

*n*-heptyl thiovinyl-1',2',2'-*d*<sub>3</sub> ether (XIIIh) followed that for protio thioether XIII through ethyl 2-*S*-*n*-heptylmercaptoacetate. Two exchanges of the latter material in ethanol-*O*-*d*<sup>27</sup> containing 0.3 *M* potassium ethoxide at reflux gave ethyl 2-*S*-*n*-heptylmercaptoacetate-2,2-*d*<sub>2</sub> which was reduced with lithium aluminum deuteride in ether to yield 2-*S*-*n*-heptylmercaptoethyl-1,1,2,2-*d*<sub>4</sub> alcohol. Conversion of 2-*S*-*n*-heptylmercaptoethyl-1,1,2,2-*d*<sub>4</sub> alcohol to *n*-heptyl thiovinyl-1',2',2'-*d*<sub>3</sub> ether (XIIIh) through the corresponding bromide followed the procedures for XIII.

*cis*- and *trans*-2-Methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb). The preparation of *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb) employed a procedure similar to that of Naylor.<sup>38</sup> Under nitrogen a mixture of 0.80 g of phosphorus pentasulfide, 1.5 g of sand, and 200 mg of a crude mixture of *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrofuran (VIIIa, VIIIb) was held at 100° for 3.5 hr. The reaction mixture was slurried several times in ether, and the combined extracts were dried over sodium sulfate. Rotary evaporation of ether yielded 309 mg of an oil containing *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb). By glc (10 ft × 0.25 in. aluminum column packed with 10% SE-30 on 80–100 mesh acid-washed Chromosorb W) the ratio of isomers was 4:1, and they were preparatively separated and yielded almost identical mass spectra.

*Anal.* Calcd for C<sub>9</sub>H<sub>16</sub>S: mol wt, 158. Found: (M<sup>+</sup>), 158.

The nmr spectrum (deuteriochloroform) of a mixture of XXIa and XXIb displayed a complex series of signals from δ 0.65 to 3.18 with doublets at δ 1.15, *J* = 7 Hz, and δ 1.30, *J* = 7 Hz (2-methyl protons).

*cis*- and *trans*-2-Methyl-3-*n*-propyltetrahydrothiopyran (XXIIa, XXIIb). The preparation of *cis*- and *trans*-2-methyl-3-*n*-propyltetrahydrothiopyran (XXIIa, XXIIb) from a crude mixture of *cis*- and *trans*-2-methyl-3-*n*-propyltetrahydropyran (IXa, IXb) employed the procedure of Naylor<sup>38</sup> as modified above for XXI. By glc conditions employed for XXI the ratio of isomers in the crude XXII was ~10:1; the major isomer was preparatively collected.

Ethyl *cis*-4-Heptenyl Thioether (XXIIIa). The conversion of *cis*-4-hepten-1-ol, prepared above, to 1-bromo-4-heptene followed

the procedure of Wood and Horning.<sup>28</sup> Under nitrogen, 300 mg (7.68 mg-atoms) of potassium was dissolved in a solution of 4.2 g (67.5 mmol) of ethanethiol in 20 ml of anhydrous ether. Then 562 mg (3.18 mmol) of 1-bromo-4-heptene was added, and the mixture was refluxed overnight, added to water, and extracted with ether. The combined extracts were dried over sodium sulfate and yielded crude ethyl *cis*-4-heptenyl thioether. Preparative glc (10 ft × 0.25 in. aluminum column packed with 15% Carbowax 20M on 80–100 mesh acid-washed Chromosorb W) gave pure XXIIIa.

*Anal.* Calcd for C<sub>9</sub>H<sub>16</sub>S: C, 68.28; H, 11.46. Found: C, 68.55; H, 11.42.

The nmr spectra (deuteriochloroform) of XXIIIa displayed a complex multiplet from δ 5.01 to 5.78 (vinyl protons, 1.90); a complex multiplet from δ 0.89 to 2.85 (16.1 H) containing two triplets at δ 0.97, *J* = 7.0 Hz, and δ 1.12, *J* = 7.0 Hz (4-heptenyl and ethyl methyl protons, respectively); and a quartet at δ 2.26, *J* = 7.0 Hz, overlapping with a triplet at δ 2.27, *J* = 7.0 Hz.

Ethyl-2-*d* *cis*-4-Heptenyl Thioether (XXIIIb). The preparation of ethyl-2-*d* *cis*-4-heptenyl thioether followed the procedure for the protio material XXIIIa through *cis*-4-hepten-1-ol. Using the procedure of Smith and Williams,<sup>39</sup> *cis*-4-hepten-1-ol was converted to *cis*-4-heptenyl tosylate. Under nitrogen 150 mg (6.52 mg-atom) of sodium was dissolved in a solution of 2 ml of absolute ethanol and 10 ml of THF. Then 0.77 g (6.41 mmol) of ethyl 2-mercaptoacetate was added followed by 1.16 g (4.32 mmol) of *cis*-4-heptenyl tosylate. The reaction mixture was refluxed for 2 hr and stirred overnight at 25°, and 10 ml of water was added. The THF was removed by rotary evaporation, and the residue was extracted with ether. The combined extracts were dried over sodium sulfate and yielded 0.784 g of a mixture of 2-*S*-(*cis*-4-heptenyl) mercaptoacetate and ethyl 2-mercaptoacetate. This mixture was reduced with lithium aluminum hydride in ether to give 480 mg of 2-*S*-(*cis*-4-heptenyl)mercaptoethanol, which was converted to 562 mg (86%) of 2-*S*-(*cis*-4-heptenyl)mercaptoethyl bromide. Reduction of this material with lithium aluminum deuteride in ether at reflux yielded ethyl-2-*d* *cis*-4-heptenyl thioether (XXIIIb) which was purified by preparative glc as was XXIIIa.

(37) D. J. Pasto and G. R. Meyer, *J. Org. Chem.*, **33**, 1257 (1968).

(38) R. F. Naylor, *J. Chem. Soc.*, 1106 (1947).

(39) G. A. Smith and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 5254 (1969).

## Mass Spectrometry in Structural and Stereochemical Problems. CCXIV.<sup>1</sup> Electron Impact Induced Fragmentation of Simple Acetylenes<sup>2</sup>

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**Abstract:** The mass spectra of a series of isomeric nonynes and decynes have been investigated with the aid of deuterium labeling, metastable analysis, and metastable defocusing. Although the spectra indicate retention of identity of the individual alkynes to a large extent under electron bombardment, evidence is presented which is consistent with some triple bond migration prior to the formation of some fragments. Hydrogen scrambling is extensive in the ions which arise by multiple fragmentation pathways. Most of the simple cleavage modes which occur in the straight-chain alkynes are suppressed in their branched-chain isomers, where the McLafferty rearrangement and β-fission processes become dominant.

The use of mass spectrometry as a routine analytical probe for structure determination demands retention of the identity of the molecule under investigation subsequent to electron impact and prior to frag-

mentation. Although simple olefinic hydrocarbons have been extensively investigated,<sup>5</sup> mechanistic interpretation of decomposition pathways is often seriously complicated by ubiquitous 1,2- and 1,3-hydrogen transfers, and consequent double bond migration, prior to

(1) For preceding paper see S. Popov, G. Eadon, and C. Djerassi, *J. Org. Chem.*, **37**, 155 (1972).

