

# Organic Radical Cations Abstract Methylene from Ketene To Produce Stable Distonic Ions

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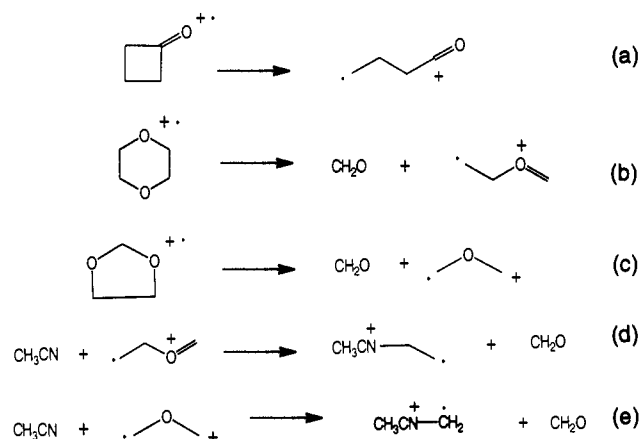
**Abstract:** Gas-phase reactions of neutral ketene can be used to generate a variety of stable distonic radical cations, *i.e.*, ions with a carbon radical center separated from the charge site by differing numbers of methylene units. Conventional radical cations abstract one to three CH<sub>2</sub> groups (accompanied by loss of CO) from neutral ketene in consecutive reactions, the number of CH<sub>2</sub> abstractions depending upon the structure of the reactant ion. All the product ions studied were found to have distonic structures. For example, ionized acetone abstracts a CH<sub>2</sub> group from ketene to generate (CH<sub>3</sub>)<sub>2</sub>C<sup>+</sup>OCH<sub>2</sub>·, an ion proposed earlier to occur as a transient intermediate during dissociation of ionized 1,2-epoxy-2-methylpropene. Besides conventional radical cations, distonic radical cations such as ·CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup> and ·CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CO<sup>+</sup> also abstract methylene from ketene. The current evidence for these reactions supports a simple radical addition/elimination mechanism involving the terminal carbon of neutral ketene and the radical site of the ion. Hence, this approach can be used to homologate distonic radical cations.

## Introduction

Distonic radical cations (ions with a formally separate charge and radical site) have been the focus of intense research since the discovery<sup>1</sup> in 1984 that these ions are surprisingly stable, sometimes more so than their conventional counterparts.<sup>1,2</sup> Indeed, many long-lived organic molecular ions spontaneously rearrange to a stable distonic ion in the gas phase<sup>3</sup> as well as in the condensed phases.<sup>2</sup> Distonic ions are also known to occur as intermediates in unimolecular dissociation reactions of gaseous radical cations, the best known example being the McLafferty rearrangement of the molecular ions of carbonyl compounds.<sup>2</sup> In solution, these ions are generated as transient intermediates for example in the Hofmann–Löffler–Freitag reaction.<sup>2</sup> It is becoming increasingly clear that a better knowledge of the properties of distonic ions will improve the understanding of various important chemical processes involving organic radical cations.

The examination of the reactivity of gaseous distonic ions is currently limited by the inability to generate *stable long-chain* distonic ions. Since distonic ions do not usually have stable neutral counterparts, they cannot be formed simply by removing an electron from a stable neutral molecule. The approaches developed to produce distonic ions in the gas phase include isomerization and dissociation of conventional radical cations (Schemes Ia–c)<sup>2</sup> and bimolecular reactions of the distonic ions formed in these unimolecular reactions.<sup>4</sup> The best known examples of the latter approach involve transfer of CH<sub>2</sub><sup>+</sup> and CH<sub>2</sub>CH<sub>2</sub><sup>+</sup> from ions such as ·CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup> and ·CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup>, respectively, to neutral molecules to produce new  $\alpha$ - and  $\beta$ -distonic ions (Schemes Id and Ie). We report here a simple method based

## Scheme I



on the reactions of neutral ketene which allows the homologation of gaseous distonic ions and the generation of a variety of stable distonic ions.

## Experimental Section

Ketene was synthesized by using a modified literature procedure.<sup>5</sup> Acetone vapors were pyrolyzed by heating a 5-mm coil of number 24 gauge Chromel A wire placed approximately 3 mm above the liquid acetone. Unpyrolyzed acetone was condensed in a trap immersed in a calcium chloride–ice bath (–5 °C). Ketene was collected in another trap which was immersed in a dry ice–acetone bath (–78 °C). The collected ketene was analyzed mass spectrometrically and occasionally found to contain ethane impurity.

All other reagents were obtained commercially. Their purity was checked by gas chromatography and by mass spectrometry. Dimethyl sulfide, 1,3-dioxolane, isopropenyl methyl ether, ethyl vinyl ether, dimethyl disulfide, and cyclobutanone were obtained from Aldrich. Acetone (Fisher Chemical) and cyclopentanone (Fluka Chemika Buchs, Switzerland) were also used.

All the experiments were carried out with use of an Extrel Model 2001 FT/MS system. This Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) has been described in detail previously.<sup>3a,6</sup> The instrument contains a differentially pumped dual cell which is aligned

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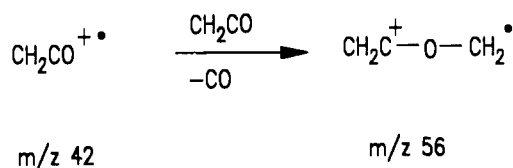
(1) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* 1984, 106, 5805. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* 1986, 42, 6225.

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## Scheme II



collinerally in the magnetic field produced by a 2.3 T superconducting magnet. The base pressure in the instrument is  $<10^{-9}$  Torr, which is maintained by two turbomolecular pumps. The two cells are separated by a common wall (the conductance limit plate) which contains a 2-mm hole in the center. Ions were transferred from one cell into the other by grounding the conductance limit plate for approximately 100  $\mu\text{s}$ . At all other times, this plate and the other two trapping plates perpendicular to the magnetic field lines were kept at +2 V.

Samples were introduced into the FT-ICR by using a Varian leak valve and two Extrel FT/MS heated single batch inlets equipped with variable leak valves. The reagents were used at a nominal pressure of  $1 \times 10^{-7}$  Torr, as measured by an ionization gauge on each side of the dual cell. Molecular ions and fragment ions were generated by electron ionization. The electron energy (typically 20–30 V), emission current (typically 8–10  $\mu\text{A}$ ), and ionization time (typically 40–100 ms) were optimized for each reaction. In some instances, the desired ions were generated by allowing one of these initially formed ions to react with neutral molecules introduced into the cell. After being generated in one cell, the ions were transferred into the other cell to study their reactions. Prior to ion transfer, any ions generated in the analyzer cell by the electron beam were removed from the cell by applying a negative potential (–10 V) to the analyzer trap plate (typically for 5–10 ms). The transferred ions were internally and kinetically relaxed through collisions (50–100) with argon which was temporarily introduced into the cell (nominal peak pressure  $1 \times 10^{-5}$  Torr) through a set of two pulsed valves.

