents the deformation (out-of-plane bending) corresponding to the presence of four adjacent aromatic protons, indicating that the compound contains an ortho-disubstituted benzene ring. The two bands at 3350 and 3450 cm^{-1} result from the symmetric and asymmetric $\text{N}-\text{H}$ stretching vibrations of an NH_2 group, the band at 2520 cm^{-1} is the particular $\text{S}-\text{H}$ stretching characteristic of thiols.

Mass Spectrum

The peak at 125 (100%) is that of the molecular ion. This odd mass shows the presence of an odd number of nitrogen atoms. The molecular ion has isotope peaks at 126 (8.9%) and 127 (4.8%). Only sulfur and silicon could give such a value of $M+2$ (Cl and Br would give a much stronger $M+2$ peak). Silicon has isotope ratios for $M+1$ (5.07) and $M+2$ (3.36), sulfur has $M+1$ (0.80) and $M+2$ (4.44), and nitrogen $M+1$ (0.36). The size of the observed $M+2$ peak is larger than expected for a silicon atom, but fits well with the presence of one sulfur atom in the molecule. Also, considering the contribution expected from a nitrogen and six carbons of the benzene ring, silicon would give a $M+1$ of 12.03 ($0.36 + 5.07 + 6 \times 1.1$). The compound contains sulfur, and in light of the contribution of 4.4% (^{34}S) per atom of S, there is one S in this compound.

^{13}C NMR

The spectrum has signals for six carbon atoms, all in the aromatic region: four CH carbons (doublets in OR) and two quaternary carbons (signals disappear in DEPT). The signal at 147.1 ppm corresponds to a quaternary carbon bearing a nitrogen atom, and the signal at 111.8 ppm corresponds to a quaternary carbon bearing a sulfur atom.

^1H NMR

There are signals from four aromatic protons and two protons on heteroatoms proton, with integration ratios of 1:1:2:3 for the peaks at 7.3, 7.0, 6.6 and 3–4 ppm. The signals between 3 and 4 ppm are very broad, corresponding to the hydrogens on the heteroatoms, two on the nitrogen and one on the sulfur. The doublet at 7.3 is the proton ortho to the sulfur, and the triplet at 7.04 is para to the sulfur. The two upfield protons at 6.6 ppm, belong to one that is ortho to, and the one that is para to, the amino group (resonance donor).

Conclusion

The benzene ring has two substituents, a thiol group and a primary amino group in an ortho orientation, giving the structure: *o*-aminothiophenol, $\text{HSC}_6\text{H}_4\text{NH}_2$.

Příklad 24

Exercise 040 (070)

Infrared

The infrared spectrum gives a clear indication of the functional group in the molecule. The spectrum has bands that are characteristic of an alcohol group in a dilute solution. The sharp band at 3650 cm^{-1} represents the free OH stretching vibration, and the broad band centred near 3350 cm^{-1} represents the hydrogen-bonded OH stretching vibrations. The band near 1100 cm^{-1} corresponds to the C–O stretching of secondary alcohols. The out-of-plane deformation band of the O–H, which is normally seen near 640 cm^{-1} , is not observed in this spectrum because the carbon tetrachloride solvent absorbs in this region.

^{13}C NMR

There are signals for four types of carbon in the compound. The DEPT spectrum shows the presence of one CH_2 (inverted signal) at 32 ppm. In the off-resonance spectrum the assignments are straightforward: the doublet at 69 ppm corresponds to a CH bearing the alcohol group, the quartet at 23 ppm corresponds to a CH_3 situated α to the carbon carrying the OH, and the quartet at 10 ppm corresponds to another CH_3 .

^1H NMR

The ^1H NMR spectrum shows the presence of five signals, with integration ratios of 1 (3.7 ppm) : 1 (2.2 ppm) : 2 (1.5 ppm) : 3 (1.2 ppm) : 3 (0.9 ppm). The multiplet of integration 1 at 3.1 ppm corresponds to a CH bearing the hydroxyl group (–OH), to which it is coupled. The OH is seen at 2.2 ppm as a doublet ($J = 4\text{ Hz}$). The CH at 3.1 ppm is also coupled to a CH_3 (signal at 1.2 ppm) and to the CH_2 protons (signal at 1.5 ppm). The multiplet of

integration 2 at 1.5 ppm corresponds to the two protons of the CH_2 . One might expect the CH_2 to be split into five by the four adjacent protons, but the pattern is much more complex than that. The protons of the CH_2 group are non-equivalent, being next to a chiral carbon. They have different chemical shifts, are mutually coupled and appear as a more complex pattern. Finally, the triplet of integration 3 at 0.9 ppm corresponds to a CH_3 coupled to the two protons of the CH_2 group.

