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The $C_3H_5^-$ Isomers. Experimental and Theoretical Studies of Tautomeric Propenyl Ions and the Cyclopropyl Anion in the Gas Phase

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Abstract: Isomeric allyl ($CH_2CHCH_2^-$), 2-propenyl ($CH_3C^-{=}CH_2$), 1-propenyl ($CH_3CH{=}CH^-$), and cyclopropyl ($(CH_2)_2CH^-$) anions, as well as the parent unsubstituted vinyl anion ($C_2H_3^-$) have been generated in the gas phase by collision-induced dissociation of the corresponding carboxylate anions by using a Fourier transform mass spectrometer (FTMS). Ion–molecule reactions of each $C_3H_5^-$ ion with selected neutral reagents are described, and distinct, non-interconverting isomeric ion structures are indicated by the results. Each of the vinylic anions and the cyclopropyl anion proton abstracts from ammonia and D_2O while the more stable allylic isomer, $CH_2CHCH_2^-$, is unreactive with the former and undergoes four hydrogen–deuterium exchanges with the latter. Sulfur abstraction from CS_2 is observed with each of the vinyl anions and the cyclopropyl anion, while the allylic ion reacts by addition followed by loss of H_2S. Four unique sets of products are produced by each of the $C_3H_5^-$ isomers in the presence of N_2O which are consistent with the expected structures. Ab initio SCF–MO calculations for each $C_3H_5^-$ ion are also described which provide additional insight into their structures and relative energies.

Rapid and significant progress in gas-phase carbanion chemistry over the last two decades has promoted many new insights into the properties and intrinsic reactivity of this important class of organic reactive intermediate.[1] Gas-phase acidity measurements, negative ion photoelectron spectroscopy, and photodetachment techniques all have made valuable new thermodynamic information available for assessing relative carbanion stabilities.[2-7] Parallel advances in the theoretical treatment of negative ions using ab initio MO methods have also produced new thermochemical and structural data for isolated carbanions which exhibit impressive accuracy when compared with experimental results.[8] These data have significantly influenced current theories concerning delocalization, aromaticity, substituent effects, and anionic hyperconjugation in organic negative ions. Furthermore, the experimentally observed behavior of gas-phase carbanions documented over the last 20 years has repeatedly shown that reaction mechanisms developed for the corresponding species in solution can be successfully applied with only minor variation.[9,10]

While the manifold achievements in gas-phase carbanion chemistry generally have been encouraging, certain key problems in the field have proven difficult to study. For instance, simple, unsubstituted alkyl anions, vinyl anions, and cyclopropyl anions—the carbanion progenitors—are not generally accessible by conventional ionization methods such as electron impact (EI) or proton transfer (CI) and, therefore, their chemistry is virtually unexplored. This is because most alkanes and ethylene either do not produce abundant carbanion fragments upon EI,[11] or are too weakly acidic to give up a proton to the strongest gas-phase bases which are normally available (NH_2^- or OH^-). For example, methane ($\Delta H_{acid}(CH_4) = 416.6$ kcal/mol),[2] the only alkane for which a gas-phase acidity is firmly established, is over 12 kcal/mol less acidic than ammonia ($\Delta H_{acid}(NH_3) = 403.6$ kcal/mol).[2] Moreover, the higher alkanes are predicted by theory[12] and by a recent semiempirical experimental technique[13] to be even weaker acids. In fact, the discouraging conclusion was reached in these studies that alkyl anions beyond CH_3^- are unstable toward electron detachment and, therefore, incapable of isolated existence in the gas phase. Vinyl anion, $C_2H_3^-$, has been observed as a product of a suprathermal proton-transfer reaction between either NH_2^- or OH^- and C_2H_4 in a drift-tube,[14,15] and the best current estimate for the gas-phase acidity of ethylene is 408 ± 3 kcal/mol.[16] Cyclopropane is also estimated to be too weakly acidic to react with NH_2^- at thermal energy ($\Delta H_{acid}(CH_2)_3 \approx 412$ kcal/mol),[13] and no product identifiable as the cyclopropyl anion is formed even with strong-base anions kinetically excited in a drift field.[16] However, substituted vinyl and cyclopropyl anions in the gas phase have been studied since the early 1970's. For instance, vinyl carbanions and related species have been generated by proton abstraction from fluoro-[17] and chloroethylenes,[18] norbornene,[19] norbornadiene,[19,20] cyclooctatetraene,[21] and $CH_2{=}CH{-}X$ de-

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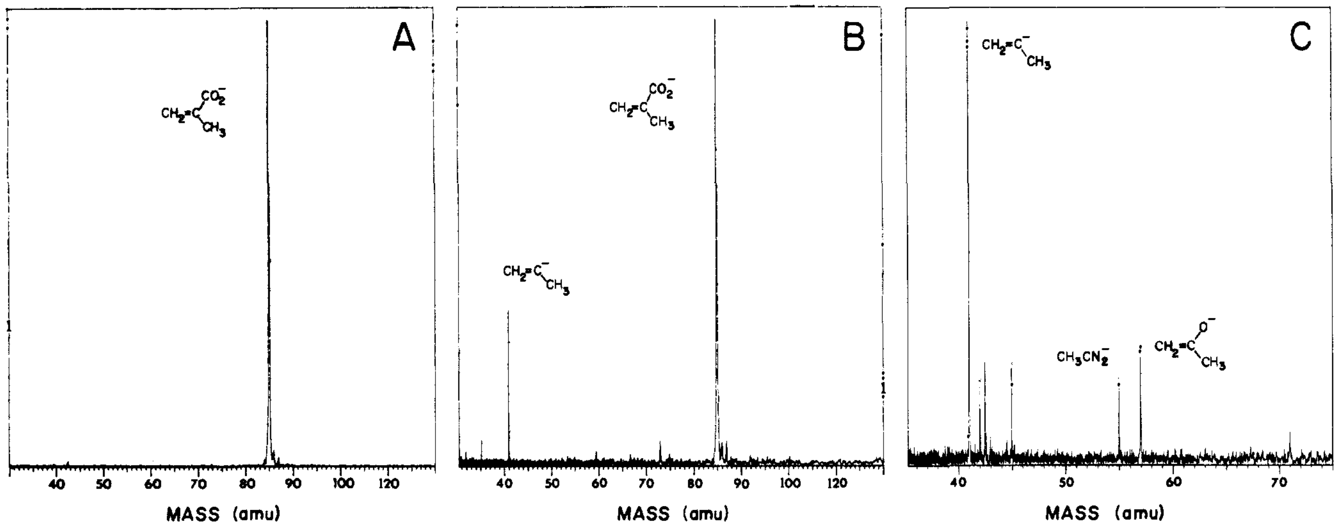


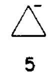
Figure 1. Fourier-transformed mass spectra illustrating the generation of the 2-propenyl anion from (A) electron-impact ionization of trimethylsilyl methacrylate followed by double-resonance isolation of methacrylate ion (m/z 85); (B) irradiation of $CH_2C(CH_3)CO_2^-$ at its cyclotron frequency with a 5.9 V, 0.10 ms CID pulse in the presence of 2 × 10^{-6} torr of Ar; (C) the product spectrum resulting from isolation of the 2-propenyl anion followed by a 250 ms reaction interval in the presence of 2 × 10^{-7} torr of N_2O. Peaks labeled X are identifiable impurities or artifacts. All plots are normalized to the largest peak in the spectrum.

rivatives where X = CN,[22,23] C_6H_5,[23] CHO,[23] NO_2,[22] OCH_3,[24] $CH{=}CH_2$,[25] and $(CH_3)_3C$.[26] Furthermore, the gas-phase reactivity of phenyl- and cyano-substituted cyclopropyl anions has been investigated recently[27,28] and has been shown to differ from that of the corresponding allylic isomers.

We have recently developed a new approach for generating novel ions in the gas phase by collision-induced dissociation (CID) in a Fourier transform mass spectrometer (FTMS). In the present work, we describe an application of this approach to the problem outlined above. Collision-induced dissociation, in its many forms, is the single-most powerful tool available for investigating the structures of gas-phase ions.[29] Used in a different way, CID may also serve as a synthetic tool for creating unusual or otherwise unobtainable ions as fragments from collisional activation of strategically selected precursor ions. For example, we have produced atomic transition metal anions by CID of the corresponding metal carbonyl anions,[30] and we have also shown CID to be useful as a double-bond-forming reaction for creating novel multiply bonded silicon anions.[31] In this paper we demonstrate the use of collision-induced decarboxylation (eq 1) as a method for *regiospecific* carbanion preparation. We illustrate an application of this method to the synthesis of vinyl and cyclopropyl anions in the gas phase, in particular, the series of tautomeric propenyl anions and the parent cyclopropyl and vinyl anions shown below. We also describe molecular orbital calculations on these ions at a uniform level of theory which give insight into their detailed structures and relative stabilities.

$$R{-}CO_2^- \xrightarrow{\text{CID}} R^- + CO_2 \qquad (1)$$

$CH_2{=}CH^-$ 1 $CH_2CHCH_2^-$ 2 $CH_3{-}\bar{C}{=}CH_2$ 3 $CH_3CH{=}CH^-$ 4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Experimental

All experiments were carried out with a prototype Nicolet FTMS-1000 which has been fully documented previously.[32] Briefly, the system incorporates a 5.2 cm cubic trapping cell located between the pole faces of an electromagnet maintained at 0.9 T. Neutral reactant gases were introduced into the cell by means of either a metering-valve manifold or a General Valve Corp. Series-9 pulsed-solenoid valve inlet.[33] The cell pressure was monitored with an uncalibrated Bayard-Alpert ionization gauge which was shut off during data collection intervals to avoid potential problems from neutral pyrolysis.[34] Initial sample ionization was achieved by using either a pulsed electron beam or laser-desorbed electrons generated from a pulsed Nd-YAG laser focussed on a metal target in the cell.

