Mass Spectrometry in Structural and Stereochemical Problems. 247.[1] Electron-Impact Induced Fragmentation of Allenes

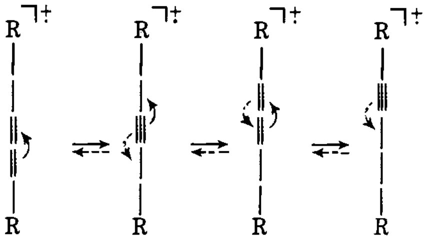
James R. Wiersig, Adrian N. H. Yeo, and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received July 6, 1976*

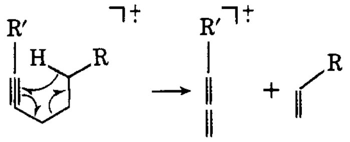
Abstract: Through extensive use of isotopic labeling and metastable peak analysis the course of the principal mass spectral fragmentation modes of allenes has been elucidated. Acetylenes and allenes do not interconvert to an important degree after electron impact. The McLafferty rearrangement is a very significant process, and depending upon the site of the diene system and especially the presence of branching, hydrogen transfer can occur either to the central carbon or the terminus of the diene system. The other major fragmentation mode proceeds by simple carbon-carbon fission, and frequently the apparently unfavorable vinylic cleavage predominates over allylic fission, thus indicating possible cyclization prior to bond rupture.

In connection with a mass spectral study of acetylenes,[2] we concluded that an investigation of the fragmentation pattern of allenes was indicated in order to answer two points raised by the acetylene study.[2] (1) Do acetylenes undergo isomerization after electron impact (see Scheme I) to give the corresponding allenes? Furthermore, do ionized allenes interconvert to acetylenes, so that triple bond migration along the carbon chain of the acetylenes is possible? (2) In the mass spectra of the acetylenes, the McLafferty rearrangement (Scheme II), which is a prominent feature, should lead to the formation of an allene. Is there any evidence in the latter's mass spectra to suggest that allenes are indeed intermediate species in the fragmentation of acetylenes after electron impact? To these two points the present mass spectral study of some allenes provides evidence which suggests that acetylenes and allenes do not interconvert after electron impact (Scheme I) and that allenes are indeed intermediates obtained when acetylenes undergo the McLafferty rearrangement (Scheme II).

Scheme I



Scheme II

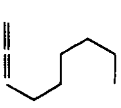


Only slight attention has been paid to the mass spectra of allenes.[3-7] Already in 1962, Polyakova and co-workers[3] investigated the mass spectra of several 3,4-octadienes and 2,3-octadienes. They concluded on the basis of low-resolution spectra and without isotopic labeling that simple cleavage α to the allenic functional group was of primary importance in the 3,4-octadienes, while β cleavage with hydrogen transfer (now known as the McLafferty rearrangement) was the source of the base peak in the 2,3-octadienes. In their study[4] of *tert*-butyl and *n*-butyl β-substituted 3,4-dienes they found that simple β cleavage was the predominant feature of the mass spectra.

Bohlmann and co-workers[5] investigated the mass spectra of 4,5-decadiene, 5,6-undecadiene, and the isomeric acetylenes and found that the McLafferty rearrangement was important in both the acetylenes and the allenes. However, the question of possible interconversion between the molecular ions of the acetylenes and the allenes prior to the McLafferty rearrangements was left open. Allenes were also suggested as the intermediate ions formed via the McLafferty rearrangement of the acetylenic carboxylic esters examined by them. In a mass spectral study of simple acetylenes using deuterium labeling, our group[2] suggested that the McLafferty rearrangement of the acetylenes leads to allenes as intermediates. In a recent study Bogentoft and co-workers[7] concluded that mass spectrometry was a useful method for distinguishing between isomeric allenic and acetylenic alcohols. They found that the allenic alcohols mainly fragment through α cleavage. In summary, the time was clearly ripe to undertake a systematic study of allenes with the aid of isotopically labeled substrates. At the outset, we selected the isomeric nonadienes because a nine-carbon chain offers sufficient scope for examining different double bond locations as well as multiple origins in bond cleavages or hydrogen rearrangements.

Discussion and Results

A. Nonadienes. The principal peaks in the mass spectra of 1,2-nonadiene (**1**, Figure 1), 2,3-nonadiene (**2**, Figure 2), 3,4-nonadiene (**3**, Figure 3), 4,5-nonadiene (**4**, Figure 4), and 7-methyl-3,4-octadiene (**5**, Figure 5) along with their variously labeled analogues are collected in Tables I and II, while the metastable peak data are summarized in Table III. All of the spectra of the nonadienes (**1-5**) show generally the same peaks; however, the relative intensities differ so greatly one from another at both 70 and 12 eV that it can be concluded that the allenes largely retain their positional integrity after electron impact unlike the alkenes[8] and, to a lesser extent, the acetylenes.[2]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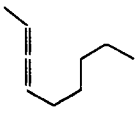
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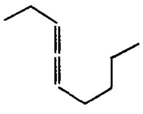
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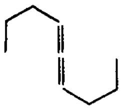
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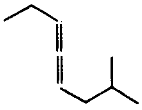
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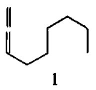
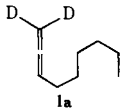
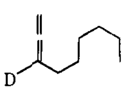
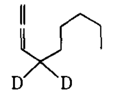
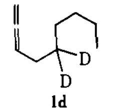
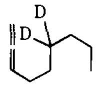
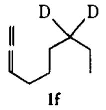
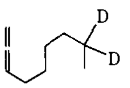
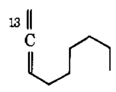
Table I. Principal Peaks (>*m/e* 51) in the Mass Spectra of 1,2-Nonadiene (1) and Its Labeled Analogues (% Relative Intensity)[a]

	 **1**		 **1a**		 **1b**		 **1c**		 **1d**		 **1e**		 **1f**		 **1g**		 **1h**	
eV	70	12	70	12	70	12	70	12	70	12	70	12	70	12	70	12	70	12
111			1	2			1	5	3	10	2	5	2	3	1	4		
110					1	2											0.5	4
109	1	2																
98			3	6			11	54	13	56	7	25	10	24	9	47		
97		1	10	18	3	6	11	37	39	100	24	64	12	25	3	12	2	10
96	10	20	9	20	13	27	4	11	3	8	4	10	3	7	4	12	11	48
95	9	16	2	4	1	3		2	1	1	1	2	1	1	6	17	2	9
85			1	2			2	4	1	4	1	4	2	3	1	3		
84			9	17		1	12	49	10	38	8	25	5	11	7	25		2
83	1	2	17	21	6	13	15	34	23	41	22	43	13	25	7	23	5	21
82	11	22	8	14	15	24	5	12	6	9	8	16	13	22	4	10	13	36
81	13	16	4	3	3	4	4	3	6	2	4	3	13	16	11	20	3	6
71			2	3			1	3	9	8	4	4	5	5	4	6		
70	2	3	12	16	3	5	12	21	21	34	11	14	9	9	6	5	3	5
69	6	7	21	18	13	19	28	36	32	22	20	30	15	21	7	14	12	25
68	14	20	10	10	20	17	13	18	17	8	22	21	17	19	14	29	20	22
67	27	19	10	9	10	9	6	5	7	2	13	6	16	11	19	17	10	14
58									2		3	1	3	2	2			
57	2	1	10	8	2	2	11	8	12	1	8	2	10	4	8	2	2	1
56	2	1	100	100	10	7	100	100	15	4	20	11	13	6	7	2	8	6
55	24	11	32	11	100	100	55	21	33	13	100	100	22	17	14	9	100	100
54	100	100	5	2	18	4	9	4	100	65	31	15	100	100	100	100	24	11
53	19		4		5		4		18		16		15		14		6	

[a] Peaks are not corrected for ^{13}C contributions or isotopic purity.

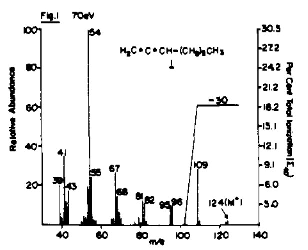


Figure 1. 70 eV mass spectrum of 1,2-nonadiene (1).

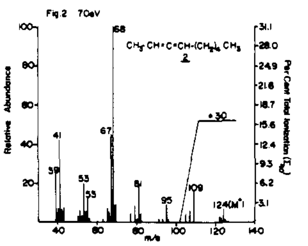


Figure 2. 70 eV mass spectrum of 2,3-nonadiene (2).