Mass Spectrum

The peak at 73 is not the molecular ion, but a fragment ion due to the loss of a hydrogen atom. The loss of H from the OH is not a characteristic of alcohols. The loss of a hydrogen from the α carbon is possible, but it is usually not the preferred fragmentation. If there are other groups on the α carbon, the larger more stable radicals are preferentially lost. In this example, peaks are found for three α cleavages: M–1 (loss of H), 73 (1%); M–15 (loss of CH_3), 59 (20%); M–29 (loss of CH_3CH_2), 45 (100%). This is compatible with a secondary alcohol having a methyl and an ethyl group on the α carbon. The ion at 28 is probably $\text{CH}_2 = \text{CH}_2^+$, resulting from a rearrangement mechanism where the molecule loses the equivalent of water and ethylene.

Conclusion

The accumulated evidence indicates that the compound is a four-carbon alcohol with a methyl group and ethyl group on the carbon bearing the hydroxyl group. The only alcohol that fits this is 2-butanol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

Příklad 25

Exercise 076 (064)

Preliminary Observation

The IR spectrum has strong bands at 1730 and 1290 cm^{-1} which indicate that the compound is an ester. The symmetrical splitting pattern of the aromatic protons in the ^1H NMR spectrum shows that there is a symmetrically substituted benzene ring.

^{13}C NMR

Because of the symmetrical substitution, there are only three peaks in the aromatic region, two CH and one quaternary carbon. The carbonyl of the ester gives a peak at 168 ppm . The triplet at 62 ppm corresponds to a CH_2 attached to the oxygen of an ester. Finally, the signal at 14 ppm corresponds to a CH_3 group.

Mass Spectrum

The molecular ion shows a weak peak at 222 (3.3%). The fragment at 177 (27.4%) represents the loss of 45 ($\text{CH}_3\text{CH}_2\text{O}$) which suggests that the ester is an ethyl ester. A further loss of CO gives the base peak at 149 . The weak peak at 194 is due to the loss of ethylene by a McLafferty rearrangement of the ethyl ester. The ions at 39 , 50 , 51 , 76 and 77 are typical of benzene rings.

^1H NMR

The typical symmetrical AA'BB' splitting pattern of a benzene ring with two identical ortho substituents is seen in the aromatic region. The peaks are shifted downfield by the electron-withdrawing substituents. The quartet at 4.3 ppm and triplet at 1.4 ppm together represent the ethyl group of the ester.

Infrared

The band at 1730 cm^{-1} is at the high end of the range for a conjugated ester. The other typical band for the $=\text{C}-\text{O}$ and $\text{O}-\text{C}$ stretching of the ester is seen at 1290 cm^{-1} . The bands between 1500 and 1600 cm^{-1} show the presence of an aromatic ring ($>\text{C}=\text{C}<$). The band near 750 cm^{-1} represents the deformations corresponding to four adjacent hydrogens (ortho-disubstituted ring).

Conclusion

The components of the structure identified from the spectra include an ortho-disubstituted benzene ring and an ethyl ester. The mass spectrum requires two of the ethyl ester groups to arrive at the molecular formula of $\text{C}_{12}\text{H}_{14}\text{O}_4$. Assembly of these components gives the compound: diethyl phthalate, $\text{C}_6\text{H}_4(\text{COOCH}_2\text{CH}_3)_2$.

Příklad 26

Exercise 045 (008)

Preliminary Observation

Counting the clusters in the mass spectrum indicates that there are eight first-row elements (C, O, N) in the molecule. The strong sharp peak well below 1700 cm^{-1} is significant.

Infrared

The band at 1640 cm^{-1} indicates the presence of a carbonyl group. The relatively low frequency for a carbonyl group indicates that it is an amide, in this case a tertiary amide because no NH bands are seen above 3000 cm^{-1} . There is nothing particularly noteworthy that may be discerned from the other bands in the spectrum.

Mass Spectrum

The odd-mass ion at 115 (33.5%) and even-mass fragment ion as a base peak, 58 (100%), suggests that the compound has an odd number of nitrogens. The isotope peak at 116 (2.4%) has a relative intensity 7.2% of the 115 ion ($100 \times 2.4/33.5$) indicating that it contains six or seven carbons.