The general strategy and variable pulse sequences employed for CID experiments in the FTMS have been described previously.[32b] In the present work, the cell is initially charged with a static pressure of ca. 2 × 10^{-6} torr of argon collision gas, plus approximately 2 × 10^{-7} torr of a reactive neutral substrate such as N_2O or CS_2. A typical operating sequence is illustrated in Figure 1. It begins with a quench pulse to remove all ions present from the cell followed by a pressure burst from the pulsed-valve of the trimethylsilyl ester reagent used as a precursor for the carboxylate ion (vida infra). As a result, the reagent gas fills the vacuum chamber to a maximum pressure of ca. 1 × 10^{-5} torr and is pumped away within 250 ms by the 5-in. diffusion pump.[33] A 5-10 V, 200 ms electron beam pulse or 7 ns laser pulse is triggered during this high-pressure interval, thus allowing carboxylate ion formation by electron impact on the silyl ester. In a few experiments, a partial pressure of ammonia was also pulsed in along with the trimethylsilyl ester to aid in carboxylate ion formation by NH_2^- chemical ionization.

After a 1.0-s-delay period to permit buildup of carboxylate ion concentration and precursor-gas removal, the cell is cleared of all other ions with broad-band double resonance ejection pulses. Figure 1A shows the resulting mass spectrum of the methacrylate ion, $CH_2C(CH_3)CO_2^-$ (m/z 85). Application of a CID pulse of typically 5.9-V amplitude and 0.1-ms width at the resonant frequency of the carboxylate ion is followed by an additional 35-ms-delay period during which time carboxylate ion frag-

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mentation occurs as a result of multiple activating collisions with the target gas (Figure 1B). Subsequent delay periods of 250-500 ms prior to ion detection enable examination of its ion-molecule reactions. Figure 1C shows the two primary reaction products at *m/z* 55 and 57 which appear when $CH_3CCH_2^-$ is trapped for 250 ms in the presence of N_2O at ca. 2×10^{-7} torr.

A few of the N_2O experiments required accurate mass measurements in order to distinguish possible isobaric product ions. While high resolution operation of the FTMS requires low-pressure conditions,[35] CID experiments and ion-molecule reaction studies normally require higher pressures (10^{-6} torr).[32,36] Pulsed valve addition of the collision gas and/or neutral reagents may alleviate this inconsistency by permitting high resolution ion detection after the target or reagent gas pulse is pumped away.[33] However, in the present work the single pulsed-valve inlet had to be dedicated to the trimethylsilyl ester precursor. Consequently, we adopted a compromise wherein the N_2O reagent gas also served as the collision gas at a static pressure of ca. 5×10^{-7} torr. Under these conditions, a moderate mass resolution (m/Δm) of 4500 could be obtained at nominal mass 41 (64K data points) which was sufficient to distinguish isobars on the basis of differences between calculated and observed masses. Mass calibrant ions were the typical negative ion impurities, CN^- (*m/z* 26.00362) and $^{35}Cl^-$ (*m/z* 34.96940).

Materials. Each of the gaseous reagents described in this study were obtained from commercial vendors and were used as supplied. The nominal purities are Ar (99.995%), NH_3 (anhydrous, 99.99%), N_2O (99.0%), C_2H_4 (99.5%), and C_3H_6 (99.0%). Liquid samples were also obtained from commercial suppliers and were subjected to multiple freeze-pump-thaw cycles prior to use. The D_2O was 99.8 atom % d_2.

Calculations. The ab initio SCF MO calculations were performed with use of a modified version of the GAUSSIAN 76 family of programs[37] on a CDC 6600. Geometry optimizations were carried out by using analytically evaluated gradients and a 3-21G split-valence basis set augmented with a set of diffuse s and p functions for carbon (3-21+G//3-21+G).[8,38] For the cyclopropyl species, the effects of basis set size and polarization functions were evaluated from single point energy calculations with a 6-31+G* basis set when the 3-21+G geometries were used (6-31+G*//3-21+G). In a few cases, correlation corrections were applied by using Møller-Plesset perturbation theory at second (MP2) and third (MP3) order.[39]

Results

Anion Formation. Carbon dioxide loss from substituted benzoate ions subjected to high-energy collisions (7 keV) in a tandem mass spectrometer was first demonstrated by Cooks and coworkers and its analytical utility in mixture analysis was presented.[40] Our initial attempts at exploiting this type of fragmentation in the synthesis of vinyl and cyclopropyl carbanions in the FTMS met with certain difficulties. Consider, for example, the parent vinyl anion ($C_2H_3^-$, *m/z* 27) which may be derived by CO_2 loss from acrylate ion ($CH_2CHCO_2^-$, *m/z* 71). Since carboxylate ions are readily generated from dissociative electron capture by the corresponding neutral carboxylic acid,[11,41] we simply admitted a partial pressure of acrylic acid into the FTMS cell along with argon collision gas and produced an intense acrylate ion signal by electron impact. Subsequent application of a CID-pulse sequence with this parent ion produced a small, though rapidly decaying population of the desired $C_2H_3^-$ fragment. Under these conditions, the highly basic vinyl anion rapidly reacts by proton transfer with the acrylic acid precursor present in the cell. The transient nature of the $C_2H_3^-$ ion signal generated in this way all but precluded an examination of its subsequent reactions with other added substrates. Clearly, the presence of an acidic precursor is inconsistent with the study of a highly basic species in a static system. A better approach would be to utilize the pulsed-valve inlet for admitting the carboxylic acid into the cell only during the initial ionization period and then allowing it to pump out prior to initiating the CID sequence. Unfortunately, acrylic acid and most other carboxylic acids are not sufficiently volatile for direct use with a pulsed valve. Therefore, our final solution involved ex situ derivatization of the acrylic acid with a volatilization agent. Trimethylsilyl esters have been successfully employed in the past as volatile derivatives for use in analytical mass spectrometry—particularly for applications involving carboxylic acids.[42] For our studies, an approximately 1:4 mixture (v/v) of the silylating agent *N,O*-bis(trimethylsilyl)acetamide (BSA, $CH_3C[{=}NSi(CH_3)_3]OSi(CH_3)_3$) and acrylic acid were directly attached to the pulsed valve inlet manifold and the vapors of the resulting trimethylsilylacrylate ester were easily pulsed directly into the FTMS cell during the electron beam interval. Abundant starting concentrations of acrylate ion could be achieved in this way, and after approximately 250 ms the FTMS cell was pumped free of the precursor ester. Subsequent CID of the acrylate ion produced considerably more stable signals of the vinyl anion fragment which could be trapped for up to ca. 1 s, thus allowing more tractable investigation of its ion-molecule reactions. Equation 2 illustrates the synthesis of the vinyl anion by the CID procedure. It appears to be of general utility and we have fashioned a variety of gas-phase

$$CH_2CHCO_2H \xrightarrow{BSA} CH_2CHCO_2SiMe_3 \xrightarrow[\text{pulsed valve}]{e^-} CH_2CHCO_2^- \xrightarrow{CID} CH_2CH^- \quad (2)$$

carbanions by this approach, including enolate ions, benzylic anions, and aryl anions.[43] Table I provides a listing of the anion fragments relevant to this study which we have generated by CID, entries **2–5** representing the $C_3H_5^-$ isomers. We are presently engaged in a detailed examination of the formation and reactions of vinyl ions from *cis*-crotonic acid and homologous cis/trans acids in pursuit of experimental evidence for the configurational stability of gaseous vinyl carbanions. The full details of these studies will be presented in a subsequent publication. In order to simplify the present discussion, the carbanion structures shown in Table

Table I. Gas-Phase Carbanions Produced by Collision-Induced Decarboxylation

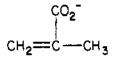
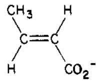
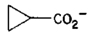
RCO_2^-	R^-	entry
$CH_2{=}CHCO_2^-$	$CH_2{=}CH^-$	**1**
$CH_2{=}CH{-}CH_2CO_2^-$	$CH_2CHCH_2^-$	**2a**
 $CH_2{=}\overset{CO_2^-}{\overset{\vert}{C}}{-}CH_3$	$CH_3{-}\bar{C}{=}CH_2$	**3**
	$CH_3CH{=}CH^-$	**4**
		**5**

Table II. Acid-Base Reactions

	carbanion	source[a]	reaction products[b] D₂O	NH₃
1	$CH_2{=}CH^-$	CID	OD^-	NH_2^-
2a	$CH_2CHCH_2^-$	CID	OD^- + 4 H/D exchanges	NR
2b	$CH_2CHCH_2^-$	NH_2^- + CH_3CHCH_2	OD^- + 4 H/D exchanges	NR
3	$CH_3{-}\bar{C}{=}CH_2$	CID	OD^-	NH_2^-
4	$CH_3CH{=}CH^-$	CID	OD^-	NH_2^-
5		CID	OD^-	NH_2^-

[a] Carbanions derived by carboxylate ion fragmentation indicated by "CID". [b] Product ion/reactant ion relationships confirmed by double resonance.

