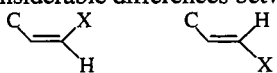
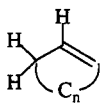
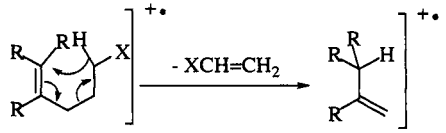
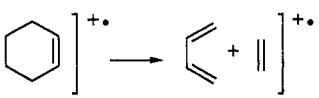


## 3 Combination Tables

### 3.1 Alkanes, Cycloalkanes

Assignment	Range	Comments	
CH <sub>3</sub>	5–35 ppm	CH <sub>3</sub> , CH <sub>2</sub> , CH, and C can be differentiated by multipulse experiments (DEPT, APT), off-resonance decoupling, 2D CH correlation spectra, or based on relaxation times Lower shift values in three-membered rings	<sup>13</sup> C NMR
CH <sub>2</sub>	5–45 ppm		
CH	25–60 ppm		
C	30–60 ppm		
CH <sub>3</sub>	0.8–1.2 ppm	Lower shift values in three-membered rings	<sup>1</sup> H NMR
CH <sub>2</sub>	1.1–1.8 ppm		
CH	1.1–1.8 ppm		
CH st	3000–2840 cm <sup>-1</sup>	Higher frequency in three-membered rings Doublet for <i>geminal</i> methyl groups In C-(CH <sub>2</sub> ) <sub>n</sub> -C with n ≥ 4 at ca. 720 cm <sup>-1</sup>	IR
CH <sub>3</sub> δ as	≈1460 cm <sup>-1</sup>		
CH <sub>2</sub> δ	≈1460 cm <sup>-1</sup>		
CH <sub>3</sub> δ sy	≈1380 cm <sup>-1</sup>		
CH <sub>2</sub> γ	770–720 cm <sup>-1</sup>		
Molecular ion	m/z 14n + 2	Weak in <i>n</i> -alkanes Very weak in isoalkanes	MS
Fragments		<i>n</i> -Alkanes: local maxima at 14n + 1, intensity variations: smooth, minimum at [M-15] <sup>+</sup> Isoalkanes: local maxima at 14n + 1, intensity distribution: irregular (relative maxima due to fragmentation at branching points with charge retention at the most substituted C)	
Rearrangements	m/z 14n m/z 14n - 2	<i>n</i> -Alkanes: unspecific Isoalkanes: elimination of alkanes Monocycloalkanes: elimination of alkanes	
		No absorption above 200 nm	UV

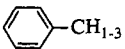
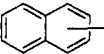
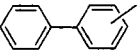
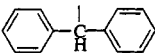
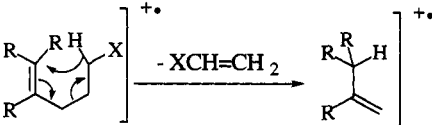
### 3.2 Alkenes, Cycloalkenes

	Assignment	Range	Comments
<b><sup>13</sup>C NMR</b>	C=C	100–150 ppm	Considerable differences between Z and E: 
	C–(C=C)	10–60 ppm	
<b><sup>1</sup>H NMR</b>	H–(C=C)	4.5–6.5 ppm	Coupling constants,  J : <i>geminal</i> 0–3 Hz, <i>cis</i> 5–12 Hz, <i>trans</i> 12–18 Hz
	CH <sub>3</sub> –(C=C)	≈1.7 ppm	Coupling constants, <sup>3</sup> J <sub>CH<sub>2</sub>–CH=C</sub> ≈7 Hz
	CH <sub>2</sub> –(C=C)	≈2.0 ppm	In rings,  J  smaller:
			 $n=2 \approx 0.5 \text{ Hz}$ $n=3 \approx 1.5 \text{ Hz}$ $n=4 \approx 4.0 \text{ Hz}$
			Long-range coupling constants <sup>4</sup> J <sub>HC–C=CH</sub> 0–2 Hz
<b>IR</b>	H–C(=C) st	3100–3000 cm <sup>–1</sup>	
	C=C st	1690–1635 cm <sup>–1</sup>	
	H–C(=C) δ oop	1000– 675 cm <sup>–1</sup>	
	CH <sub>2</sub> –(C=C) δ	1440 cm <sup>–1</sup>	
<b>MS</b>	Molecular ion	m/z 14n m/z 14n - 2	Alkenes: moderate Monocycloalkenes: medium intensity
	Fragments	14n - 1 14n - 3	Local maxima for alkenes Local maxima for monocyclic alkenes Usually, double bonds cannot be localized
	Rearrange- ments		<i>n</i> -Alkenes: unspecific Specific for:
			
			Cyclohexenes: retro-Diels–Alder reaction:
			
<b>UV</b>	C=C π→π*	< 210 nm (log ε 3–4)	Isolated double bonds; for highly substituted double bonds often absorption tail
	(C=C) <sub>2</sub> π→π*	215–280 nm (log ε 3.5–4.5)	


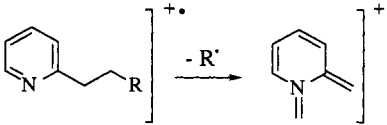
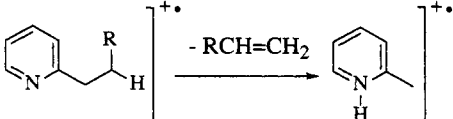
### 3.3 Alkynes

