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STUDIES IN CHEMICAL IONIZATION MASS SPECTROMETRY III[1]

CI-SPECTRA OF OLEFINS

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Zusammenfassung—Verschiedene Reaktandgase (CH_4, i-C_4H_{10}, NO, N_2O, Amine, Äther, $(CH_3)_4Si$) wurden auf ihre Brauchbarkeit bei der Bestimmung der Lage von Doppelbindungen durch chemische Ionisations-Massenspektrometrie untersucht. Positive Resultate konnten mit i-C_4H_{10}, NO und CH_3NH_2 erhalten werden.

Abstract—Various reactant gases (CH_4, i-C_4H_{10}, NO, N_2O, amines, ethers, $(CH_3)_4Si$) have been tested for their usefulness in determining the position of double bonds by chemical ionization mass spectrometry. Positive results have been obtained with i-C_4H_{10}, NO and CH_3NH_2.

The molecular ions of linear alkenes generated by electron impact (EI) show facile isomerisation into a mixture of rapidly interconverting structures which is complete within 10^{-9} sec after ionization for decomposing ions and extensive even for non-decomposing species after 10^{-5} sec[2]. Hence, localisation of the double bond from an enhanced abundance of ions formed by cleavage of an allylically activated bond is possible only if mass spectra are obtained from ions decomposing within $\sim 10^{-11}$ sec after ionization. Such ions can be selected either by the field ionization kinetic[2] (FIK) or possibly by the excess kinetic energy[3] (KE) method neither of which can be used with a commercial mass spectrometer. The data available[4] on field ionization (FI) spectra are—in spite of statements to the contrary*—somewhat contradictory regarding the significance of ions formed by allylic cleavage. Thus, with the exception of certain branched[6] and cyclic olefins[7] which give characteristic fragments in EI mass spectrometry the mass spectrometric investigation of derivatives has to be resorted to.[8,9] This procedure is disadvantageous especially since in natural products chemistry (e.g., pheromones[10]) frequently sufficient material for chemical derivatisation is not available.

CI *analysis of olefins*

General considerations. EI data show that isomerisation of alkene molecular ions occurs even in species having little excess energy. Yet, if it is possible to add by an ion molecule reaction a cationic group to the olefinic bond the position of the latter will be fixed and, in case the added group triggers fragmentation in a characteristic manner, the fragments formed are indicative of the location of the original double bond. The ideal reactant gas ought to have the following properties:

- readily available in high purity (to avoid side reactions caused by admixtures)
- not aggressive to the source or the vacuum system
- yielding by itself only few types of ions of relatively low mass (high abundance of plasma ions can be detrimental to the SEV system and frequently the dynamic range of data systems is insufficient to record both abundant plasma and low intensity fragment ions. Those parts of the mass spectra which contain the former are, therefore, usually not recorded.† Hence, plasma ions should not interfere with mass regions where characteristic substance ions are to be expected).
- the recombination energy of the plasma ions should not exceed ~ 9.5 eV (Since the IP's of n-alkenes are ~ 9.0–9.5 eV higher recombination energies as, e.g., for Ar^+ (15.8 eV) result in an increasing portion of ionization by charge exchange (CE) which in turn produces EI-type spectra).
- ionization should not be effected by proton transfer (*v. infra*).
- the product of an electrophilic attack by a plasma ion at the double bond ought to induce the

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* The data reported[4] by Rang and by Levsen differ grossly for some compounds discussed. Competing field desorption (FD (*cf* Ref. 5) the relative importance of which is highly dependent on experimental parameters as the state of the emitters, field strength etc.) which is accompanied by rearrangement reactions could be an explanation for these discrepancies. In addition, one of the main problems of FI is the low abundance of fragment ions (few percent rel. int. for the most abundant species).

† Quadrupole instruments allow to some extent omission of single masses during the scan (*cf.* the absence of *m/e* 131, 145 and 161—*cf* Ref. 11—in Fig. 1), a procedure normally not possible with magnetic instruments where the scan has to be started above the mass of the highest abundant plasma ion—a series problem esp. if working with low molecular weight compounds.

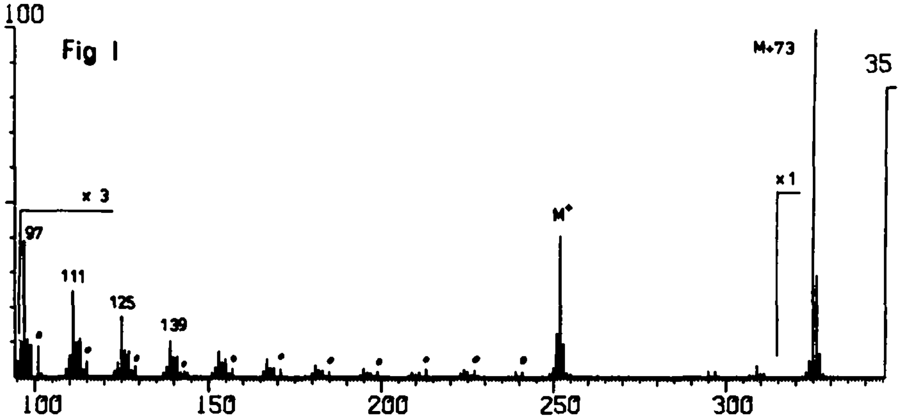


Fig. 1. CI(Si(CH$_3$)$_4$) mass spectrum of octadecene-6 (Si(CH$_3$)$_3$(CH$_2$)$_n^+$ ions are marked by a •).

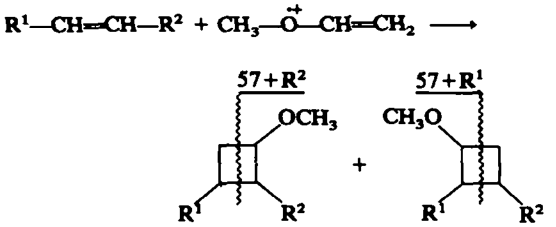
formation of characteristic fragment ions; competing isomerisation reactions should occur with much lower rates.

The following examples will illustrate these points.

(CH$_3$)$_4$Si has been suggested[11] as a suitable CI-reactant gas for its low IP (9.8 eV) and the electrophilic character of the plasma ion Me$_3$Si$^+$ (*m/e* 73), but deposits of decomposition products render the source insulators conducting within few minutes. In addition, plasma ions reach forbiddingly high masses (up to *m/e* 161, [(CH$_3$)$_3$Si-Si(CH$_3$)$_4$]$^+$).[11] The high abundance of [M+73]$^+$ in the mass spectrum (Fig. 1) of octadecene-6 as compared with long chain alkanes[11] demonstrates the attack of the π-system, but the series of Si containing ions ([73+14.n]$^+$) does not give any indication of the position of the double bond: R—CH$^+$—CH(SiMe$_3$)R′ apparently undergoes rearrangement reactions as described for EI spectra.