(2) Financial support by the National Institutes of Health (Grant No. AM 12758) is gratefully acknowledged. One of us (K. K. M.) wishes to thank the Deutsche Forschungsgemeinschaft, West Germany, for a stipend.

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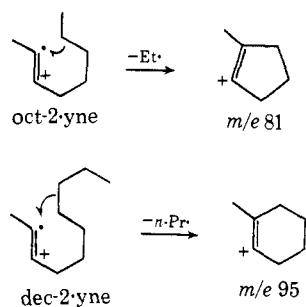
(4) Postdoctoral Research Associate, 1970–1971; on leave from the University of Regensburg, West Germany.

(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

fragmentation.<sup>6,7</sup> Insofar as alkynes are concerned, the mass spectra of some simple compounds have been recorded,<sup>8,9</sup> and evidence has been presented to support hydrogen scrambling in the molecular ion,<sup>10,11</sup> but surprisingly little isotopic labeling and metastable data are available to enable the precise fragmentation modes of simple alkynes (*i.e.*, containing no heteroatom) to be determined.<sup>11a</sup> Bohlmann and coworkers<sup>12</sup> have made extensive studies of the mass spectra of polyacetylenes, and their results are supported in some cases by deuterium labeling data, but in most instances the molecules contained additional heteroatomic functional groups (*e.g.*,  $-\text{CO}_2\text{CH}_3$ ,  $-\text{CH}=\text{O}$ ,  $-\text{CH}_2\text{OH}$ ) which would be expected to direct the major fragmentation pathways, thus obscuring the electron impact behavior of the "naked" alkyne.

The data tabulated by Rondeau and Harrah<sup>8</sup> for the fragmentation of homologous series of alkynes from but-2-yne to dec-2-yne, hex-3-yne to dec-3-yne, and oct-4-yne to non-4-yne show peaks due to the simple cleavages ( $M - \text{CH}_3$ ), ( $M - \text{C}_2\text{H}_5$ ), ( $M - \text{C}_3\text{H}_7$ ), etc., in all cases. Formally this corresponds to alkyl group scission and cyclization of the charged residue<sup>13</sup> (Scheme I). Hence, six-membered ring formation predominates

Scheme I



in dec-2-yne (18.7% of the total ionization current), whereas five-membered ring formation is predominant in oct-2-yne (13.6%).

In addition to the simple cleavage series, a rearrangement series occurs at ( $M - 28$ ), ( $M - 42$ ), ( $M - 56$ ), etc., involving hydrogen migration prior to or during cleavage. The question of triple bond mobility is important here, since the genesis of this series could involve sequential bond migration-McLafferty rearrangement steps; for instance, in non-2-yne, Scheme II. Migration of the triple bond is also indicated by consideration of the spectra of positional isomers, *e.g.*, oct-2-yne, oct-3-yne, and oct-4-yne. All show an

(6) A. F. Gerrard and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 6808 (1969), and references cited therein.

(7) M. Kraft and G. Spittler, *Org. Mass Spectrom.*, **2**, 865 (1969).

(8) R. E. Rondeau and L. A. Harrah, *J. Chem. Eng. Data*, **13**, 109 (1968).

(9) A. A. Polyakova, R. A. Khmel'nitskii, and A. A. Petrov, *Usp. Khim.*, **35**, 1671 (1966).

(10) J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **80**, 1568 (1958).

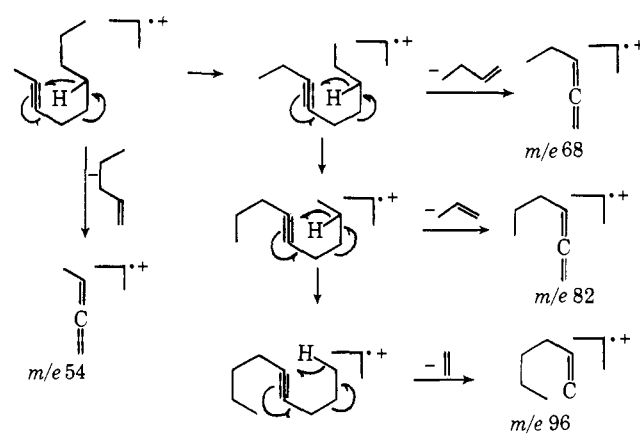
(11) Z. Dolejšek, V. Hanus, and K. Vokac, *Advan. Mass Spectrom.*, **3**, 503 (1966).

(11a) NOTE ADDED IN PROOF: After submission of our paper, an article appeared by H. Luftman and G. Spittler, *Org. Mass Spectrom.*, **5**, 1073 (1971), which described the mass spectrometric behavior of some mono- and dialkylacetylenes.

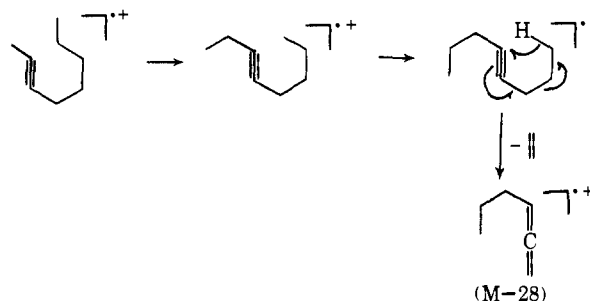
(12) F. Bohlmann and H. Bethke, *Chem. Ber.*, **104**, 11 (1971), and preceding papers.

(13) Many of the fragment ions are formulated herein as cyclic vinyl cations. While this is done in part for the sake of convenience, there is ample precedent in the recent literature for the occurrence of such species as reactive intermediates in solution; for example, M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970).

Scheme II



( $M - 28$ ) fragment ion, the formation of which is most easily rationalized on the basis of migration of the unsaturated site prior to McLafferty rearrangement.



The rearrangement series  $m/e$  96, 82, 68, etc., may also lose an alkyl radical and generate the formally simple cleavage series  $m/e$  81, 67, 53, etc., in a multiple-step process from the molecular ion (see later). There is also a second rearrangement series observed in, *e.g.*, non-2-yne at ( $M - 27$ ), ( $M - 41$ ), etc., which corresponds either to double hydrogen transfer concomitant with simple cleavage or to triple bond migration and subsequent cleavage.

Insofar as hydrogen scrambling prior to fragmentation is concerned, the Czech workers<sup>11</sup> state that ions in the simple cleavage series from alk-1-yne "are formed after an extensive exchange of hydrogen atoms, which is probably connected with the isomerization of the molecular ion," and that the only fragments originating solely from simple dissociation of a carbon-carbon bond are (a) alkyl species corresponding to  $\beta$ -fission and (b) fragment ions formed by an "energetically favorable cyclic shift of bonding electrons." From an investigation of propyne- $d_3$ <sup>10</sup> and but-1-yne-4,4,4- $d_3$ ,<sup>14</sup> it was concluded that extensive migration of hydrogen occurs in the propyne molecular ion since loss of H and D occurred statistically. Deuterium-labeling data for some polyacetylenic alcohols<sup>15</sup> and substituted diphenylacetylenes<sup>16</sup> are also consistent with electron impact induced randomization of hydrogen atoms. The similarity of the mass spectra of a number of polyacetylenes and their related (by cyclization) aromatic species<sup>17,18</sup> indicates that at least some

(14) W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956).

(15) R. T. Aplin and S. Safe, *ibid.*, **47**, 1599 (1969).

(16) S. Safe, *Org. Mass Spectrom.*, **3**, 239 (1970).