^{13}C NMR

There are at least six types of carbon in the compound. The DEPT spectrum shows the presence of two CH_2 groups (inverted signals) and one quaternary carbon (signal at 170 ppm disappears). In view of the chemical shift, the quaternary carbon is a carbonyl attached to a heteroatom. The off-resonance spectrum confirms the presence of two CH_2 groups, and also shows three types of CH_3 . The methyl group on the carbonyl is more highly deshielded than the other two.

^1H NMR

The ^1H NMR spectrum shows the presence of five signals. The cluster of peaks at 1.2 consists of two triplets, and the one at 3.3 ppm consists of two quartets. The integration gives a ratio of 4:3:6, for a total of 13 hydrogens. The two quartets at about 3.3 ppm, and the two triplets at about 1.2 ppm, are due to the presence of two ethyl groups, (CH_3CH_2-), that have only slightly different chemical shifts. The singlet at 2.1 ppm has a chemical shift that corresponds to that of a $\text{CH}_3\text{C}=\text{O}$ group.

Summary

From the ^{13}C NMR spectrum, there are six carbons. The infrared spectrum shows the presence of a carbonyl and the ^1H NMR integration indicates 13 hydrogens. This gives a partial formula of $\text{C}_6\text{H}_{13}\text{O}$, which adds up to a mass of 101 ($6 \times 12 + 13 + 16$). But the mass spectrum gives a molecular weight of 115, which means that another 14 are needed (one N atom). The molecular formula would then become $\text{C}_6\text{H}_{13}\text{NO}$. The ^1H NMR indicates that there are two CH_3CH_2- group and one $\text{CH}_3\text{CO}-$ group. There is a nitrogen atom, but the IR shows no bands for the N-H stretching, indicating that there is no $>\text{N}-\text{H}$ or $-\text{NH}_2$. This fits with a structure having N attached to two ethyl groups and the acetyl group. The compound is N,N-diethylacetamide. The slight difference that is observed in the chemical shifts of the two ethyl groups reflects hindered rotation about the N-(CO) bond, as is frequently observed in amides. This is due to the resonance donor effect of the nitrogen which increases the double bond character of the C-N bond, restricting rotation, and decreases the double bond character of the C=O bond, lowering the frequency of the C=O vibration in the IR.

Příklad 27

Exercise 048 (032)

Preliminary Observation

There is an indication of alkyl and aryl hydrogens from the peaks straddling 3000 cm^{-1} . There is no evidence of any other functional group.

Mass Spectrum

The molecular ion at 134 (29.4%) has an M+1 isotope peak, 135 (3.3%), that has a relative intensity of 11% indicating the presence of 10 carbons. The base peak at 119 (100%) is due to the loss of a methyl group from the molecular ion. One of the peaks has a m/z value of 57.5, which obviously belongs to a doubly charged ion (115). These doubly charged ions are sometimes observed in molecules that have a large system of non-bonding or π electrons.

^{13}C NMR

In counting the carbons in the aromatic region, note that the three peaks near 126 ppm are all doublets in the OR spectrum. There are six carbons in the aromatic region, two of them quaternary, suggesting the presence of a non-symmetrically disubstituted benzene ring. There are peaks for three types of aliphatic carbon, one methine carbon and two kinds of methyl group.

^1H NMR

The integration ratios are 4:1:3:6 respectively for the signals at 7.0 to 7.3, 3.1, 2.3 and 1.2 ppm. The doublet at 1.22 ppm represents two CH_3 groups attached to a CH carbon. The

singlet at 2.33 ppm represents a CH_3 on an aromatic ring. The multiplet (septet) at 3.12 ppm represents the ring substituent CH, which bears the two CH_3 groups. The signals between 7.0 and 7.3 ppm represent the ring CH protons. The $^3J_{\text{ortho}}$ coupling can be seen to split the signals into a triplet (7.06), a doublet (7.11), a triplet (7.16) and a doublet (7.23). The meta couplings broaden the peaks, but are not clearly resolved.

Infrared

The aromatic ring is indicated by the bands between 3000 and 3100 cm^{-1} , at 1500 and 1600 cm^{-1} , and at 720 and 760 cm^{-1} (out-of-plane bending of four adjacent hydrogens). The doublet of the same intensity near 1380 cm^{-1} is due to the presence of the *gem*-dimethyl group $(\text{CH}_3)_2\text{CH}-$.

Summary

The evidence indicates that the benzene ring has two substituents, a methyl group and an isopropyl group. They cannot be in a para position because there are six different aromatic carbon signals in the ^{13}C spectrum, and the ^1H NMR data are not compatible with symmetrical substitution. The ^1H NMR splitting pattern indicates that the ring is ortho substituted. The appearance of two triplets and two doublets of $^3J_{\text{ortho}}$ couplings in the ^1H NMR spectrum is compatible with ortho substitution, but not meta substitution, which would have one proton with no ortho coupling. The presence of out-of-plane bending bands between 740 and 770 cm^{-1} in the IR spectrum support this assignment. The compound is *o*-cymene, $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2$.

