

**Table III.** Quantities Used in the Independent Systems Discussion

Molecule	$\alpha_x,$ cm <sup>-1</sup>	$\alpha_y,$ cm <sup>-1</sup>	$\beta,$ cm <sup>-1</sup>	$\mu_x,$ Å	$\mu_y,$ Å
Allene <sup>a</sup>	59,360	59,360	-1060	0.37	0.37
TMA	62,460	62,460	-3360	0.61	0.61
DMA	62,460	59,360	-2170	0.61	0.37

<sup>a</sup> See ref 3 for the allene  $\pi^* \leftarrow \pi$  data.

fore four forms of eq 3. The fifth equation is the relationship of  $\beta_{\text{TMA}}$  to  $\beta_{\text{A}}$  obtained from eq 1. Simultaneous solution of the five equations results in the  $\alpha$  and  $\beta$  values given in Table III.

The only test of validity of the foregoing application of IS theory is the comparison of the calculated intensities of the two DMA transitions with those observed. The resultant transition dipoles of the low energy ( $\mu_l$ ) and high energy ( $\mu_h$ ) bands are calculated to be

$$\mu_l = 0.889\mu_A + 0.458\mu_{\text{TMA}} = 0.608 \text{ Å}$$

$$\mu_h = 0.889\mu_{\text{TMA}} - 0.458\mu_A = 0.373 \text{ Å}$$

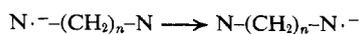
## Mass Spectra of the Hydrocarbons ( $\alpha$ -naphthyl)-(CH<sub>2</sub>)<sub>n</sub>- ( $\alpha$ -naphthyl). The Effect of the Neutral $\alpha$ -Naphthyl End Group Stabilizing the Molecular Ion

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**Abstract:** A series of hydrocarbons N-(CH<sub>2</sub>)<sub>n</sub>-N were prepared, N denoting an  $\alpha$ -naphthyl group and  $n$  varying from 2 to 16. Inspection of their mass spectra revealed that the originally formed molecular ion N-(CH<sub>2</sub>)<sub>n</sub>-N<sup>+</sup> becomes stabilized through an intramolecular collision with the other naphthyl moiety forming an intramolecular dimer (1). Interesting fragmentation patterns were observed, especially for the ion N-(CH<sub>2</sub>)<sub>3</sub>-N<sup>+</sup>. The results are interpreted and discussed.

We determined recently<sup>1,2</sup> the rate of intramolecular electron transfer in the system



N denoting  $\alpha$ -naphthyl moiety and N<sup>·-</sup> its radical anion. Under conditions prevailing in those experiments every collision seems to be effective and therefore the rate of the transfer is given by one-half of the frequency of the intramolecular collisions occurring in solution between two N groups separated by a chain of  $n$  (CH<sub>2</sub>) units ( $n$  varying from 3 to 16).

In the course of preparation and identification of the N-(CH<sub>2</sub>)<sub>n</sub>-N hydrocarbons their mass spectra were examined. It was found that the molecular ion, N<sup>·+</sup>-(CH<sub>2</sub>)<sub>n</sub>-N, undergoes intramolecular collisions during its lifetime. Such collisions stabilize the ion,

Using these values to calculate the oscillator strengths results in values of 0.47 and 0.19 for the low and high energy bands, respectively. The calculated values compare quite favorably with the observed values of 0.52 and 0.23.

### Conclusions

The  $\pi^* \leftarrow \pi$  transition energies and intensities of allene,<sup>3</sup> TMA, and DMA have been shown to be amenable to MO interpretation, utilizing symmetry to determine which excited states are obtainable by dipole radiation. However, the technique of independent systems, which can be viewed as an attempt to describe the actual transition state of a molecule, appears to be equally successful in light of existing data. The apparent success of the IS model in these few systems suggests the possibility that the allenes may serve as good systems in which to study the interactions of transition moments of  $\pi$  systems.

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presumably by the formation of an intramolecular complex (1) and retard therefore its fragmentation.



The details of our finding and their significance are reported below.

### Experimental Section

Hydrocarbons N-(CH<sub>2</sub>)<sub>n</sub>-N with  $n$  varying from 2 to 16 were prepared. Those corresponding to  $n > 4$  have not yet been described in the literature.