(CH$_3$)$_2$O (*cf*[12]) and (CH$_2$)$_2$O (reactant gases which are not aggressive to the source) yield quasi-molecular ions ([M+45]$^+$ and [M+43]$^+$, resp), but no characteristic fragments are observed for long-chain olefins.

CH$_3$—O—CH═CH$_2$ has been shown by Jennings[13] to give via a 2+2 cycloaddition[14] two isomeric cyclobutane derivatives as quasi-molecular ions. These may decompose by alternative ring opening yielding substituted vinyl ether ions from the mass of which the position of the original double bond can be deduced (*m/e* 212 corresponding to C$_{11}$H$_{23}$CH═CHOCH$_3^+$ for octadecene-6 in Fig. 2, further loss of CH$_3$OH yields *m/e* 180).[15] Since methyl vinyl ether undergoes ion molecule reactions within the reactant gas it has to be diluted by CO$_2$ or Ar which in turn act by themselves as ionizing agents by CE enhancing the EI character of the spectra. Thus in Fig. 2 the mass region below *m/e* 150 is crowded with hydrocarbon ions which do not allow to recognize any structure specific fragments (as the second cleavage product C$_5$H$_{11}$CH═CHOCH$_3^+$, *m/e* 128, in Fig. 2).


$$R^1\text{—CH═CH—}R^2 + CH_3\text{—}\overset{\cdot+}{O}\text{—CH═CH}_2 \longrightarrow$$

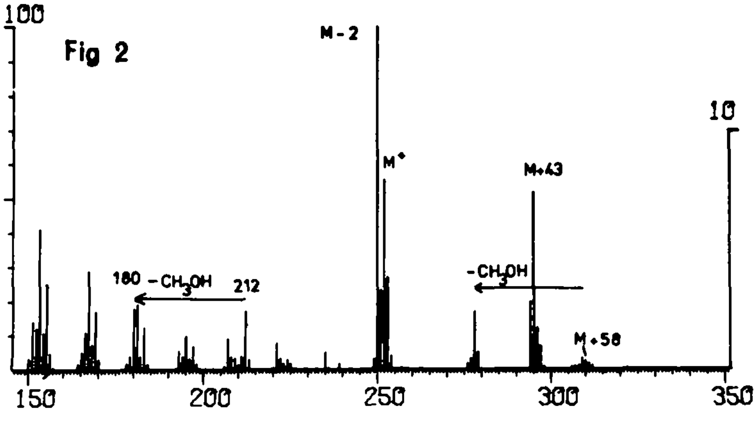


Fig. 2. CI(CH$_3$OCH═CH$_2$) mass spectrum of octadecene-6.

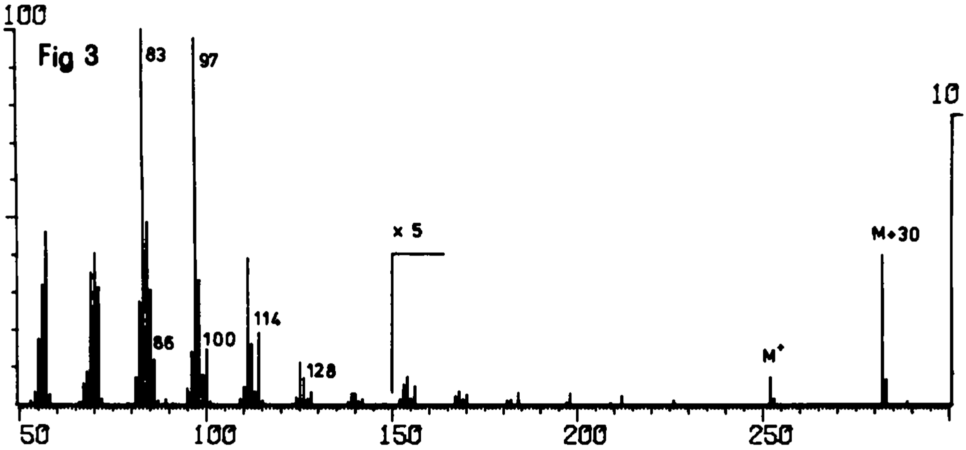


Fig. 3. CI(N_2O) mass spectrum of octadecene-1.

NO which will be discussed below in detail is corrosive to the hot cathode. Generation of NO^+ from N_2O is possible but again the high IP (12.9 eV) leads competitively to ionization by CE and to enhanced formation of unspecific hydrocarbon ions (*cf* the relative abundance of the characteristic series $[86+14n]^+$ in Figs 3 and 4).

CI with hydrocarbon reactant gases

The first systematic investigation by Field[16] was concerned with the reactions induced by a CH_4 plasma (mainly CH_5^+ and $C_2H_5^+$) which shows attack both at the double bond (yielding preferentially alkyl ions) and in the aliphatic portion of the molecule (yielding alkyl and alkenyl ions) (*cf* Scheme 1). The various ionization reactions[16–18] (protonation of the double bond, hydride abstraction from various loci in the chain, addition of $C_2H_5^+$) are strongly exothermic, the surplus energy allowing ready hydride and alkyl migrations which render CH_4 a reactant gas unsuitable for our purposes (Fig. 5).

i-C_4H_{10} (~90% of the plasma consists of $C_4H_9^+$) differs from CH_4 insofar as due to its higher proton affinity (807 for $C_4H_9^+$ as compared with 527 kJ/mole for CH_5^+) protonation reactions are only slightly exothermic. Hence formation of alkenyl ions which are formed[16–18] primarily by a statistical attack of H^+ at the various σ-bonds is reduced (*cf* Figs 5 and 6). The conclusion that the acid strength of $C_4H_9^+$ is barely sufficient to protonate and subsequently to cleave C,C σ-bonds is corroborated by the fact that in the i-C_4H_{10} spectrum of n-$C_{18}H_{38}$ essentially no fragment ions are observed. An exception are 1-alkenes where in CI (i-C_4H_{10}) spectra alkenyl ions prevail. Whether the somewhat lower (~8 kJ/mole) proton affinity of the terminal double bond can account by itself for this drastical difference (*cf* Figs 6 and 8) is a moot point.