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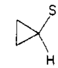
Table III. Reactions with CS_2

reactant ion	product(s)	(m/z)
1	$CH_2{=}CH{-}S^-$	(59)
2a, **2b**	$CH_2{=}CH{-}C{\equiv}C{-}S^-$	(83)
3	$CH_3C(S)CH_2^-$	(73)
4	$CH_3CH{=}CHS^-$	(73)
	trace HS^-	(33)
5		(73)

I are those derived directly from decarboxylation of the corresponding carboxylate. In the following sections we present a description of the reactivity of each of these ions with various structure-probing neutral reagents which supports the given structural assignments.

Acid–Base Reactions. Proton transfer and H/D exchange reactions involving several of the ions listed in Table I were investigated in order to obtain estimates of their basicities, as well as to aid in identifying and distinguishing among the $C_3H_5^-$ isomers. Table II summarizes the results of these experiments. For comparison purposes, an authentic allyl anion ($CH_2CHCH_2^-$, m/z 41) was generated independently by proton transfer to NH_2^- and OH^- from propene. Its well-documented acid–base behavior[2,25,44,45] was reconfirmed under conditions identical with those employed for the CID-generated ions and is included in Table II. In the presence of D_2O, each of the carbanions listed in Table II reacts to produce OD^-, as confirmed by double resonance ejection experiments which unambiguously identify the carbanions as precursors for m/z 18. In addition, ion **2a** and the authentic allylic anion formed by proton abstraction (**2b**) also produce deuterated carbanion products by H/D exchange.[25] When ammonia is present, ions **1**, **3**, **4**, and **5** all react by neutralization to produce NH_2^-, again confirmed by double resonance. In contrast, the allylic ions **2a** and **2b** do not react with NH_3. In one additional experiment not listed in the table, we trapped ion **5** in the presence of ethylene for 500 ms; however, no apparent proton transfer occurred.

Reactions with CS_2. Carbon disulfide has also proven to be a useful structure-probing neutral reagent for gas-phase carbanion studies. Its utility has been developed largely at higher pressures in flowing afterglow experiments where termolecular addition reactions are frequently observed.[46] In the FTMS, each of the ions **1–5** readily reacts with CS_2, in most cases by sulfur abstraction to yield an $(M + 32)^-$ product (Table III). Condensation-type products corresponding to CS_2 addition followed by loss of H_2S are also observed for ions **2a** and **2b**. A trace amount of HS^- (m/z 33) is also observed with **4**. While CS_2^- (m/z 76) was also observed in the mass spectra for several of the ions in Table III, it could not be identified unambiguously as a reaction product from **1–5** due to its persistent formation from trapped thermal electrons.[6]

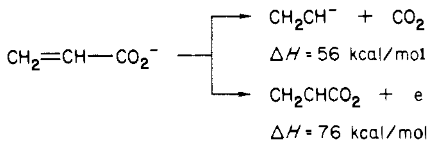
Reactions with Nitrous Oxide. As described in the preceding paper,[47] N_2O is a versatile reagent for gas-phase carbanion studies which has often been useful in the solution of ion structural problems. This is particularly so in the present work, as will become evident in later discussion.

Each of the anions listed in Table I were observed to react rapidly with N_2O which was added to the FTMS cell at a static pressure of approximately 2×10^{-7} torr. Table IV presents a summary of the products observed in each case along with the tentative ion structure assignments based on near-exact mass measurements and the unified mechanistic rationale described in the Discussion section. Approximate branching ratios are also provided when more than one product was observed.

The parent vinyl anion gives three products. The ion appearing at nominal mass 41 (m/z(obsd) = 41.0128 daltons) is assigned as the conjugate base anion of diazomethane, HCN_2^- (m/z(calcd) = 41.014 52 daltons), as opposed to deprotonated ketene, HC_2O^- (m/z(calcd) = 41.003 28 daltons), which could conceivably arise by H_2 loss from m/z 43 (CH_2CHO^-). Similarly, the 2-propenyl anion **3** produces the diazoethane anion $CH_3CN_2^-$ (m/z(obsd) = 55.0317 daltons, m/z(calcd) = 55.030 17 daltons) and not the isobar $C_3H_3O^-$ (m/z(calcd) = 55.018 94 daltons). Acetone enolate, $CH_3C(O)CH_2^-$ (m/z(obsd) = 57.0292 daltons, m/z(calcd) = 57.034 59 daltons), is the only other observed product with ion **3** (Figure 1C). Identifying N_2O reaction products from the various $C_3H_5^-$ ions was a particularly challenging exercise since two conceivable products (HCN_2^- and HC_2O^-) possess the same nominal mass as the reactant ions ($C_3H_5^-$, m/z(calcd) = 41.039 67 daltons). Fortunately, all three isobars could just be distinguished under the near-high-resolution conditions achieved in independent control experiments. As shown in Table IV, only isomer **4** produced a new m/z 41 product in the presence of N_2O which was shown to be HCN_2^-. Two other product ions at m/z 39 and m/z 67 are also produced by **4**. Ion **5** gives rise to a single product corresponding to loss of H_2 (m/z 39), while both **2a** and **2b** show identical behavior in producing a sole product at m/z 67. It is important to emphasize here that each of the $C_3H_5^-$ isomers **2–5** produced a distinct set of product ions in the presence of N_2O.

Discussion

In order to put our ion synthesis method into proper perspective, we first present a brief discussion of the energetics for collision-induced decarboxylation. In general, low-energy collisional activation of a gaseous negative ion may result in fragmentation and/or electron detachment, with the branching mainly controlled by the relative potential energy barriers and densities of microscopic pathways available for each channel.[48] In the present system, the large electron binding energies of carboxylate ions (>75 kcal/mol)[2,49] make decarboxylation the favored mode of decomposition in every case considered. For example, estimates of the thermochemistry for CO_2 dissociation vs. electron detachment from acrylate ion indicate that the former reaction is favored by approximately 20 kcal/mol (eq 3).[50] Similarly, for cyclopropanecarboxylate and 3-butenoate ions, CO_2 loss is favored over detachment by roughly 15 and 37 kcal/mol, respectively.[50]



(3)

This situation should be generally true. However, since many carbanions are only weakly bound species with electron binding energies typically less than 1 eV, we must also consider the

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(44) (a) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131–140. (b) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153–5159.

(45) (a) Dawson, J. H. J.; Noest, A. J.; Nibbering, N. M. M. *Int. J. Mass. Spectrom. Ion. Phys.* **1979**, *29*, 205–222. (b) Klass, G.; Trenerry, V. L.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519–529.

(46) (a) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389–1393. (b) Anderson, D. R.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 4244–4248. (c) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556.

(47) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.*, preceding paper in this issue.

(48) Acharya, P. K.; Kendall, R. A.; Simons, J. *J. Am. Chem. Soc.* **1984**, *106*, 3402–3407.

(49) Bartmess, J. E. *J. Phys. Chem. Ref. Data, Suppl.*, in press.

(50) $\Delta H_f[CH_2CH^-,g]$ = 53.3 kcal/mol (ref 16); $\Delta H_f[CH_2{=}CHCO_2H,g]$ = −76.7 kcal/mol, based on the measured liquid phase value (−91.7 ± 0.2 kcal/mol, ref 51) and an estimated ΔH_{vap} = 15.0 kcal/mol; $\Delta H_f[CH_2{=}CHCO_2^-,g]$ = −96.4 kcal/mol, based on an estimate for ΔH_{acid} $CH_2{=}CHCO_2H$ ≈ 346 kcal/mol; $\Delta H_f[(CH_2)_2CH^-,g]$ = 59 ± 3 kcal/mol, based on $\Delta H_{acid}[(CH_2)_3]$ = 412 kcal/mol (ref 13) and $\Delta H_f[(CH_2)_3]$ = 12.74 ± 0.12 kcal/mol (ref 51); $\Delta H_f[(CH_2)_2CHCO_2^-,g]$ = −96.9 kcal/mol, based on $\Delta H_f[(CH_2)_2CHCO_2H,g]$ = −77.2 kcal/mol (ref 52) and an estimated acidity for this compound of ≈346 kcal/mol. $\Delta H_f[CH_2CHCH_2^-,g]$ = 29.5 ± 0.9 kcal/mol (ref 53); $\Delta H_f[CH_2{=}CHCH_2CO_2^-,g]$ = −101.8 kcal/mol, based on $\Delta H_f[CH_2{=}CHCH_2CO_2H,g]$ = −82.2 kcal/mol (ref 52) and an estimated acidity of ≈346 kcal/mol; $\Delta H_f[CO_2,g]$ = −94.05 kcal/mol (ref 51).