1,2-Bis( $\alpha$ -naphthyl)ethane, N-(CH<sub>2</sub>)<sub>2</sub>-N, was prepared according to the method of Copeland, Dean, and McNeil.<sup>3</sup> 1,3-Bis( $\alpha$ -naphthyl)propane, N-(CH<sub>2</sub>)<sub>3</sub>-N, was synthesized by condensing  $\alpha$ -naphthylaldehyde with  $\alpha$ -acetylnaphthalene as described by Chandross

(1) K. Shimada, G. Moshuk, H. D. Connor, P. Caluwe, and M. Szwarc, *Chem. Phys. Lett.*, **14**, 396, 402 (1972).

(2) H. D. Connor, K. Shimada, and M. Szwarc, *Macromolecules*, **5**, 801 (1972).

(3) P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, 1232 (1961).

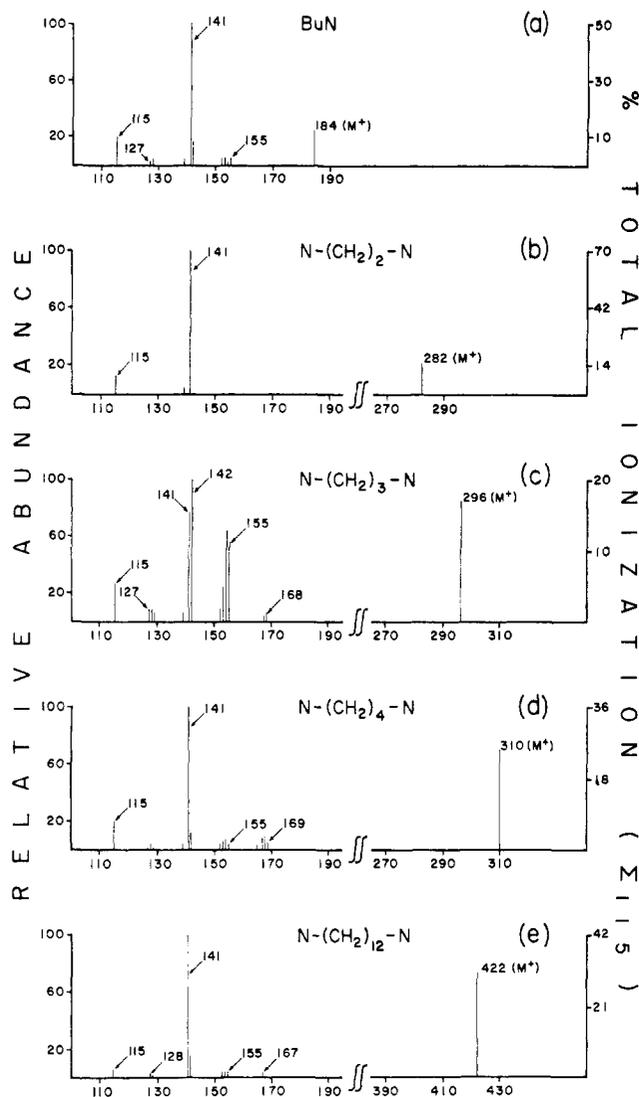


Figure 1.

and Dempster.<sup>4</sup> Their procedure<sup>4</sup> (radical coupling of the Grignard reagent of 2-( $\alpha$ -naphthyl)ethyl bromide induced by AgBr) was used in the preparation of 1,4-bis( $\alpha$ -naphthyl)butane, N-(CH<sub>2</sub>)<sub>4</sub>-N. The remaining hydrocarbons, N-(CH<sub>2</sub>)<sub>n</sub>-N, with  $n = 5, 6, 8, 10, 12$ , and 16 were prepared by Wurtz-Fittig reaction, *i.e.*, by coupling  $\alpha$ -bromonaphthalene with the appropriate  $\alpha,\omega$ -dibromoalkane. A typical procedure is described below for 1,6-bis( $\alpha$ -naphthyl)hexane, N-(CH<sub>2</sub>)<sub>6</sub>-N.