(17) R. T. Aplin and S. Safe, *Chem. Commun.*, 140 (1967).

(18) S. Safe, W. D. Jamieson, W. R. Pilgrim, and S. Wolfe, *Can. J. Chem.*, **48**, 1171 (1970).

**Table I.** Principal Peaks ( $>m/e$  51) in the Mass Spectra of Nonynes I-IV and Their Deuterated Analogs (% Relative Intensity)<sup>a</sup>

Compd	eV	$m/e$																									
		112	111	109	99	98	97	96	95	85	84	83	82	81	71	70	69	68	67	58	57	56	55	54	53		
Non-1-yne	70			6			7	53	6	5	10	23	100		7	25	37	82		13	28	64	33	20			
	12			10			8	68	5	8	14	40	100		85	19	40	56		4	11	15	19				
3,3- <i>d</i> <sub>2</sub>			6			6	53	5	4	5	27	100	19	16	5	18	79	41	20	2	20	50	68	15	8		
			8			8	63	6	3	5	36	100	20	13	4	16	57	32	9		3	14	18	2			
4,4- <i>d</i> <sub>2</sub>			6			6	54	6	4	11	28	100	17	16	12	23	83	44	16	4	9	37	59	39	17		
			9			9	63	8	3	13	37	100	16	7	6	18	61	33	6	5	8	19	9	3			
5,5- <i>d</i> <sub>2</sub>			5			7	55	5	2	8	29	100	16	12	9	30	63	39	13	8	30	47	36	31	11		
			7			7	61	6			8	35	100	14	6	7	26	55	26	7	3	8	18	14	13		
Non-2-yne	70			9			5	100				3	10	32		4	16	32	40		2	36	31	33	22		
	12			10			10	100				2	10	16			7	20	6			1	3	8			
1,1,1- <i>d</i> <sub>3</sub>		7		6	10	100	6	5	24	9	27	5	12	11	37	27	33	21	25	16	50	35	34	10	9		
		8		7	10	100	6	2	26	8	31	2	5	2	21	4	9	7	6	3	11	2					
4,4- <i>d</i> <sub>2</sub>			9			10	100	10	8		8	31	8	10	6	22	40	24	11		14	42	33	12	7		
			10			10	100	10	2		8	20	4			13	14	7	1		2	9	2				
6,6- <i>d</i> <sub>2</sub>			9			10	100	8	3		7	24	17	5		5	15	29	35		12	19	32	12	17		
			11			10	100	8	2		6	15	5	2	2	8	12	14					2	6			
7,7- <i>d</i> <sub>2</sub>			11			12	100	20	13	2	6	14	19	32	6	12	44	43	23	4	17	23	19	49	29		
			11			12	100	18	11	2	6	9	10	15	3	9	22	12	3		2	3	2	11			
8,8- <i>d</i> <sub>2</sub>			10				23	17	100	2	4	8	10	32	10	8	18	38	31	4	11	12	19	37	22		
			12			3	23	18	100	2	4	5	6	17	4	3	8	16	3				2	7			
Non-3-yne	70			13			9	94				2	23	45		2	13	43	100		7	6	34	8	25		
	12			14			10	100				2	29	24		1	4	19	16				4	1	3		
1,1,1- <i>d</i> <sub>3</sub>		13		5	5	41	3	10	100	18	20	5	24	43	57	65	38	25	59	10	16	17	37	17	16		
		15		6	5	31	3	8	100	18	14	2	20	30	13	3	2	5	6		1	1	1				
5,5- <i>d</i> <sub>2</sub>			13			10	100	6	8		21	38	15	14		15	43	97	48		18	21	33	20	11		
			16			11	100	7	5	2	23	28	8	3	8	23	20	8	2		1	2	3				
6,6- <i>d</i> <sub>2</sub>			14			10	100	14	9	2	24	43	17	18	2	10	64	78	81	5	18	19	18	15	21		
			16			10	100	14	6		26	31	9	2	1	5	18	25	8		2	1	1				
7,7- <i>d</i> <sub>2</sub>			13			10	100	11	6	2	14	32	25	18	4	26	60	75	58	4	13	22	16	15	20		
			16			10	100	10	3		16	25	19	3		8	24	13	7		1	2	1				
8,8- <i>d</i> <sub>2</sub>			18			11	93	25	37	5	10	42	24	32	6	19	37	100	98	6	21	27	25	11	29		
			23			12	100	25	28	5	12	32	16	19	3	7	11	25	6		2	4					
Non-4-yne	70			7			5	38				2	15	40			4	14	100		1	3	24	27	21		
	12			26			21	100				41	57			5	18	63					3	14			
1,1,1- <i>d</i> <sub>3</sub>		8		5	4	22	4	6	48	13	32	4	23	50	6	34	39	33	100	8	9	13	45	24	27		
		21		16	11	48	5	13	100	21	28	6	40	66	7	20	28	23	37		2	4	12	7			
2,2- <i>d</i> <sub>2</sub>			13			6	23	14	46	2	11	33	16	51	2	11	100	67	47		11	21	33	47	24		
			39			18	52	36	100	5	28	56	23	78	3	11	84	48	22		3	6	7	25			
3,3- <i>d</i> <sub>2</sub>			11			6	53	9	4	2	11	32	19	40	1	13	100	61	28	1	17	53	36	24	12		
			18			13	100	20	2	3	27	35	21	44	2	10	66	28	9		2	18	4	3			
6,6- <i>d</i> <sub>2</sub>			13			11	65	11	8	2	25	67	18	20	4	15	100	68	60	4	18	58	38	26	8		
			27			19	100	17	9	4	40	67	13	7		12	36	24	37		2	19	5	2			
7,7- <i>d</i> <sub>2</sub>		70		11			32	3	10	2	12	38	18	24	3	8	34	37	100	2	11	19	22	42	20		
		12		28			19	100	21	9	3	28	60	26	14		9	19	15	63		1	3	4	18		
9,9,9- <i>d</i> <sub>3</sub>			4			5	4	34	4	3	14	9	27	3	13	21	6	8	11	18	100	7	6	7	17	31	21
			17			19	8	100	15	5	43	33	64	8	28	26	13	3	7	16	91	1	2	3	24		

<sup>a</sup> M<sup>+</sup> and (M - 1) peaks were of negligible importance (<1%) in most cases.

of the decomposing ions in each series have the same structure and energy.

Thus, the literature data indicate that hydrogen scrambling, presumably concomitant with triple bond migration, is an important, although complicating, feature of the fragmentation of alkynes. It should be noted that the technique of prior derivatization has been used<sup>19</sup> to facilitate the localization of triple bonds by mass spectrometry. However, it is obviously advantageous to have a deeper knowledge of the mass spectral behavior of the "naked" alkyne using metastable analysis, the metastable defocusing technique,<sup>20</sup> and extensive deuterium labeling, and the research reported here was undertaken for this reason.

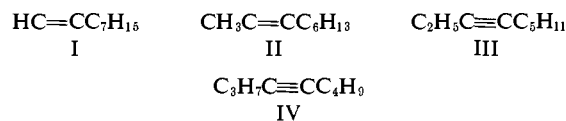
## Discussion and Results

**A. Nonynes.** The principal peaks in the mass spectra of non-1-yne (I, Figure 1), non-2-yne (II, Figure 2),

(19) H. E. Audier, J. P. Begue, P. Cadiot, and M. Fetizon, *Chem. Commun.*, 200 (1967).