(51) Pedley, J. B.; Rylance, J. Sussex-NPL Computer Analyzed Thermochemical Data, V. Sussex, 1977.

(52) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

Table IV. Reactions with Nitrous Oxide

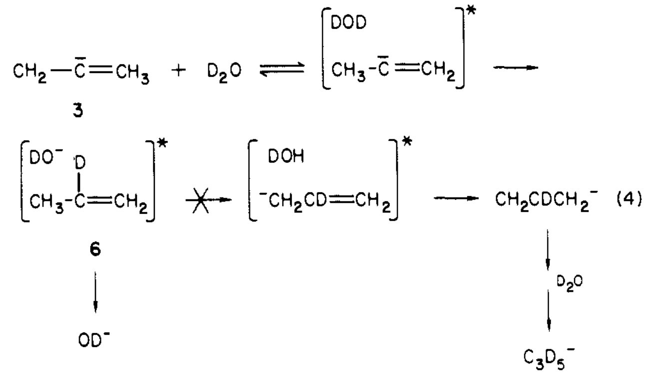
reactant ion		(*m*/*z*, obsd)	product(s)	(*m*/*z*, obsd)	path[a]	%
1	$CH_2{=}CH^-$	(27)	HC_2^-	(25)	D	74
			HCN_2^-	(41.0128)	M	13
			CH_2CHO^-	(43)	O	13
2a	$CH_2CHCH_2^-$	(41)	$CH_2{=}CHCN_2^-$	(67)	V	100
2b	$CH_2CHCH_2^-$	(41)	$CH_2{=}CHCN_2^-$	(67)	V	100
3	$CH_3{-}\bar{C}{=}CH_2$	(41)	$CH_3CN_2^-$	(55.0317)	M	50
			$CH_2{=}C(O)CH_3^-$	(57.0292)	O	50
4	$CH_3CH{=}CH$-	(41.0397)	$CH_3C{\equiv}C^-$	(39)	D	50
			HCN_2^-	(41.010)	M	*b*
			$CH_2{=}CHCN_2^-$	(67)	V	50
5		(41)		(39)	D	100

[a] Product-formation mechanisms: dehydrogenation (D), oxygen/diazo metathesis (M), oxygen abstraction (O), and vinyldiazomethane anion formation (V). See text for discussion. [b] Relative yield of this product ion not determinable under the conditions required for its detection.

possibility that electron detachment may occur from the initially formed organic anion. This can happen, for example, if the carbanion fragment retains a significant amount of internal and/or kinetic energy from collisional activation above the decarboxylation threshold. Low CID efficiencies were observed with most of the ions in this study (~5%), indicating either significant daughter ion loss or low CID cross sections. In the case at hand, vinyl anion has an estimated electron binding energy of 13.6 ± 6 kcal/mol.[16] Its appearance in our experiments implies that this species is sufficiently stable to survive its "violent" birth and does not completely succumb to collision-induced detachment once it is formed. Anticipating the ion–structure proofs in the next section, we may apply this same conclusion to the parent cyclopropyl anion since it was also observed. The best current estimate for its electron binding energy is 8 kcal/mol.[13] It is worthwhile to note in this context that the enthalpy of isomerization of cyclopropyl anion to the allyl anion is approximately 30 kcal/mol.[45c] If such a rearrangement were to occur as a result of the CID synthesis, then an allyl anion with an internal energy in excess of its own electron binding energy (8.35 ± 0.46 kcal/mol)[20,53,54] would result. Under the low-pressure conditions of the FTMS, autodetachment of the electron would be likely to follow.

Reactivity and Structure. The observed behavior of each of the CID-generated ions in the presence of various neutral reagents provides good support for the structures depicted in Table I. First of all, the occurrence of proton abstraction from both D_2O (ΔH_{acid} = 392.9 kcal/mol)[49] and NH_3 (ΔH_{acid} = 403.6 kcal/mol)[2,49] by ions **1** and **3**–**5** is consistent with the expected basicity of vinyl and cyclopropyl carbanions. That is, the parent vinyl ion has an estimated proton affinity of 408 ± 3 kcal/mol,[16] and the methylated derivatives **3** and **4** should have similar values (vide infra). The cyclopropyl anion **5** is estimated to have an even greater basicity. However, this is inherently difficult to substantiate by direct proton transfer reactions since ethylene is the only neutral compound whose acidity is known to lie between that of methane and ammonia.[2] Under our conditions, no proton transfer from C_2H_4 to ion **5** could be observed when these species were trapped together in the FTMS cell for up to 500 ms. The absence of observable reaction in this case is likely to be kinetic in origin since the thermodynamic driving force for proton transfer between cyclopropyl anion and ethylene is not expected to be large (ca. 4 kcal/mol), and reduced rates of reaction between nonpolar hydrocarbon acids and either delocalized or localized carbanion bases are common.[55,56]

The occurrence of 4 H/D exchanges in ion **2a** with D_2O plus its lack of reactivity in the presence of NH_3 clearly differentiates this species from the other *m*/*z* 41 ions and, by comparison with the behavior of **2b**, verifies its identity as the allyl anion (PA = 391.3 kcal/mol).[25,45] At the same time, these results suggest that an allyl anion generated by CID behaves "normally" and, therefore, that ions **3**–**5** are not just different vibrationally excited forms of $CH_2CHCH_2^-$.[54] If this were the case, then the allyl anion derived from 3-butenoate decarboxylate might be expected to exhibit anomalous behavior which was similar to that of **3**–**5**. The complete absence of H/D exchange in reactions between D_2O and either **3** or **4** has some interesting implications. Evidently, dissociation of the energy-rich ion–molecule complex **6** following exothermic deuterium transfer to the vinyl position is so fast that reabstraction of an allylic proton does not occur (eq 4). If it did, then an isomerized carbanion would result which is capable of undergoing further H/D exchange. This may be contrasted with



results from higher pressure experiments in a SIFT apparatus (0.4 torr) which demonstrated that multiple proton exchanges may occur within an ion–molecule collision complex, even during the course of a highly exothermic proton transfer reaction.[57]

The observed CS_2 reaction products also serve to differentiate the allylic ions **2a** and **2b** from the vinyl and cyclopropyl anions (Table III). It has previously been noted that strongly basic anions such as aryl and vinyl ions generally react with CS_2 by sulfur abstraction.[46] Furthermore, weaker base carbanions or delocalized species either do not react at all or undergo condensation reactions in which H_2S or HS^- is eliminated from an initial CS_2 adduct. This is precisely the behavior exhibited by **1**–**5**. Thus, each of the proposed vinyl anions and the cyclopropyl anion react by sulfur transfer, while the allylic ions **2a** and **2b** react identically and produce condensation products ($C_3H_5^- + CS_2 - H_2S$, *m*/*z* 83). The thioketenyl anion product structure depicted in Table III is derived by analogy with related CS_2 reaction products recently reported by DePuy and co-workers.[46]

We now turn to an analysis of the reactions involving N_2O which have proven to be the most structurally illuminating. The parent vinyl anion **1** and the authentic allylic carbanion **2b** shall serve as prototype reactants for this discussion since their structures are established and the mechanisms by which they react have been found to be generally applicable. Nitrous oxide reacts with allyl anion **2b** by an addition–dehydration mechanism first proposed

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(53) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734–7741.

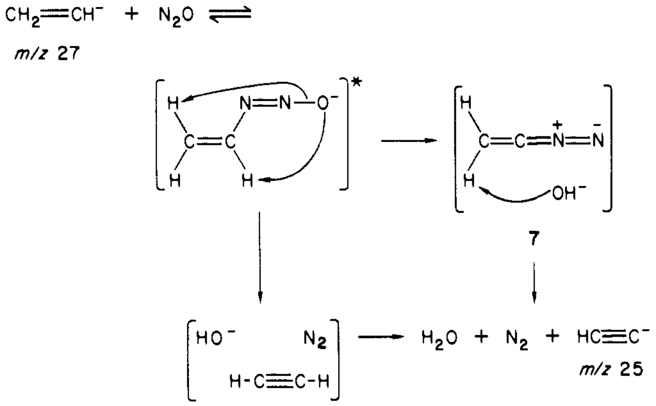
(54) Wight, C. A.; Beauchamp, J. L. *J. Phys. Chem.* **1984**, *88*, 4426–4430.

(55) Albritton, D. L. *At. Data. Nucl. Data Tables* **1978**, *22*, 1-101.