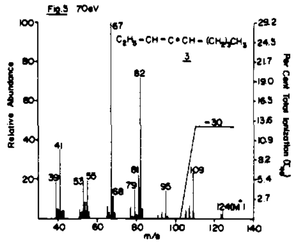


Figure 3. 70 eV mass spectrum of 3,4-nonadiene (3).

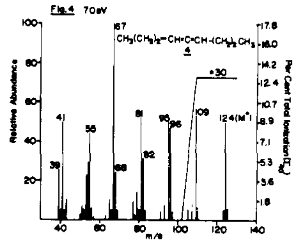


Figure 4. 70 eV mass spectrum of 4,5-nonadiene (4).

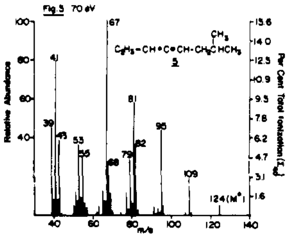
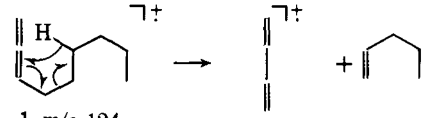


Figure 5. 70 eV mass spectrum of 7-methyl-3,4-octadiene (5).

The mass spectra of the nonadienes are characterized by a prominent peak due to a McLafferty rearrangement in which one hydrogen atom is transferred to the middle carbon of the allenic system (Scheme III). The McLafferty rearrangement leads to the base peak in all of the spectra of the straight-chain nonadienes at 12 eV and leads to either the base peak or the precursor of the base peak at 70 eV. While, admittedly, we have no direct experimental evidence for hydrogen transfer to the center carbon of the allenic system, the rearrangement proposed represents a highly favorable six-membered transition state which rationalizes the observed experimental results.

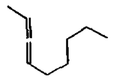
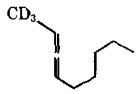
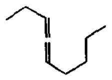
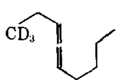
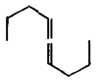
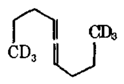
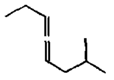
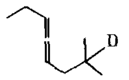
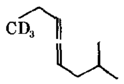
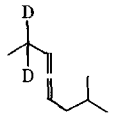
Scheme III



1, *m/e* 124

a, *m/e* 54

Table II. Principal Peaks (≥*m/e* 51) in the Mass Spectra of Nonadienes 2, 3, 4, and 5 and Their Deuterated Analogues (% Relative Intensity)[a]

	 **2**		 **2a**		 **3**		 **3a**		 **4**		 **4a**		 **5**		 **5a**		 **5b**		 **5c**	
eV	70	15	70	15	70	12	70	12	70	12	70	15	70	12	70	12	70	15	70	15
112			0.33	0.33							3.5	4					36	46	2.5	5
111															2.5	2.5	1	1	31	49
110													1.5	5	26	30	2	2	1.5	2
109	0.5	0.6	0.27	0.30	1	1	0.5		2	3			19	54	2	1.5	6	6	4	5
102											8.5	17								
101											6	11								
100											48	100								
99			1	1			1.5	1			11	10					1.5	1.5		
98			6	6			12	3			100	68					12	14	1	1
97									4	8	4.5	3.5		1	7	7	3	3	9	13
96	1	1			1	1	2	0.5	47	100	6	1	5	14	66	57	9	9	18	28
95	8	9	3	3	14	8	13	6	49	58	3		44	98	9	7	80	100	67	100
86			1				7	7			5	6.5					5	6		
85			2	1			100	100			50	71		4			55	75	3	5
84			15	8.5			23	3			80	45		1	1	1.5	65	41	43	74
83			1		5	7	4	1	5	8	9	4	3	11	16	17	11	6	53	44
82	5	5	6	4	72	100	19	11	31	56	15	3	36	100	100	100	48	32	32	35
81	18	10	5	1	22	6	16	4	52	34	7		58	62	50	21	59	51	58	54
72			6	6			1.5				9.5	4					8	6	1	
71			100	100			10	1.5			38	28		1	1		36	45	6	5
70			26	8			38	3			37	7	2	2	9	4	54	24	20	23
69	8	7	14	4	2		29	2	5	3	45	12	11	7	29	23	51	25	100	72
68	100	100	7	2	11	4	27	2.5	24	20	42	7	26	46	51	15	41	18	65	36
67	45	13	11	4	100	23	67	7	100	31	43	7	100	16	81	20	100	37	56	23
66	5		1		3		4		4	3	6		7	1	7		9		11	1
65	7		10		6		5.5		9		8		12		8.5		14		7	
59											6.5						1			
58			4				8				31	1			3		16	3	1.5	
57			4				8		1		23	1	3	2	4		16	4	17	5
56			10	1	3		10		6	2	20	1	6	2	19	1.5	28	6.5	26	18
55	13	2	13	1	19	1	23		44	4	50	10	30	2	20	1	55	8	44	9
54	5	1	7		8		11		29	10	16	1	9		12		27	2.5	33	5
53	19	1	6		17		12		22		16		37		32		25	1	29	1.5
52	3		4		3		5		5		9		7		6		14		14	
51	6		3		4		6		7		9		12		8		18		16	

[a] Peaks are not corrected for ^{13}C contributions or isotopic purity.

Table III. Summary of Metastable Peaks of the Nonadienes **1–5**

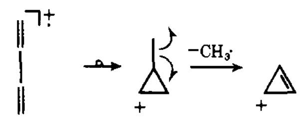
M*	Transition	Expelled fragment	M*	Transition	Expelled fragment
95.8	124→109[a]	CH_3	47.3	95→67	C_2H_4
74.3	124→96[a]	C_2H_4	89.1	93→91	H_2
72.8	124→95[a]	C_2H_5	54.7	82→67	CH_3
54.2	124→82[b]	C_3H_6	77.1	81→79	H_2
52.9	124→81[b]	C_3H_7	53.7	81→66[e]	CH_3
37.3	124→68	C_4H_8	75.1	79→77	H_2
24.4	124→55	C_5H_9	66.0	68→67	H
105.0	109→107[a]	H_2	64.1	68→66	H_2
60.2	109→81[b]	C_2H_4	41.3	68→53[b]	CH_3
27.8	109→55	C_4H_6	63.1	67→65	H_2
15.3	109→41	C_5H_8	25.1	67→41	C_2H_2
49.1	97→69	C_2H_4	51.1	55→53	H_2
68.3	96→81[c]	CH_3	28.2	54→39	CH_3
48.2	96→68[d]	C_2H_4	39.1	43→41	H_2
46.8	96→67[d]	C_2H_5	40.0	42→41[f]	H
91.1	95→93	H_2	37.1	41→39	H_2

[a] Absent in **1–3.** [b] Absent in **1–4.** [c] Absent in **5.** [d] Absent in **3–5.** [e] Absent in **2–5.** [f] Absent in **2–4.**

Another general feature of all of the straight-chain nonadienes studied is the very low abundance of the molecular ion at both 70 and 12 eV. Participation in the total ionization current (Σ_{40}) varies from 0.015% in 1,2-nonadiene to 0.36% in 4,5-nonadiene at 70 eV and from 0.053% to 1.2% at 12 eV. This contrasts with the much greater molecular ion abundance of the branched allene 7-methyl-3,4-octadiene (**5**) (1.0% Σ_{40} at 70 eV vs. 9.5% Σ_{40} at 12 eV). A similar behavior has previously been noted[2] in the case of the branched acetylenes. No obvious rationale for the significant differences in molecular ion intensities can be advanced at present.

1,2-Nonadiene (1). The McLafferty rearrangement (Scheme III) leading to the *m/e* 54 peak provides the base peak at both 70 and 12 eV (Figure 1, Table I), but no metastable peak has been detected in either the second or first field-free regions of the MS-9 double-focusing mass spectrometer (Tables III and IV). This contrasts with results from the other nonadienes studied which do show metastable peaks for the McLafferty rearrangement in both the first and second (except for 3,4-nonadiene (**3**)) field-free regions. A metastable peak is observed for the "McLafferty + 1" rearrangement[9a] (*m/e* 55 peak, Figure 1) which is known to have a lower frequency factor and a lower activation energy than the McLafferty rearrangement.[9b] Extensive deuterium labeling (Table I) and metastable analysis of the deuterated compounds (not shown) suggest that the "extra" hydrogen comes from all carbons in the lost neutral fragment except C-6. Further decomposition of the McLafferty rearrangement ion (hypothesized as ionized 1,3-butadiene) by the loss of a methyl radical is supported by the presence of a metastable peak (Table III) as well as by the defocusing results (Table IV). This suggests that rearrangement of the $C_4H_6^+$ ion (a), possibly to ionized methylcyclopropane (b), precedes decomposition (Scheme IV).