Příklad 28

Exercise 053 (042)

Infrared

The spectrum has a very strong band at 1736 cm^{-1} , typical of a carboxylic acid ester. It appears to be a non-conjugated ester. Conjugation on the carbonyl side lowers the frequency, while conjugation with the alkyl oxygen raises the frequency. An ester also has bands for the C–O single bond vibrations which are found in the region of 1000 to 1250 cm^{-1} .

^{13}C NMR

There are peaks for four different carbons, a quaternary carbon at 172 ppm ($\text{C}=\text{O}$ of ester), a methylene carbon at 60 ppm ($-\text{CH}_2-\text{O}$), a methylene carbon at 29 ppm ($-\text{CH}_2-\text{C}=\text{O}$) and a methyl carbon at 14 ppm (CH_3-C).

^1H NMR

There are only three signals, a triplet at 1.2 ppm that is coupled to a quartet at 4.1 ppm , and finally, a singlet at 2.6 ppm . The integration yields ratios of 2:2:3 for a total of seven hydrogens, an odd number which suggests the presence of a symmetry element that creates a molecule with an even number of protons. The mutually coupled quartet and triplet are the protons of an ethyl group bonded to the oxygen of the ester: $\text{CH}_3\text{CH}_2\text{O}(\text{C}=\text{O})-\text{R}$. The singlet at 2.6 ppm belongs to the CH_2 bonded to the carbonyl of the ester, giving a substructure of $-\text{CH}_2(\text{C}=\text{O})\text{OCH}_2\text{CH}_3$. The complete molecule can be made by joining two of these substructures. The two CH_2 groups situated on both sides of the centre of symmetry are isochronous and show no coupling.

Mass Spectrum

There is a peak for the molecular ion ($\text{C}_8\text{H}_{14}\text{O}_4$) at 174 . Esters generally have very weak peaks for their molecular ions. The fragment at 147 is due to a rearrangement, with the loss of 27 to give the $\text{CH}_3\text{CH}_2\text{O}(\text{CO})\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2^+$ ion. This type of ion, a protonated acid, is a typical product of the fragmentation of esters. The large peak at 129 corresponds to $\text{M}-45$, from the loss of the OCH_2CH_3 radical by the classical α cleavage at the carbonyl. A further loss of 28 yields the base peak at 101 . The peak at 73 is likely due to the $\text{CH}_3\text{CH}_2\text{O}(\text{C}=\text{O})$ ion, resulting from α cleavage.

Summary

The very strong sharp peak at 1736 cm^{-1} in the infrared spectrum, and the peaks for the strongly deshielded ethyl group in the ^1H and ^{13}C NMR spectra reveal the presence of an ethyl ester. The only other peaks in the NMR spectra are those of a CH_2 group. Two methylene groups are needed between the esters groups because of the molecular mass and the chemical shift of the CH_2 . A single CH_2 would be deshielded by two carbonyl groups (about 3.4 ppm), whereas a two-carbon bridge would have CH_2 groups bonded to only one carbonyl (about 2.6 ppm). The ^1H NMR integration and the mass spectrum provide more direct evidence for the presence of two methylene groups between the esters. The compound is diethyl succinate, $\text{CH}_3\text{CH}_2\text{O}(\text{CO})\text{CH}_2\text{CH}_2(\text{CO})\text{OCH}_2\text{CH}_3$.

Příklad 29

Exercise 055 (048)

Preliminary Observation

The strong sharp at 1690 cm^{-1} in the IR spectrum indicates there is a carbonyl in the molecule, probably conjugated. The two peaks near 3400 and 3300 cm^{-1} suggest the presence of an NH_2 group. The nitrogen is also indicated by what appears to be an odd-mass molecular ion. The IR and NMR spectra indicate that there is an aromatic ring in the compound.

Mass Spectrum

The molecule has a molecular mass of 165. The odd mass number agrees with the presence of a nitrogen atom. The peaks at 150 ($M-15$), 137 ($M-28$, loss of $\text{CH}_2=\text{CH}_2$, perhaps by McLafferty rearrangement) and the base peak at 120 ($M-45$, loss of OCH_2CH_3 by α cleavage) indicate the presence of an ethyl ester. The loss of carbon monoxide ($\text{C}\equiv\text{O}$) from the base peak ($120 - 28$) gives the fragment at 92, ($\text{C}_6\text{H}_6\text{N}^+$), which is similar to the tropylium ion (C_7H_7^+ , 91). Loss of $\text{HC}\equiv\text{N}$ (27) from the $\text{C}_6\text{H}_6\text{N}^+$ ion gives the peak at 65, and the loss of $\text{HC}\equiv\text{CH}$ (26) gives the weak peak at 66.