While—as expected—the relative abundances of *alkenyl* ions are independant from the position of the double bond (for large alkenes $C_7H_{13}^+$, *m/e* 97 always has the highest intensity) in the series of *alkyl* ($C_nH_{2n+1}^+$) ions those formed by α-cleavage accompanied by H-transfer (H^+-addition to the double bond as depicted schematically in Scheme 1) prevail as can be seen from Table 1. The smaller ionic fragment is always observed with higher intensity than its neighbors and thus clearly recognizable, while the larger one is somewhat obscured

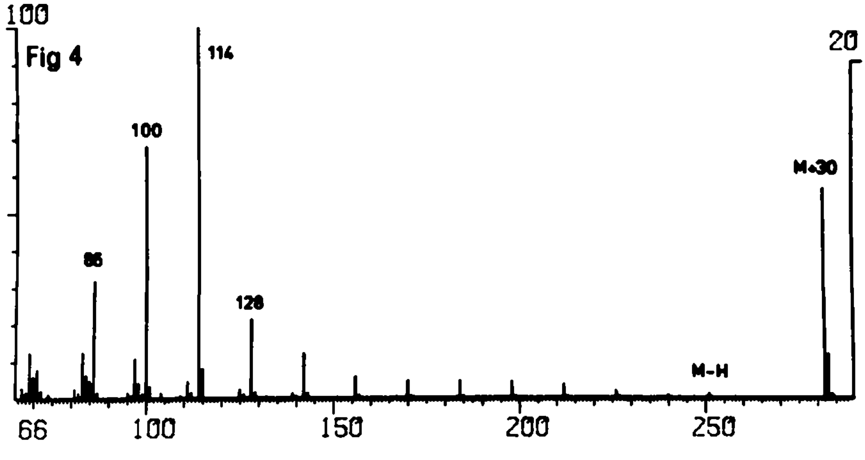
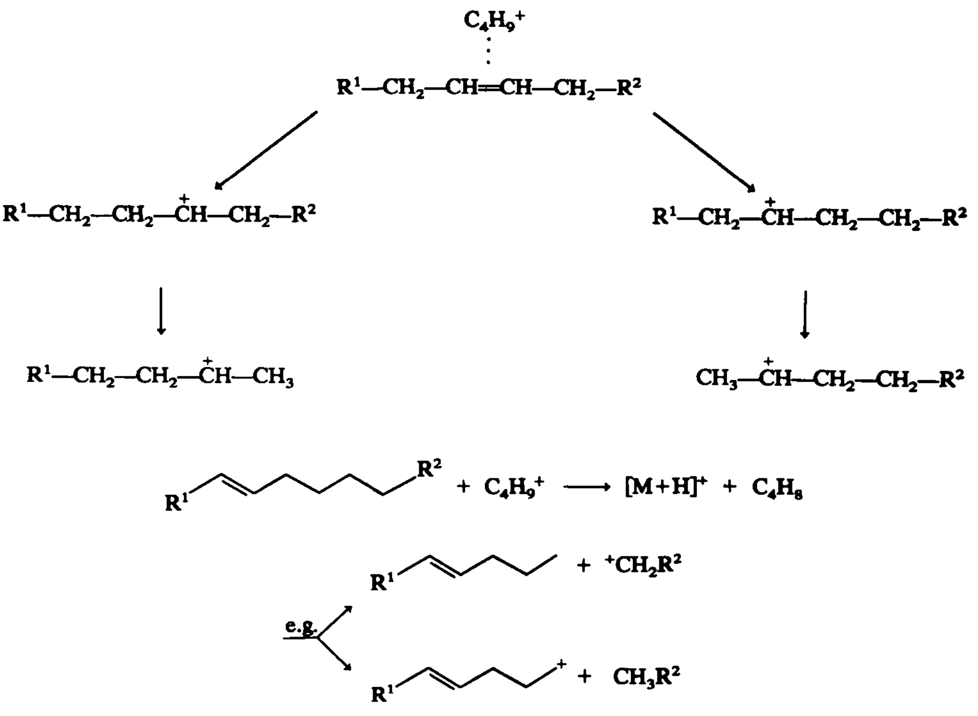


Fig. 4. CI(NO) mass spectrum of octadecene-1.



Scheme 1. Formation of alkyl (specific and unspecific process) and alkenyl ions (unspecific process) from protonated alkenes. For additional processes, rearrangement reactions etc, see Refs.[16–18]

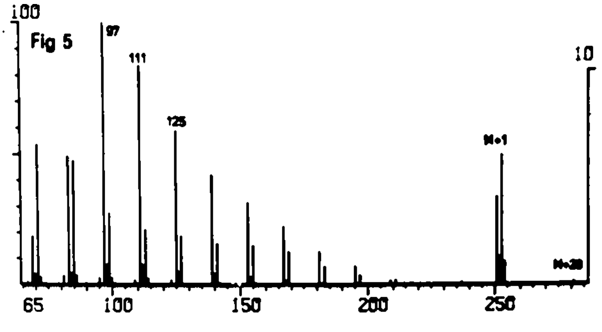


Fig. 5. CI(CH_4) mass spectrum of Z-octadecene-6.

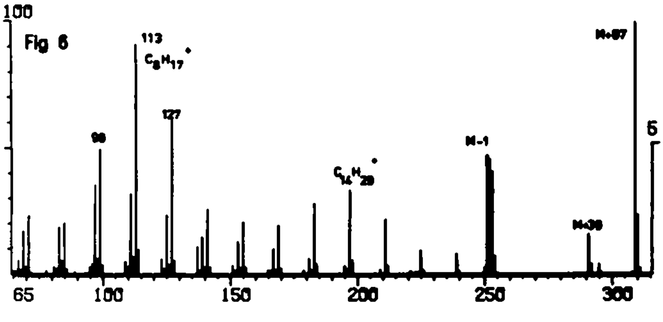


Fig. 6. CI(i-C_4H_{10}) mass spectrum of Z-octadecene-6.

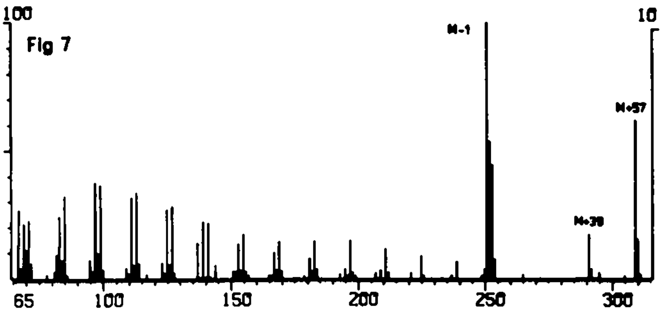


Fig. 7. CI(i-C_4H_{10}) mass spectrum of E-octadecene-6.

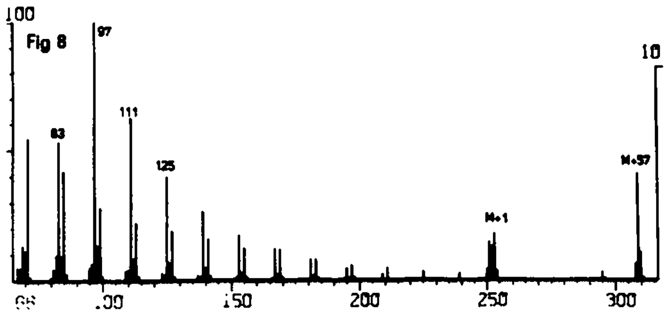


Fig. 8. CI(i-C_4H_{10}) mass spectrum of octadecene-1.