Assignment	Range	Comments	
$C\equiv C$	65–85 ppm	Coupling constant $^2J_{HC\equiv^{13}C} \approx 50$ Hz; often leading to unexpected signs of signals in DEPT spectra	$^{13}C$ NMR
$C-(C\equiv C)$	0–30 ppm		
$H-(C\equiv C)$	1.5–3.0 ppm	Coupling constants $ J $ $^4J_{CH-C\equiv CH} \approx 3$ Hz $^5J_{CH-C\equiv C-CH} \approx 3$ Hz	$^1H$ NMR
$CH_3-(C\equiv C)$	$\approx 1.8$ ppm		
$CH_2-(C\equiv C)$	$\approx 2.2$ ppm		
$CH-(C\equiv C)$	$\approx 2.6$ ppm		
$H-C\equiv C$ st	$3340\text{--}3250\text{ cm}^{-1}$	Sharp, intense	IR
$C\equiv C$ st	$2260\text{--}2100\text{ cm}^{-1}$	Sometimes very weak	
Molecular ion		Weak, for 1-alkynes up to $C_7$ often absent	MS
Fragments and rearrangements		Vary in extent between alkanes and aromatics	
$C\equiv C \pi \rightarrow \pi^*$	$< 210$ nm (log $\epsilon$ 3.7–4.0)	absorption tail, often a few weak bands $< 240$ nm	UV

### 3.4 Aromatic Hydrocarbons

	Assignment	Range	Comments
<b><sup>13</sup>C NMR</b>	ar C	120–150 ppm	Same ranges for polycyclic aromatic hydrocarbons
	ar CH	110–130 ppm	
	al C–(C ar)	10–60 ppm	
<b><sup>1</sup>H NMR</b>	H–(C ar)	6.5–7.5 ppm	In polycyclic aromatic hydrocarbons up to ≈9 ppm Coupling constants: <sup>3</sup> J <sub>ortho</sub> ≈7 Hz, <sup>4</sup> J <sub>meta</sub> ≈2 Hz, <sup>5</sup> J <sub>para</sub> <1 Hz
	CH <sub>3</sub> –(C ar)	≈2.3 ppm	Often line broadening due to long-range coupling with aromatic protons
	CH <sub>2</sub> –(C ar)	≈2.6 ppm	
	CH–(C ar)	≈2.9 ppm	
<b>IR</b>	ar C–H st	3080–3030 cm <sup>-1</sup>	Often multiple bands, weak
	comb	2000–1650 cm <sup>-1</sup>	Very weak
	ar C–C st	≈1600 cm <sup>-1</sup> ≈1500 cm <sup>-1</sup> ≈1450 cm <sup>-1</sup>	Often split, sometimes not all three bands observable
	ar C–H δ oop	900–650 cm <sup>-1</sup>	Strong, frequently multiple bands
<b>MS</b>	Molecular ion		Strong, often base peak
	Fragments	m/z 39, 50–53, 63–65, 75–78 [M–26] <sup>+</sup> , [M–39] <sup>+</sup> benzylic cleavage	Often doubly charged fragment ions
		 CH <sub>1-3</sub>	m/z 90–92
			m/z 127
			m/z 152, 153
<b>Rearrangements</b>			m/z 152, 165
			
<b>UV</b>		≈200–210 nm (log ε ≈4)	In benzene
		≈260 nm (log ε ≈2.4)	and alkylbenzenes

### 3.5 Heteroaromatic Compounds

Assignment	Range	Comments	
ar C-X	120–160 ppm		<sup>13</sup> C NMR
ar C-C	100–150 ppm		
H-(C ar)	6–9 ppm	Coupling constants in 6-membered rings similar to those in aromatic hydrocarbons; in 5-membered heteroaromatic rings smaller	<sup>1</sup> H NMR
H-(N ar)	7–14 ppm	Strongly solvent dependent, generally broad	
ar C-H st	3100–3000 cm <sup>-1</sup>	Often multiple bands, weak	IR
ar N-H st	3500–2800 cm <sup>-1</sup>		
ar C-C st	≈1600 cm <sup>-1</sup> ≈1500 cm <sup>-1</sup> ≈1450 cm <sup>-1</sup>		
ar C-H δ oop	1000–650 cm <sup>-1</sup>	Often strong, frequently multiple bands	
Molecular ion		Strong, often base peak	MS
Fragments	m/z 39, 50–53, 63–65, 75–78 [M-26] <sup>+</sup> , [M-39] <sup>+</sup> benzyl-analogous cleavage	Often doubly charged fragment ions	
		 m/z 78	
Rearrange-ments		Loss of HCN (N-heteroaromatics) Loss of CO (O-heteroaromatics) Loss of CS (S-heteroaromatics) S-Heteroaromatics	
	m/z 45 [CHS] <sup>+</sup>		
			

cf. UV/Vis Reference Spectra, Chapter 8.5.3.

