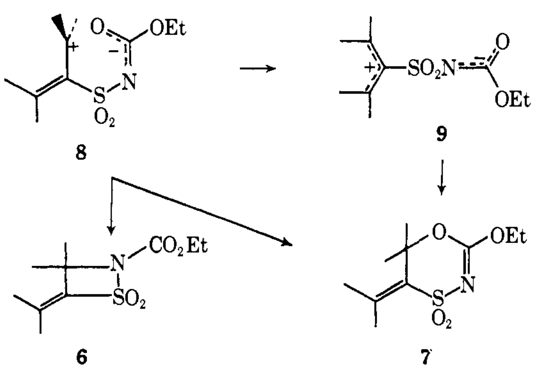
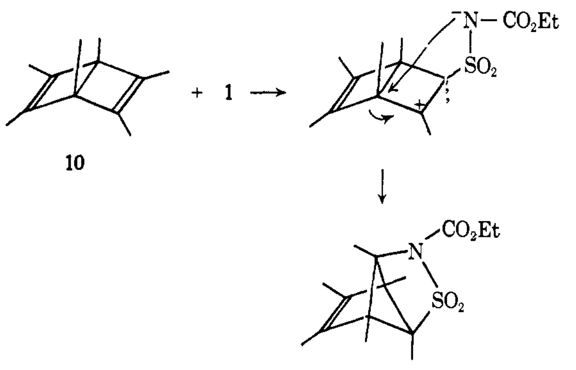


60 Mc) signals at τ 5.60 (quartet, 2 H, $J = 7$ Hz), 8.62 (triplet, 3 H, $J = 7$ Hz), 7.65, 7.96 (singlets, 3 H), and 8.19 (singlet, 6 H), while in the infrared the C═N stretching frequency occurred at 1615 cm^{-1}. 2-Carbethoxy-3,3-dimethyl-4-isopropylidene-1,2-thiazetidine 1,1-dioxide (**6**), mp 150–151°, was characterized by the appearance of C═O absorption at 1725 cm^{-1} in the infrared region and nmr ($CDCl_3$, 60 Mc) signals at τ 5.58 (quartet, 2 H, $J = 7$ Hz), 8.65 (triplet, 3 H, $J = 7$ Hz), 7.90, 8.09 (singlets, 3 H), and 8.24 (singlet, 6 H). We envision these adducts from this nonconcerted[11] cycloaddition as arising from subsequent closure of the nonplanar[12] zwitterion **8** resulting from electrophilic attack on the allenic central[13] carbon atom. The partition of **8** between **6** and **7** may reflect the additional strain imposed by the exocyclic double bond on the geometry of the transition state leading to **6**.[14] The genesis of **7** may also involve rotation of **8** to the allylic cation **9**, whose geometry will only permit closure to this heterocycle.

When **2** was treated with hexamethylbicyclo[2.2.0]-hexa-2,5-diene (**10**), at 60° in acetonitrile solution, a 70% yield of a 1:1 cycloadduct, mp 140–141°, was isolated. The appearance of nmr ($CDCl_3$, 60 Mc) signals, *inter alia*, at τ 8.27 (6 H), 8.75 (6 H), 8.51 (3 H), and 8.72 (3 H) as sharp singlets suggests a symmetrical structure for this product. This symmetry is reflected in the nmr ($CDCl_3$, 60 Mc) absorption at τ 8.91 (doublet, 6 H, $J = 7$ Hz), 8.82 (singlet, 9 H), 8.38 (singlet, 3 H), and 7.95 (multiplet, 2 H) of a dihydro derivative, mp 157–158°, isolated from catalytic hydrogenation of this cycloadduct.

Since only one structure is consistent with these symmetry requirements, formula **11** is assigned to this cycloadduct, whose origin appears to result from steric control of the approach of the electrophilic heterocumulene toward the *exo* surface of **10**.[15]



Acknowledgments. We wish to sincerely thank the Petroleum Research Foundation for a research grant (2965), the National Science Foundation for funds used to purchase a mass spectrometer, and Professor L. Paquette for stimulating discussions.

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(11) An ideal concerted thermal *cis* 2 + 2 cycloaddition is energetically unfavorable from orbital symmetry considerations: R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(12) The restriction to rotational isomerism in similar systems has been demonstrated, *i.e.*, chlorosulfonyl isocyanate stereospecifically adds to isomeric β-methylstyrenes: E. J. Moriconi and J. F. Kelley, *Tetrahedron Letters*, 1435 (1968).

(13) The greater stability of the tertiary *vs.* the vinyl carbonium ion formed by bonding the electrophile at this center has been determinative in the orientation of other tetramethylallene cycloadditions: E. J. Moriconi and J. F. Kelley, *J. Am. Chem. Soc.*, **88**, 3657 (1966).