Scheme IV



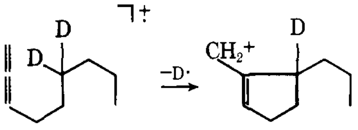
a, *m/e* 54 b *m/e* 39

Deuterium labeling results (Table I) show that the hydrogen transferred in the McLafferty rearrangement comes mainly from C-6 (consistent with Scheme III) with minor contributions from C-4 and C-5. Labeling results also show that the hydrogen lost from the molecular ion comes mainly from C-6 (Scheme V).

Table IV. Metastable Defocusing Data of 1,2-Nonadiene (**1**)

Daughter ions	Parent ions (% rel intensity)
96	124 (100)
95	124 (100)
82	124 (90), 97 (10)
81	124 (11), 109 (5), 96 (84)
69	124 (27), 97 (5), 84 (68)
68	124 (35), 97 (7), 89 (10), 69 (48)
67	109 (2), 96 (10), 82 (16), 68 (72)
55	124 (0.5), 95 (1.5), 83 (53), 70 (28)
54	96 (25), 82 (37), 69 (38)
53	81 (10), 68 (4), 55 (23), 54 (63)
43	109 (9), 85 (8), 71 (83)
42	70 (34), 68 (3), 58 (4), 44 (32), 43 (27)
41	69 (7), 67 (5), 57 (3), 56 (2), 43 (58), 42 (25)
39	65 (1), 54 (27), 41 (41), 40 (31)

Scheme V



1e, *m/e* 126 *m/e* 124

Other significant peaks in the mass spectrum, which assume greater importance at low eV, are due to the loss of ethylene (*m/e* 96) and an ethyl radical (*m/e* 95) from the molecular ion. High-resolution measurements (resolution 1:50 000) on 1,2-nonadiene-*6,6-d*$_2$ (**1e**) show that the hydrogens from C-6 are involved in both the loss of ethyl and ethylene. In the case of the ethyl expulsion the molecular ion shows a loss of 80% $C_2H_5\cdot$ and 20% $C_2H_4D\cdot$; while in the loss of ethylene, measurements show a loss of 30% C_2H_4 and 70% C_2H_3D. High-resolution measurements on the *3-d*$_1$ labeled compound (**1b**) show a loss of ethyl composed of 80% $C_2H_5\cdot$ and 20% $C_2H_4D\cdot$; while the ethylene loss consists of 20% C_2H_4 and 80% C_2H_3D. Labeling results (Table I) wxthout high-resolution measurements indicate that hydrogens from C-5 are also involved in the loss of ethylene. Thus the data from the *8,8-d*$_2$ compound (**1g**) indicate that the label is largely retained in the $M^+ - C_2H_5$ ion. However, in addition to simple loss of ethyl by fission of the 7–8 bond (path A, Scheme VI, *m/e* 95), another process is also involved to the extent of ca. 35% in which hydrogen from

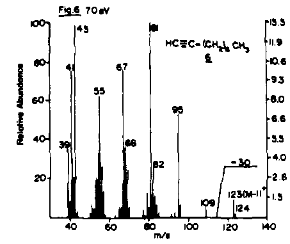
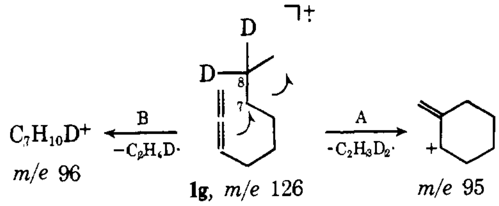


Figure 6. 70 eV mass spectrum of 1 nonyne (6).

Scheme VI



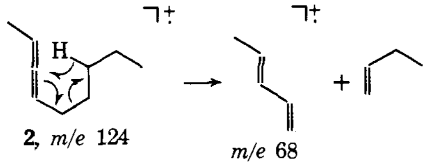
C-8 is transferred to the charge-retaining moiety (path B, Scheme VI, *m/e* 96). The *1,1-d_2* compound (**1a**) yields peaks at *m/e* 97 ($M^+ - C_2H_5\cdot$) and *m/e* 96 ($M^+ - C_2H_2D_2$). Results from the *2-^{13}C* compound (**1h**) show an ethyl loss composed of 80% $C_2H_5\cdot$ and 20% $C^{13}CH_5\cdot$; while the ethylene loss is composed of 20% C_2H_4 and 80% $C^{13}CH_4$ (after extrapolation to 100% isotopic purity). In summary, the results show that C-1 and C-2 are largely ejected as ethylene and C-8 and C-9 are the major sources for the ethyl radical.

High-resolution measurements on the *5,5-d_2* (**1d**) and *6,6-d_2* (**1e**) analogues indicate that the hydrogens from C-6 are not involved in the loss of propylene from the molecular ion but that the hydrogens from C-5 are lost to some extent. The *3-d_1* analogue (**1b**) shows a loss of 50% each of C_3H_6 and C_3H_5D. The *2-^{13}C* analogue (**1h**) shows a propylene loss of 45% $C_2{}^{13}CH_6$ and 55% C_3H_6. The origins of the other peaks (*m/e* 67, 68, and 81) in the spectrum of 1,2-nonadiene are more difficult to assign because they are formed via multiple fragmentation processes (Tables III and IV).

Comparison of the mass spectrum (Figure 1) of 1,2-nonadiene (**1**) with the spectra of 1-nonyne (**6**, Figure 6) and 2-nonyne (**7**, Figure 7) indicates that they are quite dissimilar. In 1,2-nonadiene the base peak at both 70 and 12 eV is the McLafferty rearrangement peak, *m/e* 54, due to the McLafferty ion a; in contrast, 1-nonyne and 2-nonyne show base peaks at *m/e* 81 and *m/e* 95, respectively, at both 70 and 12 eV. Since 1-nonyne and 2-nonyne are acetylenes to which 1,2-nonadiene could rearrange via bond migration (Scheme I), it can be concluded that there is little or no interconversion between acetylenes and allenes after electron impact.

2,3-Nonadiene (2). The McLafferty rearrangement (Scheme VII) is again responsible for the base peak (*m/e* 68) in the spectrum (Figure 2, Table II) at both 70 and 12 eV. In contrast to the 1,2-isomer **1**, a metastable peak is observed for this process in **2** (see Tables III and V). Defocusing results (Table V) show that its importance increases at 12 eV as expected.

Scheme VII



The second most intense peak at 70 eV occurs at *m/e* 67. Metastable analysis (Tables III and V) indicates that this peak is formed (Scheme VIII) from the *m/e* 96 peak (loss of $C_2H_5\cdot$), the *m/e* 95 peak (loss of C_2H_4), the *m/e* 82 peak (loss of $CH_3\cdot$), and the *m/e* 68 peak (loss of H·). The intensity of this peak suggests that the conjugated allylic carbonium ion c may be important. In fact, this peak becomes the most intense one in the 70 eV mass spectra of 3,4-nonadiene (**3**, Figure 3) and 4,5-nonadiene (**4**, Figure 4). Consistent with the fact that the ion is formed via secondary decompositions, the abundances drop drastically with a decrease in electron voltage.

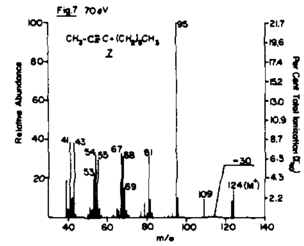
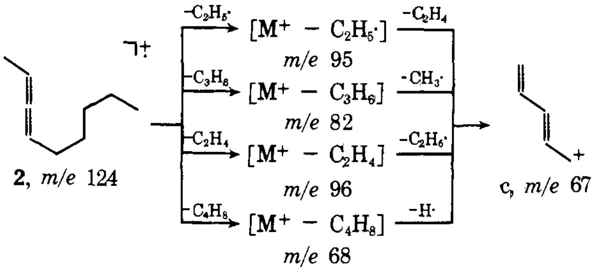


Figure 7. 70 eV mass spectrum of 2-nonyne (7).