### 3.6 Halogen Compounds

	Assignment	Range	Comments
<sup>13</sup> C NMR	al C-F	70–100 ppm	CF <sub>3</sub> : ≈115 ppm
	(C)=C-F	125–175 ppm	Coupling with <sup>19</sup> F (isotope abundance,
	C=(C-F)	65–115 ppm	100%; I = 1/2): <sup>1</sup> J <sub>CF</sub> 100–300 Hz;
	ar C-F	135–165 ppm	<sup>2</sup> J <sub>CF</sub> 10–40 Hz; <sup>3</sup> J <sub>CF</sub> 5–10 Hz; <sup>4</sup> J <sub>CF</sub> 0–5 Hz
	ar C-(C-F)	105–135 ppm	
	al C-Cl	30–60 ppm	
	(C)=C-Cl	100–150 ppm	
	C=(C-Cl)	100–155 ppm	
	ar C-Cl	120–150 ppm	
	al C-Br	10–45 ppm	
	(C)=C-Br	90–140 ppm	
	C=(C-Br)	90–140 ppm	
	ar C-Br	110–140 ppm	
	al C-I	-20 to +30 ppm	
	(C)=C-I	60–110 ppm	
	C=(C-I)	120–150 ppm	
	ar C-I	85–115 ppm	
<sup>1</sup> H NMR	-CH <sub>2</sub> -F	≈4.3 ppm	Coupling with <sup>19</sup> F (isotope abundance,
			100%; I = 1/2): <sup>2</sup> J <sub>HF</sub> 40–80 Hz;
			<sup>3</sup> J <sub>HF</sub> 0–50 Hz; <sup>4</sup> J <sub>HF</sub> 0–5 Hz
	-CH <sub>2</sub> -Cl	≈3.5 ppm	
	-CH <sub>2</sub> -Br	≈3.4 ppm	
	-CH <sub>2</sub> -I	≈3.1 ppm	
			Alkenes: <i>geminal</i> protons strongly deshielded
			by all halogens; <i>vicinal</i> protons are shielded
			by F and deshielded by the other halogens
			Aromatics: shielding by F in <i>o</i> - and <i>p</i> -
IR	C-F st	1400–1000 cm <sup>-1</sup>	Strong
	C-Cl st	< 850 cm <sup>-1</sup>	
	C-Br st	< 700 cm <sup>-1</sup>	
	C-I st	< 600 cm <sup>-1</sup>	

Assignment	Range	Comments
Molecular ion		For saturated aliphatic halogen compounds often weak, for polyhalogenated compounds often absent Characteristic isotope patterns for Cl and Br
Fragments	m/z 69 [M-50] <sup>+</sup> or [Frag-50] <sup>+</sup>	CF <sub>3</sub> CF <sub>2</sub>  $\text{R}-\overset{\leftarrow}{\text{C}}-\text{hal} > \text{R}-\overset{\rightarrow}{\text{C}}-\text{hal}$
Rearrange-ments	[M-20] <sup>+</sup> [M-36] <sup>+</sup>	HF elimination HCl elimination
hal n→π*	≤ 280 nm (log ε ≈ 2.5)	For C-I; for C-Br and C-Cl in general only absorption tail, for C-F no absorption

MS

UV

### 3.7 Oxygen Compounds

#### 3.7.1 Alcohols and Phenols

	Assignment	Range	Comments
<sup>13</sup> C NMR	al C-OH	50–100 ppm	Shift with respect to corresponding C-H: ≈+50 ppm
	al C-(C-OH)	10–60 ppm	Hardly any shift with respect to C-(C-CH <sub>3</sub> )
	al C-(C-C-OH)	10–60 ppm	Shift with respect to C-(C-C-CH <sub>3</sub> ) ≈-5 ppm
	ar C-OH	135–155 ppm	Shift with respect to C-H ≈+25 ppm
	ar C-(C-OH)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> ≈-13 ppm, <i>meta</i> ≈+1 ppm, <i>para</i> ≈-8 ppm
<sup>1</sup> H NMR	al C-OH	0.5–5 ppm	Position and shape strongly depend on experimental conditions
	ar C-OH	5–8 ppm	
	-CH <sub>2</sub> -OH	3.5–4.0 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> ≈-0.6 ppm, <i>meta</i> ≈-0.1 ppm, <i>para</i> ≈-0.5 ppm
	-CH-OH	3.8–4.2 ppm	
	ar CH-(C-OH)	6.5–7.0 ppm	
IR	O-H st	3650–3200 cm <sup>-1</sup>	Position and shape depend on degree of association; often different bands for H- bonded and free OH
	C-O(H) st	1260–970 cm <sup>-1</sup>	Strong
MS	Molecular ion		Aliphatic: weak, often missing for primary and highly branched alcohols; in this case, peaks at highest mass are often due to [M-18] <sup>++</sup> or [M-15] <sup>+</sup> Aromatic: strong
	Fragments	Aliphatic: m/z 31, 45, 59,... [M-18] <sup>++</sup> [M-33] <sup>+</sup> [M-46] <sup>++</sup>  Aromatic: [ar-O] <sup>++</sup> [M-28] <sup>++</sup> (CO) [M-29] <sup>+</sup> (CHO)	Primary: m/z 31 > m/z 45 ≈ m/z 59 Secondary, tertiary: local maxima due to α- cleavage: $\text{R}-\overset{\text{R}}{\underset{\text{CH}}{\text{C}}}-\text{OH} \xrightarrow{+\cdot} \text{R}-\overset{+\cdot}{\text{C}}-\text{OH} \xrightarrow{-\text{R}\cdot} \text{R}-\overset{+}{\text{C}}=\text{OH}$