Table 1. Relative intensities of the C_nH_{2n+1} ions in the CI(i$-C_4H_{10}$) mass spectra of isomeric n-octadecenes. Ions formed by allylic cleavage are underlined

	n	5	6	7	8	9	10	11	12	13	14	15	16	17	M+H	M+43	M+57
Δ	m/e	71	85	99	113	127	141	155	169	183	197	211	225	239	253	295	309
4		35	$\underline{57}$	49	26	22	14	13	10	8	8	15	$\underline{20}$	13	44	4	100
5		32	46	$\underline{100}$	65	27	19	15	14	12	20	$\underline{24}$	14	8	28	5	63
6		22	20	55	$\underline{90}$	60	25	19	19	27	$\underline{33}$	21	9	8	39	4	100
7		16	10	16	27	$\underline{42}$	30	24	23	$\underline{21}$	13	8	9	8	45	7	100
8		22	13	20	23	46	$\underline{78}$	55	$\underline{46}$	30	11	9	7	3	39	4	100
9		30	28	24	27	30	67	$\underline{100}$	65	24	15	12	10	8	47	3	95

when the double bond moves towards the center of the chain.

Alkyl ions are not only formed by the specific process depicted in Scheme 1 (attack of $C_4H_9^+$ at the double bond). Hence clear-cut mass shifts should not be expected from deuterium labelled analogs. Nevertheless, two things become evident from Table 2: The ions corresponding in mass to those formed by allylic cleavage (underlined in Table 2) show unexpectedly pronounced deficiency of the label as compared with losses from other positions (*cf* [3,3-D_2]octadecene-5 and [12, 12-D_2]-hexadecene-5). Apparently no scrambling of all hydrogens occurs.* Some specific mechanism seems to be responsible also for the formation of the alkyl ions formally arising from homoallylic cleavage with H-transfer as can be judged from the high degree of retention of the vinylic deuterium atoms in these ions.

Correlations between the stereochemistry of a

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* Since alkyl ions apparently are formed in a competitive manner at least from $[M+H]^+$ and from $[M+C_4H_9]^+$ (Scheme 1) reliable conclusions could only be reached after extensive labelling and measurements with C_4D_{10} as reactant gas. One gets, however, an approximate fit between calculated and observed values (which should be considered with all due caution) if one assumes for the smaller one of the alkyl ions under consideration ($C_8H_{17}^+$ for octadecene-6) that (*cf* the discussion of the spectra of Z- and E-octadecene-6) about 1/3 is formed (*cf* Refs 16 and 17) via

$$C_5H_{11}—CD{=}CD—(CH_2)_3—C_8H_{17}+C_4H_9^+ \rightarrow$$

$$C_5H_{11}—CD{=}CD—(CH_2)_2CH_3+C_8H_{17}^+ + C_4H_8$$

thus containing no lable, and about 2/3 via the specific process (Scheme 1) *after* scrambling of the vinylic D with the H's from $C_4H_9^+$. One would then expect 29% d_1 and 4% d_2. Obviously for the non-specific portion of the larger alkyl ion ($C_{14}H_{29}^+$ for octadecene-6) some other way of formation must be invoked and consequently one observes a different degree of retention of the label (Table 2).

Table 2. Abundance of the d_1- and d_2-analogs of the C_nH_{2n+1} ions formed in the CI(i-C_4H_{10}) spectra of olefins.

compounds	numbers of C-atoms																									
	5		6		7		8		9		10		11		12		13		14		15		16		17	
[3,3-D_2] octadecene-5	29	3	19	51	12	83	13	85	25	55	26	50	27	46	24	40	20	36	13	16	8	15	22	24	20	66
[4,5-D_2] octadecene-4	21	7	17	5	29	67	47	38	42	36	47	39	48	33	44	33	34	29	33	26	23	21	62	17	20	71
[5,6-D_2] octadecene-5	39	5	22	5	20	6	32	60	42	35	39	39	39	32	41	32	35	19	26	17	28	24	28	61	34	56
[6,7-D_2] octadecene-6	16	2	70	28	23	6	24	10	28	65	36	34	45	34	37	28	27	17	26	20	28	68	34	52	32	58
[12,12-D_2] hexadecene-5	14	12	10	8	10	6	10	6	28	18	35	29	26	51	16	84	10	80	12	82	7	85				

compound and the relative abundance of quasi-molecular ions have been recognized occasionally in CI-spectra as, e.g., the enhanced portion of total ion current (TI) carried by $[M+H]^+$ of stereoisomers for which conformers are possible where the proton can be stabilized by two or more non-bonding electron pairs of O-substituents.[19] For olefins a phenomenon not yet reported in literature is observed: *Sterical hindrance* seems to control the relative abundance of the quasi-molecular ions $[M-H]^+$ and $[M+C_4H_9]^+$. As can be seen from Table 3 and Figs 6 and 7 $[M—H]^+$ (together with $[M+H]^+$) prevails for the E-, while the opposite is true for the Z-isomer. Here the π-system is shielded to a lesser degree allowing the $C_4H_9^+$ ion to approach more readily. On the other hand, H^- abstraction from the various CH_2 groups (resulting in $[M-H]^+$] is hardly affected by the configuration of the double bond.

The decrease in relative abundance of $[M+C_4H_9]^+$ for the E-isomer goes hand in hand with a decrease of the portion of the TI made up from alkyl ions the intensity distribution of which now follows that of the alkenyl ions showing a maximum for C_7. The preponderance of the ions formed by allylic cleavage cannot be recognized any more with certainty since alkyl ions arising from M^+ and $[M+H]^+$ (rather than from $[M+C_4H_9]^+$) are formed in an unspecific way.

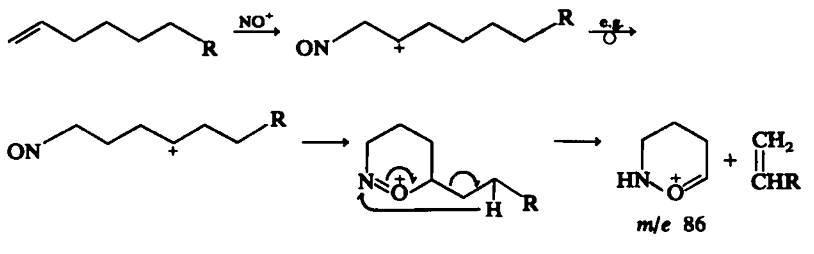
Table 3. Ratios $[M+C_4H_9]^+/[M-H]^+$ for Z- and E-olefins in their CI(i-C_4H_{10}) spectra.

Z-isomer		E-isomer	
octadecene-6	2,11	octadecene-6	0,62
octadecene-7	1,46	octadecene-7	0,89
octadecene-9	1,97	hexadecene-5	0,72
heptadecene-4	1,95		

CI *with* NO *as reactant gas*

NO^+ (the major component of the NO plasma) has a recombination energy of 8.3 eV too small for ionization of alkenes by CE (IP ~9.0–9.5 eV); it is a mild hydride abstractor (hydride affinity 1028 kJ/mole) and a strong electrophile.[17] The main quasi-molecular ions of olefins are, therefore, $[M-H]^+$ and $[M+NO]^+$.