After collisional cooling of the ions, the ion of interest was isolated by ejecting all unwanted ions from the cell through the application of a series of single frequency excitation pulses and radio frequency sweeps to the excitation plates of the analyzer cell, or by using a stored waveform inverse Fourier transform excitation pulse (by using the Extrel FTMS SWIFT module).<sup>7</sup> During the application of the sweeps and pulses, care was taken to avoid excitation of the ion of interest. After the ion was isolated, it was allowed to undergo reactions with the desired neutral reagent for a variable time period (usually from 500 ms up to 12 s). For rate measurements, pressure reading of the ion gauges was corrected for the sensitivity of the gauge toward the neutral molecule. In order to correct for the pressure differential in the instrument, the ion gauges were also calibrated for each neutral reagent by measuring rates for reactions with known rate constants,<sup>8</sup> as described previously.<sup>3</sup> Precision of the rate measurements was better than  $\pm 10\%$  and the accuracy is estimated to be better than  $\pm 50\%$ . All the spectra shown are an average of at least ten spectra acquired using an excitation sweep with 124 V<sub>p-p</sub> amplitude, 2.7 MHz bandwidth, and 2.8–3.0 kHz/ $\mu\text{s}$  sweep rate. The spectra were recorded as 32K data points and subjected to one zero fill before Fourier transformation.

Collision-activated dissociation was carried out on a few of the ions.<sup>3</sup> In these experiments, the isolated ions were allowed to collide with argon (for 100 or 500 ms) introduced into the cell at a static nominal pressure of  $1.2 \times 10^{-7}$  Torr. Prior to collisions, the ions were kinetically excited by using a short single-frequency pulse with an amplitude of 3.5 V and a variable duration. The duration of the excitation pulse determines the final kinetic energy of the ions.<sup>3,6</sup>

## Results and Discussion

Ketene<sup>9</sup> and methylketene<sup>10</sup> were reported some 15 years ago to transfer one to three CH<sub>2</sub> or CH<sub>3</sub>CH groups, respectively, to the molecular ions of ketene, methylketene, and acetone in a quadrupole ion trap as well as in an ion cyclotron resonance mass

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## Scheme III

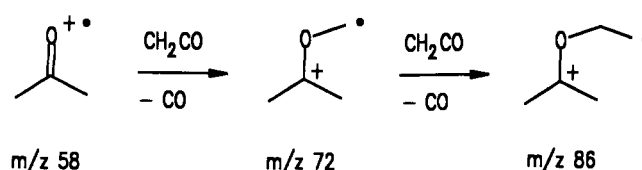


Table I. Reactions of Various Organic Radical Cations with Neutral Ketene (MW 42)

reactant ion (m/z)	ionic products <sup>a</sup> (m/z)	branching ratio, %	k <sup>b</sup>	k <sub>ADO</sub> <sup>c</sup>	k/k <sub>ADO</sub>
CH <sub>2</sub> CO <sup>+</sup> (42)	43 (p)	66	d	18	
	56 (p)	34			
	70				
	84				
CH <sub>3</sub> C(O)CH <sub>3</sub> <sup>+</sup> (58)	43 (p)	10	5.5	26	0.2
	59 (p)	33			
	72 (p)	57			
	86				
CH <sub>3</sub> SCH <sub>3</sub> <sup>+</sup> (62)	76 (p)	100	0.35	17	0.02
	86 (p)	100			
CH <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub> <sup>+</sup> (72)	86 (p)	100	4.6	16	0.3
	100				
cyclopentanone (84)	85 (p)	45	0.55	16	0.03
	98 (p)	39			
	125				
•CH <sub>2</sub> OCH <sub>2</sub> <sup>+</sup> (44)	126 (p)	16	1.8	18	0.1
	57 (p)	72			
	58 (p)	28			
	72				
•CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sup>+</sup> (70)	86		3.7	16	0.2
	83 (p)	63			
	84 (p)	37			
	98				

<sup>a</sup> (p) denotes primary products. <sup>b</sup> k in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>c</sup> k<sub>ADO</sub> is the collision rate, given in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>d</sup> The rate was not measured for this reaction due to contamination of the ketene with acetone.

spectrometer. Resonance ejection was used to verify the stepwise nature of some of these reactions.<sup>10</sup> The structures of the product ions were not investigated. However, it was suggested<sup>9,10</sup> that some of the product ions might, at least initially, have a structure with the odd spin remote from the charge site on the terminal carbon of a methylene chain, i.e., a distonic structure (Schemes II and III). This is an intriguing proposition, considering the difficulty in generating stable long-chain distonic ions by the currently used approaches.<sup>4</sup>

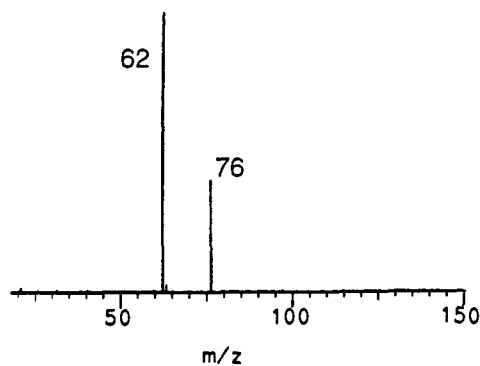
In order to examine the generality of the abstraction of a CH<sub>2</sub> group from ketene, the limiting number of CH<sub>2</sub> groups which can be transferred to a reactant ion, and the structures of the product ions, various radical cations were allowed to react with neutral ketene. It is demonstrated that reactions of ketene provide a general approach for the generation of stable gaseous distonic ions.