Assignment	Range	Comments
Rearrange- ments		<p>Aliphatic: elimination of <math>\text{H}_2\text{O}</math> from <math>\text{M}^{+\bullet}</math> and from products of <math>\alpha</math>-cleavage; elimination of <math>\text{H}_2\text{O}</math> followed by alkene elimination</p> <p>Unsaturated:</p> <p>vinylcarbinols: spectra similar to those of ketones</p> <p>allyl alcohols: specific, aldehyde elimination:</p> $\left[ \text{R}_1-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{R}_2 \right]^{+\bullet} \xrightarrow{-\text{R}_2\text{CHO}} \left[ \text{R}_1-\text{CH}=\text{CH}-\text{CH}=\text{R}_2 \right]^{+\bullet}$ <p>Aromatic: <i>ortho</i> effect with appropriate substituents:</p> $\left[ \text{C}_6\text{H}_4(\text{Y})(\text{Z})-\text{O}-\text{H} \right]^{+\bullet} \longrightarrow \left[ \text{C}_6\text{H}_4(\text{Y})(\text{Z})=\text{O} \right]^{+\bullet} + \text{H} \cdot / \text{Z} \cdot$ <p><math>-\text{Y}-\text{Z}</math>: <math>-\text{CO}-\text{OR}</math>, <math>-\text{C}-\text{hal}</math>, <math>-\text{O}-\text{R}</math>, and similar</p> <p>Aliphatic: no absorption above 200 nm</p> <p>Aromatic: in alkaline solution, shift to longer wavelength and intensity increase due to deprotonation</p>

UV

### 3.7.2 Ethers

Assignment	Range	Comments
al C-O	50–100 ppm	Oxiranes: outside the normal range
al C-(C-O)	10–60 ppm	Hardly any shift with respect to C-(C-CH <sub>3</sub> )
al C-(C-C-O)	10–60 ppm	Shift with respect to C-(C-C-CH <sub>3</sub> ) $\approx$ -5 ppm
O-C-O	85–110 ppm	
(C)=C-O	115–165 ppm	Shift with respect to (C)=C-C $\approx$ +15 ppm
C=(C-O)	70–120 ppm	Shift with respect to C=(C-C) $\approx$ -30 ppm
ar C-O	135–155 ppm	Shift with respect to C-H $\approx$ +25 ppm
ar C-(C-O)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> $\approx$ -15 ppm, <i>meta</i> $\approx$ +1 ppm, <i>para</i> $\approx$ -8 ppm

<sup>13</sup>C NMR

	Assignment	Range	Comments
<b><sup>1</sup>H NMR</b>	CH <sub>3</sub> -O	3.3–4.0 ppm	Singlet
	CH <sub>2</sub> -O	3.4–4.2 ppm	
	O-CH <sub>2</sub> -O	4.5–6.0 ppm	
	CH-O	3.5–4.3 ppm	
	CH-(O) <sub>3</sub>	≈5–6 ppm	
	H-C(O)=C	5.7–7.5 ppm	Shift with respect to H-C(H)=C ≈ +1.2 ppm
	H-C(=C-O)	3.5–5.0 ppm	Shift with respect to H-C(=C-H) ≈ -1 ppm
	ar CH-(C-O)	6.6–7.6 ppm	
<b>IR</b>	H-C(-O) st	2880–2815 cm <sup>-1</sup>	For CH <sub>3</sub> -O and CH <sub>2</sub> -O; similar range for amines
	H-CH(-O) <sub>2</sub> st	2880–2750 cm <sup>-1</sup>	Two bands
	C-O-C st as	1310–1000 cm <sup>-1</sup>	Strong, sometimes two bands
<b>MS</b>	Molecular ion		Aliphatic: weak, tendency to protonate Aromatic: strong
	Fragments	Aliphatic: m/z 31, 45, 59,... [M-18] <sup>++</sup> [M-33] <sup>+</sup> [M-46] <sup>++</sup>	Base peak of aliphatic ethers, generally due to fragmentation of the bond next to the ether bond: $R_1-C-O-R_2 \left[ ^{++} - R_1^{\bullet} \right] \longrightarrow C=O^+-R_2$ or due to heterolytic cleavage of the C-O bond, especially for polyethers: $R_1-O-R_2 \left[ ^{++} - R_1-O^{\bullet} \right] \longrightarrow R_2^+$
			Aryl alkyl ethers: preferential loss of the alkyl chain
			Diaryl ethers: preferential loss of CO (28) from M <sup>++</sup> and/or [M-H] <sup>+</sup> as well as: $ar_1-O-\overset{\curvearrowright}{\text{ar}_2}$
	Rearrange- ments		Aliphatic: elimination of alcohol Aromatic ethyl and higher alkyl ethers: alkene elimination to the phenol: $\left[ \text{C}_6\text{H}_5-O-\overset{\text{H}}{\underset{\text{R}}{\text{CH}_2}} \right] ^{++} \xrightarrow{-RCH=CH_2} \left[ \text{C}_6\text{H}_5-OH \right] ^{++}$
<b>UV</b>			Aliphatic: no absorption above 200 nm Aromatic: shift to higher wavelength and more intense due to the ether group