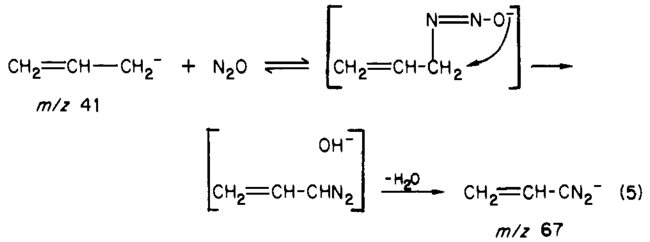
(56) (a) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891-7898. (b) Brauman, J. I. In "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979.

(57) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185-5192.

Scheme I



by Bierbaum et al.[58] (eq 5). This reaction has also been observed in a Fourier transform ion cyclotron resonance spectrometer (FT–ICR) by Nibbering and co-workers,[45c] who employed deuterium-labeled allyl anions to confirm the proposed mechanism

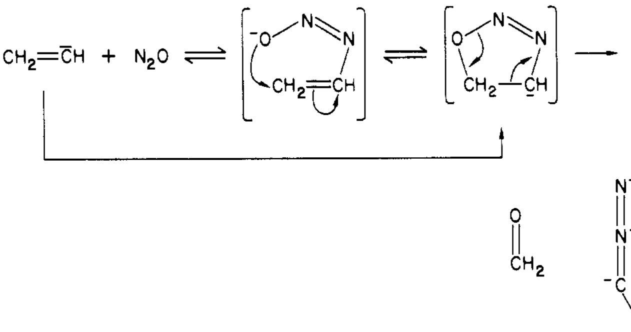


(5)

and demonstrate the absence of hydrogen scrambling in gaseous allyl anions. Initial addition of most carbanions to N_2O has been shown to occur at the terminal nitrogen.[59] Subsequent intramolecular proton transfer followed by expulsion of H_2O leads to the vinyldiazomethane anion (*m/z* 67). Interestingly, a second product is produced when this reaction is carried out under flowing afterglow conditions (0.5 torr) which corresponds to overall H_2 loss (*m/z* 39). As described in the preceding paper,[47] this product has been assigned the allenyl anion structure, CH_2CCH^-. It is not observed in the present study for either ion **2a** or **2b**, nor was it observed as a product in the earlier FT–ICR work.[45c] The origins of this inconsistency are not immediately obvious but may lie in differing lifetimes for the reactive ion–molecule collision complexes at high (0.5 torr) and low (10^{-6} torr) pressure.[60]

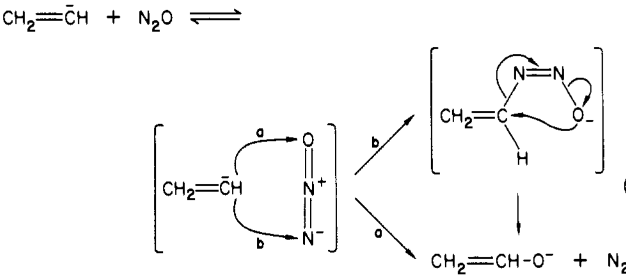
The parent vinyl anion $C_2H_3^-$ nicely illustrates the three commonly observed reactions of N_2O with this class of carbanion. This particular pair of reactants has also been examined previously in a higher pressure SIFT-drift experiment and the same three products were observed.[16] The dehydrogenation product (*m/z* 25) can arise by at least two conceivable stepwise mechanisms (Scheme I). Initial addition at the terminal nitrogen of N_2O produces an excited diazenyl oxide ion which can decompose by intramolecular abstraction of either the α or cis-β proton. In the former case, the resulting hydroxide ion can induce elimination of nitrogen from diazoethylene in a manner reminiscent of the Bamford–Stevens reaction.[61] Alternatively, initial attack at the β-hydrogen produces an acetylene, nitrogen, and hydroxide ion complex which can decompose to the same products. Dehydrogenation of a variety of cyclic and acyclic allylic anions by N_2O is described in the preceding paper.[47] For these reactions, mechanisms involving diazo-type intermediates analogous to complex **7** are proposed since the alternative (triple-bond-forming) mechanism is improbable for the smaller ring allylic ions examined.

Scheme II



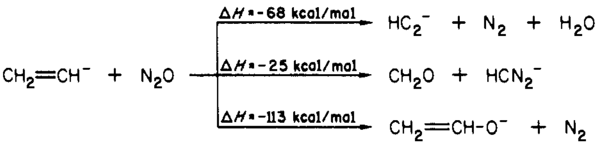
The diazomethane anion product derives from a metathesis-type mechanism which is believed to involve a cyclic intermediate (Scheme II). This species may be formed in an allowed 1,3-dipolar [π^4s + π^2s] cycloaddition,[62] or in a stepwise fashion via the diazenyl oxide ion adduct. This same type of reaction is observed with the (M − H)⁻ ion from 1,3-butadiene[58] and is postulated to account for the formation of phenoxide ion from the reaction between $C_6H_5^-$ and N_2O.[47] It appears to be a general reaction for vinyl carbanions.

Finally, oxygen transfer to give CH_2CHO^- (*m/z* 43) may occur by direct attack at oxygen or by an ipso mechanism involving the initial diazenyl oxide adduct (eq 6). Experimental evidence has been reported which supports the latter mechanism and demonstrates that oxygen transfer from N_2O is a general reaction for vinyl and aryl anions with proton affinities ≥ ca. 390 kcal/mol.[47]



(6)

The three reactions observed for the parent vinyl anion with N_2O are strongly exothermic (eq 7).[63] Considering the extremely large enthalpy for oxygen transfer, it is somewhat surprising that the observed *m/z* 41 product ion is *not* HC_2O^-, formed by H_2 loss from CH_2CHO^-, but rather the diazomethane anion (HCN_2^-). It can be shown independently that CH_2CHO^- does indeed eliminate H_2 when collisionally activated.[64] Evidently, either the N_2 product from the oxygen transfer must be apportioned an appreciable amount of the overall reaction exothermicity or H_2 elimination is slow under the present conditions.



(7)

In order to facilitate discussion of how these four general reactions of N_2O apply to ions **3**–**5**, they will be referred to as V for vinyldiazomethane anion formation (eq 5), D for dehydrogenation (Scheme I), M for the oxygen/diazo metathesis reaction (Scheme II), and O for oxygen abstraction (eq 6). The appropriate labels are indicated for each reaction product in Table IV.

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[58] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800–5802. See also: Smit, A. L. C.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 6471.

[59] (a) Dawson, J. H. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1928–1929. (b) Tiernan, T. O.; Clow, R. P. *Adv. Mass Spectrom.* **1974**, *6*, 295–302.

[60] For pertinent comments on this point, see: King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133–7140. Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959–966.

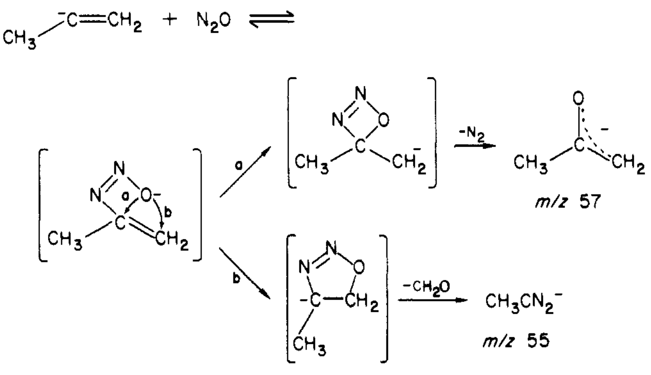
[61] Bamford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735–4740.

[62] Huisgen, R. *Angew. Chem., Intl. Ed. Engl.* **1963**, *2*, 565–632.

[63] $\Delta H_f[HCN_2^-,g]$ = 75.3 kcal/mol, based on $\Delta H_f[H_2CN_2,g]$ = 71 kcal/mol (ref 52) and an estimated acidity for diazomethane of ≈370 kcal/mol. All other heats of formation taken from ref 49 or 51.

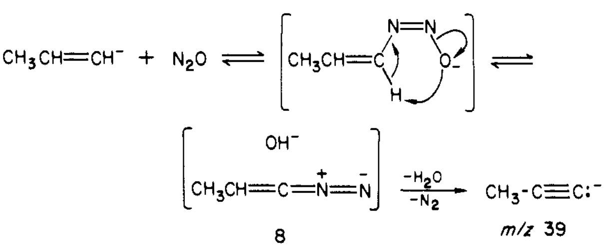
[64] Froelicher, S. W.; Lee, R. E.; Squires, R. R.; Freiser, B. S. *Org. Mass Spectrom.* **1985**, *20*, 4–9.