Hunt[17] observed for 1-alkenes a series of ions of the general composition $(CH_2)_nNO^+$ with an intensity maximum which shifts from n = 4 to n = 6 with increasing chain length. He suggests that NO^+ is added to the terminal CH_2-group (Markovnikov orientation). The positive charge then migrates from C-2 by a series of 1,2-hydride shifts towards the center of the chain. Nucleophilic substitution by the terminal O results in cyclic ions (preferentially 6- to 8-membered) which eliminate an alkene via a McLafferty rearrangement—formulated here for b_2 (n = 4) (*cf* Fig 4 and Table 6):

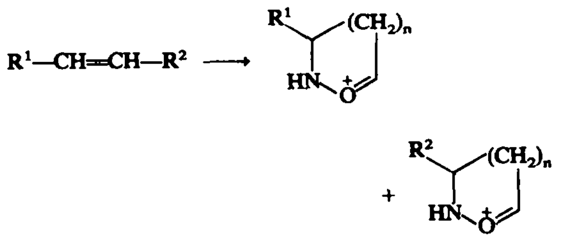


For alkenes with the double bond in other positions Hunt only comments on the low abundance of fragments, a rather undesirable situation. Systematic investigation, however, of the various parameters influencing the appearance of a CI spectrum shows that variation of the electron energy (80–150 eV) and cathode emission (0.5–1.0 mA) had no major influence on the spectra in contrast to source temperature and reactant gas pressure (Table 4): at high temperatures and low pressure EI-type spectra

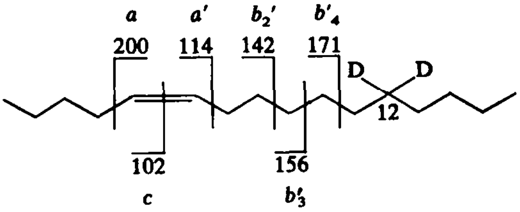
Table 4. Temperature and NO pressure dependence of the CI(NO) spectrum of octadecene-5.

t °C	P Pa	% TI			
		$[M+NO]^+$	$[M-H]^+$	ΣNO-containing fragments	Σalkenyl ions
60	31	42	25	18	15
120		22	7	7	25
180		4	negl.	1	55
100	20	8	5	2	35
	35	32	13	8	20

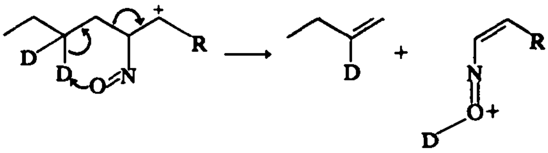
are obtained, where NO-containing fragments become negligible, while at 60°C and 30 Pa NO-containing fragments with up to 50% rel. int. are observed. The higher abundance of NO-containing fragment ions thus obtained by us allows also the analysis of CI(NO) spectra of alkenes with central double bonds. Fragmentation as depicted above should be possible here, too, but since the reaction enthalpies for the addition of NO^+ to either terminus of the double bond are now rather similar one should expect two series of fragments provided the alkyl groups R^1 and R^2 are long enough to allow the rearrangement (b-series).



Accordingly, in the spectrum (Fig. 9) of octadecene-5 ions at *m/e* 142, 156...are found, and the maximum intensity (Table 5, column b_3) lies with a 7-membered ring. That the fragment formation follows the mechanism suggested above for 1-alkenes with high specificity is evidenced by the mass shifts upon labelling (Table 5), especially by the transfer of one D only in the spectrum of [12, 12-D_2]hexadecene-5 during the formation of *m/e* 171. This rearrangement is accompanied by a drastic isotope effect (0.4). Such isotope effects have been observed[20] in cases where the mobility of the decomposing ion is reduced (especially cyclic compounds) in a way that the shorter bond length of C–D becomes important.



In the spectrum of octadecene-5 (Fig. 9) the ions *m/e* 226 and 114 formally belong also to the series $(CH_2)_nNO^+$ but they are formed—as shown by labelling—by a highly specific McLafferty rearrangement:



Finally, an ion (*c*) is observed which is formed by cleavage of the double bond and transfer of 2H ($C_nH_{2n+2}NO^+$). Of the two possible ions only the smaller one seems to occur in the spectra (*m/e* 102 in Fig. 9). As can be seen from Table 5, for 5,6-unsaturation both D's from C-3 and one from the double bond are retained and no migration from C-12 does take place. Based on these incomplete labelling data speculations as to the genesis of this ion seem to be unwarranted. Summarizing one can state that the NO-containing ions are formed without preceding H-scrambling in contrast to the hydrocarbon ions where partial mass shifts are observed after labelling at any position in the molecule.

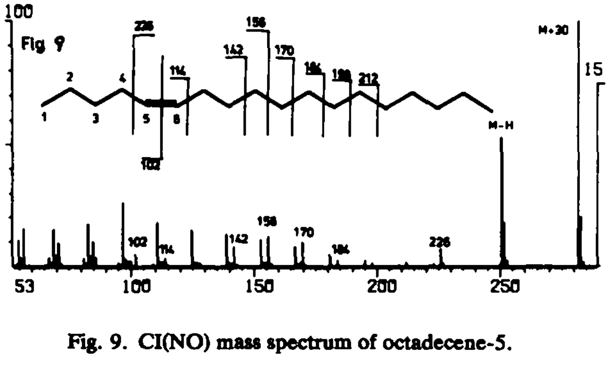
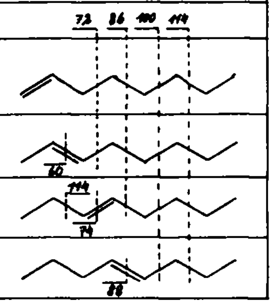


Fig. 9. CI(NO) mass spectrum of octadecene-5.

Table 5. Mass and rel. intensity of the characteristic NO-containing ions in the CI(NO) spectra of olefins.