## 3.8 Nitrogen Compounds

### 3.8.1 Amines

Assignment	Range	Comments	
al C-N	25–80 ppm	Shift with respect to C-H $\approx$ +20 to +30 ppm	<sup>13</sup> C NMR
al C-(C-N)	10–60 ppm	Shift with respect to C-(C-C) $\approx$ +2 ppm	
al C-(C-C-N)	10–60 ppm	Shift with respect to C-(C-C-C) $\approx$ -2 ppm	
(C)=C-N	120–170 ppm	Shift with respect to (C)=C-C $\approx$ +20 ppm	
C=(C-N)	75–125 ppm	Shift with respect to C=(C-C) $\approx$ -25 ppm	
ar C-N	130–150 ppm	Shift with respect to C-H $\approx$ +20 ppm	
ar C-(C-N)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> $\approx$ -15 ppm, <i>meta</i> $\approx$ +1 ppm, <i>para</i> $\approx$ -10 ppm	
al C-NH	0.5–4.0 ppm		<sup>1</sup> H NMR
ar C-NH	2.5–5.0 ppm		
al or ar N <sup>+</sup> H	6.0–9.0 ppm	Often broad	
CH <sub>3</sub> -N	2.3–3.1 ppm	Singlet	
CH <sub>2</sub> -N	2.5–3.5 ppm		
CH-N	3.0–3.7 ppm		
CH-N <sup>+</sup>	3.2–4.0 ppm		
ar CH-(C-N)	6.0–7.5 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> $\approx$ -0.8 ppm, <i>meta</i> $\approx$ -0.2 ppm, <i>para</i> $\approx$ -0.7 ppm	IR
ar CH-(C-N <sup>+</sup> )	7.5–8.0 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> $\approx$ +0.7 ppm <i>meta</i> $\approx$ +0.4 ppm, <i>para</i> $\approx$ +0.3 ppm	
N-H st	3500–3200 cm <sup>-1</sup>	Position depends on extent of association, often different bands for H-bonded and free NH; always at least two bands for NH <sub>2</sub>	
N <sup>+</sup> -H st	3000–2000 cm <sup>-1</sup>	Broad, similar to COOH band but more structured	
N-H $\delta$	1650–1550 cm <sup>-1</sup>	Weak or absent	
N <sup>+</sup> -H $\delta$	1600–1460 cm <sup>-1</sup>	Often weak	
H-C(-N) st	2850–2750 cm <sup>-1</sup>	For CH <sub>3</sub> (-N) and CH <sub>2</sub> (-N); similar range for ethers	

	Assignment	Range	Comments
MS	Molecular ion		Odd mass number for odd number of nitrogens Aliphatic: weak, tendency to protonate Aromatic: strong, no tendency to protonate [M+H] <sup>+</sup> is often important
	Fragments	Aliphatic: m/z 30, 44, 58,...	Base peak of aliphatic amines generally due to fragmentation of the bond next to the amine bond: $\begin{array}{c} \text{R}_1 \\   \\ \text{R}_2 - \text{N} - \text{CH}_2 - \text{R}_3 \end{array} \left[ \right]^{+\bullet} \xrightarrow{-\text{R}_3\cdot} \begin{array}{c} \text{R}_1 \\   \\ \text{R}_2 - \text{N}^+ = \text{CH}_2 \end{array}$
	Rearrangements		Elimination of alkenes following amine cleavage: $\begin{array}{c} \text{R}_1 \\   \\ \text{R}_2 - \text{N}^+ = \text{CH}_2 \end{array} \longrightarrow \text{R}_1 - \text{NH}^+ = \text{CH}_2$
UV			Aliphatic: no absorption maximum above 200 nm Aromatic: in acidic solution, shift to lower wavelength and decrease in intensity

### 3.8.2 Nitro Compounds

	Assignment	Range	Comments
<sup>13</sup> C NMR	al C-NO <sub>2</sub>	55–110 ppm	Shift with respect to C-H ≈ +50 ppm
	al C-(C-NO <sub>2</sub> )	10–50 ppm	Shift with respect to C-(C-C) ≈ -6 ppm
	al C-(CCNO <sub>2</sub> )	10–60 ppm	Shift with respect to C-(C-C-C) ≈ -2 ppm
	ar C-NO <sub>2</sub>	130–150 ppm	Shift with respect to C-H ≈ +20 ppm
	ar C-(C-NO <sub>2</sub> )	120–140 ppm	Shift with respect to C-(C-H): <i>ortho</i> ≈ -5 ppm, <i>meta</i> ≈ +1 ppm, <i>para</i> ≈ +6 ppm
<sup>1</sup> H NMR	al CH-NO <sub>2</sub>	4.2–4.6 ppm	
	ar CH-(C-NO <sub>2</sub> )	7.5–8.5 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> ≈ +1.0 ppm, <i>meta</i> ≈ +0.3 ppm, <i>para</i> ≈ +0.4 ppm
IR	NO <sub>2</sub> st as	1660–1490 cm <sup>-1</sup>	Strong to very strong
	NO <sub>2</sub> st sy	1390–1260 cm <sup>-1</sup>	Strong to very strong

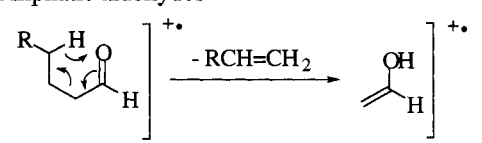
Assignment	Range	Comments	
Molecular ion		Odd mass number for odd number of nitrogens Aliphatic: weak or absent Aromatic: strong	MS
Fragments	[M-16] <sup>+</sup> , [M-46] <sup>+</sup>		
Rearrange- ments	m/z 30, [M-17] <sup>+</sup> , [M-30] <sup>+</sup> , [M-47] <sup>+</sup>		
	≈275 nm (log ε <2) Aliphatic ≈350 nm (log ε ≈2) Aromatic		UV