Scheme III



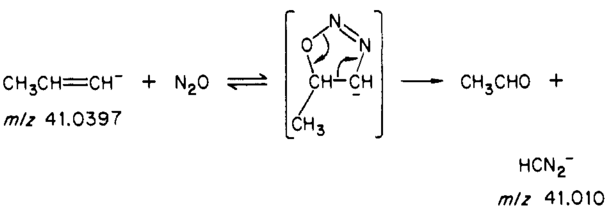
The $C_3H_5^-$ derived from 3-butenoate decarboxylation **2a** reacts exclusively by path V. This further supports the allylic ion structural formulation and provides an additional example of "normal" behavior for the CID-generated carbanion. In contrast, ion **3** gives two products via paths M and O. The complete absence of dehydrogenation (D) in this case is significant. It supports the view that an α-hydrogen at the charged site of the carbanion is required for this reaction and strongly suggests that diazoalkene or alkane ions such as **7** are obligatory intermediates. Scheme III outlines the mechanisms proposed for ion **3**, which derive from straightforward analogy with the mechanisms for the parent vinyl ion. It is interesting to note that ion **3** is the only $C_3H_5^-$ isomer which produces an oxygen abstraction product. This may be due to the fact that oxygen transfer is an inherently slower reaction which becomes unmasked when faster reactions such as dehydrogenation are precluded.

The $C_3H_5^-$ ion from *trans*-crotonate (**4**) gives N_2O reaction products assignable to pathways D, M, and V. The $C_3H_3^-$ dehydrogenation product ion is assigned the acetylide structure as opposed to the propargylic (allenyl) structure since the former derives from the putative 1-diazopropylene intermediate **8** (eq 8). The metathesis product, HCN_2^-, is produced in the same way as



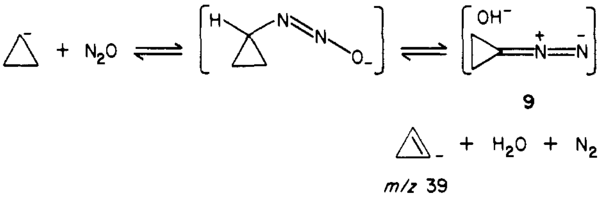
(8)

it is formed from the parent vinyl anion; in this case acetaldehyde is the neutral product (eq 9). Vinyldiazomethane anion formation (V) proceeds somewhat differently, however. The neutral 1-diazopropylene in complex **8** above is simply a tautomeric form of vinyldiazomethane as depicted in eq 5. Thus, proton abstraction from the methyl group in **8** followed by dissociation of water from the complex directly produces the observed vinyldiazomethane anion product (*m/z* 67).

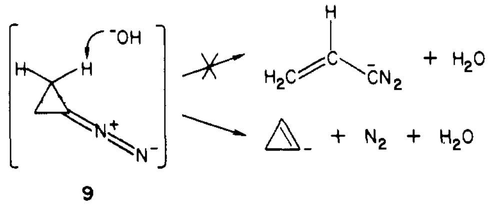


(9)

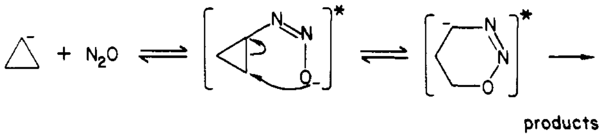
Cyclopropyl anion **5** undergoes exclusive dehydrogenation in the presence of N_2O. On the strength of the foregoing discussion, it is reasonable to presume that the observed *m/z* 39 product is the 1-cyclopropenyl anion derived by N_2 elimination from diazocyclopropane (eq 10). Experiments to rigorously test this hypothesis by comparison of the reactivity of this product ion with that of an authentic 1-cyclopropenyl carbanion are currently in progress. The absence of pathway V or M in the case of ion **5** has some interesting implications. Evidently, elimination within complex **9** by C–N cleavage occurs preferentially over the C–C cleavage which would be required for vinyldiazomethane anion formation (eq 11). An alternative possibility here is that vinyldiazomethane anion *is* produced as in eq 11 but it rapidly fragments by N_2 loss to yield the observed $C_3H_3^-$ product. This is made unlikely, however, since an independently generated vinyldiazomethane anion (from **2b** + N_2O) did *not* produce a $C_3H_3^-$ daughter ion when subjected to collisional activation.[65] It may also be noted that if the "usual" metathesis mechanism were to proceed with ion **5**, it would produce a highly vibrationally excited oxadiazinyl anion (eq 12). Apparently, either the ring-opening reaction shown above does not occur or the oxadiazinyl ion intermediate further fragments to either $C_3H_3^-$ or undetected products (e.g., free electrons and neutral molecules).



(10)



(11)



(12)

We conclude from the differing reactivity exhibited by ions **2–5** that they are distinct chemical species which do not interconvert under the conditions of the experiments. Furthermore, the specific behavior shown by each $C_3H_5^-$ ion in the presence of N_2O is consistent with our expectations based on the known reactions of N_2O and the anion structures assigned in Table I. Thus, collision-induced decarboxylation of carboxylate ions can be used to synthesize gas-phase vinyl carbanions with complete regiospecificity. Moreover, the method appears to be applicable to the production of highly basic and reactive species, such as the cyclopropyl anion, under conditions where subsequent examination of their bimolecular reactions is possible.

Theoretical Studies. In order to provide additional insight into the structures and relative energies of the $C_3H_5^-$ isomers which have been generated in this study, we present here ab initio HF/SCF-MO calculations on each ion and the corresponding conjugate acids. Analogous calculations for ethylene and the parent vinyl anion are also included for comparison. Calculations on these ions at similar or higher levels of theory have recently been reported by Schleyer and co-workers.[8] For the present investigation, we required additional calculations of the structures and energies of the corresponding inversion transition states for each ion; therefore an entire set of computations at a uniform level of theory was performed. Table V presents a summary of the computational results, including absolute and relative energies for each species along with the resulting proton affinities and inversion barriers for each negative ion. Following the recommendations of Schleyer,[8b] methyl stabilization energies as defined by eq 13 are also tabulated for each ion. Molecular geometries

$$CH_3^- + RH \rightarrow CH_4 + R^- \qquad (13)$$

optimized within the constraints of C_s symmetry when a 3-21+G

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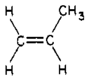
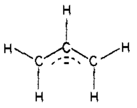
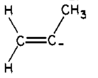
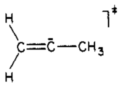
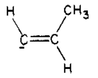
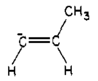
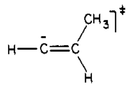
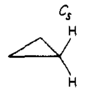
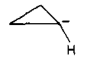
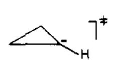
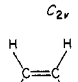
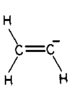
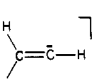
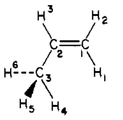
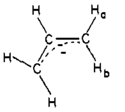
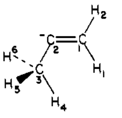
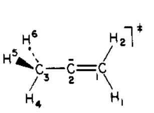
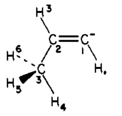
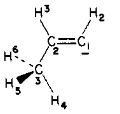
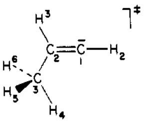
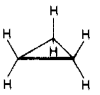
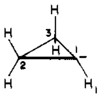
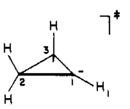
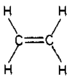
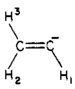
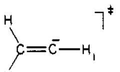
(65) Froelicher, S. W.; Freiser, B. S.; Squires, R. R., unpublished results. For related examples where nitrogen loss is observed, see ref 46c.

Table V. Calculated Total Energies, Stabilization Energies, Proton Affinities, and Inversion Barriers for Vinyl and Cyclopropyl Anions[a]

species	-E(3-21+G// 3-21+G)	$\Delta E(13)$[b]	proton affinity	ΔE_{inv}[c]
 C_s	116.432 77			
 C_{2v}	115.789 12	-27.8	403.9	
 C_s	115.764 04	-12.1	419.6	42.2
 C_s	115.696 81			
 C_s	115.759 26	-9.1	422.6	28.5
 C_s	115.759 23	-9.0	422.7	28.5
 C_s	115.713 77			
 D_{3h}	116.406 43[d]			
 C_s	115.718 67[d]	-0.1	431.6	18.4
 C_{2v}	115.689 35			
 D_{2d}	77.607 92[e]			
 C_s	76.937 81[e]	-11.2	420.5	30.4
 C_{2v}	76.889 29			

[a] Total energies in hartrees; relative energies and proton affinities given in kcal/mol. [b] Methyl stabilization energies as defined by eq 13. E(3-21+G//3-21+G): CH_3^- = -39.290 75 au; CH_4 = -39.978 71 au taken from ref 38. [c] Energy difference between minimum energy (bent) structure and carbanion inversion transition structure. [d] E(6-31+G*//3-21+G): $(CH_2)_3$ = -117.060 47 au; $(CH_2)_2CH^-$ = -116.371 27 au. The computed proton affinity for cyclopropyl anion at this level is 432.5 kcal/mol. [e] E(MP2/3-21+G//3-21+G): C_2H_4 = -77.789 81 au; $C_2H_3^-(C_s)$ = -77.127 83 au; $C_2H_3^-(C_{2v})$ = -77.082 71 au. E(MP3/3-21+G//3-21+G): C_2H_4 = -77.806 33 au; $C_2H_3^-(C_s)$ = -77.139 80 au; $C_2H_3^-(C_{2v})$ = -77.093 29 au. The proton affinities and inversion barriers at these two levels are 415.4 (28.3) and 418.3 (29.2) kcal/mol, respectively.