**Reactions of Molecular Ions.** All the molecular ions examined were found to abstract at least one CH<sub>2</sub> group from ketene (Table I). Ionized dimethyl sulfide reacts with ketene by a very slow but clean abstraction of one methylene group (efficiency, or reaction rate/collision rate,<sup>11</sup> is 0.02; Figure 1). This reaction yields an ion which almost certainly has the distonic structure<sup>12,13</sup> (CH<sub>3</sub>)<sub>2</sub>S<sup>+</sup>–CH<sub>2</sub>•. The ion (CH<sub>3</sub>)<sub>2</sub>S<sup>+</sup>–CH<sub>2</sub>• has been generated earlier by transfer of CH<sub>2</sub><sup>+</sup> either from ionized ethylene oxide or from ionized cyclobutanone to neutral dimethyl sulfide,<sup>12,13</sup> and found to be stable toward isomerization to ionized ethyl methyl sulfide.<sup>12,13</sup> Ketene reacts with ionized cyclopentanone by slowly

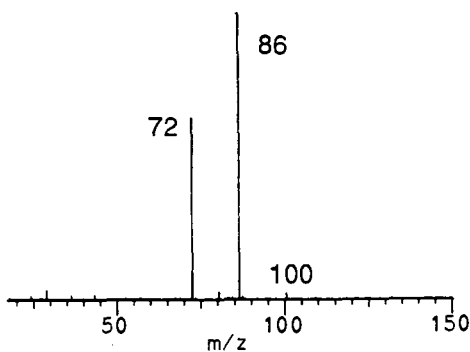
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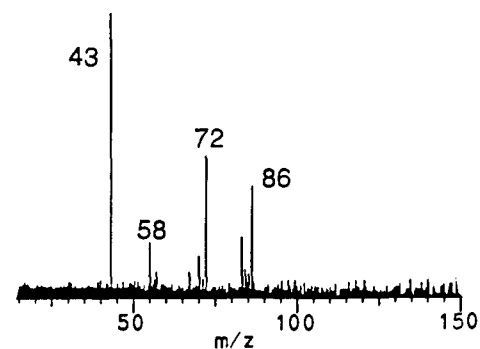
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**Figure 1.** Ionized dimethyl sulfide ( $m/z$  62) slowly abstracts a methylene group from neutral ketene, yielding the ion of  $m/z$  76. The nominal ketene pressure was  $1.2 \times 10^{-7}$  Torr and the reaction time was 5 s.



**Figure 2.** Reaction of ionized ethyl vinyl ether ( $m/z$  72) with neutral ketene ( $1.2 \times 10^{-7}$  Torr) for 1 s yields the product ions of  $m/z$  86 and 100 from transfer of one and two  $\text{CH}_2$  groups, respectively.



**Figure 3.** Reaction of neutral ketene ( $1.3 \times 10^{-7}$  Torr) with ionized acetone ( $m/z$  58) for 6 s.

transferring one  $\text{CH}_2$  group (Table I). Adduct formation ( $m/z$  126; Table I) and abstraction of a hydrogen atom by ionized cyclopentanone ( $m/z$  85) was also observed (the latter reaction may involve the ethane impurity present in ketene; see the Experimental Section).

Two conventional radical cations were found to react with ketene to yield product ions corresponding to the consecutive abstraction of two methylene groups: ionized ethyl vinyl ether (Figure 2) and ionized acetone (Figure 3; Table I). The reaction of ionized acetone has been suggested<sup>9</sup> to yield the ions shown in Scheme III; however, the structures of the ions and the mechanism of the reaction were not investigated. If methylene transfer to ionized ethyl vinyl ether occurs according to Scheme III and involves C–C bond formation at the most nucleophilic site in the ion, without any other structural change accompanying the reaction, then the abstraction of two methylene groups by this ion leads to distonic ions with one and two methylenes separating the charge site and the radical site:  $\cdot\text{CH}_2\text{CH}_2\text{CH}^+-\text{OCH}_2\text{CH}_3$  and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}^+-\text{OCH}_2\text{CH}_3$ .

Ionized ketene abstracts three methylene groups from neutral ketene molecules (generation of ions of  $m/z$  56, 70, and 84; Table I). These reactions were found to occur in a consecutive manner,

in support of earlier reports:<sup>9a</sup> the abundance of the higher homologs increases relative to the lower homologs as a function of reaction time. The only other reaction is proton transfer to neutral ketene generating an abundant ion of  $m/z$  43 (Table I).

The results discussed above demonstrate that it is common for radical cations to abstract at least one  $\text{CH}_2$  group from ketene. In order to gain more insight into the mechanisms of these reactions, the structures of the product ions obtained upon reaction of ionized acetone with ketene were investigated.

**$\text{CH}_2$  Transfer to Ionized Acetone.** As mentioned above, ionized acetone reacts with neutral ketene to yield two radical cations, corresponding to the abstraction of one and two methylene groups, respectively (formation of the ions of  $m/z$  72 and  $m/z$  86). No further  $\text{CH}_2$ -transfer reactions were observed (Table I; Figure 3). When the ion of  $m/z$  72 was continuously ejected from the cell during the reaction, the ion of  $m/z$  86 completely disappeared. This finding indicates a stepwise transfer of the methylene groups from neutral ketene to the acetone ion, in agreement with earlier results.<sup>9a</sup> The structure of the ion resulting from abstraction of one methylene group by ionized acetone was examined by using ion–molecule reactions.

Many distonic ions with a hydrocarbon radical chain attached to a heteroatom at the charge site have been identified on the basis of their ability to transfer the radical chain as a radical cation to nucleophiles.<sup>2,4</sup> For example, the distonic ion  $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$  (which can be viewed as formaldehyde with an ethylene radical chain attached to the carbonyl oxygen) transfers  $\text{CH}_2\text{CH}_2^{\cdot+}$  to acetone, releasing formaldehyde.<sup>2,4</sup> Hence, if the ion formed by abstraction of one methylene group by ionized acetone has the distonic structure shown in Scheme III one would expect to be able to replace acetone with a larger ketone, such as cyclopentanone.

In order to follow the fate of the methylene group transferred from ketene to acetone, the partially deuterated analog  $(\text{CD}_3)_2\text{C}^+-\text{OCH}_2$  ( $m/z$  78) was studied. This ion was generated in one side of the dual cell by the reaction of ionized acetone- $d_6$  with neutral ketene (Scheme IVa) and then transferred into the other side of the dual cell for reaction with cyclopentanone. Transfer of  $\text{CH}_2^{\cdot+}$  to cyclopentanone dominates the reaction (Figure 4a: the ion of  $m/z$  98; the ion of  $m/z$  144 arises from the loss of  $\text{CD}_3$  from the collision complex). This observation provides strong support for the distonic structure  $(\text{CD}_3)_2\text{C}^+-\text{OCH}_2$  for the reactant ion. Further support is obtained from the examination of the reaction of cyclopentanone with a reference ion with the proposed  $\alpha$ -distonic structure. The reference ion<sup>12</sup> was generated by transferring  $\text{CH}_2^{\cdot+}$  from  $\cdot\text{CH}_2\text{OCH}_2^+$  to acetone- $d_6$ <sup>14</sup> ( $\Delta H_{\text{reaction}} \approx -19$  kcal/mol;<sup>15,16</sup> Scheme IVb). The distonic structure of this reference ion has been previously confirmed<sup>12</sup> on the basis of its reactions with various neutral reagents, such as dimethyl disulfide: thiomethyl abstraction verified a distonic structure; the conventional isomer, ionized isopropenyl methyl ether, reacts with dimethyl disulfide by fast charge exchange.<sup>12</sup> This reference ion reacts with cyclopentanone at the same rate (the apparent rate is  $1.5 \times 10^{-10}$   $\text{cm}^3$  molecule $^{-1}\text{s}^{-1}$ ) and yields a similar product distribution (Figure 4) as the ion generated by transfer of a methylene group from ketene to ionized acetone- $d_6$ . These findings unambiguously show that the two ions have the same structure.