### 3.9 Thiols and Sulfides

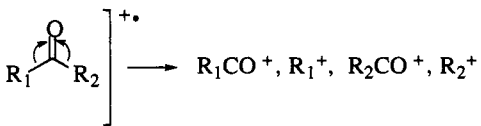
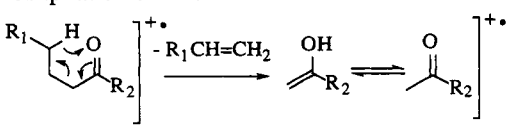
	Assignment	Range	Comments
<b><sup>13</sup>C NMR</b>	al C-S	5-60 ppm	No significant shift with respect to C-C
	ar C-S	120-140 ppm	
<b><sup>1</sup>H NMR</b>	al C-SH	1.0-2.0 ppm	<i>Vicinal</i> coupling constant, $J \approx 5-9$ Hz
	ar C-SH	2.0-4.0 ppm	
	al CH-S	2.0-3.2 ppm	
	ar CH-S	7.0-7.5 ppm	
<b>IR</b>	S-H st	2600-2540 cm <sup>-1</sup>	Frequently weak
<b>MS</b>	Molecular ion		<sup>34</sup> S-isotope peak at $[M+2]^+ \approx 4.5\%$ Aliphatic: intensity higher than for corresponding alcohols and ethers
	Fragments	$m/z$ 47, 61, 75,...	Sulfide cleavage: $R_1-S-CH_2-R_2 \left[ ^+ \cdot \right] \xrightarrow{-R_2 \cdot} R_1-\overset{+}{S}=CH_2$
	Rearrange- ments	$m/z$ 34, 35, 48 $[M-33]^+$ , $[M-34]^+$	Alkene elimination after sulfide cleavage
<b>UV</b>		<225 nm (log $\epsilon$ 3-4)	In aliphatic compounds
		220-250 nm (log $\epsilon$ 2-3)	

## 3.10 Carbonyl Compounds

### 3.10.1 Aldehydes

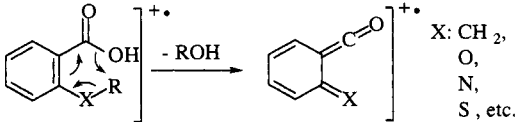
Assignment	Range	Comments	
CHO	190–205 ppm	Coupling constant $^1J_{CH}$ 172 Hz	$^{13}C$ NMR
al C–(CHO)	30–70 ppm	Coupling constant $^2J_{CH}$ 20–50 Hz	
al C–(C–CHO)	5–50 ppm	Shift with respect to C–(C–CH <sub>3</sub> ) $\approx$ -10 ppm	
(C)=C–(CHO)	110–160 ppm		
C=(C–CHO)	110–160 ppm		
ar C–(CHO)	120–150 ppm		
H–(C=O)	9.0–10.5 ppm		$^1H$ NMR
al CH–(CHO)	2.0–2.5 ppm	$^3J_{HH}$ 0–3 Hz	
CH=CH–(CHO)	5.5–7.0 ppm	$^3J_{HH} \approx$ 8 Hz	
ar CH–(C–CHO)	7.2–8.0 ppm	For C–aromatics, shift with respect to CH–(C–H): <i>ortho</i> : $\approx$ +0.6 ppm, <i>meta</i> : $\approx$ +0.2 ppm, <i>para</i> : $\approx$ +0.3 ppm	
comb	2900–2700 cm <sup>-1</sup>	Two weak bands	IR
C=O st	1765–1645 cm <sup>-1</sup>	Aliphatic: $\approx$ 1730 cm <sup>-1</sup> Conjugated: $\approx$ 1690 cm <sup>-1</sup>	
Molecular ion		Aliphatic: moderate Aromatic: strong	MS
Fragments	[M-1] <sup>+</sup>  [M-29] <sup>+</sup>	For aliphatic aldehydes, only significant up to C <sub>7</sub>	
Rearrange- ments	m/z 44, [M-44] <sup>+</sup>	Aliphatic aldehydes 	
n $\rightarrow\pi^*$	270–310 nm (log $\epsilon \approx$ 1) $\geq$ 207 nm (log $\epsilon \approx$ 4) $\geq$ 250 nm (log $\epsilon >$ 3)	Saturated aldehydes $\alpha,\beta$ -Unsaturated aldehydes Aromatic aldehydes	UV

### 3.10.2 Ketones

	Assignment	Range	Comments
<sup>13</sup> C NMR	C=O	195–220 ppm	
	al C–(C=O)	25–70 ppm	
	al C–(C–C=O)	5–50 ppm	Shift with respect to C–(C–CH <sub>3</sub> ) ≈ -6 ppm
	(C)=C–(C=O)	105–160 ppm	
	C=(C–C=O)	105–160 ppm	
	ar C–(C=O)	120–150 ppm	
<sup>1</sup> H NMR	al CH–(C=O)	2.0–3.6 ppm	CH–CO–al 2.0–2.6 ppm CH–CO–ar 2.5–3.6 ppm
	CH=CH–(C=O)	5.5–7.0 ppm	
	ar CH–(C–C=O)	7.2–8.0 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.6 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
IR	C=O st	1775–1650 cm <sup>-1</sup>	Aliphatic: ≈ 1715 cm <sup>-1</sup> Cyclic: ring size ≥ 6: ≈ 1715 cm <sup>-1</sup> ring size < 6: ≥ 1750 cm <sup>-1</sup> Conjugated: ≈ 1690–1665 cm <sup>-1</sup>
MS	Molecular ion		Aliphatic: moderate Aromatic: strong
	Fragments		Ketone cleavages:
			