compounds	i o n s																							
	M+30	MW	a		b_1		b_2		b_3		b_4		a'		b_1'		b_2'		b_3'		b_4'		c	
	I	m/e	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I
octene-2	22,4	112	128	-	-	-	-	-	-	-	-	-	72	-	86	1,3	100	16,1	114	5,1	-	-	60	-
E-octene-3	6,8	112	114	b_2'	-	-	-	-	-	-	-	-	86	<1	100	-	114	1,0	-	-	-	-	74	-
E-octene-4	5,3	112	100	a'	114	b_1'	-	-	-	-	-	-	100	<1	114	-	-	-	-	-	-	-	88	<1
dodecene-5	27,1	168	142	b_2'	156	b_3'	170	-	-	-	-	-	114	3,6	128	3,9	142	10,1	156	2,0	170	-	102	1,5
dodecene-6	48,9	168	128	a'	142	b_1'	156	b_2'	170	b_3'	-	-	128	15,8	142	3,5	156	2,8	170	-	-	-	116	4,6
pentadecene-5	100	210	184	13,0	198	<1	212	<1	-	-	-	-	114	3,9	128	1,3	142	8,1	156	13,0	170	11,3	102	4,9
E-hexadecene-5	88,1	224	198	5,6	212	<1	226	-	-	-	-	-	114	2,6	128	3,2	142	6,7	156	10,5	170	9,6	102	3,8
[12,12-D_2] hexadecene-5	100	226	200	10,0	214	-	228	-	-	-	-	-	114	4,6	128	5,3	142	8,3	156	10,5	171	5,5	102	4,4
4-methyl pentadecene-4	5,3	224	212	-	226	-	-	-	-	-	-	-	114	-	128	-	142	-	156	-	170	-	102	-
heptadecene-4	100	238	226	4,2	240	-	-	-	-	-	-	-	100	2,9	114	2,6	128	12,9	142	19,7	156	19,6	88	8,9
heptadecene-5	100	238	212	9,2	228	-	240	-	-	-	-	-	114	2,9	128	2,0	142	8,9	156	10,9	170	9,2	102	4,6
octadecene-4	100	252	240	2,6	254	<1	-	-	-	-	-	-	100	3,9	114	8,1	128	22,3	142	29,6	156	28,9	88	15,1
[4,5-D_2] octadecene-4	100	254	242	2,8	256	-	-	-	-	-	-	-	102	<1	116	<1	130	9,2	144	14,5	158	11,6	89	5,3
octadecene-5	100	252	226	5,3	240	-	254	-	-	-	-	-	114	2,9	128	1,2	142	7,2	156	11,8	170	9,4	102	4,6
[3,3-D_2] octadecene-5	100	254	227	3,9	240	-	256	-	-	-	-	-	116	2,7	130	1,0	144	8,5	158	14,5	172	10,9	104	5,7
[5,6-D_2] octadecene-5	100	254	228	6,5	242	-	256	-	-	-	-	-	116	2,0	130	<1	144	6,3	158	9,5	172	8,1	103	3,8
octadecene-6	100	252	212	12,8	226	<1	240	-	254	-	-	-	128	13,2	142	3,0	156	10,5	170	14,8	184	10,8	116	5,9
octadecene-7	100	252	198	11,8	212	1,1	226	<1	240	-	254	-	142	7,8	156	2,9	170	3,9	184	7,9	198	11,8	130	1,4
octadecene-8	100	252	184	b_2'	198	b_3'	212	b_4'	226	2	240	-	156	10,5	170	1,5	184	13,3	198	3,0	212	2,6	144	2,0
octadecene-9	100	252	170	a'	184	b_1'	198	b_2'	212	b_3'	226	b_4'	170	51,8	184	3,2	198	7,9	212	8,1	226	2,8	158	5,0
dodecylidene cyclohexane	8	250	-	-	-	-	-	-	-	-	-	-	126	2,2	140	<1	154	-	168	-	182	-	114	-
1-cyclohexyl tridecene-1	100	264	212	5,4	-	-	-	-	-	-	-	-	140	2,0	154	-	168	-	182	-	196	-	128	-
4-propyl hexadecene-4	-	266	254	-	268	-	-	-	-	-	-	-	142	-	156	-	170	-	184	-	198	-	130	-
eicosene-6	100	280	240	8,6	254	<1	268	-	282	-	-	-	128	11,6	142	1,9	156	7,6	170	14,5	184	10,5	116	6,6
eicosene-9	100	280	198	11,2	212	b_3'	226	b_4'	240	1	254	1	170	13,1	184	2,9	198	11,2	212	3,9	226	2,0	158	1,3
tricosene-9	100	322	240	5,4	254	-	268	<1	282	2	296	-	170	12,7	184	<1	198	1,8	212	3,1	226	2,1	158	1,7
ergost-22-ene	9,2	384	344	1,6	372	-	-	-	-	-	-	-	128	48,0	156	1	-	-	-	-	-	-	116	2

Table 6. Relative intensities of the main ions in the CI(NO) mass spectra of isomeric n-octenes.

ion	C_nH_{2n+1}			$(CH_2)_nNO$ (a + b)				$C_nH_{2n+2}NO$ (c)			$M^+ - H$	M^+	$M^+ + NO$	fragmenation
n	4	5	6	3	4	5	6	2	3	4				
m/e	55	69	83	72	86	100	114	60	74	88	111	112	142	
octene-1	9	8	4	13	100	64	11	†	-	-	11	3	26	
octene-2	6	8	3	1	2	16	5	†	-	-	100	17	23	
octene-3	7	10	4	-	1	-	2	†	1	-	100	28	7	
octene-4	4	3	1	-	-	1	-	†	-	1	100	17	5	

†) coincides with $(NO)_2^+$

For practical purposes the ions *a* and *a'* (the sum of which amounts to M+2NO+28) and *c* will be the most important species, the *b*-series giving corroborating evidence only. Difficulties will arise with olefins with less than 10 C-atoms. Not only that the portion of the TI carried by the NO-containing fragments decreases with decreasing chain length (see octene-3 and -4, Table 6) these ions shift into the part of the spectrum occupied by more abundant hydrocarbon ions. In addition, certain fragments the formation of which requires a minimum chain length are missing. Thus, one would have to resort to rather minute differences to distinguish between octene-3 and octene-4 by CI(NO).

Olefins with a trisubstituted double bond are not amenable to positional analysis by CI(NO): due to the lower ionization potential and to steric hinderance (*vide infra* E-olefins) M^+ is increased relative to $M+NO^+$ and hence NO-containing fragments are essentially missing in the mass spectra.

Since, fortunately, these compounds give characteristic EI spectra[6] the two methods are complementary. Branching in allylic or more remote position is of no influence (Table 5). Even in the spectrum of ergost-22-ene[21] the characteristic *a* fragments are clearly discernible.

As observed for the CI(i-C_4H_{10}) spectra the ratio of the intensities $[M+30]^+/[M-H]^+$ is strikingly different for E- and Z-isomers (see Table 7), the more hindered E-isomer rendering NO^+ addition to the double bond less likely.

Table 7. Ratios $[M+NO]^+/[M-H]^+$ for Z- and E-olefins in their CI(NO) spectra.

Z-isomer		E-isomer	
octadecene-6	2,11	octadecene-6	0,57
octadecene-7	1,43	octadecene-7	0,64
octadecene-9	1,38	hexadecene-5	0,88
heptadecene-4	2,49		

CI spectra with amines as reactant gases

The plasma ions[22] of CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ are $[M+H]^+$, $[M-H]^+$ and higher adducts as $[2M+H]^+$. The high proton affinity of the ammonium ions (882 and 911 kJ/mole, resp., for $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$) renders them mild protonizing agents for highly basic compounds[23]. Alternatively, addition of plasma ions has been observed in cases where formation of hydrogen bridges between the ammonium ion and the compound to be ionized is possible. Neither of these processes is to be expected with olefins. Nevertheless, it was hoped that amine radical ions formed by primary ionization of the reactant gas (e.g., $CH_3NH_2^{+\cdot}$) might react with the π-electrons of an olefinic system. Quasi-molecular ions formed in this way would be isomeric with molecular ions of aliphatic amines formed by EI. Since amines give very characteristic mass spectra localisation of double bonds might be possible using CI(amine).