(14) The analogous internal ion pair ii from the reaction of N-sulfonylbenzamide with ethyl vinyl ether closes through a four-membered transition state although a more strain-free pathway is available. See ref 1.

$$\overset{+}{\text{EtO}}\text{=\!=CHCH}_2\text{SO}_2\text{N}\text{=\!=C(}\overset{-}{\text{O}}\text{)C}_6\text{H}_5$$

ii

(15) Electronic considerations appear to control the *endo* attack of chlorosulfonyl isocyanate on **10** leading to a dihydroazasemibullvalene system: L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 2133 (1968); L. A. Paquette, *ibid.*, 2139 (1968).

(16) National Institutes of Health Predoctoral Fellow, 1963–1968.

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Metastable Ion Characteristics. VII. Collision-Induced Metastables

Sir:

It has recently been shown that the structures of gaseous ions can be characterized by the metastable decomposition reactions which they undergo.[1] Such metastable ion characteristics include the kinetic energy of the transition, the effect of the number of vibrational degrees of freedom in the molecular ion, and the ratio of abundances of two metastable ions from the same precursor ion. Application of the technique to the structures of many ions has been limited by the requirements of these characteristics. We report here that collision-induced metastables appear to provide an additional characteristic of broad applicability. This method produces additional metastable peaks whose relative abundances not only are high, but appear to be nearly independent of the energy of their precursor ions. Thus the structure of an ion can be characterized by the abundance of a single collision-induced metastable ion.

The possible structures of the $C_3H_7^+$ ion has been a classic problem in mass spectrometry, with Meyerson and coworkers giving persuasive evidence that most $C_3H_7^+$ ions have been isomerized to a protonated cyclopropane structure.[2-4] The metastable ion charac-

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(1) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967); M. L. Gross and F. W. McLafferty, *Chem. Commun.*, 254 (1968), and references cited therein.

(2) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963; see also F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *J. Am. Chem. Soc.*, **90**, 2222 (1968).

Table I. Metastable Peaks from $C_3H_7^+ \xrightarrow{m_1^*} C_3H_5^+ + H_2$ and $C_3H_7^+ \xrightarrow{m_2^*} C_2H_3^+ + CH_4$

	<10^{-6} torr[a]		5 × 10^{-6} torr[a]			1 × 10^{-5} torr[a]		
	KE of m_1^*, eV	$[m_1^*]^f/[C_3H_7^+]$	$\Delta[m_1^*]^{b,f}/[C_3H_7^+]$	$[m_2^*]^f/[C_3H_7^+]$	$\Delta[m_1^*]/[m_2^*]$	$\Delta[m_1^*]^{b,f}/[C_3H_7^+]$	$[m_2^*]^f/[C_3H_7^+]$	$\Delta[m_1^*]/[m_2^*]$
n-Hexane	0.20	1.60	0.98	0.67	1.46	1.88	1.24	1.52
2-Methylpentane	0.20	1.18	0.91	0.67	1.36	2.04	1.33	1.53
3-Methylpentane	0.21	1.10	*c*	0.64		1.91	1.29	1.48
2,2-Dimethylbutane	0.21	0.59	0.99	0.68	1.44	1.85	1.24	1.49
2,3-Dimethylbutane	0.20	1.09	*d*	0.64		*d*	1.25	
2-Bromopropane	0.21	1.61	*c*	0.67		1.85	1.27	1.46
1-Bromopropane	0.20	1.71	*c*	*c*		2.32[e]	1.50[e]	1.54

[a] Approximate pressure in drift region. [b] Abundance in excess of that at <10^{-6} torr. [c] Data not determined. [d] Interference from $C_3H_6^+ \rightarrow C_3H_5^+$ metastable. [e] Pressure in drift region approximately 1.3 × 10^{-5} torr. [f] Per cent.

teristics of Table I confirm this and illustrate the use of collision-induced metastables.