	Rearrange- ments	m/z 44 [M-44] <sup>+</sup>	Aliphatic ketones
			
UV	π→π*	<200 nm (log ε 3–4)	Saturated
	n→π*	250–300 nm (log ε 1–2)	ketones
		≥ 215 nm (log ε ≈ 4)	α,β-Unsaturated ketones
		≥ 245 nm (log ε > 3)	Aromatic ketones



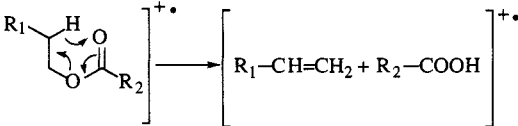
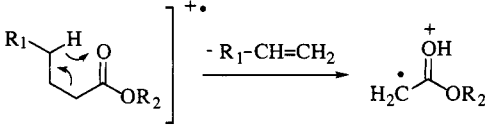
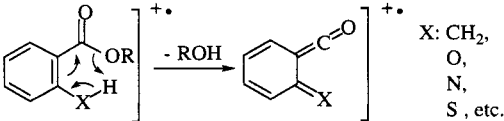
### 3.10.3 Carboxylic Acids

Assignment	Range	Comments	
COOH	170–185 ppm	In COO <sup>-</sup> , shift with respect to COOH: 0 to +8 ppm	<sup>13</sup> C NMR
al C–(COOH)	25–70 ppm		
al C–(C–COOH)	5–50 ppm	Shift with respect to C–(C–CH <sub>3</sub> ) ≈ -6 ppm	
(C)=C–(COOH)	105–160 ppm		
C=(C–COOH)	105–160 ppm		
ar C–(COOH)	120–150 ppm		
COOH	10.0–13.0 ppm	Position and shape strongly depend on experimental conditions	<sup>1</sup> H NMR
al CH–(COOH)	2.0–2.6 ppm		
CH=CH–(COOH)	5.2–7.5 ppm		
ar CH–(C–COOH)	7.2–8.0 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.8 ppm, <i>meta</i> ≈ +0.2 ppm, <i>para</i> ≈ +0.3 ppm	
COO–H st	3550–2500 cm <sup>-1</sup>	Broad	IR
C=O st	1800–1650 cm <sup>-1</sup>	Aliphatic: ≈ 1715 cm <sup>-1</sup> Conjugated: ≈ 1695 cm <sup>-1</sup> In COO <sup>-</sup> two bands: 1580 and 1420 cm <sup>-1</sup>	
CO–OH δ oop	≈ 920 cm <sup>-1</sup>	For dimers	
Molecular ion		Aliphatic: moderate, strong for long chains, tendency to protonate Aromatic: strong	MS
Fragments	[M-17] <sup>+</sup> [M-45] <sup>+</sup>	Strong for aromatic acids	
Rearrange-ments	m/z 60, 61 [M-18] <sup>+</sup>	Aliphatic acids Aliphatic acids <i>Ortho</i> effect with aromatic acids:	
			
n→π*	<220 nm (log ε 1–2) ≥193 nm (log ε ≈ 4) ≥230 nm (log ε > 3)	Saturated acids α,β-Unsaturated acids Aromatic acids	UV

## 3.10.4

## Carboxylic Esters and Lactones

	Assignment	Range	Comments
<sup>13</sup> C NMR	COOR	165–180 ppm	Shift with respect to COOH: -5 to -10 ppm
	al C–(COOR)	20–70 ppm	
	al C–(C–COOR)	5–50 ppm	Shift with respect to C–(C–CH <sub>3</sub> ) ≈ -6 ppm
	al C–(OCOR)	50–100 ppm	Shift with respect to C–(OH) +2 to +10 ppm
	(C)=C–(COOR)	105–160 ppm	
	C=(C–COOR)	105–160 ppm	
	(C)=C–(OCOR)	100–150 ppm	
	C=(C–OCOR)	80–130 ppm	
	ar C–(COOR)	120–150 ppm	
	ar C–(OCOR)	100–160 ppm	
<sup>1</sup> H NMR	al CH–(COOR)	2.0–2.5 ppm	CH <sub>3</sub> COOR ≈ 2.0 ppm; CH <sub>2</sub> COOR ≈ 2.3 ppm CHCOOR ≈ 2.5 ppm
	al CH–(OCOR)	3.5–5.3 ppm	CH <sub>3</sub> OCOR ≈ 3.5–3.9 ppm CH <sub>2</sub> OCOR ≈ 4.0–4.5 ppm CHOCOR ≈ 4.8–5.3 ppm
	CH=CH–(COOR)	5.2–7.5 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +0.8 ppm, <i>cis</i> ≈ +1.1 ppm, <i>trans</i> : ≈ +0.5 ppm
	C=CH–(OCOR)	6.0–8.0 ppm	Shift with respect to CH=CH–H:
	CH=C–(OCOR)	4.5–6.0 ppm	<i>geminal</i> ≈ +2.1 ppm, <i>cis</i> ≈ -0.4 ppm, <i>trans</i> ≈ -0.6 ppm
	ar CH–(C–COOR)	7.5–8.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.7 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
	ar CH–(C–OCOR)	6.8–7.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ -0.2 ppm, <i>meta</i> ≈ 0 ppm, <i>para</i> ≈ -0.1 ppm
IR	C=O st	1745–1730 cm <sup>-1</sup>	Strong; range for aliphatic esters Higher wavenumbers for hal–C–COO, COO–C=C, COO–ar, and for small-ring lactones Lower wavenumbers for C=C–COOR and ar–COOR
	C–O st	1330–1050 cm <sup>-1</sup>	Mostly two bands, at least one of them strong

