

Figure 3. Pulse radiolysis of methanol in  $D_2O$ . Methanol is at 3.5 ppm.

at 1.15 ppm ( $Me_4Si$ ) and AE quartet at 2.3 ppm. Methane (actually  $CH_3D$ ) is seen at  $\sim 0.2$ – $0.3$  ppm and is in enhanced absorption (A), since in this system it is the radical with the smallest  $g$  factor.<sup>6</sup> Combination of two acetate radicals gives succinic acid which is seen at 2.6 ppm, and is weakly polarized. In the pulse radiolysis of methanol alone (Figure 3) only ethylene glycol can be seen at 3.7 ppm in enhanced absorption (A).<sup>7</sup>

A mixture of methanol and acetate yields, in addition to the products mentioned above, ethanol and  $\beta$ -hydroxypropionic acid ( $OHCH_2CH_2COO^-$ ). Ethanol has AE triplet at 1.25 ppm and AE quartet at 3.7 ppm, and  $OHCH_2CH_2COO^-$  has two AE triplets at  $\sim 3.7$  and  $\sim 2.4$  ppm. As more methanol is added to acetate solutions, propionate is displaced by ethanol (Figure 1 A–E) as the dominant polarized product.

While this example deals with radicals produced by the OH-abstraction reaction, we have also studied examples of the  $e_{aq}^-$  reaction in the  $CH_3I-CH_3OH$  system. Details of this and numerous other systems that exhibit CIDNP in pulse radiolysis will be discussed elsewhere.<sup>8</sup>

Several important features of pulse radiolysis NMR–CIDNP experiments should be mentioned. The intensities of polarized NMR signals are dominated by the nuclear spin lattice relaxation time ( $T_1$ ) of the products in question. Thus products with very short  $T_1$  may not be seen at all if the transfer time between the irradiating magnet and the NMR magnet is not comparable to the  $T_1$  of that product. Substantial concentrations of radicals are produced by irradiation and the typical radical half-lives are in the range of microseconds or less.<sup>9</sup> This is considerably shorter than the nuclear  $T_1$  in these radicals ( $\sim 10^{-4}$  s) and sometimes it is shorter than the electron  $T_1$  in some of these radicals. Under these conditions polarization transfer may be occurring.<sup>10</sup> This is being investigated.

The overall polarization pattern of NMR multiplets is AE (enhanced absorption low field lines and emission high field lines of the multiplet) as expected for independently generated radicals.<sup>11</sup> However, the relative signal intensities of the polarized NMR multiplets can be complex. The residence time of radicals in the irradiating magnet may affect the relative multiplet intensities.<sup>12</sup> The effect of flow rate on the NMR signal intensity should also be considered.<sup>13</sup> The CIDNP in varying magnetic fields can also be easily studied, and provides additional details on polarization in various products.

We hope to have illustrated how this novel application of nuclear magnetic resonance spectroscopy to pulse radiolysis can be used to study various radical products and their reaction mechanisms. The more detailed analysis of CIDNP can yield information on the radical–radical interaction in solution. We believe that CIDNP study in radiation chemistry will prove to be a simple and useful analytical tool.

## References and Notes

- (1) Work performed under the auspices of the USERDA.
- (2) For general references see M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", The M.I.T. Press, Cambridge, Mass., 1969.
- (3) A. D. Trifunac and M. C. Thurnauer, *J. Chem. Phys.*, **62**, 4884 (1975).
- (4) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization", Wiley Interscience, New York, N.Y., 1973; G. L. Closs, *Adv. Magn. Reson.*, **7**, 157 (1974).
- (5) A similar flow system has been described by R. G. Lawler and M. Halfon, *Rev. Sci. Instrum.*, **45**, 84 (1974). Flow systems have also been used to study CIDNP in the chemically produced  $OH\cdot$  radical reaction products. M. Covivera, C. A. Fyfe, S. P. Vaish, and H. E. Chen, *J. Am. Chem. Soc.*, **96**, 1611 (1974).
- (6) G. L. Closs and A. D. Trifunac, *J. Am. Chem. Soc.*, **92**, 2183 (1970).
- (7) This unusual polarization (A) has also been observed in other systems,<sup>8</sup> and remains to be explained.
- (8) A. D. Trifunac, to be submitted for publication.
- (9) These estimates of radical half-lives are based on our measurements of the  $\cdot CH_2COO^-$  radical half-life at somewhat lower electron beam intensities. A. D. Trifunac, *J. Am. Chem. Soc.*, in press.
- (10) The observed CIDNP effect of a given product can be the result of a "co-operative" effect of the singlet–triplet evolution of the primary and the secondary (and subsequent) radical pairs. J. A. Den Hollander, *Chem. Phys.*, **10**, 167 (1975).
- (11) G. L. Closs and A. D. Trifunac, *J. Am. Chem. Soc.*, **92**, 2186 (1970).
- (12) R. Kaptein, Ph.D. Thesis, Leiden, 1971.
- (13) D. W. Jones and T. F. Child, *Adv. Magn. Reson.*, **8**, 123 (1976).