Table V. Metastable Defocusing Data of 2,3-Nonadiene (**2**)

Daughter ions	Parent ions (% rel intensity)
95	124 (100)
82	124 (90), 97 (10)
81	124 (30), 109 (12), 96 (58)
79	94 (1), 81 (99)
69	84 (100)
68 (70 eV)	124 (5), 95 (1), 83 (2), 69 (92)
68 (12 eV)	124 (15), 83 (7), 69 (78)
67	82 (1), 68 (99)

Scheme VIII



Simple cleavage associated with the loss of methyl (*m/e* 109), ethyl (*m/e* 95), and propyl (*m/e* 81) radicals is also evident in the spectrum. Comparison of the *1,1,1-d_3* analogue (**2a**) with the unlabeled compound (**2**) shows that loss of methyl occurs 40% by loss of C-1 and 60% by loss of another carbon—most likely C-9 (Table II). C-1 is also involved to some extent in the loss of ethyl (35%) and propyl (25%) radicals from the molecular ion. These results demonstrate that some rearrangement must occur prior to loss of the ethyl and propyl groups.

3,4-Nonadiene (3). The McLafferty rearrangement peak (*m/e* 82) is important (19.5% Σ_{40}), but the base peak in the 70 eV mass spectrum (Figure 3, Table II) is at *m/e* 67 (hypothesized to be due to the conjugated allylic carbonium ion c). Its importance is due to its formation from the McLafferty rearrangement ion (d, *m/e* 82) via an allylic cleavage with loss of a methyl radical (Scheme IX). This pathway is supported

Scheme IX

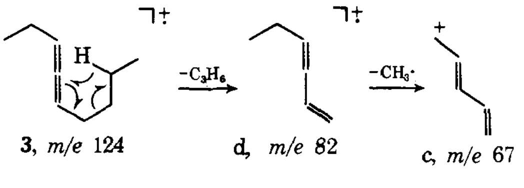


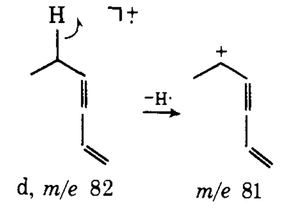
Table VI. Metastable Defocusing Data of 3,4-Nonadiene (**3**)

Daughter ions	Parent ions (% rel intensity)
82	124 (54), 97 (8), 83 (38)
81	124 (8), 109 (4), 96 (17), 82 (71)
68	124 (3), 110 (1), 96 (9), 83 (68), 69 (19)
67	109 (1.5), 95 (8.5), 82 (70), 68 (20)

by an intense metastable peak as well as by the metastable defocusing results (Tables III and VI). At 12 eV the base peak is due to the McLafferty ion d.

Other significant peaks appear at *m/e* 81 and *m/e* 95. Metastable defocusing data (Table VI) show that the mass 81 ion arises mainly by secondary processes such as the loss of hydrogen (e.g., as in Scheme X) from the McLafferty ion (d).

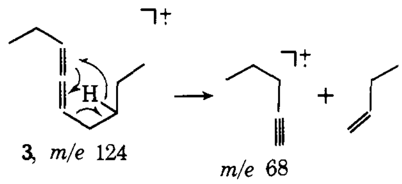
Scheme X



Consistent with this fact is the great reduction in its abundance upon lowering the electron voltage. Labeling results (Table II) from the *1,1,1*-d_3 analogue (**3a**) reveal that the *m/e* 95 peak (ethyl loss) arises ca. 50% by vinylic cleavage between C-2 and C-3 and ca. 50% by loss of C-8 and C-9 (most likely). The results from **3a** also show that the loss of methyl radical from the molecular ion (leading to *m/e* 109) occurs 65% by loss of C-9 (most likely) and 35% by loss of C-1 via allylic cleavage.

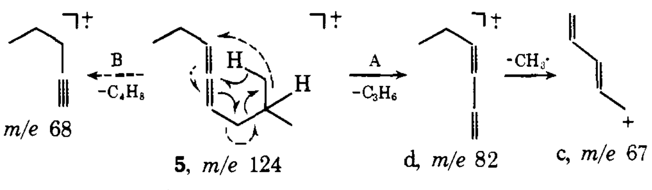
An alternative McLafferty rearrangement of 3,4-nonadiene (**3**) which involves hydrogen transfer to the terminus of the allenic system should give rise to an ion of mass 68 (Scheme XI). Its very low abundance (Figure 3) suggests that this pathway is unfavorable in this instance; therefore, it was considered important to prepare a 3,4-allene with a branched chain (e.g., **5**) in order to determine whether the known[10,11] preference for tertiary hydrogen transfer would enhance this alternative McLafferty rearrangement.

Scheme XI



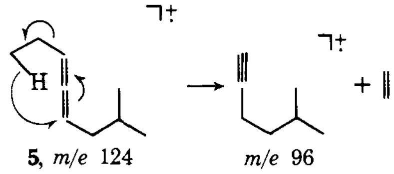
7-Methyl-3,4-octadiene (5). Indeed, when 7-methyl-3,4-octadiene (**5**) was prepared and its mass spectrum (Figure 5, Table II) measured, the alternative McLafferty rearrangement with hydrogen transfer to C-3 (pathway B, Scheme XII) was approximately half as prevalent (3.4% Σ_{40} vs. 5.0% Σ_{40} at 70 eV; 9.3% Σ_{40} vs. 19.1% Σ_{40} at 12 eV) as the "normal" McLafferty rearrangement with hydrogen transfer to C-4 (pathway A, Scheme XII).

Scheme XII



Of minor importance (0.2% Σ_{40} at 70 eV; 1.2% Σ_{40} at 12 eV) is the alternative McLafferty rearrangement in which a primary hydrogen from C-1 is transferred to C-5 (Scheme XIII).

Scheme XIII



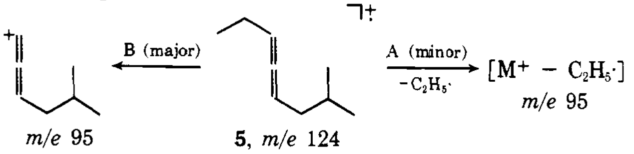
Metastable peaks (Tables III and VIII) for all three processes from the molecular ion are observed. It is clear, therefore, that the nature of the transferred hydrogen is of considerable importance.

Just like in the unbranched isomer **3**, the base peak at 70 eV in the spectrum of **5** is at *m/e* 67—most likely due to the conjugated allylic carbonium ion c resulting from multiple pathways (see Tables III and VIII). The base peak in the 70 eV mass spectrum of 7-methyl-3,4-octadiene-*7*-d_1 (**5a**, Table II) is due to the "normal" McLafferty rearrangement ion of mass 82; however, high-resolution measurements on **5a** show that ions of composition $C_5(H,D)_7$ carry a larger portion of the ion current than the ions of composition $C_6(H,D)_{10}$ (i.e., part of the *m/e* 67 peak is shifted to *m/e* 68 due to isotopic substitution).

The transfer of the deuterium to the center carbon of the allene system (pathway A, Scheme XII) leading to the mass 69 ion is less important (3.1% Σ_{40}) than the ion of mass 68 in the unlabeled compound (**5**, 3.4% Σ_{40}). High-resolution data on the *7*-d_1 compound (**5a**) show that 70% of the *m/e* 69 peak has the composition C_5H_7D, the McLafferty product, while 25% has the composition C_5H_9. The data seem to indicate a significant isotope effect. The origin of $C_5H_9{}^+$ is unknown but probably results from a rearrangement which precedes fragmentation.

Other significant peaks in the spectrum (Figure 5) include those due to simple cleavages—*m/e* 109, 95, and 81 (loss of methyl, ethyl, and propyl radicals, respectively). The spectrum (Table II) of the *1,1,1*-d_3 analogue (**5b**) shows that methyl loss occurs 85% from the isopropyl group and 15% by allylic cleavage between C-1 and C-2. The loss of an ethyl radical from the molecular ion (supported by the metastable data) suggests either rearrangement of the molecular ion prior to fragmentation (Scheme XIV, pathway A) or a cleavage of the vinylic bond (pathway B, Scheme XIV). The data (Table II) from the *1,1,1*-d_3 analogue (**5a**) indicate that 87% of the ethyl loss arises from vinylic cleavage (pathway B) and 13% originates by some other process (pathway A). The results (Table II) from the *2,2*-d_2 compound **5c** show 80% loss of $C_2H_3D_2$ (vinylic cleavage), 10% loss of C_2H_4D, and 10% loss of C_2H_5. These results indicate that there must be some process other than vinylic cleavage which contributes to a small extent to formation of the $M^+ - C_2H_5$ ion.