Table VI. Calculated 3-21+G Geometries

species	point group	bond distances Å		angles (deg)	
	C_s	C_1C_2 C_2H_3 C_1H_1 C_1H_2 C_2H_3 C_3H_4 C_3H_5	1.321 1.510 1.076 1.074 1.078 1.084 1.086	$C_1C_2C_3$ $H_1C_1C_2$ $H_2C_1C_2$ $H_3C_2C_1$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	124.8 121.9 121.6 119.4 111.3 110.7 120.5
	C_{2v}	CC CH CH_a CH_b	1.387 1.086 1.077 1.078	CCC HCC H_aCC H_bCC	131.2 114.4 120.9 121.7
	C_s	C_1C_2 C_2C_3 C_1H_1 C_1H_2 C_3H_4 C_3H_5	1.350 1.547 1.098 1.081 1.102 1.089	$C_1C_2C_3$ $H_1C_1C_2$ $H_2C_1C_2$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	114.7 123.6 122.2 114.1 109.9 121.5
	C_s	C_1C_2 C_2C_3 C_1H_1 C_1H_2 C_3H_4 C_3H_5	1.313 1.460 1.112 1.113 1.114 1.097	$C_1C_2C_3$ $H_1C_1C_2$ $H_2C_1C_2$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	181.7 125.7 125.6 118.3 111.2 121.5
	C_s	C_1C_2 C_2C_3 C_1H_1 C_2H_3 C_3H_4 C_3H_5	1.350 1.538 1.113 1.086 1.088 1.093	$C_1C_2C_3$ $H_1C_1C_2$ $H_3C_2C_1$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	127.9 110.7 119.8 110.2 111.9 120.0
	C_s	C_1C_2 C_2C_3 C_1H_2 C_2H_3 C_3H_4 C_3H_5	1.348 1.534 1.106 1.093 1.092 1.088	$C_1C_2C_3$ $H_2C_1C_2$ $H_3C_2C_1$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	123.0 110.8 123.9 111.4 111.1 120.4
	C_s	C_1C_2 C_2C_3 C_1H_2 C_2H_3 C_3H_4 C_3H_5	1.304 1.557 1.055 1.108 1.084 1.094	$C_1C_2C_3$ $H_2C_1C_2$ $H_3C_2C_1$ $H_4C_3C_2$ $H_5C_3C_2$ $\angle H_5C_3C_2C_1$	127.4 181.3 124.3 109.3 110.8 120.5
	D_{3h}	CC CH	1.515 1.073	HCH	114.8
	C_s	C_1C_2 C_2C_3 C_1H_1 C_2H_2 C_2H_3	1.562 1.531 1.097 1.078	$C_1C_2C_3$ $H_2C_2C_3$ $H_3C_2C_3$ $H_1C_1C_2$	60.6 115.6 118.7 111.9
	C_{2v}	C_1C_2 C_2C_3 C_1H_1 C_2H_2	1.471 1.571 1.060 1.092	$C_1C_2C_3$ $H_2C_2C_3$	64.6 115.9
	D_{2d}	CC CH	1.320 1.074	CCH	121.8
	C_s	CC CH_1 CH_2 CH_3	1.358 1.109 1.094 1.083	CCH_1 CCH_2 CCH_3	110.5 125.3 121.5
	C_{2v}	CC CH_1 CH_2	1.315 1.055 1.103	CCH_2	125.1

basis set is used are provided in Table VI.

Geometries. The present results may be compared with previous calculations on acyclic $C_3H_5^-$ ions by Schleyer and co-workers,[8] Mackay, Lien, Hopkinson, and Bohme (MLHB),[45a] and Boerth and Streitwieser (BS).[66] On the whole, the computed geometries in Table VI are in reasonable agreement with those reported in the earlier studies. The most recent calculations[8b] employed complete optimizations with a 4-31+G basis, while MLHB and BS utilized full and/or partial geometry optimizations with a minimal (STO-3G) basis set. The most outstanding structural feature, which has long been recognized computationally,[8,67] is that simple vinyl and cyclopropyl carbanions favor bent and pyramidal geometries, respectively. Analogous geometrical preferences have been found experimentally for the corresponding isoelectronic imines and aziridines.[68] Vinyl and cyclopropyl radicals also exhibit bent structures, albeit with small inversion barriers, and vinyl cations are shown by theory to favor bridged geometries.[69,70] The bent structures favored by vinyl carbanions represent a balance between minimal bonding electron pair repulsions in the linear $C{=}C^-{-}R$ geometry (although maximal lone pair/bond pair repulsion) and optimal lone-pair orbital stability in the perpendicular geometry. For cyclopropyl anion, the small internuclear bond angles about the deprotonated carbon are best accommodated by sp^3-like (pyramidal) hybridization. Nonlinearity in vinyl carbanions produces additional structural consequences. As noted in previous theoretical studies,[8,66,67] vinylic carbanions generally exhibit increased bond lengths to and decreased bond angles between the two substituents flanking the deprotonated carbon relative to the parent olefin. For example, the CCC angle in propene shrinks by $\sim 10°$, and the C_1–C_2 and C_2–C_3 distances increase by 0.03–0.04 Å as a result of proton removal from the central carbon atom. Similarly, a 0.04-Å increase in $r(C_1\text{–}H)$ and an 11° decrease in $\angle C_2C_1H$ can be seen in comparing propene with the 1-propenyl anion. This has been rationalized in VSEPR terms as an effect of lone pair/bond pair repulsion.[45a] A complementary view can be formulated by using simple hybridization arguments. As the bond angle between the α-substituent and the double bond decreases, the lone pair orbital is stabilized by the corresponding increase in s-character. Accompanying this is an increased p-character in the bond to the α-substituent and a concomitant bond lengthening. In the limiting case of a 90° bond angle, an sp-hybridized lone pair and pure p bond to the α-substituent would result. A clear manifestation of this same type of rehybridization is also apparent in the inversion transition-state structures for vinyl and both propenyl ions, where significantly shortened α(C–C) and α(C–H) distances are found. As pointed out by Streitwieser,[67a] the geometry changes noted above couple vinyl carbanions to α-elimination reactions. That is, were the α-substituent to be an electronegative group, complete dissociation *via* a near-perpendicular geometry could occur to yield a vinylidene carbene. An analogous interplay among geometrical parameters is evident for the cyclopropyl anion. The three bonds to the negatively charged carbon are longest in the pyramidal anion, shortest in the planar inversion transition structure, and of intermediate length in cyclopropane. Accompanying the pyramidal-to-planar interconversion is an increase in the $C_2C_1C_3$ bond angle and, correspondingly, the C_2C_3 distance.

Energies. In accordance with experimental observations[45] and previous theoretical studies,[8,66,67] the allylic $C_3H_5^-$ isomer is determined to be the most stable by a large margin, and the cyclopropyl anion is found to be the highest energy species (Table V). Of the vinyl anions, the 2-propenyl isomer is the most stable by 3 kcal/mol. No difference in energy between the *cis*- and *trans*-1-propenyl diastereomers is evident at this level of theory, although a barrier of 28.5 kcal/mol is calculated for their interconversion via the near-linear C_s transition structure. The present results are generally in good agreement with the computed energy differences for isomeric $C_3H_5^-$ ions recently reported by the Erlangen group.[8b] The computed proton affinities listed in Table V are ca. 12–13 kcal/mol too high compared to the experimental values for allyl (391.3 kcal/mol)[45a] and vinyl (408 ± 3 kcal/mol).[16] Larger basis sets and/or inclusion or correlation corrections (MP3/3-21+G//3-21+G) reduce the differences by 2–3 kcal/mol. Incorporation of zero-point energy corrections determined from the computed vibrational frequencies may further reduce the errors somewhat.[8,71] We note that the difference between calculated and experimental proton affinities for allyl and vinyl anions is roughly constant at 13 ± 1 kcal/mol. If we apply this correction factor to the computed proton affinities for the remaining $C_3H_5^-$ ions, we arrive at final estimates of 407 kcal/mol for the 2-propenyl anion, 410 kcal/mol for both (*Z*)- and (*E*)-1-propenyl anions, and 419 kcal/mol for the cyclopropyl anion. These estimates are consistent with the experimentally observed acid–base behavior of each ion. However, the corrected proton affinity for cyclopropyl anion is ca. 7 kcal/mol greater than the experimental estimate given by DePuy et al. (412 kcal/mol),[13,45c] and it seems unlikely that it should exceed that for the methyl anion (416.6 kcal/mol).[2] We note in this context that ab initio calculations involving cyclopropane and its derivatives are often found to require polarization functions for an adequate description of the severely distorted σ bonds.[72] However, in the present system the diffuse s- and p-type functions apparently provide sufficient flexibility in the smaller 3-21+G basis set since the computed 6-31G* and 3-21+G geometries and proton affinities for cyclopropyl anion are very nearly the same.[38]