$\alpha$ -Bromonaphthalene (0.2 mol), 1,6-dibromohexane (0.1 mol), and Na (0.4 mol) were refluxed in 100 ml of ether for 1 week. Unreacted sodium was filtered off under nitrogen, and the filtrate treated with excess MeOH and water. The ether layer was separated, washed with water, dried (CaCl<sub>2</sub>), and evaporated. Naphthalene was removed from the crude product by vacuum sublimation. The oily, viscous residue was dissolved in petroleum ether (bp 40–50°). Upon cooling a viscous oil separated. The decanted solution was concentrated, cooled, and decanted until no more oily residue separated. The remaining solution was put in the refrigerator for crystallization (several days). The crystalline material was further purified by repeated chromatography on silica gel/CCl<sub>4</sub>, treated with activated carbon (until complete removal of fluorescent material) and finally recrystallized from petroleum ether. The final product yields a single spot on the tlc.

The prepared compounds have been characterized by their melting points and mass spectra; see Table I. The nmr spectra of all these hydrocarbons in carbon disulfide show a multiplet for aromatic protons ( $\delta$  7.2–8.0) a triplet for benzylic protons ( $\delta$  2.85–3.12),

(4) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).

Table I

	Mp, °C	M <sup>+</sup>	Formula
N-(CH <sub>2</sub> ) <sub>5</sub> -N	71	324	C <sub>25</sub> H <sub>24</sub>
N-(CH <sub>2</sub> ) <sub>6</sub> -N	84	338	C <sub>26</sub> H <sub>26</sub>
N-(CH <sub>2</sub> ) <sub>8</sub> -N	43	366	C <sub>28</sub> H <sub>30</sub>
N-(CH <sub>2</sub> ) <sub>10</sub> -N	37–38	394	C <sub>30</sub> H <sub>34</sub>
N-(CH <sub>2</sub> ) <sub>12</sub> -N	50–55	422	C <sub>32</sub> H <sub>38</sub>
N-(CH <sub>2</sub> ) <sub>16</sub> -N	59–60	478	C <sub>36</sub> H <sub>46</sub>

and a broad signal centered at about  $\delta$  1.5 for the remaining aliphatic protons. The integration gives the expected ratios of intensities.

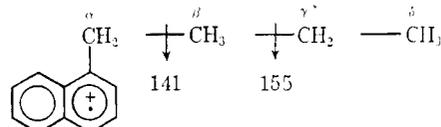
We also synthesized 1-( $\alpha$ -naphthyl)butane, Bu-N, which served as a reference compound. This hydrocarbon was prepared by Wurtz-Fittig reaction from  $\alpha$ -bromonaphthalene and *n*-butyl bromide. The resulting liquid was purified by glc and finally distilled under high vacuum. Its nmr spectrum in carbon disulfide shows a multiplet of aromatic protons at  $\delta$  7.1–8.0, a triplet of benzylic protons centered at  $\delta$  2.92, multiplet of the methylene protons at  $\delta$  1.05–1.8, and a triplet of methyl protons centered at  $\delta$  0.9, the respective protons being in the ratio 7:2:4:3. The mass spectrum gives M<sup>+</sup> 184.

**Mass Spectra.** The mass spectra were obtained on a Hitachi Perkin-Elmer Instrument, RMU6E. The investigated hydrocarbons, except butyl naphthalene, were melted in high vacuum to remove traces of solvents incorporated in the crystals and introduced through the direct inlet system. The spectra were taken at 70 eV and recorded 15 min after the introduction of the sample to ascertain the constancy of the ionization current. Under these conditions the results were reproducible. The abundance for each fragment (including its isotope satellite) was calculated as per cent of the ion current of all fragments with  $m/e$ 's  $\geq 115$  ( $\Sigma \geq 115 = 100$ ). The ions of  $m/e \geq 115$  represent 95% of all the ions formed in the mass spectrometer from the studied compounds.