(20) J. H. Futrell, K. R. Ryan, and L. W. Sieck, K. R. Jennings, *J. Chem. Phys.*, 43, 1832 (1965).

non-3-yne (III, Figure 3), and non-4-yne (IV, Figure 4),



together with their appropriately deuterated analogs, are collected in Table I. Although all the alkynes I-IV show the same peaks, their relative intensities differ markedly at both 70 and 12 eV, indicating that the acetylenes retain their identity to a large degree under electron bombardment. Some triple bond mobility, is, however, evidenced by the labeling data.

At 70 eV the spectra (Figures 1-4) are dominated by a series of formally simple cleavage ions ( $m/e$  123, 109, 95, 81, 67). Some of the even-mass ions ( $m/e$  96, 82, 68, 54), which must arise by rearrangement processes, assume greater importance at 12 eV. Metastable analysis (Table II) and metastable defocusing data (Table III) show that the odd-numbered ions of lower mass arise from several precursor ions. The regular-

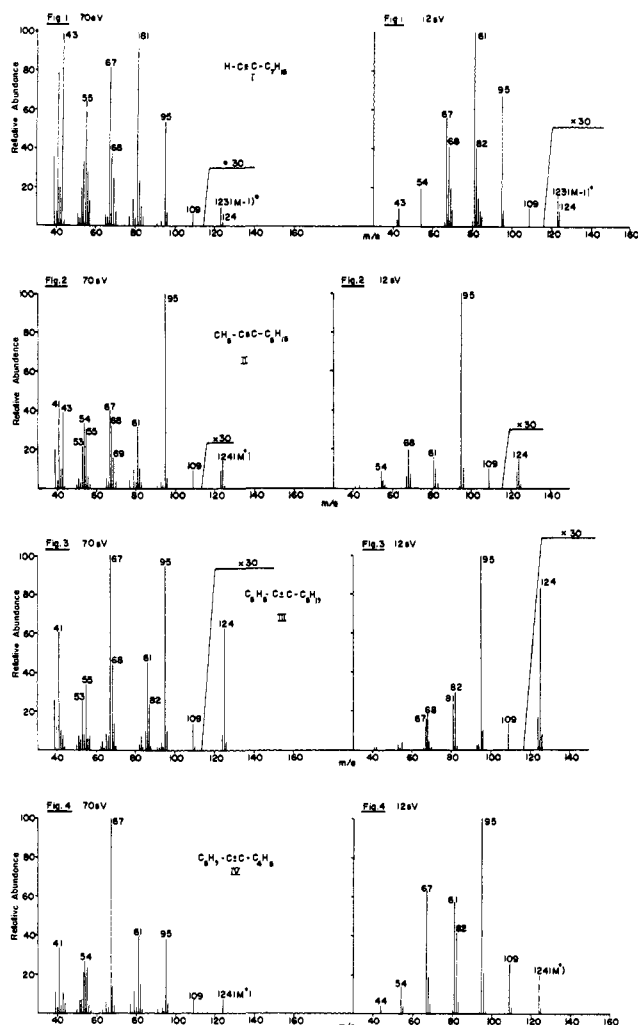


Figure 1. Mass spectrum of non-1-yne.  
 Figure 2. Mass spectrum of non-2-yne.  
 Figure 3. Mass spectrum of non-3-yne.  
 Figure 4. Mass spectrum of non-4-yne.

shaped peaks indicating metastable transitions in the spectra of the unlabeled compounds become diffuse, broadened clusters for the deuterated analogs, thus

**Table II.** Metastable Transitions in the Mass Spectra of Nonynes I-IV

M*	Transition	M*	Transition
85.8	124 → 109	91.1	95 → 93
74.4	124 → 96 <sup>a</sup>	47.2	95 → 67
72.8	124 → 95	89.1	93 → 91
54.2	124 → 82 <sup>b</sup>	54.8	82 → 67
52.9	124 → 81 <sup>c</sup>	77.1	81 → 79
37.2	124 → 68	75.1	79 → 77
36.2	124 → 67 <sup>d</sup>	41.1	68 → 53
24.4	124 → 55	63.1	67 → 65
105.1	109 → 107 <sup>e</sup>	25.1	67 → 41
41.2	109 → 67	28.2	54 → 39
68.4	96 → 81	39.1	43 → 41
48.2	96 → 68	37.1	41 → 39
46.7	96 → 67		

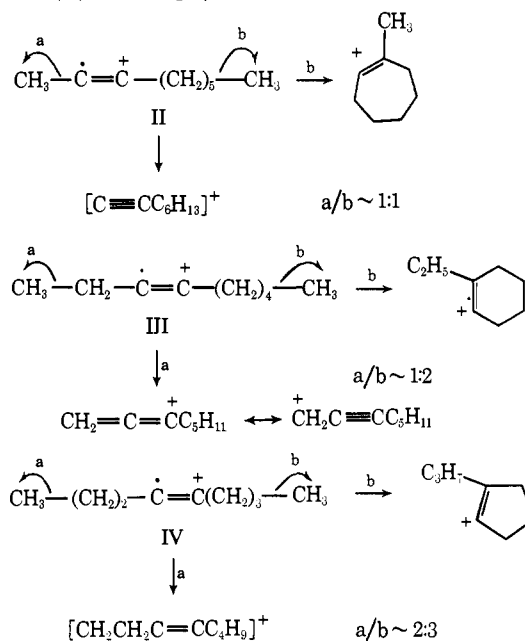
<sup>a</sup> Absent in I, II, and III. <sup>b</sup> Absent in II. <sup>c</sup> Absent in I and II.  
<sup>d</sup> Absent in II. <sup>e</sup> Absent in I.

demonstrating hydrogen scrambling. This scrambling is particularly evident when a fragment ion is itself the source of further fragmentation reactions.

**Simple Cleavage Ions.** The  $(M - H)^+$  ions are of negligible intensity in I-IV, and the deuteration data (not recorded in Table I) indicate nonspecific loss of a hydrogen radical. As previously noted by Hanus and coworkers,<sup>11</sup> deuterium is mostly retained in terminally labeled 1-alkynes; for oct-1-yne-*I-d*<sub>1</sub> we recorded 82% (70 eV) and 84% (12 eV) retention of deuterium in  $(M - 1)^+$ .

The  $(M - CH_3)^+$  ions of mass 109 are of moderate intensity at both 70 eV (6-13% rel intensity) and 12 eV (10-26% rel intensity). The deuterated analogs show this fragment ion cleanly shifted to *m/e* 111 in all cases except when the terminal carbon atom is labeled. Thus, in non-2-yne-*I, I, I-d*<sub>3</sub> the peak is split between *m/e* 109 (45%) and 112 (55%); in non-3-yne-*I, I, I-d*<sub>3</sub> between *m/e* 109 (30%) and 112 (70%); and in non-4-yne-*I, I, I-d*<sub>3</sub> and non-4-yne-*9,9,9-d*<sub>3</sub> between *m/e* 109 (40 and 55%, respectively) and 112 (50 and 45%, respectively). Hence, in II-IV the methyl radical is lost from both ends of the molecule to varying extents (Scheme III).