Scheme XIV



The origin of the *m/e* 81 peak is more complex—major sources (see Table VIII) are the molecular ion (loss of propyl) and the *m/e* 109 ion (loss of ethylene). The most likely source for the propyl loss is expected to be allylic cleavage with the

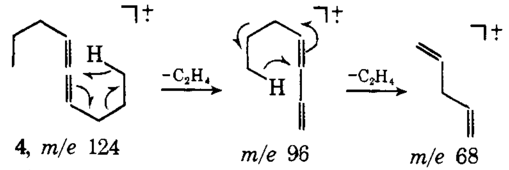
Table VII. Metastable Defocusing Data of 4,5-Nonadiene (**4**)

Daughter ions	Parent ions (% rel intensity)
82	124 (95), 97 (5)
81	124 (8), 109 (3), 96 (71), 82 (18)
68	124 (21), 110 (2), 96 (19), 83 (25), 69 (33)
67	109 (3), 95 (25), 82 (38), 68 (34)

loss of the isopropyl group, but the labeling data suggest also some loss of propyl (ca. 50%) from other sources.

4,5-Nonadiene (4). This is the shortest straight-chain allene capable of undergoing two consecutive McLafferty rearrangements (*m/e* 96 and 68 in Figure 4) from the molecular ion (Scheme XV). The first rearrangement is supported by a metastable peak; however, there is no metastable peak in the second field-free region for the second McLafferty rearrangement. Metastable defocusing results (Table VII) show sources in addition to the mass 96 ion for the *m/e* 68 peak.

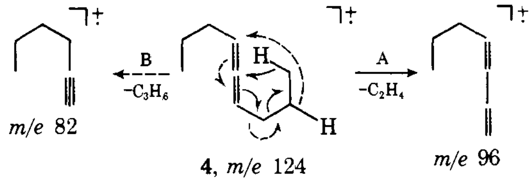
Scheme XV



The base peak (*m/e* 67) in the 70 eV spectrum (Figure 4) is again due to the conjugated allylic carbonium ion c, which arises by multiple pathways (Table VII) and hence is decreased greatly at 12 eV (8.75% Σ_{40} vs. 17.76% Σ_{40} at 70 eV).

A peak at *m/e* 82 which increases in importance with decreasing electron voltage (5.3% Σ_{40} at 70 eV to 15.6% Σ_{40} at 12 eV) suggests that the alternative McLafferty rearrangement with transfer of a secondary hydrogen to the terminus of the diene at C-4 (Scheme XVI, pathway B) competes well with the "normal" McLafferty rearrangement with transfer of a primary hydrogen to the center (C-5) of the diene (Scheme VI, pathway A).

Scheme XVI



The two first McLafferty rearrangements (pathways A and B, Scheme XVI) are well supported by the mass spectrum (Table II) of the *1,1,1,9,9,9-d*$_6$ compound **4a,** in which the *m/e* 96 peak is cleanly shifted to *m/e* 100 and the *m/e* 82 peak is mainly shifted to *m/e* 85 (20% remains unshifted). A metastable peak supports the 130 → 85 transition. However, the second McLafferty rearrangement (96 → 68, Scheme XV) leading to the *m/e* 70 peak in the d_6 analogue **4a** cannot be clearly detected due to peak overlap in the 67–72 area. High-resolution data indicate that only 7% of the *m/e* 70 peak results from this second McLafferty rearrangement.

The loss of an ethyl radical (resulting in the *m/e* 95 peak) from the unlabeled compound is an important process at both high and low electron voltage (8.7% Σ_{40} at 70 eV; 16.9% Σ_{40} at 15 eV) and is clearly due to allylic fission (Scheme XVII) in this symmetrical molecule. This is well supported by the loss of 32 mass units ($M^+ - C_2H_2D_3$, *m/e* 98) from the d_6 compound (**4a,** Table II). This *m/e* 98 peak is the most intense one at 70 eV, which contrasts with a base peak at *m/e* 67 in the unlabeled compound. However, high-resolution measurements indicate that the ions with the composition $C_5(H,D)_7{}^+$ in the *m/e* 67–71 region actually carry a much larger portion of the ion current than does the mass 98 ion.

Scheme XVII

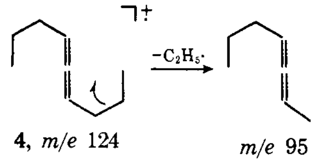


Table VIII. Metastable Defocusing Data of 7-Methyl-3,4-octadiene (**5**)

Daughter ions	Parent ions (% rel intensity)
95	124 (100)
82	124 (91), 110 (8), 97 (1)
81	124 (45), 109 (31), 96 (7), 82 (17)
68	124 (53), 110 (8), 96 (6), 83 (18), 69 (15)
67	109 (18), 95 (13), 82 (38), 68 (31)

The *m/e* 85 peak associated with the McLafferty rearrangement (Scheme XVI, pathway B) of the d_6 analogue **4a** through transfer of a secondary *hydrogen* is of almost the same importance (4.7% Σ_{40} vs. 4.9% Σ_{40}) as the mass 100 peak resulting from transfer of a primary *deuterium* (Scheme XVI, pathway A). This probably indicates an isotope effect since in the unlabeled compound (**4**) the ions of mass 82 carry 4.9% of the total ion current (Σ_{40}) while those of mass 96 carry 7.6% of the total ion current.

The mass spectrum (Table II) of the d_6 analogue **4a** shows a peak at *m/e* 102 ($M^+ - C_2H_4$) which suggests that the *m/e* 96 peak in the unlabeled compound must also originate by a loss (ca. 15%) of ethylene via a process that is different from the McLafferty rearrangement.

The loss of methyl from the molecular ion (leading to the *m/e* 109 peak in the unlabeled compound) is shown by the d_6 analogue to arise mainly (80%) by loss of one of the terminal methyl groups. However, there is a small (20%) loss of unlabeled methyl from the molecular ion which suggests loss of methyl by some process other than simple cleavage.

The other significant peak in the spectrum (Figure 4) of 4,5-nonadiene occurs at *m/e* 81. Metastable defocusing (Table VII) results show that the peak is formed via multiple pathways including vinylic cleavage of the molecular ion ($M^+ - C_3H_7$).

B. Undecadiene. 5,6-Undecadiene (8). 5,6-Undecadiene (**8**) was prepared in order to compare the importance of the normal (Scheme XVIII, pathway A) and alternative (Scheme XVIII, pathway B) McLafferty rearrangements when a secondary hydrogen is being transferred in both cases. In the 70 eV spectrum (Figure 8) as well as the 12 eV spectrum, the alternative McLafferty rearrangement (pathway B) is almost completely suppressed (0.4% Σ_{40} at 70 eV; 1.2% Σ_{40} at 12 eV)

Scheme XVIII

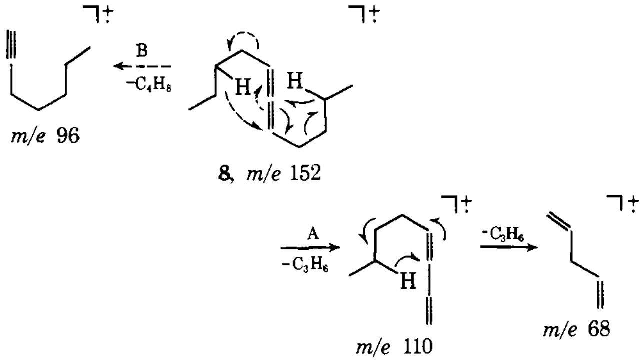


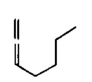
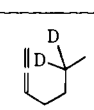
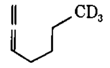
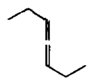
Table IX. Summary of Metastable Peaks of 5,6-Undecadiene (**8**)