^1H NMR

The five signals have integration ratios of 2:2:2:2:3 (7.8, 6.6, 4.3, 4.1, 1.4 ppm) for a total count of 11 protons. The doublets at 7.8 and 6.6 ppm represent four protons of a para-disubstituted aromatic ring (AA'XX' system). The two protons at 7.8 ppm are ortho to a deshielding group (carbonyl group), while the two protons at 6.6 ppm are ortho to a shielding group (NH_2). The mutually coupled triplet (1.4 ppm) and quartet (4.1 ppm) are the protons of an ethyl group. The chemical shifts are compatible with the ethoxy chain $\text{CH}_3\text{CH}_2\text{O}-(\text{C}=\text{O})-$ of an ester. The final signal is a singlet at 4.3 ppm, corresponding to an NH_2 group.

^{13}C NMR

Three peaks disappear in the DEPT spectrum, one from a carbonyl carbon (167) and two from quaternary aromatic carbons (119, 151). The carbon at 151 ppm is shifted downfield by

the inductive withdrawal effect of its substituent NH_2 (ipso $\Delta\delta = +18.2$) and the resonance withdrawal from the ester carbonyl (para $\Delta\delta = +3.9$). The other quaternary ring carbon (119) is slightly deshielded by its substituent ester carbonyl (ipso $\Delta\delta = +2.1$) and shielded by the resonance donation from the NH_2 (para $\Delta\delta = -10.0$). The carbons (114) ortho to the NH_2 group are shielded (ortho $\Delta\delta = -13.4$) by the NH_2 and slightly shielded by the ester (meta $\Delta\delta = -0.5$). The carbons (131) ortho to the ester are slightly deshielded (ortho $\Delta\delta = +1.0$) by the carbonyl and by the ester ($\Delta\delta = +0.8$). The signal at 60 ppm represents the CH_2 of the ethyl group, and at 14 ppm represents the CH_3 group.

Infrared

The band at 1690 cm^{-1} corresponds to the carbonyl of a conjugated ester. The other peaks of the ester are found between 1000 and 1300 cm^{-1} . Peaks for the aromatic ring are found at 3000 – 3100 , between 1500 and 1650 , and at 780 cm^{-1} . The strong bands at 3430 and 3350 cm^{-1} are due to N–H, the asymmetric and symmetric stretching vibrations characteristic of an NH_2 group. The third band at 3230 cm^{-1} is probably due to an overtone of the N–H bending vibration. The presence of the NH_2 group is supported by the very broad band below 750 cm^{-1} representing the $>\text{N-H}$ deformations.

Summary

The compound is ethyl *p*-aminobenzoate, $\text{CH}_3\text{CH}_2\text{O}(\text{CO})\text{C}_6\text{H}_4\text{NH}_2$. The structure is easily solved by recognizing its components: the ethyl ester, the primary amine and the para-substituted benzene ring. The ester carbonyl is at a very low wavenumber (1690 cm^{-1}) because of conjugation to the aromatic ring involving the resonance donation to the carbonyl group by the para NH_2 . Note that the location of the peak for an NH_2 in the ^1H NMR spectrum is variable, depending upon sample conditions, such as solvent and temperature, and may appear at different frequencies and with different peak widths.

Příklad 30

Exercise 059 (097)

Preliminary Observation

The infrared spectrum has evidence of an aromatic ring in all of the typical frequency ranges. The ^1H NMR spectrum has peaks for the aromatic protons, but no others.

Mass Spectrum

The compound has a very stable molecular ion at 178 (100%). The $M+1$ isotope peak has a relative intensity of 15.2%, which corresponds to 14 carbons, thus requiring 10 H to complete the formula ($178 - 14 \times 12 = 10 \text{ H}$), for a molecular formula, $\text{C}_{14}\text{H}_{10}$. The molecule has 10 centres of unsaturation.

Infrared

The infrared spectrum has all the typical bands of an aromatic ring. Note the position of the strong out-of-plane bending bands. There is no indication of any other functional group, and no band between 3000 and 2900 cm^{-1} that would indicate the presence of aliphatic groups.