The mass spectrum<sup>5</sup> of BuN is shown in Figure 1a;  $m/e$  141 is large whereas the molecular ion is relatively small. This spectrum is taken as the reference in the following discussion. The spectrum of N-(CH<sub>2</sub>)<sub>2</sub>-N, seen in Figure 1b, reveals an even larger  $m/e$  141 and smaller molecular ion. The spectrum of N-(CH<sub>2</sub>)<sub>3</sub>-N, given in Figure 1c, is somewhat unusual because  $m/e$  142, 154, and 155 are exceptionally high when compared with those shown in the spectra of the other hydrocarbons. The mass spectra of the remaining hydrocarbons,  $n > 3$ , basically are similar to each other. For the sake of illustration those of N-(CH<sub>2</sub>)<sub>4</sub>-N and of N-(CH<sub>2</sub>)<sub>12</sub>-N are shown in Figures 1d and 1e, respectively.

## Discussion

The fragmentation modes of BuN<sup>+</sup> are similar to those of 1-phenylbutane.<sup>6</sup> As seen from Table II, the abundance of the molecular ion,  $m/e$  184, is relatively low amounting to 12% only, while the most abundant fragment arises from  $\beta$  cleavage,  $m/e$  141, 51%. The  $\beta$  fission, involving transfer of hydrogen atom from the  $\gamma$  methylene to the aromatic moiety, yields  $m/e$  142, 8%, and the  $\gamma$  cleavage produces  $m/e$  155, 2%.



The fragmentation patterns of N-(CH<sub>2</sub>)<sub>n</sub>-N<sup>+</sup> ions resemble that of BuN<sup>+</sup>. However, it seems that the presence of the second naphthyl moiety substantially stabilizes the molecular ion (see Table II) while the abundances of the other fragments depend, in an interesting way, on the value of  $n$ .

(5) The calculated abundance of the isotope satellite of  $m/e = X$  is added to the abundance of  $X$  and subtracted from that of  $X + 1$ .

(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 82.

**Table II.** Corrected<sup>a</sup> Abundances of Fragments Calculated as % of the Ion Current  $\Sigma \geq_{115}$  for N-(CH<sub>2</sub>)<sub>n</sub>-N

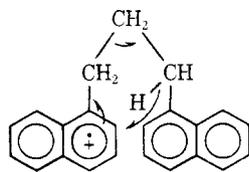
<i>m/e</i> <sup>b</sup>	BuN	<i>n</i>								
		2	3	4	5	6	8	10	12	16
115	10	9	5.5	7	7.5	6	4.5	4	3	2
141	51	70	15	36	38	40	44	41	42	43
142	8.5	0	20	4.5	4	6	7.5	7.5	7	7.5
152	2	1	2	1.5	1	1	0.8	1.0		
153	2	1	5	2.5	2	2	1.5	1.5	1	1
154			13	2.5	1.5	2.5	1.5	2	2	2
155	2		11.5	2	2	2.5	2.5	2.5	2	2.5
167			1.0	3	1	1.5	1.5	1.5	1	1.5
168			1.5	4						
169				2			0.8			
182					2					
183					4			2		
M <sup>+</sup>	12	14.5	17	25	24	25	25	28	31	29

<sup>a</sup> The abundance of the isotope satellite of *m/e* = X is added to the abundance of X and subtracted from that of X + 1. <sup>b</sup> The fragments of abundance lower than 3% are omitted in the table except for those bearing particular significance for the discussion.

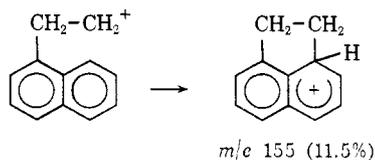
The fragmentation patterns of N-(CH<sub>2</sub>)<sub>n</sub>-N<sup>+</sup> for *n* ≥ 4 are remarkably similar. For all these compounds the abundance of the molecular ion is in the range 28 ± 3%, *i.e.*, substantially greater than 12% found for BuN<sup>+</sup>, while the abundances of *m/e* 141 and 142 decrease accordingly.

The fragmentation of N-(CH<sub>2</sub>)<sub>2</sub>-N<sup>+</sup> and N-(CH<sub>2</sub>)<sub>3</sub>-N<sup>+</sup> is somewhat different. The central C-C bond in the former ion is exceptionally weak because both fragments produced in its fission are strongly stabilized by resonance. Consequently, the proportion of *m/e* 141 is very high (70%) while the abundance of the molecular ion is low (14.5%). Moreover, no fragment *m/e* 142 (excluding the isotope satellite) is observed because the β fission accompanied by H transfer is impossible.