A. D. Trifunac,\* K. W. Johnson, R. H. Lowers

Chemistry Division, Argonne National Laboratory  
Argonne, Illinois 60439

Received May 27, 1976

## 1,6-Methano[10]annulen-11-ylidene

Sir:

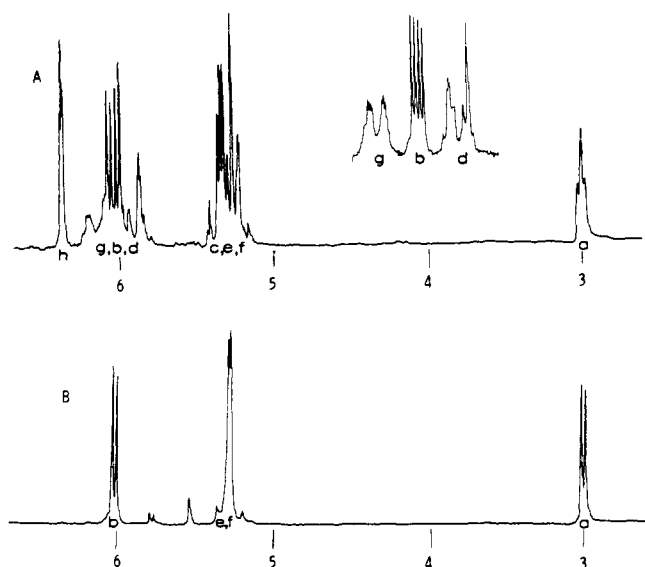
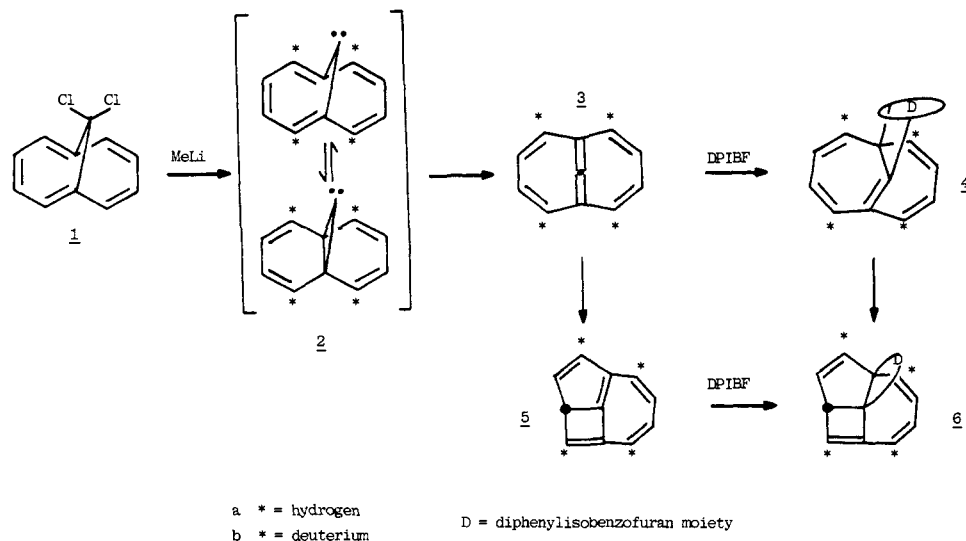
Due to the continuing interest in the phenylcarbene-cycloheptatrienylydene rearrangement,<sup>1</sup> we undertook a study of 1,6-methano[10]annulen-11-ylidene (**2**), a relative of cycloheptatrienylydene. We now wish to report the successful generation of the carbenoid equivalent of **2** and the trapping of a novel intermediate.