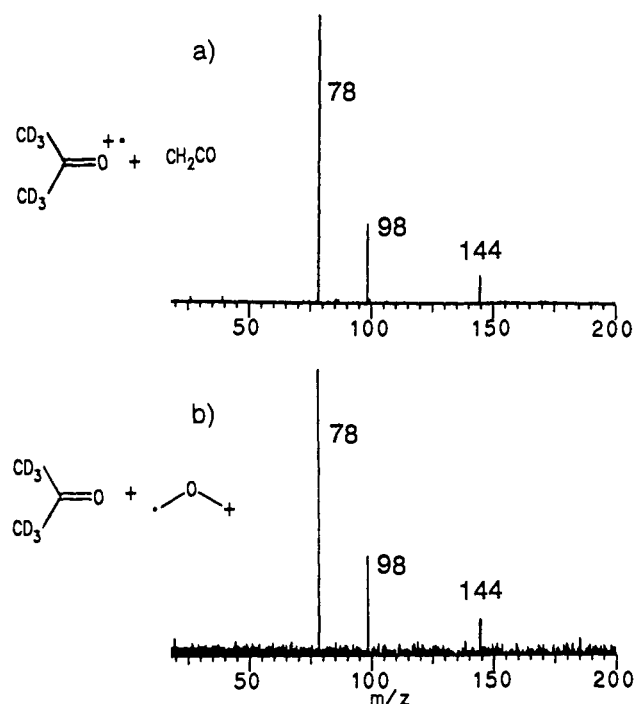
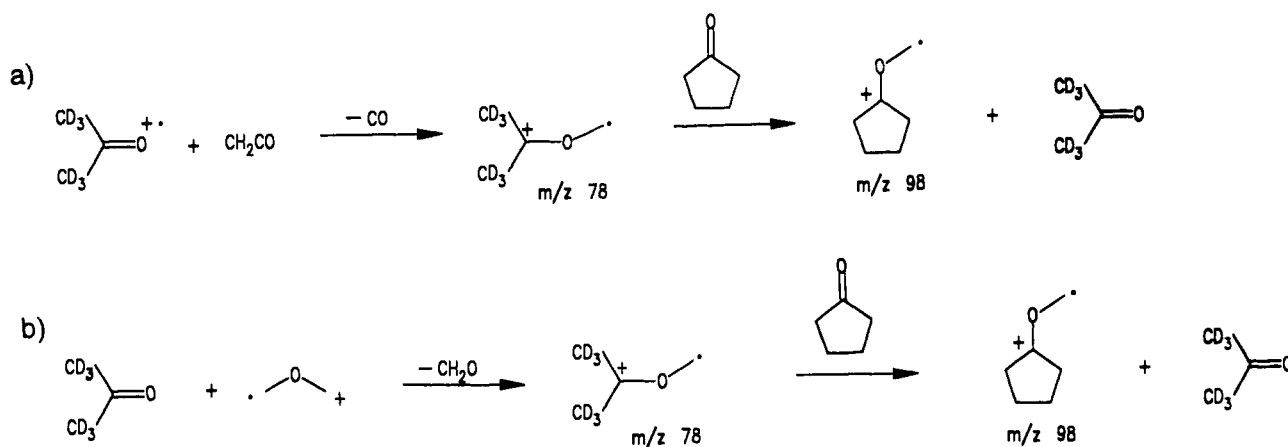
When the distonic ion  $(\text{CD}_3)_2\text{C}^+-\text{OCH}_2$  (generated from either of the two different sources described above) was given long time periods to interact with cyclopentanone, it became evident that 20–30% of these ions are unreactive toward the neutral reagent (Figure 5). Hence, some of the ions have another structure, most

(14) Acetone- $d_6$  was used instead of acetone in order to avoid interference from an abundant fragment ion of 1,3-dioxolane ( $m/z$  73).

(15) The heat of reaction was estimated using values for the heat of formation of ionized acetone, neutral ketene, and neutral carbon monoxide from ref 16. The heat of formation of the ionic product,  $(\text{CH}_3)_2\text{C}^+-\text{OCH}_2$ , has been obtained by theoretical calculations; see ref 18.

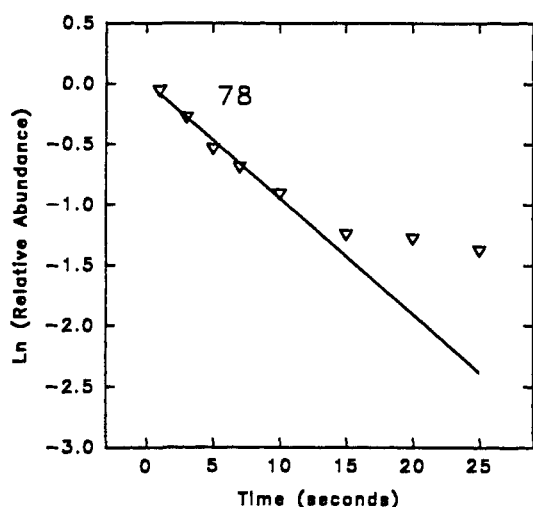
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## Scheme IV



**Figure 4.** (a) Reaction of cyclopentanone ( $1.5 \times 10^{-7}$  Torr) for 1 s with the ion of  $m/z$  78 generated by transfer of a methylene group from ketene to ionized acetone- $d_6$ . (b) Reaction of cyclopentanone ( $9.0 \times 10^{-8}$  Torr) for 3 s with the ion of  $m/z$  78 synthesized by the transfer of  $\text{CH}_2^+$  from  $\text{CH}_2\text{OCH}_2^+$  to acetone- $d_6$ .