**Scheme III** (*m/e* 109 Origin)



The  $(M - C_2H_5)^+$  ion at *m/e* 95 is an important peak in the spectra of I-IV at both 70 and 12 eV. For non-1-yne there is a clean shift to *m/e* 97 in the deuterated derivatives (Table I) consistent with simple cleavage of  $(C_8 + C_9)$  without hydrogen transfer and triple bond migration. In the case of non-2-yne, however, the isotopic labeling data (Table I) indicate isomerization of the molecular ion to some extent prior to fragmentation. Thus, in non-2-yne-*7,7-d*<sub>2</sub> the peak is split between *m/e* 97 (90%) and 95 (10%); in non-2-yne-*8,8-d*<sub>2</sub> between *m/e* 97 (20%) and 95 (80%); and in non-2-yne-*I, I, I-d*<sub>3</sub> between *m/e* 98 (80%) and 95 (20%). These data clearly indicate movement of the site of unsaturation prior to formation of *ca.* 20% of the ions of mass 95.

Although the *5,5-d*<sub>2</sub>, *6,6-d*<sub>2</sub>, and *7,7-d*<sub>2</sub> analogs of non-3-yne show the peak neatly shifted to *m/e* 97, placement of the label near the termini of the molecule causes partitioning of the peak due to ejection of an ethyl radical from either end. Thus, in non-3-yne-

**Table III.** Parent–Daughter Relationships in the Fragmentation of Nonynes (Determined by Metastable Defocusing)<sup>a</sup>

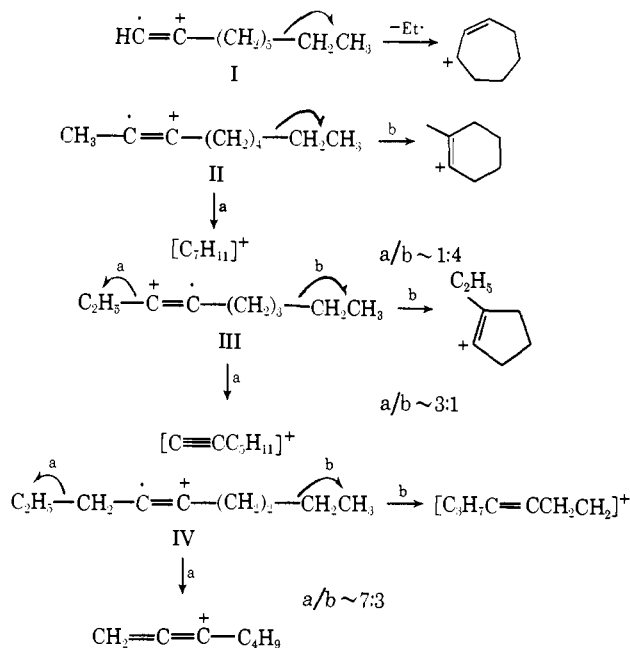
Compound	Daughter ions, <i>m/e</i>					
	82	81	68	67	55	54
Non-2-yne (II)	124 SS	124 M	124 M	124 WW	109 W	96 S
	110 W	109 M	109 M	109 M	95 M	82 S
	97 W	96 SS	96 S	95 S	83 S	69 M
Non-3-yne (III)	124 SS	124 S	124 W	124 WW	123 W	96 M
	109 W	109 W	110 W	109 W	109 W	82 S
	97 W	96 S	96 W	95 W	95 S	69 M
		82 ?	83 W	82 W	83 S	
			69 SS	68 SS	70 M	
					56 S	
Non-4-yne (IV)	124 SS	124 S	124 S	124 W	109 W	96 S
	110 W	109 S	110 W	95 M	95 M	82 S
	97 W	96 W	96 M	82 S	83 S	
		82 ?	83 S	68 SS	70 W	
			69 S		56 M	

<sup>a</sup> Parent ions (*m/e*) are listed vertically in columns. Those whose contribution to a daughter ion is greater than 30% are denoted S; between 10 and 30% denoted by M; and less than 10% denoted by W.

*1,1,1-d<sub>3</sub>* the fragment is split between *m/e* 98 (30%) and 95 (70%), while in non-3-yne-*8,8-d<sub>2</sub>* it is split between *m/e* 97 (65%) and 95 (35%). Hence, when the alkyne structure is such that there is possible a competitive loss of an alkyl radical from two loci, there is a preference for ejection of the group closest to the site of unsaturation (*C<sub>1</sub> + C<sub>2</sub>* above).

A similar correlation is observed for non-4-yne (Scheme IV). Thus, in non-4-yne-*1,1,1-d<sub>3</sub>* the peak is

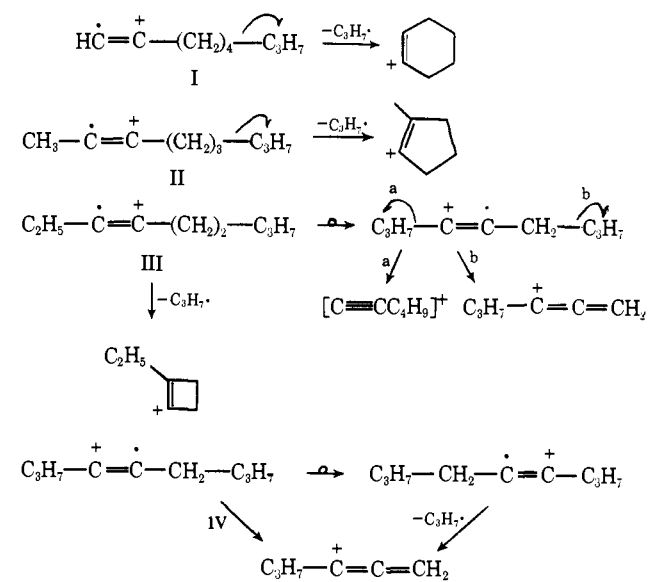
**Scheme IV** (*m/e* 95 Origin)



split between *m/e* 98 (30%) and 95 (70%); in non-4-yne-*9,9,9-d<sub>3</sub>* between *m/e* 98 (70%) and 95 (30%); and in non-4-yne-*2,2,2-d<sub>3</sub>* between *m/e* 97 (30%) and 95 (70%). The *6,6-d<sub>2</sub>* and *7,7-d<sub>2</sub>* derivatives show *ca.* 10% retention of the peak at *m/e* 95, again indicating a minor amount of hydrogen transfer and bond migration prior to decomposition.

Metastable (Table II) and ion-defocusing (Table III) data show that the ion of mass 81 (Scheme V) arises not only by loss of a propyl radical from the molecular ion, but also from *m/e* 109 by loss of ethylene and from *m/e* 96 by loss of a methyl radical. In the case of non-

**Scheme V** (*m/e* 81 Origin)



1-yne, *m/e* 81 is the base peak at both 70 and 12 eV (Table I). The fragment is shifted to *m/e* 83 to *ca.* 90% in the *3,3-d<sub>2</sub>*, *4,4-d<sub>2</sub>*, and *5,5-d<sub>2</sub>* analogs, indicating *ca.* 10% hydrogen scrambling. It is a general feature of the alkyne spectra that when an ion arises *via* multiple pathways the extent of hydrogen scrambling increases. Also, analysis of the labeling data is complicated by overlapping of peaks from the even-mass rearrangement series, because of incomplete peak shifts. For non-2-yne-*4,4-d<sub>2</sub>* and -*6,6-d<sub>2</sub>* the peak is shifted to *m/e* 83; in the *7,7-d<sub>2</sub>* and *8,8-d<sub>2</sub>* derivatives there is some evidence of hydrogen scrambling (Table I) but the peak is retained to >70% at *m/e* 81. Although the 70-eV data for non-3-yne-*5,5-d<sub>2</sub>*, -*6,6-d<sub>2</sub>*, and -*7,7-d<sub>2</sub>* indicate hydrogen scrambling (and probably isomerization of the precursor ions), the peak is shifted to *m/e* 83 at 12 eV to >90%. Further evidence of triple bond migration is provided by the spectra of non-3-yne-*1,1,1-d<sub>3</sub>* where the peak is split between *m/e* 84 (30%) and 81 (70%), and non-3-yne-*8,8-d<sub>2</sub>* where the peak is split between *m/e* 83 (55%) and 81 (45%). These values differ somewhat at 12 eV, indicating isomerization is more prevalent at higher electron energies. The same phenomenon of differential peak splitting, and thus