Comparison of the relative energies and proton affinities for the $C_3H_5^-$ ions with the parent vinyl anion permits an assessment of methyl-substituent effects on both vinyl CH acidity and vinyl carbanion inversion barriers. The calculated PA order $CH_3{-}C^-{=}CH_2 < CH_2{=}CH^- < CH_3CH{=}CH^-$ implies that α-methyl substitution on an sp^2 carbon increases C–H acidity while β-methyl substitution has an acidity decreasing effect. The latter substituent effect is analogous to that which is found experimentally for terminal alkynes, viz., acetylene is a stronger acid than propyne by 4.3 kcal/mol.[2] A similar β-effect is also evident between formic acid ($\Delta H_{\text{acid}} = 345.2$ kcal/mol) and acetic acid ($\Delta H_{\text{acid}} = 348.5$ kcal/mol) and between acetaldehyde ($\Delta H_{\text{acid}} = 366.4$ kcal/mol) and acetone ($\Delta H_{\text{acid}} = 368.8$ kcal/mol).[2] Such effects have been rationalized in terms of a stabilizing methyl hyperconjugative interaction in the neutral acids which is largely lost in the conjugate base anions.[73] That is, donation from the filled methyl π-type orbital into the empty π^* orbital of the acetylene, carboxylate, or enolate moiety is attenuated by the increase in energy of the acceptor orbital which accompanies deprotonation.[74] Analogous interactions can be envisaged for propene and 1-propenyl anion which may account, in part, for

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(67) (a) Williams, J. E.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 750-754. (b) Lehn, J. M.; Munsch, B.; Millie, P. *Theor. Chim. Acta* **1970**, *16*, 351-372. (c) Dykstra, C. E.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007-6012. (d) Hopkinson, A. C.; Lien, M. H.; Yates, K.; Mezey, P. G.; Csizmadia, I. G. *J. Chem. Phys.* **1977**, *67*, 517-523. (e) Rossi, A. R.; Remillard, B. D.; Gould, S. J. *Tetrahedron Lett.* **1978**, *45*, 4357-4360. (f) Caramella, P.; Houk, K. N. *Tetrahedron Lett.* **1981**, *22*, 819-822. (g) Clark, D. T.; Armstrong, D. R. *J. Chem. Soc., Chem. Commun.* **1969**, 850-851. (h) Tyrell, J.; Kolb, V. M.; Meyers, C. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3497-3500. (i) Radom, L. *Mod. Theor. Chem.* **1977**, *4*, 333-356.

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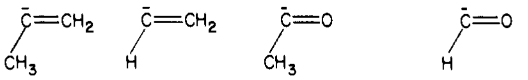
the calculated decrease in acidity at the C-1 position relative to ethylene. A destabilizing inductive effect of the β-methyl substituent is also important in these cases. Calculated charge distributions in the parent vinyl and acetylide anions with use of both Mulliken population analysis[75] and electron density distribution plots[67a] show a significant polarization of σ and π electron density away from the deprotonated carbon toward adjacent nuclei. Indeed, Mulliken analysis assigns a greater net negative charge to the β-carbon than the α-carbon in both vinyl and acetylide ions. The electron-releasing inductive effect of a β-methyl substituent opposes this polarization/stabilization mechanism and, therefore, results in net destabilization relative to the parent vinyl anion.

In the 2-propenyl anion, polarization of electron density in the double bond toward C-1 may act to attenuate the otherwise destabilizing inductive effects of an α-methyl substituent. Methyl hyperconjugation in the opposite sense as that described earlier may also contribute to the decreased basicity of the 2-propenyl anion relative to vinyl, i.e., donation from the carbanion lone pair orbital (n_{sp^2}) into the empty π* orbital of the α-methyl group [$n_{sp^2} \rightarrow \pi^*_{CH_3}$]. Note that this is the more familiar "anionic hyperconjugation" mechanism which has been invoked to account for the greater acidity of methanol relative to water.[2,3,73] However, in the present system we expect this to be a less important effect since the donor (n_{sp^2}) and acceptor ($\pi^*_{CH_3}$) orbitals are relatively widely separated in energy and the overlap between them is reduced by virtue of the small CCC angle in the carbanion. In contrast, the methyl π-interaction with the lone pair at C-2 is *maximal* in the linear inversion transition state. Here, a 4-electron repulsive interaction between filled orbitals [$n_p \leftrightarrow \pi_{CH_3}$] is dominant over [$n_p \rightarrow \pi^*_{CH_3}$] hyperconjugation, thereby causing a higher inversion barrier for 2-propenyl anion (42.2 kcal/mol) relative to vinyl (30.4 kcal/mol). This influence is analogous to the well-known "heteroatom effect" which is commonly invoked to explain the enhanced configurational stabilities of oximes, hydrazones, and *N*-haloaziridines relative to their unsubstituted counterparts.[68,76] Thus, alkyl substitution may also increase configurational stability due to the destabilizing π-interactions accompanying inversion, albeit to a lesser extent than lone pair bearing heteroatoms.

Finally, it is interesting to compare the proton affinities computed for 2-propenyl anion and the parent vinyl anion with experimental values recently made available for the related acetyl[77] and formyl[78] anions:



PA (kcal/mol)	419.6	420.5	389 ± 2	392 ± 2
Δ	0.9		3.0	

A larger difference in basicity is evident for the acyl anions. Since the CH bond energies in formaldehyde and acetaldehyde are similar,[79] the large acidity difference can be mainly attributed to the relative electron binding energies of the two acyl anions.[3,78a] Qualitatively, we can understand the difference in methyl substituent effects on vinyl and acyl ions in terms of the charge polarization mechanism alluded to earlier for vinyl and acetylide ions. Polarization of σ and π electron density to the β-atom of the unsaturated group occurs to a greater extent in the acyl anions than it does for vinyl anions since it places more electron density on oxygen. In fact, Mulliken analysis shows that charge migration in acyl anions is so pronounced that they are probably better viewed as singlet oxy-anion carbenes. As pointed out earlier, such polarization can have the effect of alleviating the destabilizing inductive/field effects of an α-methyl group and unmasking its potentially stabilizing polarizability/hyperconjugative influence. Since greater charge polarization occurs in acyl anions than in vinyl anions, a greater net effect is observed when α-methyl replaces hydrogen.

Concluding Remarks

The results reported in this paper demonstrate that collisionally activated CO_2 loss from carboxylate negative ions is a useful method for synthesizing novel gas-phase carbanions in a regiospecific manner. We have applied this technique to the formation of a series of isomeric $C_3H_5^-$ ions under conditions where their subsequent ion–molecule reactions could be observed. As a result, the reactivity of the parent cyclopropyl anion and tautomeric propenyl anions has been examined for the first time in the gas phase. The vinylic anion isomers and cyclopropyl anion exhibit acid–base behavior which is consistent with their expected high basicities. We have shown that each ion produces a unique set of products in bimolecular reactions with N_2O which is characteristic of its structure. Thus, interconversion of the $C_3H_5^-$ isomers does not occur under the conditions of our experiments, and each ion maintains the original structure derived by direct detachment of CO_2 from the precursor carboxylate. Ab initio molecular orbital calculations have been carried out in order to obtain information about the relative energies and detailed structures of the $C_3H_5^-$ isomers. Our calculations indicate that propene is more acidic than ethylene at the 2-position but less acidic at C-1. The vinyl anions and cyclopropyl anion exhibit bent and pyramidal structures, respectively, and relatively high barriers to inversion. Methyl-substituent effects on both vinyl anion basicity and inversion barriers have been rationalized in terms of charge polarization and hyperconjugative interactions in the ions.

We are currently examining the ion–molecule reactions of vinyl and cyclopropyl anions derived from CID of *stereoisomeric* carboxylate ions in search of direct experimental evidence for their configurational stabilities. The full details of these studies will appear in a future publication.

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Registry No. 1, 25012-81-1; **2a**, 1724-46-5; **3**, 65887-19-6; **4**, 65887-20-9; **5**, 1724-45-4; H_2, 1333-74-0; $CH_2{=}CHCO_2^-$, 10344-93-1; $CH_2{=}CHCH_2CO_2^-$, 54467-93-5; (*E*)-$CH_3CH{=}CHCO_2^-$, 13095-94-8; D_2O, 7789-20-0; NH_3, 7664-41-7; CS_2, 75-15-0; N_2O, 10024-97-2; $CH_2{=}C{-}HC{\equiv}CS^-$, 100840-39-9; $CH_3C(S)CH_2$, 100840-40-2; $CH_3CH{=}CHS^-$, 100840-41-3; $CH_2{=}CHS^-$, 35731-41-0; HC_2^-, 29075-95-4; HCN_2^-, 100840-43-5; CH_2CHO^-, 64723-93-9; $CH_2{=}CHN_2^-$, 100840-44-6; $CH_3CN_2^-$, 100840-45-7; $CH_3C{\equiv}C^-$, 36147-87-2; 2-methyl-2-propenoate anion, 18358-13-9; cyclopropane carboxylate anion, 18917-09-4; cyclopropane thiol anion, 100840-42-4; acetone enolate, 71695-00-6; cyclopropenyl anion, 80251-77-0.

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