^1H NMR

The two sets of peaks in the aromatic region have an integration ratio of 2 (7.5 ppm) : 3 (7.3 ppm). This pattern is typical of a monosubstituted benzene ring in which the two ortho protons are slightly more deshielded than the other three protons.

^{13}C NMR

There are four signals in the aromatic region between 123 and 132 ppm. The signal at 123.3 ppm corresponds to the substituted carbon of a phenyl ring (quaternary, signal

disappears in DEPT spectrum). The other three signals in the aromatic region (128.2, 128.3, 131.6) correspond to the para carbon and the pairs of ortho and meta carbons (all doublets in the OR spectrum). The signal at 89.4 ppm is in the range for the carbons of an alkyne group. Note that a triple-bonded carbon is a shielding substituent at the *ipso* position, which explains why the chemical shift of this carbon is at a slightly higher field (123.3 ppm) than the others.

Conclusion

The only structural features evident from the spectra are the phenyl rings and alkyne carbons. An alkyne bond with a phenyl group on each end gives the required molecular formula, $\text{C}_{14}\text{H}_{10}$. The compound is diphenylacetylene, $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$. The compound has a highly conjugated stable molecular ion with small peaks for $M-1$ (9%) and $M-2$ (14%) ions. The ions at 76 and 77 that are typically found for phenyl compounds are present but very weak. Note the ion at 152 ($P-26$) which results from the loss of acetylene from a retro Diels–Alder at a benzene ring.

The IR bands at 695 and 760 cm^{-1} are due to the out-of-plane bending of the five adjacent hydrogens. No alkyne $\text{C}\equiv\text{C}$ stretching band near 2100 cm^{-1} is observed because the alkyne is, symmetrically substituted. The stretching does not result in a dipole moment change, therefore no absorption occurs.

Příklad 31

Exercise 061 (077)

Infrared

The very broad band between 2300 and 3500 cm^{-1} has a pattern that gives a strong indication of the functional group. Other bands that characterize this group are found at 1730 , 1290 , 1420 and 900 cm^{-1} . The two bands of the same intensity at 1369 and 1388 cm^{-1} are significant.

^{13}C NMR

There are peaks for six types of carbon in the compound, two of which are clearly within functional groups. The off-resonance and DEPT spectra show that the carbons of the two functional groups are quaternary, and that there is a quaternary carbon in the aliphatic chain. There is also evidence for a methyl carbon and two methylene carbons.

^1H NMR

The ^1H NMR spectrum shows peaks for the carboxylic acid protons (11.9 ppm), as well as the two methylene groups and the methyl groups. The integration ratios indicate that there are two acid protons and two methyl groups per methylene group. The mutual splitting of the methylene signals show that the CH_2 groups are bonded to one another.

Mass Spectrum

The peak at 142 may be the molecular ion, but the IR spectrum indicates the presence of a functional group that readily loses a neutral molecule. The evidence from the other spectra indicates the presence of two carboxylic acids (2 COOH), one aliphatic quaternary

carbon (C), two methyl groups (2 CH_3) and two methylene groups (2 CH_2), which gives a molecular formula of $\text{C}_7\text{H}_{12}\text{O}_4$ and a mass of 160 . The ion at 142 is not the molecular ion, but the product arising from the loss of water, a common fragmentation reaction of carboxylic acids.

Conclusion

The parts of the structure can be put together by joining the two methylene carbons, adding the quaternary carbon containing the two methyl groups, and attaching carboxyl groups to the two ends of the chain: $\text{HOOCCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOH}$, 2,2-dimethylglutaric acid.

Notes

The extremely broad band of 2300 and 3500 cm^{-1} (asymmetric, centred around 3000 cm^{-1}), and the associated carbonyl and C–O stretching bands, are characteristic of a carboxylic acid. The two bands of the same intensity at 1369 and 1388 cm^{-1} are indicative of a pair of methyl groups on the same carbon.

The protons of the pair of non-equivalent CH_2 groups form an $\text{AA}'\text{XX}'$ system which appears as a symmetrical pattern of two four-line signals. In this example, the central lines are overlapping because of the similar sizes of J_{AX} and $J_{\text{AX}'}$.

In the mass spectrum, the ion at 115 ($M-45$) is the result of cleavage at the quaternary carbon. The ion at 97 (88%) comes from the additional loss of a molecule of water (18). The base peak at 69 corresponds to the stable allylic ion, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2^+$, resulting from the loss of carbon monoxide (CO) from the 97 ion. A McLafferty rearrangement yields the peak at 88 , $(\text{CH}_3)_2\text{CHCOOH}$, which then loses water to give the ion at 70 .