In fact, it is possible to obtain CI(CH_3NH_2) spectra of olefins, though the sensitivity is about one order of magnitude lower than for NO. Besides alkyl ions (possibly from competing EI ionization giving M^+; the IP of CH_3NH_2 (9.0 eV) is too low for CE) with increasing sample pressure a series of $C_nH_{2n+2}N^+$ ions is observed from which two pairs are of enhanced abundance (see Fig. 10). Their formation can be explained readily as shown in Scheme 2: Addition of $CH_3NH_2^{+\cdot}$ which is possible in two ways followed by 1,3-hydrogen shift results in species which are identical with the $M^{+\cdot}$ of aliphatic amines. Subsequent α-cleavage yields the four characteristic ions.

The way of formation suggested for these ions is corroborated by the appropriate quantitative shifts in the spectrum of [5,6-D_2]octadecene-5. For the remaining ions of the series $C_nH_{2n+2}N^+$ see the β-, γ,... cleavages of lower abundance typical for aliphatic amines[24]. There are, however, different paths leading to these ions since in the labelled analog shifts by 2, 0 and to a minor portion by 1 u are observed.

Use of $(CH_3)_2NH$ leads to analogous results: the characteristic ions are shifted by 14 u. $(CH_3)_3N$

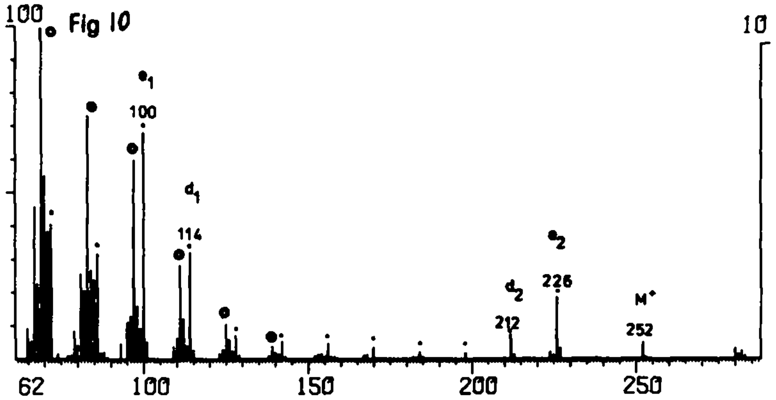
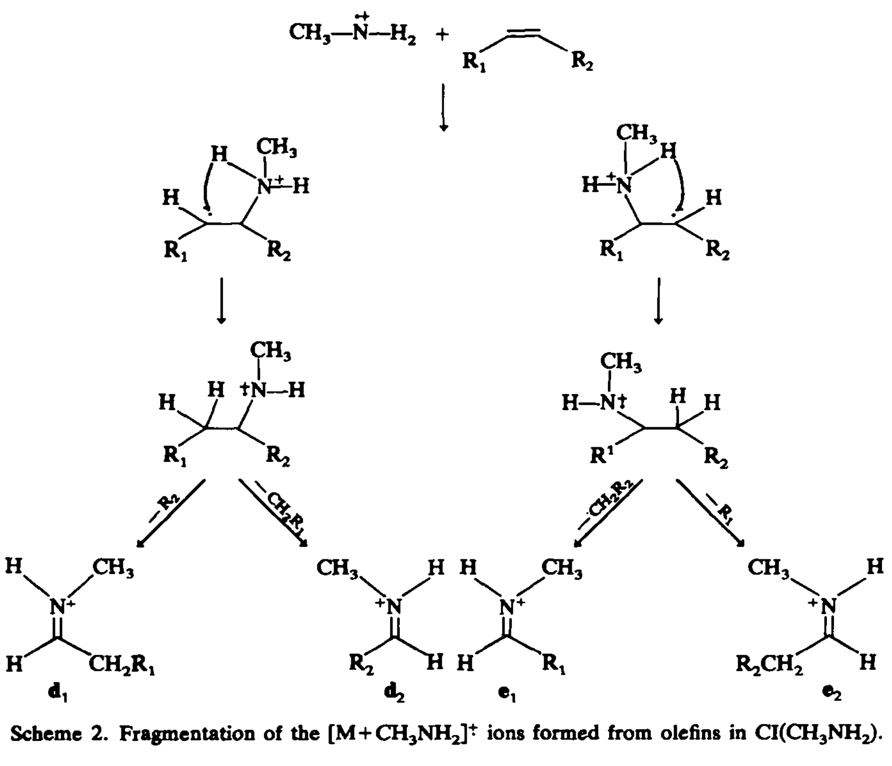


Fig. 10. CI(CH$_3$NH$_2$) mass spectrum of octadecene-5 (C$_n$H$_{2n-1}$ ions marked by a o, C$_n$H$_{2n+2}$N ions by a ·).



Scheme 2. Fragmentation of the [M+CH$_3$NH$_2$]$^{+}$ ions formed from olefins in CI(CH$_3$NH$_2$).

Table 8. Mass and rel. intensity of the characteristic amine fragments in the CI(amine) spectra of olefins.

compounds	CH$_3$NH$_2$ ions								(CH$_3$)$_2$NH ions							
	d^1		d^2		e^1		e^2		d^1		d^2		e^1		e^2	
	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I
octadecene-5	114	3,47	212	0,83	100	7,22	226	2,0	128	8,7	226	1,0	114	16,0	240	1,2
[5,6-D$_2$] octadecene-5	116	3,3	213	1,1	101	8,4	228	2,3								
octadecene-6	128	3,8	198	1,5	114	5,4	212	1,4	142	3,8	212	1,3	128	6,4	226	0,9
octadecene-7	142	3,5	184	2,1	128	4,3	198	1,8	156	2,4	198	1,2	142	1,8	212	1,3
octadecene-9	170	5,35	156	6,1	156	6,1	170	5,35	184	5,0	170	5,7	170	5,7	184	5,0
eicosene-6	128	5,1	226	1,6	114	8,0	240	2,4	142	5,0	240	1,1	128	8,1	254	1,0

Table 9. Reactant gases used.

reactant gas	purity %	source	source pressure mbar
CH_4	99,995	Messer-Griesheim, Düsseldorf	0,8
i-C_4H_{10}	99,5	Messer-Griesheim	0,45
NO	99	Merok-Schuchardt, München	0,28
N_2O	99	Messer-Griesheim	0,08
CH_3NH_2	98	Merck-Schuchardt	0,12
$(CH_3)_2NH$	99,5	Matheson, Oevel, Belgien	0,09
$(CH_3)_3N$	99,3	Matheson	0,07
$CH_3OCH{=}CH_2$	99	Messer-Griesheim	0,07
$(CH_3)_4Si$	99,8	EGA-Chemie, Steinheim	0,14
CH_3OCH_3	99,8	Messer-Griesheim	0,25
ethylene oxide	99,8	Fluka, Buchs, Schweiz	0,13

shows too little sensitivity to be useful for practical purposes. The results obtained are compiled in Table 8.