likely the more stable conventional structure:<sup>17</sup> ionized isopropenyl methyl ether (Scheme V). Ionized isopropenyl methyl ether was indeed found to be unreactive toward cyclopentanone (Scheme VI). The existence of a dynamic equilibrium between the distonic ion and the conventional structure (Scheme V) can be excluded. This would cause scrambling of the methylene and methyl hydrogens and therefore result in the transfer of partially or completely labeled  $\text{CH}_2^+$  to cyclopentanone, which was not observed (Figure 4). It is concluded that while most of the distonic reactant ions are stable toward intramolecular hydrogen transfer (Scheme V), some of these ions (20–30%) rearrange irreversibly to ionized isopropenyl ether at some point during the experiment. Note that in an earlier study,<sup>12</sup> the ions generated by the reaction of  $\text{CH}_2\text{OCH}_2^+$  with acetone- $d_6$  were concluded to partially isomerize to the conventional form within the collision complex with dimethyl disulfide. It is conceivable that the observations discussed here can also be explained on the basis of a slow



**Figure 5.** Temporal loss of the ion of  $m/z$  78 upon reaction with cyclopentanone. The ion of  $m/z$  78 was generated by transfer of a methylene group from  $\text{CH}_2\text{OCH}_2^+$  to acetone- $d_6$ .

rearrangement within the collision complex of the distonic ion and cyclopentanone.

Finally, it is of interest to note that a product ion of  $m/z$  132 resulting from transfer of  $(\text{CD}_3)_2\text{C}^+$  from the ion of  $m/z$  78 to cyclopentanone (replacement of formaldehyde) was not observed. This reaction is likely to be less exothermic than transfer of  $\text{CH}_2^+$  due to the large energy difference ( $\Delta H = 26$  kcal/mol) between the neutral products formaldehyde and acetone ( $\Delta H_f$  of formaldehyde is  $-26.0$  kcal/mol,  $\Delta H_f$  of acetone is  $-51.9$  kcal/mol).<sup>16</sup> In this sense, the ion of  $m/z$  78 reacts differently than  $\text{CH}_3\text{CH}^+\text{OCH}_2$ , which transfers either  $\text{CH}_2^+$  or  $\text{C}_2\text{H}_4^+$  to a variety of nucleophiles.<sup>4,18</sup>

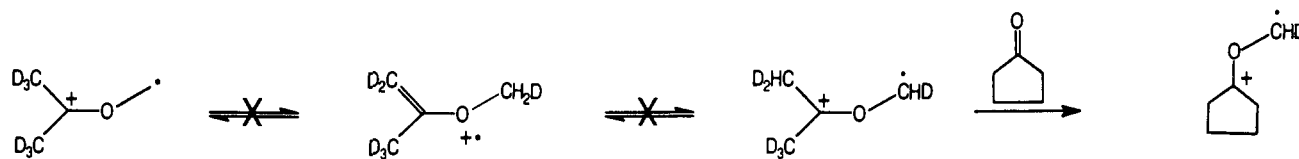
No products were observed for the even-electron analog of the ion  $(\text{CH}_3)_2\text{C}^+-\text{OCH}_2$ ; the ion  $(\text{CH}_3)_2\text{C}^+-\text{OCH}_3$  (generated by proton transfer to 2-methoxy propene; Scheme VI) even after 5 s reaction time (the distonic ion produces an observable product after 1 s: Figure 4). Indeed, even-electron analogs are known to react slower than distonic ions in these group transfer reactions.<sup>3,4</sup>

The distonic ion  $(\text{CH}_3)_2\text{C}^+-\text{OCH}_2$  has been proposed<sup>17</sup> to exist as an intermediate in the unimolecular decomposition of ionized 1,2-epoxy-2-methylpropene (Scheme VII). Ab initio molecular orbital calculations at the 3–21G level of theory suggest<sup>17</sup> that the distonic ion lies 12 kcal/mol higher in energy than ionized isopropenyl methyl ether and that the barrier to isomerization is only 6 kcal/mol. However, the experimental results shown here demonstrate that most of the distonic ions  $(\text{CH}_3)_2\text{C}^+-\text{OCH}_2$  are

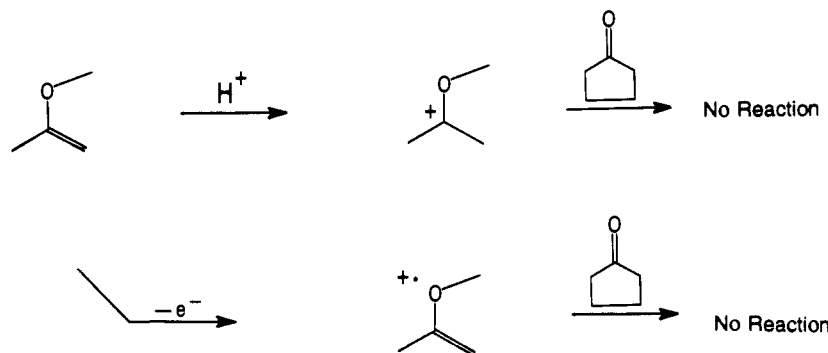
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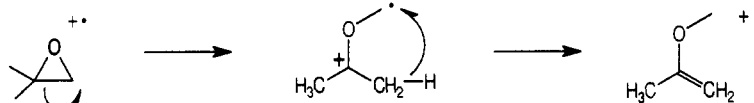
## Scheme V



## Scheme VI



## Scheme VII



stable toward rearrangement to the lower energy structure. Isomerization of the distonic ion to ionized 1,2-epoxy-2-methylpropene is ruled out on the basis of the very high heat of formation of this ion<sup>17</sup> as well as the observed reactivity. Due to the high recombination energy of ionized 1,2-epoxy-2-methylpropene,<sup>16</sup> this ion is expected to undergo facile charge exchange with the various neutral reagents studied (e.g., cyclopentanone).

**Transfer of the Second CH<sub>2</sub> Group to Ionized Acetone.** The product ion formed by the consecutive transfer of two methylene groups to ionized acetone has been earlier suggested<sup>9a</sup> to have the distonic structure (CH<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup> (Scheme III). In order to examine this possibility, the ion was subjected to collision-induced dissociation. Distonic ions of this type are known<sup>2,19,20</sup> to readily decompose by cleavage of the weak C-O bond (e.g., the lower homolog <sup>•</sup>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup> has been reported to dissociate<sup>19</sup> by loss of CH<sub>2</sub>O to yield an abundant ion CH<sub>2</sub>CH<sub>2</sub><sup>•+</sup>, as well as by loss of a hydrogen atom; the same dissociation reactions dominate in the FT-ICR). Hence, an ion with the structure (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup> would be expected to decompose to yield (CD<sub>3</sub>)<sub>2</sub>CO<sup>+</sup> and possibly also CH<sub>2</sub>CH<sub>2</sub><sup>•+</sup>. However, the secondary product of the reaction of ionized acetone with ketene does not fragment readily under the experimental conditions used here; in fact, no fragment ions were detected even at 125 eV collision energy (500 ms reaction time was used; this corresponds to several activating collisions).