Assignment	Range	Comments
Molecular ion		Aliphatic esters: weak, tendency to protonate Aliphatic lactones: medium to weak, tendency to protonate Aromatic esters and lactones: strong
Fragments	$[M - RO]^+$ $[M - ROCO]^+$	Esters Esters Lactones: loss of $\alpha$ -substituents (attached to ether carbon), decarbonylation, for aromatic lactones also double decarbonylation
Rearrangements		Alkene elimination from the alcohol moiety:  $\left[ \text{R}_1-\text{CH}(\text{H})-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{R}_2 \right]^{+\bullet} \longrightarrow \left[ \text{R}_1-\text{CH}=\text{CH}_2 + \text{R}_2-\text{COOH} \right]^{+\bullet}$ <p>Elimination of the alcohol side chain with double hydrogen transfer (for <math>&gt; \text{C}_2</math> alcohols)</p> $\left[ \text{R}_1-\text{COOR}_2 \right]^{+\bullet} \longrightarrow \text{R}_1-\text{C}(\text{OH})=\text{CH}_2$ <p>Elimination of the alkyl chain of the acid moiety as an alkene</p>  $\left[ \text{R}_1-\text{CH}(\text{H})-\text{CH}_2-\text{C}(=\text{O})-\text{OR}_2 \right]^{+\bullet} \xrightarrow{-\text{R}_1-\text{CH}=\text{CH}_2} \text{H}_2\text{C}=\text{C}(\text{OH})-\text{OR}_2$ <p>Alcohol elimination from <i>ortho</i>-substituted aromatic esters</p>  $\left[ \text{C}_6\text{H}_4(\text{OR})(\text{X})-\text{C}(=\text{O}) \right]^{+\bullet} \xrightarrow{-\text{ROH}} \left[ \text{C}_6\text{H}_4(\text{X})=\text{C}=\text{O} \right]^{+\bullet}$ <p>X: <math>\text{CH}_2</math>, O, N, S, etc.</p>
	$[M-18]^{+\bullet}$	Lactones
$n \rightarrow \pi^*$	<220 nm (log $\epsilon$ 1–2) $\geq 193$ nm (log $\epsilon \approx 4$ ) $\geq 230$ nm (log $\epsilon > 3$ )	Aliphatic esters $\alpha, \beta$ -Unsaturated esters Aromatic esters

MS

UV

## 3.10.5

## Carboxylic Amides and Lactams

	Assignment	Range	Comments
<sup>13</sup> C NMR	CONR <sub>2</sub>	165–180 ppm	
	al C–(CONR <sub>2</sub> )	20–70 ppm	
	al C–(C–CONR <sub>2</sub> )	5–50 ppm	Shift with respect to C–(C–CH <sub>3</sub> ) ≈ -6 ppm
	al C–(NCOR)	25–80 ppm	Shift with respect to C–(NH) ≈ -1 to -2 ppm
	C=C–(CONR <sub>2</sub> )	105–160 ppm	
	ar C–(CONR <sub>2</sub> )	120–150 ppm	
	ar C–(NCOR)	110–150 ppm	
<sup>1</sup> H NMR	CONH	5–10 ppm	Frequently broad to very broad; splitting due to H–N–C–H coupling often only recognizable in the CH signal
	al CH–(CONR <sub>2</sub> )	2.0–2.5 ppm	
	al CH–(NCOR)	2.7–4.8 ppm	CH <sub>3</sub> NCOR ≈ 2.7–3.0 ppm; CH <sub>2</sub> NCOR ≈ 3.1–3.5 ppm; CHNCOR ≈ 3.8–4.8 ppm
	CH=CH–(CONR <sub>2</sub> )	5.2–7.5 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +1.4 ppm, <i>cis</i> ≈ +1.0 ppm, <i>trans</i> ≈ +0.5 ppm
	C=CH–(NCOR)	6.0–8.0 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +2.1 ppm, <i>cis</i> ≈ -0.6 ppm, <i>trans</i> ≈ -0.7 ppm
	CH=C–(NCOR)	4.5–6.0 ppm	
	ar CH–C(CONR <sub>2</sub> )	7.5–8.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.6 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
	ar CH–C(NCOR)	6.8–7.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ 0 ppm, <i>meta</i> ≈ 0 ppm, <i>para</i> : ≈ 0 to -0.3 ppm
IR	N–H st	3500–3100 cm <sup>-1</sup>	Position and shape depend on extent of association, often different bands for H-bonded and free NH, always at least two bands for NH <sub>2</sub>
	C=O st (amide I)	1700–1650 cm <sup>-1</sup>	Strong, range given for amides as well as for δ- and larger lactams, higher wavenumbers for β- and γ-lactams
	N–H δ and N–C=O st sy (amide II)	1630–1510 cm <sup>-1</sup>	Often strong, missing for tertiary amides and lactams

Assignment	Range	Comments	
Molecular ion		Aliphatic amides: moderate, tendency to protonate Aromatic amides: strong	<b>MS</b>
Fragments		Amides: cleavage on both sides of the carbonyl group followed by loss of CO; large number of fragments of even mass Lactams: loss of $\alpha$ -substituent, loss of CO	
Rearrange- ments		Amides: elimination of the amine moiety, elimination of alkene from the amine or acid moiety in analogy to esters	
	$[M-18]^+$	Lactams	
$n \rightarrow \pi^*$	<220 nm (log $\epsilon$ 1–2)	Aliphatic amides and lactams	<b>UV</b>