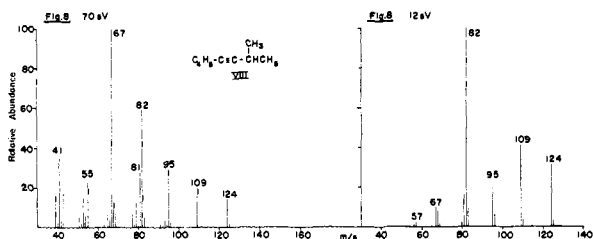
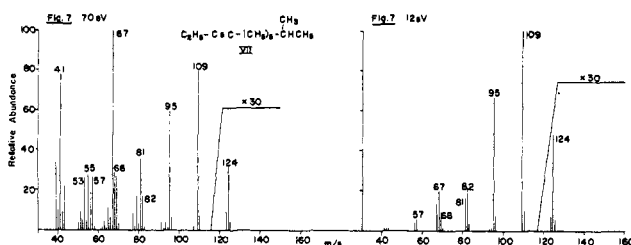
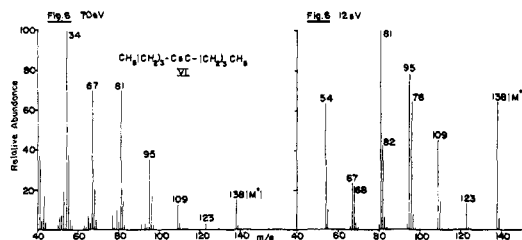
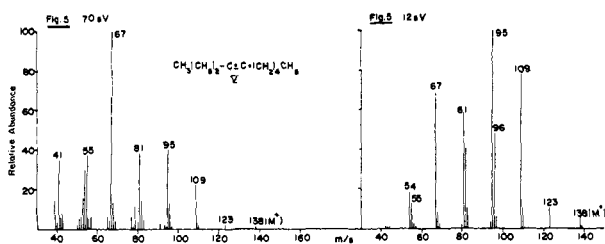


Figure 5. Mass spectrum of dec-4-yne.  
 Figure 6. Mass spectrum of dec-5-yne.  
 Figure 7. Mass spectrum of 7-methyloct-3-yne.  
 Figure 8. Mass spectrum of 2-methyloct-3-yne.

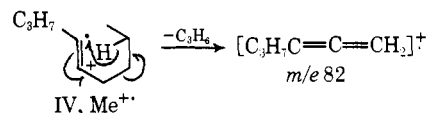
hydrogen scrambling, is observed in the spectra of non-4-yne and its deuterated analogs (Table I). In this case the 70 eV data show that the propyl radical may be lost from either side of the acetylenic bond with equal facility. Of particular interest is non-4-yne-6,6- $d_2$  which shows 25% loss of the label at 70 eV; however, because of the multiplicity of precursor ions, rationalization of the process leading to loss of the  $C_6$  hydrogens prior to formation of  $m/e$  81 in the unlabeled alkyne is not meaningful, although triple bond migration is presumably implicated. It should be noted that the intermediacy of the allene, nona-4,5-diene, during the isomerization process seems to be excluded.<sup>21</sup>

The  $(M - C_4H_9)^+$  peak at  $m/e$  67 is intense in all cases (Table I), and again metastable analysis (Tables II and III) delineates its genesis from several precursor ions. As expected, peak overlap and extensive hydrogen scrambling (Table I) prevent valid structural or mechanistic assignments.

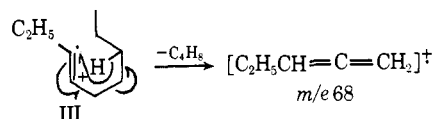
**Even-Mass Rearrangement Ions.** A series of rearrangement ions ( $m/e$  96, 82, 68, 54) is observed in the spectra of I-IV (Table I). Only  $m/e$  96 is significant

(21) A. N. H. Yeo and C. Djerassi, unpublished observation.

for non-4-yne, increasing from 2% relative intensity at 70 eV to 13% relative intensity at 12 eV. In the 2,2- $d_2$ , 3,3- $d_2$ , 6,6- $d_2$ , and 7,7- $d_2$  analogs the peak is split between  $m/e$  98 (ca. 35%) and  $m/e$  96 (ca. 65%) indicating isomerization of the triple bond in the molecular ion prior to loss of ethylene by a McLafferty rearrangement involving transfer of a primary hydrogen atom. Similarly, the  $(M - 42)$  peak at  $m/e$  82 may be represented as the product of a McLafferty rearrangement in the molecular ion after hydrogen scrambling. The peak is of comparable intensity in I, III, and IV (Table I), which is indicative of triple bond migration, and the labeling data show that both sides of, e.g., non-4-yne must be involved in the formation of this allenic rearrangement ion.

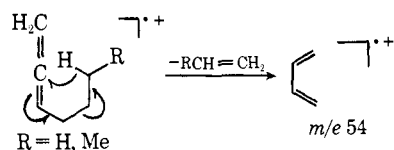


The appropriate metastable peaks (Tables II and III) demonstrate the formation of the  $(M - 56)$  ion at  $m/e$  68 by multiple fragmentation pathways. The



peak is of no importance in non-4-yne, and surprisingly is of comparable intensity in non-1-yne and non-2-yne as in non-3-yne, where it can be readily rationalized as a McLafferty ion. Again, this is indicative of triple bond migration. The spectra of all deuterated derivatives (Table I) provide evidence for hydrogen scrambling.

Metastable defocusing (Table III) showed that  $m/e$  54 is formed from the even-mass allenic rearrangement



ions at  $m/e$  96 and 82. In all four nonynes it is of moderate intensity.

**B. Decynes.** The fragmentation pathways of dec-4-yne (V, Figure 5) and dec-5-yne (VI, Figure 6) were



studied extensively by deuterium labeling (Table IV) and metastable analysis (Table V). As in the case of the nonynes, the spectra of the isomeric decynes differ appreciably. The principal decomposition pathways are analogous to those outlined above for the nonynes, viz. a simple cleavage series, and a rearrangement series.

**Simple Cleavage Series.** The  $(M - CH_3)^+$  ions at  $m/e$  123 are of appreciable intensity (ca. 10% relative intensity) at 12 eV only. In both V and VI the 1,1,1- $d_3$  analogs show the fragment split between  $m/e$  126 (90 and 60%, respectively) and  $m/e$  123 (10 and 40%, respectively). In the case of dec-4-yne (V) the data indicate preference for formation of a six-membered cyclic intermediate (Scheme VI), or possibly a competing isomerization between dec-4-yne and dec-5-yne.