When 11,11-dichloro-1,6-methano[10]annulene (**1**)<sup>2</sup> was treated with either *n*-butyllithium or methylolithium in an ether solvent,  $C_{22}H_{16}$  hydrocarbons<sup>3,4</sup> were isolated. Due to their instability and the complex nature of their  $^1H$  NMR spectrum, these  $C_{11}H_8$  dimers were neither separated nor fully characterized. However, since the  $^1H$  NMR spectrum revealed the presence of only vinyl and allylic protons, it was clear that rearrangement to 2,3-benzocycloheptatrienylydene or  $\alpha$ -naphthylcarbene had not occurred.

Our efforts were then directed towards intercepting the  $C_{11}H_8$  intermediate prior to dimerization in order to both enhance the stability and simplify spectral analysis of the product. Trapping by furan,<sup>1a,5</sup> cyclohexene,<sup>6</sup> mercaptide anion,<sup>7</sup> bis(triphenylphosphine)(ethylene)platinum,<sup>8,9</sup> anthracene, buta-1,3-diene, or 1-methoxybuta-1,3-diene proved unsuccessful. However, when **2** was generated in the presence of 1,3-diphenylisobenzofuran<sup>10</sup> (DPIBF), a 1:1 adduct,<sup>11</sup> mp 187–189 °C with decomposition, was obtained in 65% yield. The  $^1H$  NMR spectrum of this compound is partially reproduced in Figure 1A. Extensive proton decoupling experiments<sup>12</sup> permitted us to obtain the chemical shift and coupling constant data displayed in Table I. This information, in conjunction with the  $^{13}C$  NMR and the uv spectrum [ $\lambda_{max}$  (in acetonitrile) 303 nm ( $\epsilon$  3450)], still did not allow an unambiguous structural assignment.

Clear crystals of the 1,3-diphenylisobenzofuran adduct **6a** were grown by slow evaporation of an EtOAc solution at 4 °C. Diffraction symmetry was orthorhombic with accurate cell constants of  $a = 8.792$  (2),  $b = 17.037$  (5), and  $c = 14.493$  (4) Å. Systematic absences indicated the chiral space group  $P_{2_1,2_1,2_1}$  and a calculated density suggested one molecule of  $C_{31}H_{22}O$  per asymmetric unit.<sup>13</sup> All diffraction maxima with  $2\theta \leq 114^\circ$

Scheme I



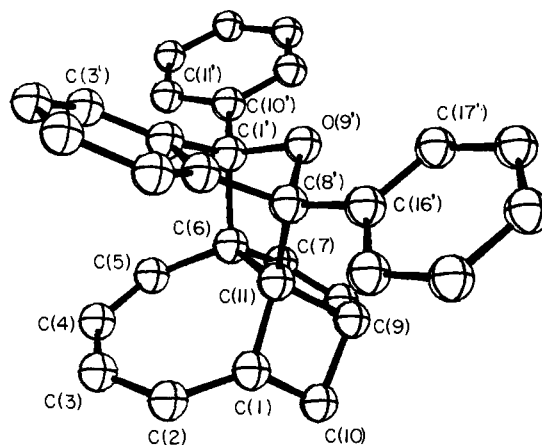
**Figure 1.** (A) The partial XL-100-15  $^1\text{H}$  NMR spectrum of **6a**, in  $\text{CDCl}_3$ , showing the signals derived from the  $\text{C}_{11}\text{H}_8$  moiety. The inset displays  $\text{H}_g$ ,  $\text{H}_b$ , and  $\text{H}_d$  at 270 MHz.<sup>12</sup> (B) The partial XL-100-15  $^1\text{H}$  NMR spectrum of **6b**, in  $\text{CDCl}_3$ , showing the signals derived from the  $\text{C}_{11}\text{H}_4\text{D}_4$  moiety.

were recorded on a Syntex P<sub>21</sub> diffractometer using an  $\omega$ -scan technique and graphite monochromated  $\text{Cu K}\alpha$  radiation (1.541 78 Å). A total of 1701 reflections were measured and after corrections for Lorentz, polarization, and background effects, 1547 (91%) were judged observed ( $F_o \geq 3\sigma(F_o)$ ).