In order to further examine the structure of the secondary product ion of ionized acetone, a reference ion expected to have the structure (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup> was generated by transfer of CH<sub>2</sub>CH<sub>2</sub><sup>•+</sup> from <sup>•</sup>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub><sup>+</sup> to acetone-*d*<sub>6</sub> (Scheme VIII).<sup>21</sup> Upon collisional activation, this ion indeed decomposes by the expected C-O bond cleavage. However, instead of losing C<sub>2</sub>H<sub>4</sub> (no such loss was observed), losses of C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> and C<sub>2</sub>HD<sub>3</sub>

dominate (also minor losses of C<sub>2</sub>D<sub>4</sub> and C<sub>2</sub>H<sub>3</sub>D were observed). This result demonstrates that the distonic ion (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>-CH<sub>2</sub><sup>•</sup> is unstable toward rearrangement to ionized ethyl isopropenyl ether CD<sub>2</sub>=C(CD<sub>3</sub>)COCH<sub>2</sub>CH<sub>2</sub>D<sup>•+</sup> (Scheme VIII). Equilibration of the two ions must occur *prior* to collisional activation of the ion. If the activated ion had the structure (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup>, a fast direct bond cleavage leading to loss of C<sub>2</sub>H<sub>4</sub> should be able to compete with the rearrangement reaction resulting in H/D scrambling; hence, a major loss of C<sub>2</sub>H<sub>4</sub> should have been observed (the observation of loss of C<sub>2</sub>D<sub>4</sub> suggests that acetone may be able to move between the two methylene carbons in the activated distonic ion). Further support for a rearranged structure for the distonic ion (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup> is obtained from its rapid reaction by charge exchange with dimethyl disulfide, cyclohexanone, triethylamine, and *sec*-butylamine. An ion with the distonic structure (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>-OCH<sub>2</sub>CH<sub>2</sub><sup>•</sup> is expected<sup>12</sup> to react similarly to the related ions (CD<sub>3</sub>)<sub>2</sub>C<sup>+</sup>OCH<sub>2</sub><sup>•</sup> and <sup>•</sup>CH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub><sup>+</sup>: by abstraction of a thiomethyl group from dimethyl disulfide and by transfer of CH<sub>2</sub>CH<sub>2</sub><sup>•+</sup> to cyclohexanone (and possibly also to the amines studied). These reactions, however, were not observed. The reactivity of the ion is consistent with a conventional vinyl ether structure. For example, ionized isopropenyl methyl ether undergoes facile charge exchange with dimethyl disulfide, as mentioned above.

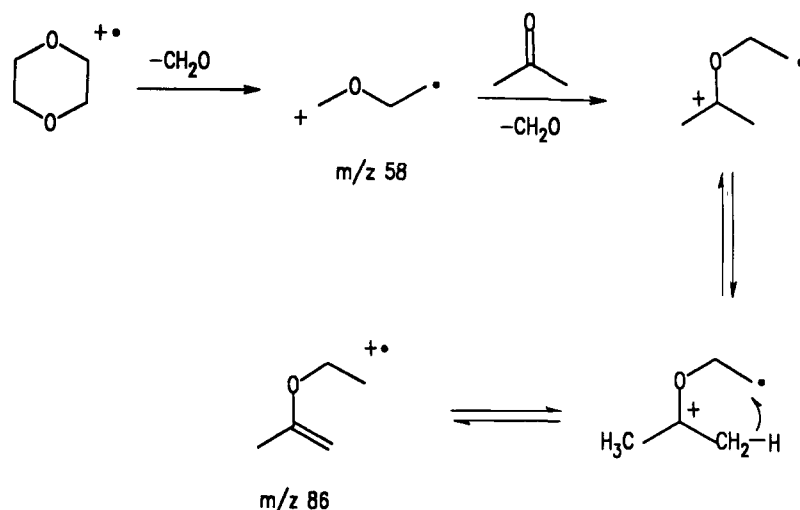
On the basis of the preceding discussion, it was initially assumed that the ion generated by transfer of two CH<sub>2</sub> groups from ketene to ionized acetone has the ionized isopropenyl ethyl ether structure. However, the ion generated in the ketene reaction did not react further with neutral ketene, a finding which is in disagreement with a conventional radical cation structure: all the conventional radical cations studied thus far abstract a methylene group from neutral ketene, and this includes ionized vinyl ethers (e.g., the molecular ion of ethyl vinyl ether discussed above; Figure 2, Table I). Most importantly, ionized ethyl isopropenyl ether (generated as described above: by rearrangement of the ion formed by transfer of CH<sub>2</sub>CH<sub>2</sub><sup>•+</sup> from <sup>•</sup>CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub> to acetone-*d*<sub>6</sub>; Scheme VIII) abstracts methylene from ketene. Furthermore, this ion fragments readily upon CAD by loss of ethylene, as mentioned above. Hence, the ion formed by

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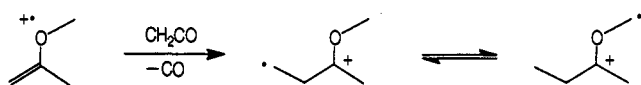
(20) Kiminkinen, L. K. M.; Stirk, K. G.; Kenttämä, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 2027.

(21) Acetone-*d*<sub>6</sub> was used instead of acetone in order to avoid interference from the molecular ion of acetone which has the same mass value as the reactant ion, <sup>•</sup>CH<sub>2</sub>OC<sub>2</sub>CH<sub>2</sub><sup>+</sup>.

## Scheme VIII



## Scheme IX



transfer of two  $\text{CH}_2$  groups from ketene to ionized acetone cannot have the ethyl isopropenyl ether structure.

Indirect support for a distonic structure for the product ion from ketene is provided by the finding that the ion does not yield observable products with dimethyl disulfide. Most conventional organic radical cations undergo facile charge exchange with dimethyl disulfide (ionization potential of dimethyl disulfide is only about  $8\text{ eV}^{16}$ ) while many distonic ions slowly abstract  $\text{CH}_3\text{S}^\bullet$  from this neutral reagent.<sup>12</sup> However, some distonic ions have been found to be unreactive toward dimethyl disulfide (e.g.,  $(\text{CH}_3\text{O})_3\text{P}^+\text{OCH}_2\text{CH}_2$ ).<sup>20</sup> For these ions, the  $\text{CH}_3\text{S}$ -abstraction reaction is probably too slow to be observed under the conditions used.