Table IV. Principal Peaks in the Mass Spectra of Decynes V and VI and Their Deuterated Analogs (% Relative Intensity)

Compd	eV	m/e																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
		70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220	1221	1222	1223	1224	1225	1226	1227	1228	1229	1230	1231	1232	1233	1234	1235	1236	1237	1238	1239	1240	1241	1242	1243	1244	1245	1246	1247	1248	1249	1250	1251	1252	1253	1254	1255	1256	1257	1258	1259	1260	1261	1262	1263	1264	1265	1266	1267	1268	1269	1270	1271	1272	1273	1274	1275	1276	1277	1278	1279	1280	1281	1282	1283	1284	1285	1286	1287	1288	1289	1290	1291	1292	1293	1294	1295	1296	1297	1298	1299	1300	1301	1302	1303	1304	1305	1306	1307	1308	1309	1310	1311	1312	1313	1314	1315	1316	1317	1318	1319	1320	1321	1322	1323	1324	1325	1326	1327	1328	1329	1330	1331	1332	1333	1334	1335	1336	1337	1338	1339	1340	1341	1342	1343	1344	1345	1346	1347	1348	1349	1350	1351	1352	1353	1354	1355	1356	1357	1358	1359	1360	1361	1362	1363	1364	1365	1366	1367	1368	1369	1370	1371	1372	1373	1374	1375	1376	1377	1378	1379	1380	1381	1382	1383	1384	1385	1386	1387	1388	1389	1390	1391	1392	1393	1394	1395	1396	1397	1398	1399	1400	1401	1402	1403	1404	1405	1406	1407	1408	1409	1410	1411	1412	1413	1414	1415	1416	1417	1418	1419	1420	1421	1422	1423	1424	1425	1426	1427	1428	1429	1430	1431	1432	1433	1434	1435	1436	1437	1438	1439	1440	1441	1442	1443	1444	1445	1446	1447	1448	1449	1450	1451	1452	1453	1454	1455	1456	1457	1458	1459	1460	1461	1462	1463	1464	1465	1466	1467	1468	1469	1470	1471	1472	1473	1474	1475	1476	1477	1478	1479	1480	1481	1482	1483	1484	1485	1486	1487	1488	1489	1490	1491	1492	1493	1494	1495	1496	1497	1498	1499	1500	1501	1502	1503	1504	1505	1506	1507	1508	1509	1510	1511	1512	1513	1514	1515	1516	1517	1518	1519	1520	1521	1522	1523	1524	1525	1526	1527	1528	1529	1530	1531

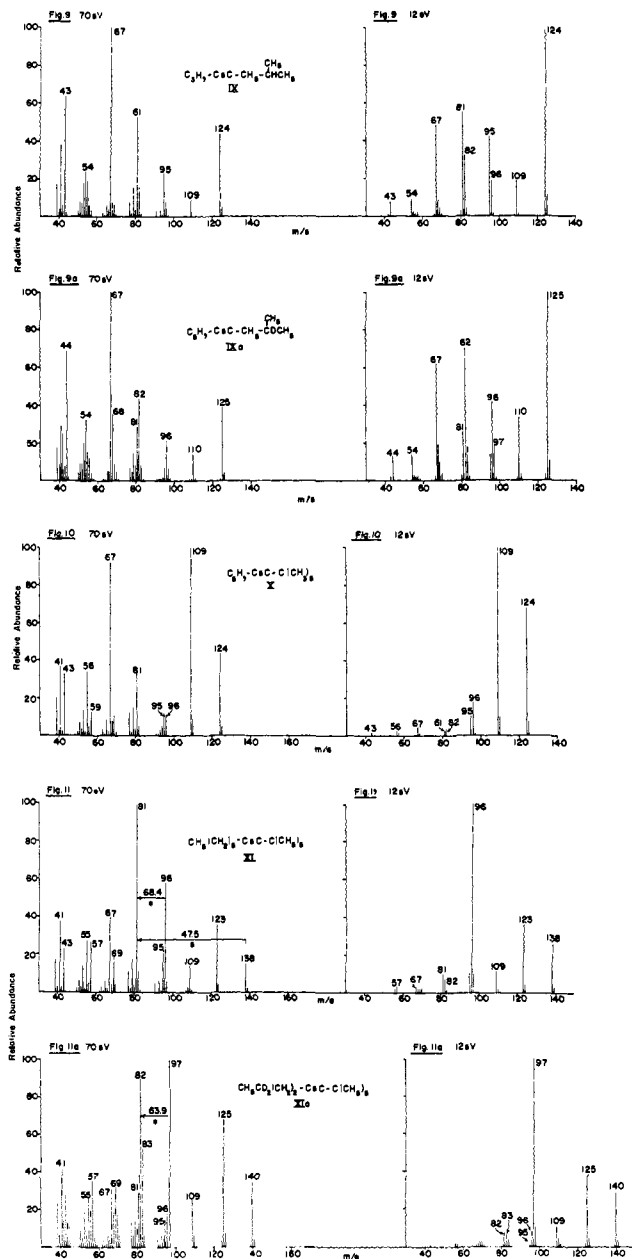
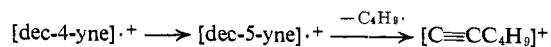


Figure 9. Mass spectrum of 7-methyloct-4-yne.  
 Figure 9a. Mass spectrum of 7-methyloct-4-yne-7- $d_1$ .  
 Figure 10. Mass spectrum of 2,2-dimethylhept-3-yne.  
 Figure 11. Mass spectrum of 2,2-dimethyloct-3-yne.  
 Figure 11a. Mass spectrum of 2,2-dimethyloct-3-yne-7,7- $d_2$ .

drogen scrambling results. However, for  $m/e$  81, predominant loss of the label is observed for the  $1,1,1-d_3$ ,  $2,2-d_2$ , and  $3,3-d_2$  analogs of dec-4-yne (Table IV) and this necessitates movement of the triple bond prior to fragmentation. The symmetrical dec-5-yne can cleave on either side of the unsaturation and the peaks are split accordingly (Scheme IX).

#### Scheme IX ( $m/e$ 81 Origin)

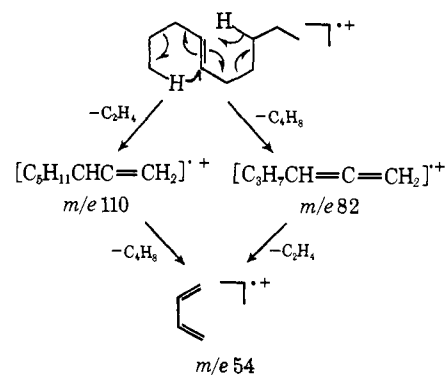


Insofar as  $m/e$  67 is concerned, valid structural and mechanistic assignments cannot be made because of extensive hydrogen scrambling and peak overlap.

**Even-Mass Rearrangement Ions.** The important rearrangement ions in the spectrum (Figure 5) of dec-4-

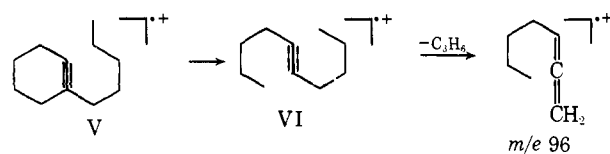
yne occur at  $m/e$  96, 82, and 54 (Table IV). Formation of  $m/e$  82 and 54 is rationalized as before by sequential McLafferty rearrangement processes (Scheme X).