Table I reports the kinetic energy released in the metastable transition, $C_3H_7^+ \rightarrow C_3H_5^+ + H_2$ (m_1^*), plus the collision-induced metastables of $C_3H_7^+$ measured on a Bendix Model 12 time-of-flight mass spectrometer specially modified for the observation of metastable ions.[5–7] Raising the pressure in the drift tube of the spectrometer with air increases the abundance of *m*$_1$* and causes an abundant new metastable to appear, corresponding to $C_3H_7^+ \rightarrow C_2H_3^+ + CH_4$ (m_2^*). The neutral fragment formed by the pressure-dependent reaction $N_2\cdot^+ \rightarrow N_2$ is used as an internal indicator of the drift tube pressure. Note that at a particular pressure *the values of* $[m_2^*]/[C_3H_7^+]$ *are equal within experimental error* for all of the molecules studied, despite the fact that the abundances of the metastable ions from the unimolecular decomposition $C_3H_7^+ \rightarrow C_3H_5^+$ are not constant. In addition, the fractions of the latter metastable ions which are caused by collision-induced fragmentation are also constant within experimental error, and the abundance ratio of the two collision-induced metastables produced at different pressures is also constant. Thus the abundance of the collision-induced metastable ion products appears to be *independent* of the original energy distribution of the precursor ions, indicating that most collisions impart considerably more energy to the $C_3H_7^+$ ions than the activation energy for the decompositions. The reaction producing m_2^* should require a higher activation energy than m_1^*, yet $\Delta[m_1^*]/[m_2^*]$ appears to be independent of the internal energy of the precursor $C_3H_7^+$ ions. Also $[m_2^*]/[C_3H_7^+]$ is independent of ionizing electron energy between 20 and 70 eV, consistent with previous observations showing that a collision-induced metastable exhibits the same ionization efficiency curve as its precursor ion.[8]

The usefulness of this tool for ion structure determination would be lowered if the collision process greatly increased the chance for isomerization of the ion.[9] We plan studies to check this; however, it is encouraging to note that the shape and width of the flat-topped metastable m_1^* appears to be identical for both the unimolecular and collision-induced processes, indicating comparable transition states for these processes. Also, in preliminary measurements collision-induced metastables, corresponding to $C_3H_6O\cdot^+ \rightarrow C_2H_3O^+ + CH_3$ in the spectra of acetone, 2-pentanone, and 4-heptanone, are produced in differing relative abundances, as would be expected from the different structures indicated for their respective $C_3H_6O\cdot^+$ ions.[10]

Thus, the abundance of a single collision-induced metastable should serve to characterize the structure of an ion. It may be possible that an even higher sensitivity for such metastables can be gained by utilizing the drift region between the ion source and electric sector of a double-focusing mass spectrometer[11] as the collision chamber, hopefully making this an ion structure tool of broad applicability.[12]

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(3) This could not be confirmed [F. W. McLafferty and T. A. Bryce, *Chem. Commun.*, 1215 (1967)] by measurement of the abundances of the metastables, as only the transition $C_3H_7^+ \rightarrow C_3H_5^+$ was found;[4] although different relative abundances were observed for different sources of $C_3H_7^+$, this could be due to the formation of the same $C_3H_7^+$ isomer structure with different energy distributions.

(4) C. Ottinger, *J. Chem. Phys.*, 47, 1452 (1967), reports the very weak transition $C_3H_7^+ \rightarrow C_3H_6^+ + H$.

(5) F. W. McLafferty, R. S. Gohlke, and R. C. Golesworthy, Annual Meeting on Mass Spectrometry, ASTM E-14, Montreal, June 1964, p 331; R. E. Ferguson, K. E. McCulloh, and H. M. Rosenstock, *J. Chem. Phys.*, 42, 100 (1965); W. W. Hunt, Jr., R. E. Huffman, J. Saari, G. Wassel, J. F. Betts, E. H. Paufve, W. Wyess, and R. A. Fluegge, *Rev. Sci. Inst.*, **35**, 88 (1964).

(6) This instrument, which will be described in a separate publication, was especially modified to defocus ions of masses higher than the precursor.

(7) Measurements on a magnetic sector instrument (Hitachi RMU-6D) of the kinetic energy released in this *m/e* 39.09 metastable peak agree well with these data, despite interference of the $C_3H_3^+$ peak.

(8) K. R. Jennings, Annual Meeting on Mass Spectrometry, ASTM E-14, Denver, Colo., June 1967, p 73.

(9) Even the activation energy for ordinary metastable ion decompositions can be sufficient to cause isomerization of the precursor ion structure (*e.g.*, $C_2H_5O^+$ ions from several types of molecules[1]). However, higher energies generally discriminate *against* reactions with low "frequency factors," such as rearrangements.

(10) W. T. Pike and F. W. McLafferty, *J. Am. Chem. Soc.*, **89**, 5953 (1967).

(11) M. Barber and R. M. Elliott, Conference on Mass Spectrometry, ASTM E-14, Montreal, June 1964, p 30; T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).

(12) The generous support of National Institutes of Health Grants GM 12755 and FR 00354 is gratefully acknowledged.

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The Mechanism and Stereochemistry of the Addition of Olefins to Bicyclo[2.1.0]pentane

Sir:

The cycloaddition of carbon–carbon multiple bonds to highly strained carbon–carbon single bonds is one of the more remarkable reactions to appear in the recent chemical literature. Although numerous ex-