M*	Transition	Expelled fragment	M*	Transition	Expelled fragment
123.5	152→137	CH_3	95→67	47.3	C_2H_4
79.6	152→110	C_3H_6	93→91	89.1	H_2
78.1	152→109	C_3H_7	82→67	54.8	CH_3
60.6	152→96	C_4H_8	81→80	79.1	H
33.9	131→68	C_5H_9	81→53	34.7	C_2H_4
94.8	123→108	CH_3	79→77	75.1	H_2
82.1	110→95	CH_3	69→41	24.4	C_2H_4
42.0	110→68	C_3H_6	68→66	64.2	H_2
105.1	109→107	H_2	68→53	41.2	CH_3
81.0	109→94	CH_3	68→40	23.5	C_2H_4
60.1	109→81	C_2H_4	67→65	63.1	H_2
27.8	109→55	C_4H_6	67→41	25.1	C_2H_2
15.4	109→41	C_5H_8	57→41	29.5	CH_4
95.1	97→96	H	57→28	13.8	C_2H_5
94.1	96→95	H	54→39	28.2	CH_3
68.3	96→81	CH_3	43→41	39.1	H_2
91.2	95→93	H_2	41→39	37.1	H_2

Table X. Metastable Defocusing Data of 5,6-Undecadiene (**8**)

Daughter ions	Parent ions (% rel intensity)
110	152 (100)
96	152 (74), 111 (26)
95	152 (11), 137 (3), 124 (4), 110 (82)
82	152 (13), 124 (5), 110 (78), 97 (4)
81	123 (6), 110 (64), 96 (30)
69	111 (88), 97 (6), 84 (6)
68	124 (1), 110 (77), 96 (3), 83 (19)
67	123 (0.5), 109 (12.5), 95 (12), 82 (43), 68 (32)
55	109 (5), 97 (5), 95 (21), 83 (42), 70 (5), 56 (22)
54	110 (42), 96 (23), 82 (35)

Table XI. Principal Peaks (≥*m/e* 40) in the Mass Spectra of Heptadienes **9** and **11** and the Deuterated Analogues of **9** (% Relative Intensity)[a]

	 **9**		 **9a**		 **9b**		 **11**	
eV	70	12	70	12	70	12	70	15
99					4	6		
98			3.5	6	1	2		
97			1	2			4	6
96	1.5	3					48	81
95	0.5	1					4	4
84			1	2	10	17		
83			16	32	1	2		
82	1	2	6	9	2	2	7	7
81	17	31	2	2	10	16	100	100
71					2	3		
70			1.5		2	1		
69			6	6	3	1		1
68	5	4	11	10	3	1	11	9
67	21	9	14	5	16	10	81	77
58			2	1	7	2	1.5	1.5
57			6	1	2			
56	2		13	11	3	1	5	2
55	15	7	100	100	8	5	32	10
54	100	100	22	10	100	100	29	20
53	25		21		21		51	5
46					4			
45			3.5		2			
44			1.5		4		1	
43	4		8		7		2	
42	4		10		5		13	2
41	30		15		16		85	5
40	5		9		6		12	

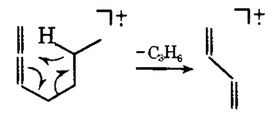
[a] Peaks are not corrected for ^{13}C contributions or isotopic purity.

in favor of the "normal" McLafferty rearrangement (pathway A, 10.6% Σ_{40} at 70 eV; 43.0% Σ_{40} at 12 eV). The importance of the nature of the transferred hydrogen is thus clearly demonstrated when these results are compared with those encountered (Figure 5) with 7-methyl-3,4-octadiene (**5**). A second McLafferty rearrangement of the mass 110 ion (supported by a metastable peak—see Table IX) results in the *m/e* 68 peak (Scheme XVIII).

The base peak at 70 eV, *m/e* 54, arises (Table X) from the mass 110 ion (loss of butylene), the mass 96 ion (loss of propylene), and the mass 82 ion (loss of ethylene). The base peak (*m/e* 110) at 12 eV is due to the McLafferty ion, which carries 43% of the total ion current (Σ_{40}). The mass 95 ion originates from multiple pathways including vinylic cleavage of the 4-5 bond of the molecular ion (see Table X). The sources of the mass 81 ion include the normal McLafferty ion (mass 110, loss of ethyl) and the alternative McLafferty ion (mass 96, loss of methyl).

C. Heptadienes. 1,2-Heptadiene (9). The base peak (*m/e* 54) of the spectrum at both 70 eV (Figure 9) and 12 eV (Table XI) is due to the McLafferty rearrangement (Scheme XIX).

Scheme XIX



9, *m/e* 96 *m/e* 54

However, just as in the case of the higher homologue **1**, no metastable peak is seen for this transformation (Table XII). The spectrum (Table XI) of the 6-d_2 analogue **9a** shows that the hydrogen transferred in the McLafferty rearrangement comes completely from the 6 position.

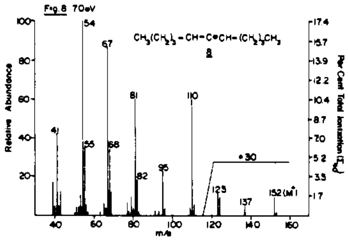


Figure 8. 70 eV mass spectrum of 5,6-undecadiene (**8**).

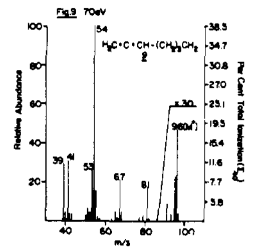


Figure 9. 70 eV mass spectrum of 1,2-heptadiene (9).

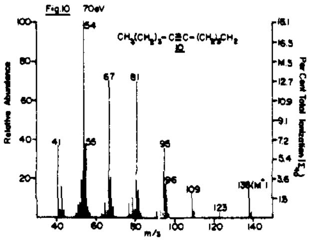


Figure 10. 70 eV mass spectrum of 5-decyne (10).

Table XII. Summary of Metastable Peaks of Heptadienes (9) and (11)

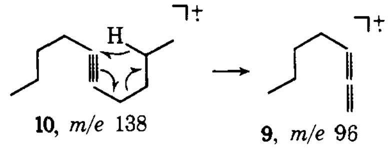
M*	Transition	Expelled fragment	M*	Transition	Expelled fragment
68.3	96→81	CH_3	41.0	68→53[b]	CH_3
48.1	96→68[a]	C_2H_4	23.5	68→40[b]	C_2H_4
46.7	96→67[b]	C_2H_5	63.1	67→65	H_2
91.1	95→93[b]	H_2	25.2	67→41	C_2H_2
89.1	93→91[b]	H_2	13.8	57→28	C_2H_5
77.1	81→79	H_2	51.1	55→53[b]	H_2
34.8	81→53[b]	C_2H_4	28.2	54→39	CH_3
75.1	79→77[b]	H_2	39.1	43→41[a]	H_2
24.4	69→41[b]	C_2H_4	40.0	42→41[b]	H
66.1	68→67	H	37.1	41→39	H_2
64.2	68→66	H_2			

[a] Absent in 11. [b] Absent in 9.

Deuterium labeling in the terminal methyl group (*7,7,7-d_3* analogue **9b**, Table XI) leads to the unexpected conclusion that only 50% of the terminal methyl group (C-7) is implicated in the important $M^+ - CH_3$ peak (18.9% Σ_{40} at 12 eV). The origin of the rest of the methyl loss is not clear. The loss of ethyl from the molecular ion appears to occur mainly by expulsion of C-6 and C-7. However, the labeling data (Table XI) seem to indicate some deuterium scrambling.

The 70 and 12 eV spectra of 1,2-heptadiene are qualitatively similar to the portion below *m/e* 96 of the spectra (Figure 10) of 5-decyne (**10**). This suggests that the McLafferty rearrangement of 5-decyne probably results in ionized 1,2-heptadiene (Scheme XX).[2] Qualitative discrepancies in relative intensities are almost certainly due to differences in the internal energy of the ions.

Scheme XX



10, *m/e* 138

9, *m/e* 96

3,4-Heptadiene (11). Unlike the other allenes studied, 3,4-heptadiene (**11**) shows (Figure 11) a remarkably abundant molecular ion peak at both 70 and 15 eV (7.3% Σ_{40} and 22.8% Σ_{40}, respectively). This compound was synthesized in order to see if the alternative McLafferty rearrangement (Scheme XXI) involving a primary hydrogen atom could be forced since in this case the "normal" McLafferty rearrangement is not possible. The intensity of the mass 68 peak is very low (1.0% Σ_{40} at 70 eV and 1.5% Σ_{40} at 15 eV), and metastable defocusing results (Table XIII) reveal that none of the mass 68 ion originates from the molecular ion. The sources of the ion are the mass 96 (M^+, 44%) and mass 69 (56%) ions.