#### Scheme X



simplest explanation for the formation of  $m/e$  96 is a McLafferty rearrangement preceded by isomerization to dec-5-yne (Scheme XI). This hypothesis is sup-

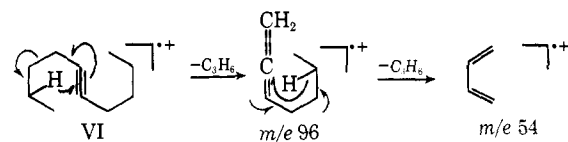
#### Scheme XI



ported by the fact that all of the even-mass ions are split in the spectra of the deuterated analogs, although exact data are difficult to determine as overlap from the even- and odd-mass fragments occurs.

In the spectrum (Figure 6) of dec-5-yne  $m/e$  54 is the base peak at 70 eV and the labeling data (Table IV) indicate that this ion is the product of a double McLafferty rearrangement (Scheme XII) although no

#### Scheme XII



metastable transitions are observed in the second field-free region (Table V). The formulation of  $m/e$  96 as an ionized hepta-1,2-diene is strongly supported by the spectrum of this independently synthesized compound.<sup>21</sup>

The data presented here provide strong evidence for isomerization of the molecular ion of simple unbranched alkynes to some extent prior to decomposition. Although all the isomeric nonynes and decynes follow the same fragmentation pathways, the relative intensity of each fragment is peculiar to each compound, thus giving rise to analytically useful spectra. In the case of the rearrangement ions, those which are derived directly from the molecular ions are (except in the case of dec-5-yne) the most important, while the less important members of the series can be rationalized by sequential isomerization-McLafferty rearrangement steps.

**C. Branched Alkynes.** It is well known<sup>7,22</sup> that in branched olefins isomerization is largely suppressed

(22) K. K. Mayer and C. Djerassi, *Org. Mass Spectrom.*, 5, 817 (1971).





The above data clearly show that branched-chain alkynes exhibit much less complicated fragmentation behavior than their straight-chain isomers. The major decomposition modes are processes of low activation energy, such as the McLafferty rearrangement and  $\beta$  fission. The *tert*-butyl group in particular exerts an anchoring effect suppressing isomerization of the molecular ion to a high degree.

### Experimental Section

The mass spectra were determined on a AEI MS-9 instrument using the heated inlet system with a source temperature of 200°. All ionizing voltages quoted are nominal values. The repeller voltages ranged between +3 to 5 V and the accelerating voltage amounted to 8000 V.

The alkynes<sup>23</sup> and their deuterated analogs were prepared in 70–95% yield by reacting the appropriate terminal acetylene (Farchan Research Laboratories, Willoughby, Ohio) with an alkyl halide. A typical detailed procedure follows.

To an ice-cold solution of hept-1-yne (0.1 mol) in hexamethylphosphoramide (0.75 ml, distilled from 13X molecular sieves) was added dropwise a solution of *n*-butyllithium in hexane (0.35 ml of 2.67 M solution). The ice bath was removed and the mixture was stirred for 5 min at ambient temperature. The ice bath was then replaced, and *n*-propyl bromide (0.077 ml) was added. After stirring at room temperature for 30 min, the mixture was poured into 1 N HCl (20 ml). Pentane (5 ml) was added, and the organic layer separated, washed with aqueous NaHCO<sub>3</sub> and water, and dried. Removal of the solvent was followed by vpc purification (20% Apiezon or 15% SE 30 on Chromosorb W) to give dec-4-yne.

(23) We thank Dr. Michele Rudler for the preparation of the unlabeled straight-chain compounds.

## Reactions of *N*-Phenyl-2-naphthylamino Radicals<sup>1</sup>

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**Abstract:** The thermal decomposition of 1,4-diphenyl-1,4-(2-naphthyl)-2-tetrazene (1) ( $\Delta H^\ddagger = 24.8$  kcal/mol,  $\Delta S^\ddagger = 0.7$  eu in benzene) produces *N*-phenyl-2-naphthylamino radicals (A·). The major products are the carbon-carbon (3) and carbon-nitrogen (4) dimers of A·, with *N*-phenyl-2-naphthylamine (2) and 7-phenyldibenzo[*c,g*]-carbazole (5) formed as minor products. No stable diarylamino radicals are detectable in the reaction mixture by electron resonance spectroscopy. Surprisingly facile hydrogen transfer reactions occur between A· and a variety of hydrocarbons. Hydrogen transfer reactions of A· with hydroperoxides, hindered phenols, thiols, phosphines, amines, and aldehydes are also described. The data show *N*-phenyl-2-naphthylamino radicals to be considerably more reactive than generally believed. The results are discussed in the context of amine inhibition of hydrocarbon autoxidations.

Diarylamino radicals are of significant historical interest to organic chemistry. The diphenylamino radical was erroneously reported<sup>2</sup> as one of the earliest examples of a stable organic free radical. This claim stood unchallenged for nearly 50 years. Musso<sup>3</sup> demonstrated that diphenylamino radicals disproportionate rapidly at 90° to a mixture of oligomers and diphenylamine. Neugebauer and Fischer<sup>4</sup> showed that the diphenylamino radical could not be observed by esr during decomposition of the hydrazine over a range of temperatures. Stable diarylamino radicals could be observed, however, if the reactive para positions were blocked by electron donating substituents, in agreement with the classic series of papers by Wieland and coworkers.<sup>5</sup>

Despite the voluminous literature on carbon-centered radicals, knowledge of nitrogen-centered radicals is surprisingly meager, and even the most rudimentary

reactions of diarylamino radicals have been attended by a good deal of confusion. Various reports<sup>6–10</sup> of hydrogen transfer reactions by the diphenylamino radical are of questionable significance because earlier workers assumed the amino radicals to be stable in solution or were unaware of the extensive disproportionation reaction, which produces about 50% yield of the apparent hydrogen abstraction product, diphenylamine.<sup>11</sup>

The absence of a comprehensive study of diarylamino radicals has prompted us to investigate the reactions of the *N*-phenyl-2-naphthylamino radical. This radical is uniquely suited for such a study because of its low degree of disproportionation and its well-defined coupling products.<sup>12,13</sup>

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March–April, 1971.

(2) H. Wieland, *Justus Liebig's Ann. Chem.*, **381**, 200 (1911).

(3) H. Musso, *Chem. Ber.*, **92**, 2881 (1959).

(4) (a) F. A. Neugebauer and P. H. H. Fischer, *ibid.*, **98**, 844 (1965).

(b) The spectrum of the short-lived diphenylamino radical was recently resolved during photolysis of the hydrazine in a flow system: F. A. Neugebauer and S. Bamberger, *Angew. Chem.*, **83**, 47 (1971).

(5) An excellent review is given by A. R. Forrester, J. M. Hay, and R. H. Thompson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 3.

(6) T. J. Wallace, J. J. Mahon, and J. M. Kelliher, *Nature (London)*, **206**, 709 (1965).

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(8) P. F. Holt and B. P. Hughes, *ibid.*, 1320 (1955).

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(10) V. D. Pokhodenko and V. A. Bidzilya, *Teor. Eksp. Khim.*, **2**, 234 (1966).

(11) For more recent studies of the disproportionation of diarylamino radicals confirming the results of ref 3, see (a) P. Welzel, *Chem. Ber.*, **103**, 1318 (1970); (b) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc., B*, 1114 (1966); (c) F. A. Neugebauer and H. Fischer, *Chem. Ber.*, **104**, 886 (1971).

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(13) R. F. Bridger, *ibid.*, **35**, 1746 (1970).