Příklad 32

Exercise 065 (074)

Preliminary Observation

A quick scan of the IR and NMR spectra indicates that the compound has an aromatic ring. The IR spectrum is noteworthy in its lack of absorption bands just below 3000 cm^{-1} in the region of sp^3 CH stretching. There is also no evidence for the presence of carbonyl groups or functions with an NH or an OH.

Mass Spectrum

The strong odd-mass peak at 141 (86%) indicates the presence of nitrogen in the molecule. The $M+1$ isotope peak 142 (6.1%) has a relative intensity of 7.1%, indicating that the molecule has six carbon atoms (6.6 for six C and 0.4 for one N). The series of peaks for the loss of 16, 30 and 46 are typical of aromatic nitro compounds. The small peak at 125 (3.9%) is due to the loss of an oxygen atom, the peak at 111 (30.1%) from the loss of nitrogen monoxide (NO) and the peak at 95 (100%) from the loss of nitrogen dioxide. The peak at 83(22.5%) is due to the loss of carbon monoxide from the 111 ion. Benzene has a mass of 78, and replacing one hydrogen with an NO_2 group increases the mass to 123. This is 18 mass units less than the required molecular mass of 141. If a hydrogen of the benzene ring is replaced by a substituent, that substituent would need to have a mass of 19, which is just that of a fluorine atom. The peak at 75 (55.1%) is due to the loss of HF from the base peak.

^1H NMR

One pair of the ring protons is found near the normal position for benzene, and the other pair at a strongly deshielded position as expected of protons to a nitro group. The splitting pattern of the protons is interesting. The upper peak has four lines with splittings of 9.2 and 8.2 Hz, and the lower signal has four lines with splittings of 9.2 and 4.9 Hz. The mutual splitting of 9.2 Hz between the two protons is that of $^3J_{\text{ortho}}$ proton-proton coupling. The other splittings are caused by coupling to the fluorine atom, $^3J_{\text{HF}} = 8.2\text{ Hz}$ and $^4J_{\text{HF}} = 4.9\text{ Hz}$.

^{13}C NMR

There are six carbons in a benzene ring; with two different substituents one would expect four carbons signals for para substitution, six for meta substitution, and six for ortho substitution. In this case there are seven lines in the broad band spectrum. However, in counting the number of carbons from the lines, one must take into account the coupling to the fluorine atom. One can see a doublet (171.57 and 161.34) centred at 166.5 ppm with a splitting of 257 Hz, a doublet (126.66 and 126.26) centred at 126.5 ppm with a splitting of 10 Hz, and a doublet (117.02 and 116.07) centred at 116.5 with a splitting of 24 Hz. The doublet centred at 166.5 ppm and the singlet at 144.6 ppm are quaternary carbons (disappear in DEPT). The one at 166.5 is clearly the one bearing the fluorine because of the large splitting ($^1J = 257\text{ Hz}$). The other quaternary carbon, which has such a small coupling it is not observed, bears the NO_2 group. The doublet at 117 ppm is ortho ($^3J = 24\text{ Hz}$) to the fluorine, and the one at 127 is meta ($^4J = 10\text{ Hz}$) to the fluorine.

Infrared

The absence of bands between 3000 and 2900 cm^{-1} indicates that there are no alkyl groups in the molecule. The typical peaks for an aromatic ring are present: bands between 3000 and 3100 cm^{-1} for C-H stretching, weak overtone-combination bands between 2000 and 1600 cm^{-1} , bands at 1500 and 1600 cm^{-1} for the $>\text{C}=\text{C}<$ stretching, and bands in the out-of-plane bending region. The bands typical of an aromatic nitro group are found at 1350 and 1520 cm^{-1} . The C-F stretching vibration is found at 1230 cm^{-1} .

Conclusion

The compound is *p*-fluoronitrobenzene.

Příklad 33

Exercise 075 (059)

Preliminary Observation

The IR spectrum has the noteworthy pattern of an aromatic ring in the overtone-combination region between 2000 and 1600 cm^{-1} . It also has the peaks expected in the other aromatic regions. The peak at 3300 cm^{-1} is possibly that of NH stretching. In the ^1H NMR spectrum there is a peak at the base of the high-field doublet which disappears in a 'D₂O shake' experiment.

^{13}C NMR

There are signals for seven types of carbon: one quaternary and three CH carbons in the aromatic region, and a CH₃, CH₂ and CH in the aliphatic region. The aromatic signals have the classical pattern for monosubstituted benzene rings, one weak signal for the quaternary carbon, a more intense signal for the para carbon, and even more intense peaks for the ortho and meta pairs. The peaks at 51 and 48 ppm represent, respectively, the CH and CH₂ carbons bonded to a nitrogen atom. Finally, the OR quartet represents two isochronous CH₃ groups.