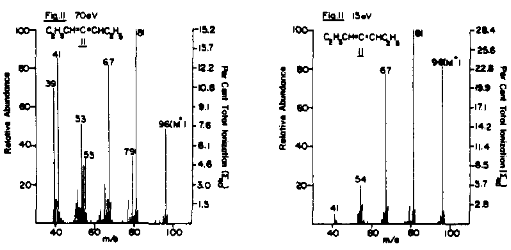
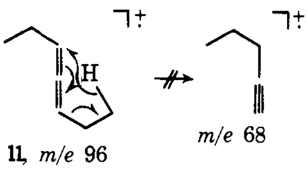


Figure 11. 70 and 15 eV mass spectrum of 3,4-heptadiene (11).

Table XIII. Metastable Defocusing Data of 3,4-Heptadiene (11)

Daughter ions	Parent ions (% rel intensity)
81	96 (100)
79	81 (100)
68	96 (44), 69 (56)
67	96 (35), 68 (65)
66	96 (49), 81 (12), 68 (39)
65	91 (1), 81 (6), 67 (83), 66 (10)
55	95 (2), 81 (18), 70 (2), 56 (78)
54	96 (35), 82 (65)
53	81 (49), 68 (2), 55 (49)
41	81 (7), 69 (2), 67 (32), 56 (4), 43 (6), 42 (49)

Scheme XXI



11, *m/e* 96

m/e 68

Other peaks of interest are due to the ions of mass 81, 67, and 55. Methyl expulsion from the molecular ion by allylic cleavage gives the *m/e* 81 peak. Defocusing experiments (Table XIII) show that 35% of the ethyl loss (*m/e* 67) is the result of vinylic cleavage of the 2,3 bond of the molecular ion and that the remainder (65%) comes from *m/e* 68 by loss of a hydrogen atom. The origin of the mass 54 peak is more obscure. Defocusing results show that 35% is a result of propylene elimination from the molecular ion and that 65% is a result of the loss of ethylene from the mass 82 precursor. Attempts to rationalize these fragmentations are not justified in the absence of isotopic labeling.

In summary, the main mass spectral fragmentation modes of allenes can be categorized as follows:

(1) The McLafferty rearrangement with transfer of a hydrogen to the central carbon of the diene system is an important process in all of the allenes studied. When branching is introduced into the allene, an alternative McLafferty rearrangement with transfer of a hydrogen to the terminal carbon of the diene system becomes important.

(2) Quite unexpectedly, the generally unfavorable vinylic cleavage was found to predominate over allylic cleavage in many cases (e.g., **3** and **5**). This suggests that the sp^2 hybridized

carbon at the terminus of the diene system becomes rehybridized to sp^3 prior to fission of the vinylic bond (most likely through cyclization prior to bond rupture).

(3) A second unexpected finding involved the loss of ethylene from 1,2-nonadiene (**1**). The labeling data (particularly from the *2-*^{13}C compound (**1h**)) indicate that ethylene is lost largely (80%) through what amounts to cleavage of the olefinic 2–3 bond rather than through the expected loss of C-8 and C-9. Multiple rearrangement prior to bond fission must be invoked in order to rationalize the results.

(4) Finally, it was found that acetylenes and allenes do not interconvert to an appreciable extent after electron impact and that, indeed, allenes do appear to be intermediates formed from the McLafferty rearrangement of the acetylenes.

Experimental Section

General. The low-resolution mass spectra were obtained by Mr. R. G. Ross on an AEI MS-9 mass spectrometer using the heated inlet system (150 °C) with a source temperature of 200 °C. The high-resolution mass spectra were recorded by Miss A. Wegmann on a Varian MAT 711 double-focusing mass spectrometer with the samples also introduced via the heated inlet system. Metastable defocusing[12,13] experiments were performed on the MS-9 instrument. All ionizing voltages quoted are nominal values.

NMR spectra were recorded on a Varian T-60 model spectrometer with $CDCl_3$ as solvent. All final products were purified by preparative gas-liquid chromatography on a Varian Aerograph gas chromatograph using a 10 ft × 0.25 in. column of either 20% Apiezon L or 15% SE-30 on Chromosorb W.

The isotopic purity (by mass spectrometry) of all of the labeled compounds was found to be >95% unless otherwise indicated. All peak shifts in the low-resolution spectra were determined without correction for isotopic purity except for those in **1h** in which the peak areas of interest were extrapolated to 100% isotopic purity. Spectral data (NMR, IR) were consistent with the indicated structures of all compounds.

Some of the allenes studied are sensitive to dehydrogenation which is apparently caused by the metal inlet system used in the MS-9 spectrometer. The appearance of a very small $(M - 2)^+$ ion was noted in several of the allenes after a slight change was made in the inlet system, but the remainder of the spectrum was essentially unchanged.

General Procedures for Preparation of Allenes. Procedure A. A suitable olefin was converted to the corresponding *gem*-dibromocyclopropane using potassium *tert*-butoxide and bromoform in pentane[14,15] or using a phase-transfer catalysis method (bromoform, 50% aqueous sodium hydroxide, olefin, benzyltriethylammonium chloride).[16,17] Conversion of the *gem*-dibromocyclopropane to the allene was accomplished with either methyllithium in ether or butyllithium in hexane at −40 °C.[14,15]

Procedure B. A Grignard reagent was reacted with a propargylic bromide at −40 °C in ether to yield the allene.[18,19]

1,2-Nonadiene (1)[14,15] was prepared using procedure A starting with 1-octene.

1,2-Nonadiene-*1,1*-d_2 (1a). Ethyl octanoate was reduced with $LiAlD_4$ to yield 1-octanol-*1,1*-d_2 which was converted to the corresponding bromide with 48% HBr and H_2SO_4. Dehydrohalogenation[20] with ethyldicyclohexylamine afforded 1-octene-*1,1*-d_2 which was converted to **1a** by procedure A.

1,2-Nonadiene-*3*-d_1 (1b). Hydroboration[21,22] of 1-octyne with disiamylborane-*d* (prepared from 2-methyl-2-butene, $LiAlD_4$, and BF_3-etherate) followed by hydrolysis with acetic acid yielded 1-octene-*2*-d_1 which was converted to **1b** by procedure A.

1,2-Nonadiene-*4,4*-d_2 (1c). Hexanoyl chloride was converted to the methyl ester by reaction with methanol. Reduction of the ester with $LiAlD_4$ followed by bromination with 48% HBr/H_2SO_4 gave the labeled bromide which was converted to the Grignard reagent and reacted with propargyl bromide (procedure B) to yield **1c.**

1,2-Nonadiene-*5,5*-d_2 (1d). Esterification of valeryl chloride with methanol followed by reduction with $LiAlD_4$ afforded 1-pentanol-*1,1*-d_2. Bromination (48% HBr/H_2SO_4) followed by conversion to the lithium reagent and reaction with paraformaldehyde gave 1-hexanol-*2,2*-d_2. Bromination (48% HBr/H_2SO_4) followed by conversion to the Grignard reagent and reaction with propargyl bromide (procedure B) gave **1d.**

1,2-Nonadiene-*6,6*-d_2 (1e). Esterification of butyryl chloride with methanol followed by reduction with $LiAlD_4$ and bromination with 48% HBr/H_2SO_4 yielded 1-bromobutane-*1,1*-d_2. Malonic ester condensation of the bromide followed by hydrolysis, decarboxylation, $LiAlH_4$ reduction, and bromination (48% HBr/H_2SO_4) afforded 1-bromohexane-*3,3*-d_2. Conversion to the Grignard reagent followed by reaction with propargyl bromide gave **1e.**

1,2-Nonadiene-*7,7*-d_2 (1f). Reduction of methyl propionate with $LiAlD_4$ followed by bromination with $NaBr/H_2SO_4$ afforded 1-bromopropane-*1,1*-d_2. Malonic ester synthesis followed by reduction ($LiAlH_4$) and bromination (48% HBr/H_2SO_4) yielded 1-bromopentane-*3,3*-d_2. Conversion to the Grignard reagent and reaction with allyl bromide gave 1-octene-*6,6*-d_2 which was converted to **1f** by procedure A.