The most interesting pattern is obtained for N-(CH<sub>2</sub>)<sub>3</sub>-N<sup>+</sup>. The abundance of *m/e* 142 (20%) is even higher than that of *m/e* 141 (15%). This is attributed to the stabilization of the C=C bond in vinylnaphthalene formed during the β fission involving H-atom transfer. The γ cleavage is exceptionally

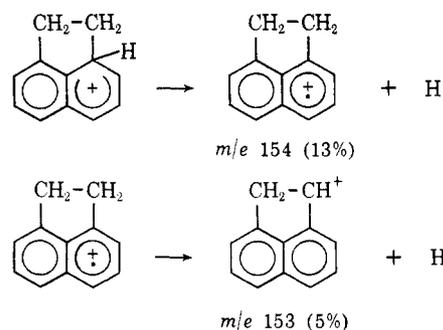


favored in this molecular ion since it leads to the formation of resonance stabilized NCH<sub>2</sub>· radical and probably also to the stabilization of the positive ion *m/e* 155 by ring closure, *viz.*



The resulting protonated acenaphthene loses a hydrogen atom yielding the *m/e* 154 radical cation and the latter may lose again an H atom, although much less readily, forming the carbonium ion *m/e* 153. This accounts for the exceptionally high abundance of these three ions in the spectrum of N-(CH<sub>2</sub>)<sub>3</sub>-N (see Table II). Indeed, we found that in the mass spectrum of acenaphthene

apart from the molecular ion the only other one having high abundance is *m/e* 153.



A similar sequence of processes takes place through δ fission in the fragmentation of N-(CH<sub>2</sub>)<sub>4</sub>-N<sup>+</sup> ions and through ε fission in N-(CH<sub>2</sub>)<sub>5</sub>-N<sup>+</sup> ions. The former yields *m/e* 169, 168, and 167 while the latter gives rise to *m/e* 183 and 182. However, the respective ring closures are less probable than in the previous case; thus, the total per cent of fragmentation leading to the relevant ions and the products of their decomposition is 30% for the *n* = 3 systems but only 9 and 6% for *n* = 4 and 5, respectively.

The stability of the *m/e* 155, 154, and 153 ions, attributed to the ring formation, is reflected in their relatively large abundance in all the systems with *n* > 3, although their formation is not facilitated, like in N-(CH<sub>2</sub>)<sub>3</sub>-N<sup>+</sup>, by the formation of resonance stabilized NCH<sub>2</sub>· radicals and hence they are less abundant than in *n* = 3.

The formation of the dimeric (1) ion stabilizes the originally produced N-(CH<sub>2</sub>)<sub>n</sub>-N<sup>+</sup>, making it longer-lived than the BuN<sup>+</sup> ion. The dimeric radical cations are formed readily in solution<sup>7</sup> and were shown to be stable.

The dimerization in the mass spectrometer arises from rapid intramolecular collisions. Intramolecular collisions occurring in solution between an N·- moiety and a naphthyl group of N-(CH<sub>2</sub>)<sub>n</sub>-N·- radical anions have been studied recently in our laboratory.<sup>1,2</sup> The extrapolation of the available data to 200° (the approximate temperature maintained in the mass spectrometer) indicates that the time between those collisions is shorter than 10<sup>-8</sup> sec, even for N-(CH<sub>2</sub>)<sub>16</sub>-N. Hence, the collisions occur in a time much shorter than the lifetime

(7) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

of the molecular ions ( $\sim 10^{-7}$  sec) and this accounts for the fact that the degree of their stabilization is independent of  $n$ , provided  $n > 3$ . The lower abundance of the molecular ion in the  $n = 3$  system is due to two modes of decomposition facile for  $n = 3$  but less favored in the other ions of this series, namely the decomposition yielding  $m/e$  142, 155.