Considering all the facts presented above, and especially the observations that (1) some of the distonic ions  $(\text{CH}_3)_2\text{C}^+\text{-OCH}_2^\bullet$  probably have isomerized (or can isomerize within a collision complex) to ionized isopropenyl methyl ether and (2) vinyl ether radical cations readily abstract a  $\text{CH}_2$  group from ketene (e.g., ionized ethyl vinyl ether; see discussion above), it seems likely that the ion generated upon transfer of two  $\text{CH}_2$  groups from ketene to ionized acetone arises from a reaction of the rearranged primary product, isopropenyl methyl ether ion, with ketene. Strong support for this proposal is obtained from the following result: ionized isopropenyl methyl ether (generated by ionization of neutral isopropenyl methyl ether) abstracts rapidly one  $\text{CH}_2$  group from ketene to yield a product ion (Scheme IX) which is unreactive toward ketene, just like the ion generated by transfer of two  $\text{CH}_2$  groups to ionized acetone. Moreover, this product ion reacts with dimethyl disulfide so slowly that only a trace of the  $\text{CH}_3\text{S}$ -abstraction product is formed at very long reaction times (12 s). This finding is in agreement with the results obtained for the ion generated from ionized acetone. In the latter case, the poor signal-to-noise ratio prevents the observation of the  $\text{CH}_3\text{S}$ -abstraction product. It is concluded that the structure of the acetone product ion is likely to be  $\text{CH}_2\text{CH}_2\text{C}^+(\text{CH}_3)\text{OCH}_3$ , perhaps in equilibrium with  $\text{CH}_3\text{CH}_2\text{C}^+(\text{CH}_3)\text{OCH}_2^\bullet$  (Scheme IX). Both of these structures are in agreement with the experimental data discussed above. These ions are not expected to decompose readily upon low-energy CAD (no simple reaction will lead to stable ionic and neutral products). Moreover, both of these ions are distonic ions and hence not expected to undergo facile charge exchange with dimethyl disulfide.

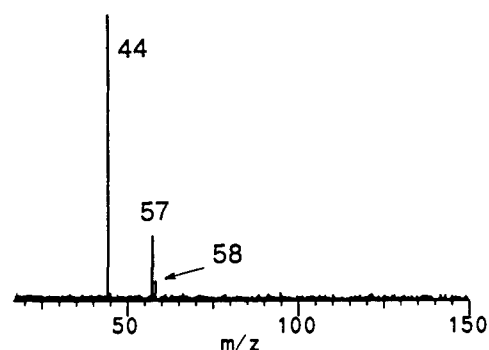
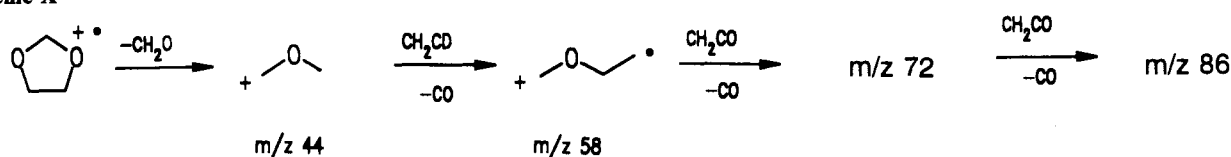


Figure 6. Reaction of  $\text{CH}_2\text{OCH}_2^+$  for 250 ms with neutral ketene ( $1.4 \times 10^{-7}$  Torr). Only primary products were observed at this short reaction time.

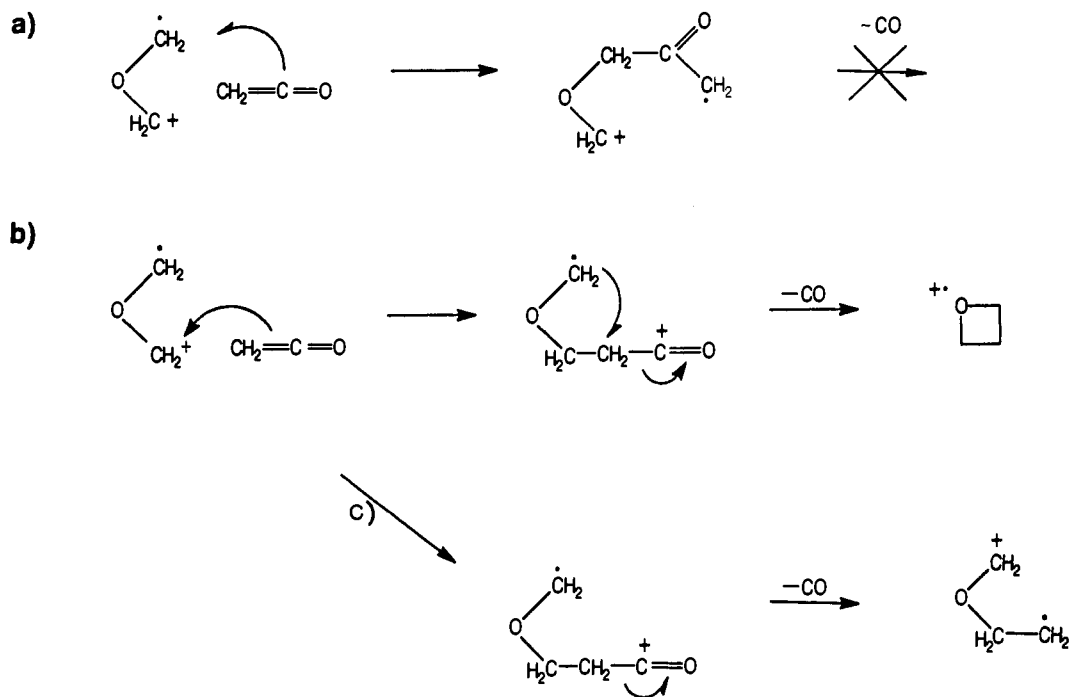
**Reaction of Distonic Ions with Ketene.** The results discussed above suggest that the distonic ion  $(\text{CH}_3)_2\text{C}^+\text{-OCH}_2^\bullet$  may not abstract a  $\text{CH}_2$  group from neutral ketene. In order to see whether distonic ions in general are unreactive toward ketene, reactions of other distonic radical cations were investigated. The well-characterized distonic ion  $^+\text{CH}_2\text{OCH}_2^\bullet$  (formed as shown in Scheme Ib from ionized 1,3-dioxolane)<sup>2,4</sup> was found to abstract a total of three methylene groups from ketene (Table I), resulting in the formation of the primary product ion of  $m/z$  58 (Figure 6) and other product ions of  $m/z$  72 and 86 (Table I; Scheme X). The ions of  $m/z$  58 almost certainly have the distonic structure  $^\bullet\text{CH}_2\text{CH}_2\text{OCH}_2^+$  (the conventional cyclic structure shown in Scheme XIb is less stable) since many of these ions spontaneously lose a hydrogen atom to form an ion of  $m/z$  57: loss of a hydrogen atom dominates the spontaneous dissociation of the metastable ions  $^\bullet\text{CH}_2\text{CH}_2\text{OCH}_2^+$ .<sup>19</sup> Another distonic ion, the ion  $^\bullet\text{CH}_2\text{CH}_2\text{-CH}_2\text{CO}^+$  generated by ionization of cyclobutanone (Scheme Ia)<sup>3b</sup> abstracts two methylene groups from ketene in a consecutive manner. Structural characterization of the ion generated by abstraction of one  $\text{CH}_2$  group by the ion  $^\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$  is reported in another paper;<sup>22</sup> this product ion was demonstrated to be a distonic ion and to have the structure  $^\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ . Note that the abstraction of a methylene group by the two distonic reactant ions  $^\bullet\text{CH}_2\text{OCH}_2^+$  and  $^\bullet\text{CH}_2\text{-CH}_2\text{CH}_2\text{CO}^+$  occurs at a relatively high efficiency: one to two collisions out of ten lead to a reaction.