1,2-Nonadiene-*8,8*-d_2 (1g). Bromoethane-*1,1*-d_2 was prepared according to the procedure of Shiner.[23] Malonic ester synthesis to butyric-*3,3*-d_2 acid followed by reduction ($LiAlH_4$) and bromination (48% HBr/H_2SO_4) yielded 1-bromobutane-*3,3*-d_2 which was converted to the Grignard reagent and reacted with paraformaldehyde to give 1-pentanol-*4,4*-d_2. Bromination (48% HBr/H_2SO_4) followed by conversion to the Grignard reagent and reaction with allyl bromide gave 1-octene-*7,7*-d_2 which afforded **1g** via procedure A.

1,2-Nonadiene-*2*-^{13}C (1h). Carbonation of heptylmagnesium bromide with $^{13}CO_2$ generated from $Ba^{13}CO_3$ with concentrated H_2SO_4 using a high-vacuum line apparatus[24] gave octanoic-*1*-^{13}C acid. Conversion to 2-nonanone-*2*-^{13}C was accomplished by formation of the lithium salt of the acid with lithium hydride in 1,2-dimethoxyethane followed by reaction with methyllithium using the general procedure of Bare and House.[25] After the ketone was converted to the ethylene ketal in the usual manner, bromination[26] with bromine in ether followed by reaction with magnesium in THF[26] gave **1h** (88% isotopic purity).

2,3-Nonadiene (2).[27] Bromination of 1-octyn-3-ol with triphenylphosphine and bromine in DMF[28] gave 3-bromo-1-octyne. Reaction with methylmagnesium iodide (procedure B) gave **2.**

2,3-Nonadiene-*1,1,1*-d_3 (2a). Reaction of methyl-d_3-magnesium iodide with 3-bromo-1-octyne as above gave **2a.**

3,4-Nonadiene (3).[27] Bromination of 1-heptyn-3-ol with triphenylphosphine and bromine in DMF[28] gave 3-bromo-1-heptyne. Reaction with ethylmagnesium bromide (procedure B) gave **3.**

3,4-Nonadiene-*1,1,1*-d_3 (3a). Acetic-d_4 acid was reduced with $LiAlH_4$ to give ethanol-*2,2,2*-d_3 which was converted to bromoethane-*2,2,2*-d_3 using PBr_3. Formation of the Grignard reagent and reaction with 3-bromo-1-heptyne (procedure B) gave **3a.**

4,5-Nonadiene (4)[29] was prepared using procedure A on *trans*-4-octene.

4,5-Nonadiene-*1,1,1,9,9,9*-d_6 (4a). di-*tert*-butyl *trans*-4-octenedioate[30] was reduced with $LiAlD_4$ in ether to *trans*-4-octene-*1,1,8,8*-d_4-1,8-diol which was converted to the ditosylate. Reduction of the ditosylate with $LiAlD_4$ in THF gave *trans*-4-octene-*1,1,1,8,8,8*-d_6 which was converted to **4a** using procedure A. (95% d_6, 5% d_5).

7-Methyl-3,4-octadiene (5).[27] Bromination of 5-methyl-1-hexyn-3-ol with PBr_3 gave 3-bromo-5-methyl-1-hexyne which was reacted with ethylmagnesium bromide (procedure B) to give **5.**

7-Methyl-3,4-octadiene-*7*-d_1 (5a). Isobutyraldehyde was converted to the enol acetate with potassium acetate in acetic anhydride. The enol acetate was hydrolyzed with D_2SO_4 in D_2O to give isobutyraldehyde-*2*-d_1. The labeled aldehyde was reduced with $LiAlH_4$, brominated with 48% HBr/H_2SO_4, converted to the Grignard reagent, and reacted with 3-bromo-1-pentyne (prepared by bromination of 1-pentyn-3-ol with PBr_3) to give **5a** via procedure B.

7-Methyl-3,4-octadiene-*1,1,1*-d_3 (5b). Reaction of ethyl-*2,2,2*-d_3-magnesium bromide with 3-bromo-1-pentyne gave **5b.**

7-Methyl-3,4-octadiene-*2,2*-d_2 (5c). Reaction of ethyl-*1,1*-d_2-magnesium bromide with 3-bromo-1-pentyne yielded **5c** via procedure B.

5,6-Undecadiene (8).[5] was prepared using Procedure A starting with *trans*-5-decene.

1,2-Heptadiene (9). Reaction of *n*-butylmagnesium bromide with propargyl bromide (procedure B) afforded **9.**

1,2-Heptadiene-*7,7,7*-d_3 (9a). Malonic ester synthesis using bromoethane-*2,2,2*-d_3 (vide supra) gave butyric-*4,4,4*-d_3 acid which was reduced to the alcohol with $LiAlH_4$. Bromination (48% HBr/H_2SO_4)

followed by conversion to the Grignard reagent and reaction with propargyl bromide (procedure B) gave **9a**.

1,2-Heptadiene-*6,6-d*$_2$ (9b) was prepared analogously to **9a** starting with bromoethane-*1,1-d*$_2$.

3,4-Heptadiene (11).[32] Reaction of ethylmagnesium bromide with 3-bromo-1-pentyne (procedure B) gave **11**.

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Structure of Nogalamycin

Paul F. Wiley,* Ronald B. Kelly, E. Louis Caron, Veronica H. Wiley,
Jian H. Johnson, Forrest A. MacKellar, and Stephen A. Mizsak

Contribution from the Research Laboratories, The Upjohn Company, Kalamazoo, Michigan 49001. *Received July 16, 1976*

Abstract: A combination of chemical degradation and spectral data has established the structure of nogalamycin to be that shown in **I**.

Nogalamycin (**1**) is an antitumor antibiotic produced by the organism *Streptomyces nogalater* var. *nogalater* sp.n.[2] Its isolation, some of its reactions, and a partial provisional structure have been reported,[1] and the structure of nogalose (**2**), the neutral sugar moiety of nogalamycin, has been published.[3] The present communication proposes a complete structure for nogalamycin (**1**), except for absolute stereochemistry, and discusses the evidence supporting the proposed structure as well as some of the chemistry of nogalamycin. It also presents a complete assignment of the carbon atoms in the ^{13}C NMR spectrum of **1**.

Nogalamycin is an orange-red solid having a molecular formulaof $C_{39}H_{45}NO_{16}$ rather than the previously reported[1] $C_{39}H_{49}NO_{17}$. Analytical values derived from **1, 3a, 3b, 3c,** and **4** are in better agreement with the formula proposed earlier, but mass spectral data derived from **1** and its degradation products establish the revised molecular formula. The analytical values obtained probably resulted from retention of solvent. Nogalamycin dissolves readily in both acids and bases, being orange-red in the former and purple in the latter. A pK_a' value of 7.45 in 60% EtOH is due to the basic nitrogen present as a dimethylamino group, as will be shown subsequently. The groups accounting for base solubility are only weakly acidic and are phenolic hydroxyls, as will also be shown later. The ultraviolet spectrum[1] of **1** is quite similar to those of the anthracycline antibiotics daunomycin[4] and aklavin[5] and suggests that nogalamycin is a member of that class. Its visible spectrum has a maximum at 480 nm, which moves to 553 nm in base. The infrared spectrum indicates the presence of hydroxyl groups (3390, 3270 cm^{-1}), a ketonic or ester carbonyl (1740 cm^{-1}), and an α-hydroxyanthraquinone in that a strong band at 1620 cm^{-1} is typical of a carbonyl hydrogen bonded to a peri hydroxyl group with a weaker band at 1670 cm^{-1} arising from a nonbonded carbonyl in an anthraquinone.[6] Sodium hydrosulfite reduction of **1** converts it to a light yellow unstable solid, confirming the presence of a quinonoid system. Pyrolysis of **1** with zinc dust gave a product in very low yield whose visible spectrum was identical with that of tetracene,[7] indicating a linear tetracyclic system in nogalamycin. These data are all consistent with the view that **1** is a member of the anthracycline family and contains a hydroxylated anthraquinone system having one or more α-hydroxyl groups. The visible spectrum is characteristic of anthraquinones having two α-hydroxyl groups in that a single maximum is present,[8-11] and the max-