The extent of stabilization of the cyclized ions is revealed even more clearly on comparison of the rate constants of their fragmentation into a specific fragment ion with the respective rate constant of fragmentation of the  $\text{BuN}^{\cdot+}$  ion. For example, the ratio of the rate constants of fragmentation of the investigated hydrocarbon and butyl naphthalene into the  $m/e$  141 ion,  $k_{141}/k_{141}^0$ , is given by the ratio of the relative abundances  $m/e$  141 and  $\text{M}^{\cdot+}$  for these two compounds. The pertinent data are collected in Table III and show that

**Table III.** Relative Rate Constants of Fragmentation of Molecular Ions  $\text{N}-(\text{CH}_2)_n-\text{N}^{\cdot+}$  Referred to  $\text{BuN}^{\cdot+}$  Taken as a Reference

$n$	$k_{141}/k_{141}^0$	$k_{142}/k_{142}^0$	$k_{155}/k_{155}^0$
2	1.1		
3	0.2	1.7	4.2
4	0.3	0.25	0.5
5	0.35	0.25	0.5
6	0.35	0.35	0.6
8	0.4	0.4	0.6
10	0.35	0.35	0.55
12	0.3	0.3	0.4
16	0.35	0.35	0.5

$k_{141}/k_{141}^0$  is nearly constant and much less than 1 for all the compounds with  $n > 2$  while it is slightly higher than 1 for  $n = 2$ . Hence, this fragmentation is retarded in all the ions  $\text{N}-(\text{CH}_2)_n-\text{N}^{\cdot+}$  ( $n > 2$ ) when compared with the analogous fragmentation of  $\text{BuN}^{\cdot+}$ .

The relative rates of fragmentation into  $m/e$  142 (excluding the contribution of the isotope satellite ion of  $m/e$  141) and into  $m/e$  155 are exceptionally high for  $\text{N}-(\text{CH}_2)_3-\text{N}^{\cdot+}$ , *i.e.*, 1.7 and 4.2, respectively. The reasons for this facile fragmentation of the  $n = 3$  ion

have been fully discussed in the preceding paragraphs. However, for all the remaining hydrocarbons ( $n > 3$ ) the relative rates of fragmentation are again low (see Table III) confirming the effect of stabilization of the molecular ions by the other naphthyl group.

It is interesting to note that the doubly charged ions  $m/2e$  appear in the mass spectra of  $\text{N}-(\text{CH}_2)_n-\text{N}$  for  $n > 2$ ; their abundance is about 1% of the total ion current. Such ions are not observed in the spectrum of  $\text{N}-(\text{CH}_2)_2-\text{N}$ . This indicates that the  $\text{N}^{\cdot+}-(\text{CH}_2)_2-\text{N}^{\cdot+}$  ion is exceptionally unstable like the analogous dinegative ion.<sup>8</sup>

The occurrence of intramolecular collisions is implied in studies<sup>9,10</sup> of mass spectra of some trimethylsilyl derivatives, *i.e.*,  $\text{TMS}-\text{X}$ , where X is linked to TMS through a long chain. This is evident from the appearance of fragments such as  $(\text{TMX}\cdot\text{X})^+$ . However, such interactions do not stabilize the molecular ion (a phenomenon demonstrated by our studies).

Finally, the following question calls for an answer. Are the intramolecular dimers (1) formed as a result of an intramolecular collision between  $\text{N}^{\cdot+}$  and N taking place *after* electron ejection or are the two N moieties associated with each other all the time and the electron ejection takes place from the associate? A definite answer could be provided by studies of photoelectron spectra of  $\text{N}-(\text{CH}_2)_n-\text{N}$  and  $\text{BuN}$ . In the absence of this information we may use the spectroscopic data obtained in solution. The electronic spectra of  $\text{N}-(\text{CH}_2)_3-\text{N}$  and  $\text{N}-(\text{CH}_2)_4-\text{N}$  in hydrocarbon solution are identical with that of  $\text{BuN}$  even at  $-80^\circ$ . Hence, it is plausible to assume that  $\text{N}-(\text{CH}_2)_n-\text{N}$  in the gas phase forms an open chain and not a ring.

**Acknowledgment.** This work was supported by the Petroleum Research Fund administered by the American Chemical Society. We wish also to acknowledge the support of the National Science Foundation in the purchase of the mass spectrometer.

(8) A. Lagendijk and M. Szwarc, *J. Amer. Chem. Soc.*, **93**, 5359 (1971).

(9) G. H. Draffan, R. N. Stillwell, and J. M. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

(10) S. Sloan, D. J. Harvey, and P. Vouros, *ibid.*, **5**, 789 (1971).