A trial structure was achieved with a multiple solution weighted tangent formula approach and recycling of plausible molecular fragments through phase refinement.<sup>14</sup> Full-matrix least-squares refinements with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogens have converged to a standard crystallographic residual of 0.035 for the observed reflections.<sup>15</sup> See the statement at the end of the paper for additional crystallographic details.

Figure 2 is a computer generated perspective drawing of the final x-ray model. In general, bond distances and angles agree well with generally accepted values. There are no abnormally short intermolecular contacts or large residual peaks on a final difference electron density synthesis.

The molecular reorganization accompanying the genesis of **6a** can be most simply explained by the mechanisms depicted in Scheme I. Precedent exists for the transformation of the



**Figure 2.** A computer generated perspective drawing of adduct **6a**. Hydrogens are omitted for clarity.

**Table I.**  $^1\text{H}$  NMR Spectrum of **6a**<sup>a</sup>

$\delta$	$\text{H}_a$	$\text{H}_b$	$\text{H}_c$	$\text{H}_d$	$\text{H}_e$	$\text{H}_f$	$\text{H}_g$	$\text{H}_h$
$\text{H}_a$	3.00	2.4	<0.5				2.4	0.6
$\text{H}_b$		6.04	5.9					0.6
$\text{H}_c$			5.32					
$\text{H}_d$				5.92	12.1			
$\text{H}_e$					5.34 <sup>b</sup>	7.2		
					(5.28)			
						5.28 <sup>b</sup>		
						(5.34)	10.6	
							6.16	0.6
							$\text{H}_h$	6.38

<sup>a</sup> Diagonal elements represent chemical shifts ( $\delta$ ) obtained in  $\text{CDCl}_3$ ; off diagonal elements are coupling constants (Hz). <sup>b</sup> Values in parentheses may be interchanged.

annulenyldiene or its norcaradienyl equivalent into the symmetric and highly strained allene, **3a**.<sup>16,17</sup> Subsequent Diels-Alder cycloaddition<sup>10</sup> to DPIBF could produce **4a**, which may close to yield **6a**. Alternately, the allene may itself close to produce **5a**, which may then, in turn, be trapped with DPIBF.<sup>18,19</sup>

The mechanisms in Scheme I were also found to be consistent with the following labeling experiment. The tetradeuterated derivative **1b** was prepared in the standard fashion.<sup>20</sup> Generation and trapping of **2b** in the usual manner provided **6b**. As can be seen in Figure 1B, the  $^1\text{H}$  NMR signals assigned to  $\text{H}_c$ ,  $\text{H}_d$ ,  $\text{H}_g$ , and  $\text{H}_h$  have vanished from the spectrum.  $\text{H}_a$

is now coupled only to  $H_b$  ( $J_{ab} = 2.4$  Hz), both signals appearing as doublets. The previously complex multiplet due to  $H_c$ ,  $H_e$ , and  $H_f$  was transformed into an AB quartet ( $\Delta\nu_{ef} = 5.06$  Hz,  $J_{ef} = 7.2$  Hz).

Distinction between the two proposed pathways may be achieved through an analysis of the  $C_{22}H_{16}$  dimers produced. A mechanism proceeding via initial allene-allene cycloaddition<sup>21</sup> can lead to but two isomers in which the bicycloheptadiene skeletons remain preserved. The alternate route, involving allene closure followed by addition across the internal bridgehead double bond,<sup>22</sup> may produce four isomers.

Further effort is currently being directed at elucidating the structure of the dimers, as well as surveying the chemistry of **6** and its allene progenitor.

**Acknowledgment** is made to the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. R.H.L. is grateful to the E. I. duPont de Nemours Company for a Young Faculty Grant and also to Professor W. Doering and two referees for their most helpful comments.