CONCLUSIONS

Localisation of olefinic double bonds in unbranched and—with some limitations—in branched olefins is generally possible. Since readily available and not aggressive to the instrument and especially to the filament i-C_4H_{10} should be tried first. Analysis of the relative abundances of the $C_nH_{2n+1}^+$ ions shows enhanced intensity of those ions which are formed by cleavage of the allylic bonds. Only in case of ambiguities NO^+ (detrimental to the filament; does not add to tri- or tetra-substituted double bonds and gives no conclusive results for chains below ~C_{10}) or CH_3NH_2/$(CH_3)_2NH$ (less sensitive) should be used. Both, i-C_4H_{10} and NO spectra allow a differenciation between Z- and E-isomers.

Abundant plasma ions can be a problem if a deflection of single ions is not possible and the scan thus can be started only beyond the plasma spectrum.

EXPERIMENTAL

Mass spectrometer: Finnigan 3200 with data system 6110. Electron energy 110–150 eV, emission current 1 mA, source temperature 60–80°C. Samples were introduced via a gas chromatograph (20 m glas capillary column OVI, Ø 0.35 mm), amount of sample 0.5–1.5 μg, for CI(amine) 4–10 μg. Reactant gas pressure (Table 9) was chosen for maximal monomeric plasma ions relative to polymeric ones.

Olefins as far as not available commercially were synthesised by Wittig reactions[25] or by Lindlar hydrogenation of alkynes the synthesis of which has been described elsewhere[1]. Especially after prolonged hydrogenation substantial amounts of E-olefins in addition to the expected Z-isomers were obtained. The mixtures could be separated by gas chromatography (*vide supra*). Pure E-octadecene-6 was prepared by reduction with Na in liquid ammonia.[26] Olefins deuterated at the double bond stem from Lindlar reduction using D_2 gas.

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REFERENCES

[1] II. Communication: E. Busker and H. Budzikiewicz, *Org. Mass Spectrom.* **14**, 222 (1979).

[2] F. Borchers, K. Levsen, H. Schwarz, Ch. Wesdemiotis, and H. U. Winkler, *J. Am. Chem. Soc.* **99**, 6359 (1977) and lit cited.

[3] M. Tsuchiya, K. Tamura, and K. Arishima, *Bunseki Kagaku* **25**, 440 (1976).

[4] [a]H. D. Beckey and P. Schult, *Z. Naturf.* **A, 20**, 1335 (1965); [b]P. Tecon, D. Stahl, and T. Gäumann, *Int. J. Mass Spectrom. Ion Phys.* **27**, 83 (1978); [c]S. A. Rang, A.-M. A. Müürisepp, M. M. Liitmaa, and O. G. Eisen, *Org. Mass Spectrom.* **13**, 181 (1978); [d]A.-M. A. Müürisepp, S. A. Rang, and O. G. Eisen, *Zh. Org. Khim.* **14**, 2017 (1978); [e]K. Levsen, R. Weber, F. Borchers, H. Heimbach, and H. D. Beckey, *Analyt. Chem.* **50**, 1655 (1978).

[5] P. Tecon, D. Stahl, and T. Gäumann, *Int. J. Mass Spectrom. Ion Phys.* **28**, 267 (1978).

[6] M. Kraft and G. Spiteller, *Org. Mass Spectrom.* **2**, 865 (1969); K. K. Mayer and C. Djerassi, *ibid.* **5**, 817 (1971).

[7] H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron* **21**, 1855 (1965).

[8] A compilation of literature may be found in Ref. 4c.

[9] Analysis of derivatives of olefins by CI has also been suggested (dideuteroalkanes: D. F. Hunt and Ch. N. McEwen, *Org. Mass Spectrom.* **7**, 441 (1973); epoxides: J. H. Tumlinson, R. R. Heath, and R. E. Doolittle, *Analyt. Chem.* **46**, 1309 (1974); diol trimethylsilyl ethers: W. Blum and H. J. Richter, *Helv. Chim. Acta* **57**, 1745 (1974) and T. Murata, T. Ariga, and E. Araki, *J. Lipid Res.* **19**, 172 (1978)).

[10] For a review see: R. Rossi, *Synthesis* 817 (1977).

[11] B. L. Jelus, B. Munson, and C. Fenselau, *Biomed. Mass*

Spectrom. **1,** 96 (1974); T. J. Odiorne, D. J. Harvey, and P. Vouros, *J. Phys. Chem.* **76,** 3217 (1972).

[12] R. v. Doorn and N. M. M. Nibbering, *Org. Mass Spectrom.* **13,** 527 (1978).

[13] A. J. V. Ferrer-Correira, K. R. Jennings, and D. K. Sen-Sharma, *Chem. Commun.* 973 (1975); *Org. Mass Spectrom.* **11,** 867 (1976); *Adv. Mass Spectrom.* **7,** 287 (1976).

[14] For cycloaddition reactions with other reagent gas ions *cf* F. P. Abramson and J. H. Futrell, *J. Phys. Chem.* **72,** 1994 (1968); J. M. Henis, *J. Chem. Phys.* **52,** 282 (1970); M. L. Gross, P.-H. Lin, and S. J. Franklin, *Analyt. Chem.* **44,** 974 (1972)

[15] For limitations and side reactions see the discussion in Ref. 13.

[16] F. H. Field, *J. Am. Chem. Soc.* **90,** 5649 (1968).

[17] D. F. Hunt and T. M. Harvey, *Analyt. Chem.* **47,** 1965 and 2136 (1975), *cf* also T. M. Harvey, Ph.D. thesis, Univ. of Virginia, 1975 (Univ. Microfilms, Ann Arbor, Mich., No. 75-28067).

[18] *cf* also A. Fiaux, D. L. Smith, and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.* **15,** 9 (1974) and **25,** 281 (1977); R. Houriet, G. Parisot, and T. Gäumann, *J. Am. Chem. Soc.* **99,** 3599 (1976); R. Houriet and T. Gäumann, *Int. J. Mass Spectrom. Ion Phys.* **28,** 93 (1978).

[19] e.g., C. C. Van de Sande, F. Van Graever, P. Sandra, and J. Monstrey, *Z. Naturf.* **32b,** 573 (1977).

[20] J. K. Macleod and C. Djerassi, *J. Am. Chem. Soc.* **89,** 5182 (1967).

[21] For the typical fragments in the EI spectra of side-chain unsaturated steroids see H. Budzikiewicz, *Biochemical Applications of Mass spectrometry* (Edited by G. Waller) Chapter 10, p. 259. Wiley, New York (1972) and 1st Supplement (to appear in 1980).

[22] P. V. Neilson, M. T. Bowers, M. Chan, W. R. Davidson, and D. H. Aue, *J. Am. Chem. Soc.* **100,** 3649 (1978).

[23] M. S. Wilson and J. A. McCloskey, *Ibid.* **97,** 3436 (1975).

[24] H. Budzikiewicz, C. Djerassi, and D. H. Williams, *Mass Spectrometry of Organic Compounds* p. 297 ff. Holden-Day, San Francisco (1967).

[25] M. Schlosser and K. F. Christmann, *Liebigs Ann.* **708,** 1 (1967).

[26] B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.* 3156 (1953).