Infrared

Peaks are found in all regions expected for a benzene ring. The broad band at 3300 cm^{-1} represents the weak N–H stretching of a secondary amine. The NH bending band of a secondary amine is found between 660 and 900 cm^{-1} , but it is very variable and not a reliable indicator for the NH group.

Mass Spectrum

The peak at 134 (41%) would be a candidate for the molecular ion, except for the fact that it is an even-mass ion and there appears to be nitrogen in the compound. There is also a

weak peak at 149 (2.3%), which is 15 units higher than the 134 peak. This suggests that it is more likely to be a fragment arising from the loss of a methyl group. The molecule has two functions that direct the fragmentation, the phenyl ring and the amino group. Cleavage at the α position of the benzene ring gives $\text{C}_6\text{H}_5\text{CH}_2^+$, which is responsible for the base peak at 91 (100%). The M–15 peak at 134 (41%) is due to α cleavage at the nitrogen. The benzyl group and nitrogen ($\text{C}_6\text{H}_5\text{CH}_2\text{N}$) contribute a mass of 105, which requires another 44 (C_3H_8) to complete the molecular formula of $\text{C}_{10}\text{H}_{15}\text{N}$.

^1H NMR

The single peak at 7.3 ppm represents the five protons of a monosubstituted benzene ring. Although there are three different types of proton on such a ring, the chemical shifts of these protons are so close that they appear as one peak in a low-field spectrometer (60 MHz). In high-field spectrometers (400 MHz) separate peaks may be observed. The singlet at 3.7 ppm represents a CH₂ bonded to an aromatic ring and to a nitrogen atom. The septet at 2.8 ppm represents the CH of an isopropyl group, and the doublet at 1.1 ppm represents its two CH₃ groups. The CH chemical shift indicates that it is bonded to nitrogen. The broad signal at 1.25 ppm represents the NH of a secondary amine (this peak disappears when the sample is shaken with one or two drops of D₂O).

Conclusion

The identified substructures are: a phenyl ring, a methylene group, >NH and an isopropyl group. This gives the structure, $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}(\text{CH}_3)_2$, isopropylbenzylamine.

Příklad 34

Exercise 076 (064)

Preliminary Observation

The IR spectrum has strong bands at 1730 and 1290 cm^{-1} which indicate that the compound is an ester. The symmetrical splitting pattern of the aromatic protons in the ^1H NMR spectrum shows that there is a symmetrically substituted benzene ring.

^{13}C NMR

Because of the symmetrical substitution, there are only three peaks in the aromatic region, two CH and one quaternary carbon. The carbonyl of the ester gives a peak at 168 ppm . The triplet at 62 ppm corresponds to a CH_2 attached to the oxygen of an ester. Finally, the signal at 14 ppm corresponds to a CH_3 group.

Mass Spectrum

The molecular ion shows a weak peak at 222 (3.3%). The fragment at 177 (27.4%) represents the loss of 45 ($\text{CH}_3\text{CH}_2\text{O}$) which suggests that the ester is an ethyl ester. A further loss of CO gives the base peak at 149 . The weak peak at 194 is due to the loss of ethylene by a McLafferty rearrangement of the ethyl ester. The ions at 39 , 50 , 51 , 76 and 77 are typical of benzene rings.

^1H NMR

The typical symmetrical AA'BB' splitting pattern of a benzene ring with two identical ortho substituents is seen in the aromatic region. The peaks are shifted downfield by the electron-withdrawing substituents. The quartet at 4.3 ppm and triplet at 1.4 ppm together represent the ethyl group of the ester.

Infrared

The band at 1730 cm^{-1} is at the high end of the range for a conjugated ester. The other typical band for the =C-O and O-C stretching of the ester is seen at 1290 cm^{-1} . The bands between 1500 and 1600 cm^{-1} show the presence of an aromatic ring ($>\text{C}=\text{C}<$). The band near 750 cm^{-1} represents the deformations corresponding to four adjacent hydrogens (ortho-disubstituted ring).

Conclusion

The components of the structure identified from the spectra include an ortho-disubstituted benzene ring and an ethyl ester. The mass spectrum requires two of the ethyl ester groups to arrive at the molecular formula of $\text{C}_{12}\text{H}_{14}\text{O}_4$. Assembly of these components gives the compound: diethyl phthalate, $\text{C}_6\text{H}_4(\text{COOCH}_2\text{CH}_3)_2$.