**Supplementary Material Available:** Fractional coordinates, bond distances, bond angles, and structure factors (12 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) (a) T. T. Coburn and W. M. Jones, *J. Am. Chem. Soc.*, **96**, 5218 (1974); (b) R. L. Tyner, W. M. Jones, Y. Öhrn, and J. R. Sabin, *ibid.*, **96**, 3765 (1974); (c) P. H. Gebert, R. W. King, R. A. LaBar, and W. M. Jones, *ibid.*, **95**, 2357 (1973); (d) R. A. LaBar and W. M. Jones, *ibid.*, **95**, 2359 (1973); (e) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *ibid.*, **95**, 826 (1973), and references therein; (f) W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970); (g) W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969).
- (2) P. H. Nelson and K. G. Untch, *Tetrahedron Lett.*, 4475 (1969).
- (3) The mass spectrum shows a parent ion at  $m/e$  280.
- (4) The  $^{13}C$  NMR spectrum contains 38 signals, some of which are clearly due to overlapping resonances, indicating the presence of more than one dimer.
- (5) P. Warner, R. LaRose, C. Lee, and J. C. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972).
- (6) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).
- (7) W. E. Billups, L. P. Lin, and W. Y. Chow, *J. Am. Chem. Soc.*, **96**, 4026 (1974).
- (8) (a) M. E. Jason, J. A. McGinnety, and K. B. Wiberg, *J. Am. Chem. Soc.*, **96**, 6531 (1974); (b) J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 3803 (1974); (c) J. P. Visser, A. J. Schipperijn, and J. Lukas, *J. Organomet. Chem.*, **47**, 433 (1973); (d) J. P. Visser and J. E. Ramakers, *J. Chem. Soc., Chem. Commun.*, 178 (1972); (e) J. P. Visser, A. J. Schipperijn, J. Lukas, D. Bright, and J. J. deBoer, *Chem. Commun.*, 1266 (1971).
- (9) We thank Dr. A. Kramer for supplying us with a sample of this platinum complex.
- (10) (a) W. G. Dauben and J. D. Robbins, *Tetrahedron Lett.*, 151 (1975); (b) K. B. Becker, *Chimia*, **28**, 726 (1974); (c) W. G. Dauben and J. Ipaktschi, *J. Am. Chem. Soc.*, **95**, 5088 (1973); (d) J. A. Chong and J. R. Wiseman, *ibid.*, **94**, 8627 (1972); (e) M. A. Battiste and C. T. Sprouse, Jr., *Tetrahedron Lett.*, 4661 (1970); (f) R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, **92**, 984 (1970); (g) G. Wittig and P. Fritze, *Justus Liebigs Ann. Chem.*, **711**, 82 (1968).
- (11) The observed exact mass was 410.166 98. For  $C_{31}H_{22}O$ , the calculated exact mass is 410.167 06. The osmometric molecular weight was found to be  $415 \pm 5\%$ .
- (12) Thanks are due to Dr. M. Saunders (Yale) and Dr. L. Neuringer (Francis Bitter National Magnet Laboratory at M.I.T.) for recording spectra at 270 MHz.
- (13) Actually space group  $P_{2,2,2}$ , was the only space group consistent with the systematic extinctions and the lack of molecular symmetry displayed in the NMR spectrum. It would be interesting to know whether this represents a case of spontaneous resolution where each macroscopic crystal contains only one enantiomer or whether the enantiomers occur in resolved microscopic domains scattered throughout the entire crystal. Unfortunately, the crystal morphology was unsuitable for a visual determination and the lack of anomalous scatterers precluded determination by an x-ray experiment. We were unable to measure any optical activity in a sample prepared by dissolving a large single crystal and thus tentatively conclude that resolution occurs only in domains.
- (14) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **24**, 274 (1970).
- (15) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL", USAEC Report IS-2625, Iowa State University-Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran

Thermal-Ellipsoid Plot Program", U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

- (16) For examples of carbenoids rearranging to allenoids, see (a) W. R. Moore and W. R. Moser, *J. Am. Chem. Soc.*, **92**, 5469 (1970); (b) *J. Org. Chem.*, **35**, 907 (1970); (c) L. Skattebøl, *Tetrahedron*, **23**, 1107 (1967); (d) E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966); (e) L. Skattebøl, *ibid.*, 167 (1961); (f) for an example of a carbenoid which does not rearrange to an allene see R. Vaidyanathaswamy and D. Devaprabhakara, *Chem. IND (London)*, 515 (1968).
- (17) For examples of carbenes rearranging to allenoids, see (a) W. R. Dolbier, Jr., O. T. Garza, and B. H. Al-Sadar, *J. Am. Chem. Soc.*, **97**, 5038 (1975); (b) M. Oda, Y. Ito, and Y. Kitahara, *Tetrahedron Lett.*, 2587 (1975); (c) R. A. LaBar and W. M. Jones, *J. Am. Chem. Soc.*, **96**, 3645 (1974); (d) G. W. Klumpp and P. M. Van Dijk, *Recl. Trav. Chim. Pays-Bas*, **90**, 381 (1971).
- (18) Depending upon the mode of closure of **4** or the direction of addition to **5**, isomers of **6a**, with the ether oxygen syn or anti to the dienyl unit, can be produced. In fact, a minor isomer (5% yield) displaying spectral characteristics analogous to **6a** (the major isomer) can be seen in Figure 1B.
- (19) For reports on the trapping of bicyclo[3.2.0]hepta-1,3,6-triene with DPIBF see (a) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *J. Am. Chem. Soc.*, **91**, 2787 (1969); (b) R. Breslow, W. Washburn, and R. C. Bergman, *ibid.*, **91**, 196 (1969).
- (20) (a) W. Böll, *Tetrahedron Lett.*, 2595 (1968); (b) F. Gerson, E. Heilbronner, W. A. Böll, and E. Vogel, *Helv. Chim. Acta*, **48**, 1494 (1965).
- (21) (a) R. A. LaBar and W. M. Jones, *J. Am. Chem. Soc.*, **96**, 3645 (1974), and references therein; (b) J. E. Baldwin and R. A. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).
- (22) For an example of such a dimerization in the parent bicyclo[3.2.0]hepta-1,3,6-triene, see ref 19 above. For a report on a benzo analogue see M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Am. Chem. Soc.*, **91**, 2379 (1969).
- (23) National Institutes of Health Trainee, 1974-present.
- (24) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee 1972-1977.

Jane Berkowitz Carlton,<sup>23</sup> Ronald H. Levin\*

Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138

Jon Clardy<sup>24</sup>

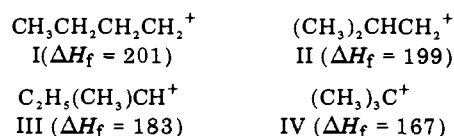
Ames Laboratory—USERDA and Department of Chemistry  
Iowa State University  
Ames, Iowa 50011

Received May 14, 1976

## Ion Structure Determination by Gas Phase Derivatization and Collisional Activation Mass Spectrometry<sup>1</sup>

Sir:

Structural studies of gaseous organic ions have commonly employed characterization by ion-molecule reactions,<sup>2,3</sup> especially utilizing ion cyclotron resonance (ICR) spectrometry,<sup>4-6</sup> and by metastable<sup>7,8</sup> and collisionally activated<sup>9</sup> decompositions occurring in a field-free drift region of the mass spectrometer. Collisional activation (CA) spectra are uniquely insensitive to differences in ion internal energies, and have been found applicable in a wide variety of problems.<sup>1,9,10</sup> However, for particular ions, especially those without functional groups, the CA spectra of isomers can be closely similar; further, isomerization may occur in the relatively long times (CA,  $\sim 10^{-5}$  s; ICR,  $> 10^{-3}$  s) before structural assay.<sup>11</sup> We report here that it is possible to alleviate these disadvantages by in situ derivatization of the newly formed ions using ion-molecule reactions, followed by characterization of the products from their CA spectra; the isomeric  $C_4H_9^+$  ions I-IV (heat of formation,<sup>12</sup> kcal/mol, in parentheses)



have been investigated using this technique.

$C_4H_9^+$  ions generated from any of the isomeric halobutanes apparently undergo metastable decomposition (lifetimes  $\sim 10^{-5}$  s) from a common structure, or mixture of structures.<sup>8</sup>