**Reaction Mechanism.** Transfer of a methylene group from ketene to a radical cation must involve bond formation at the terminal carbon of ketene. While addition to the central carbon is also conceivable, this cannot lead to elimination of CO to generate the observed products (Scheme XIa). Further, an

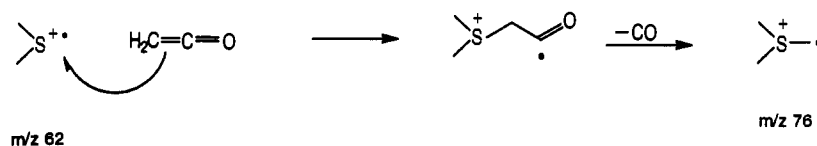
## Scheme X



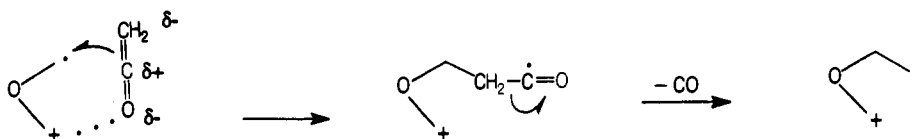
## Scheme XI



## Scheme XII



## Scheme XIII



electron-transfer mechanism is ruled out on the basis of the high endothermicity of charge exchange between ketene and the ions studied (e.g., dimethyl sulfide has an ionization energy of 8.69 eV and ketene 9.61 eV,<sup>16</sup> which makes charge exchange endothermic by 21 kcal/mol). The reactions of the conventional radical cations with ketene are likely to occur as shown in Scheme XII, involving an intermediate analogous to those occurring upon reactions of ionized ketene with neutral molecules.<sup>23</sup> There are several conceivable mechanisms through which the distonic ions can react with neutral ketene. It is clear that the radical site plays an important role: methylene abstraction from ketene does not occur for even-electron ions, such as  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ . Addition of the radical site of a distonic ion to the terminal carbon of ketene would account for the products observed (Scheme XIII). It is well-known that radical addition to carbon-carbon double

bonds is facile in solution.<sup>24</sup> Furthermore, radical-type reactions have been recently reported for distonic ions,<sup>4</sup> including the demonstration that the radical site of the distonic ion  $(\text{CH}_3)_2\text{S}^+\text{-CH}_2^{\cdot}$  adds to the carbon-carbon double bonds in alkenes.<sup>25</sup> Addition of a nucleophilic radical would be expected to involve the *central* and not terminal carbon of ketene (one-electron/two-orbital SOMO-LUMO interaction; the central carbon atom of ketene has a large LUMO coefficient).<sup>23</sup> However, distonic ions are more likely to behave as electrophilic radicals (due to the positive charge) for which the three-electron/two-orbital SOMO-HOMO interaction might be expected to dominate and to lead to addition to the terminal carbon.<sup>26</sup>

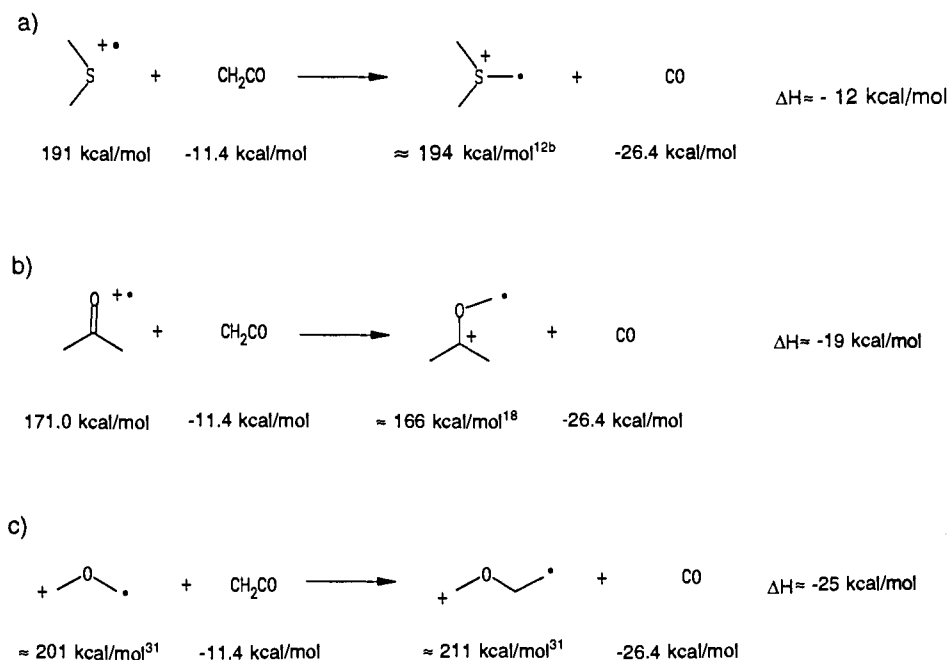
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## Scheme XIV



The participation of the charge site cannot be entirely ruled out in the reactions of distonic ions.<sup>27</sup> The reactions of some distonic ions with ketene could even involve initial addition of the terminal carbon of ketene to the charge site of the ion, followed by a reaction between the radical site of the ion and ketene (Scheme XIc). Note, however, that although the ions  $\cdot\text{CH}_2\text{OCH}_2^+$  and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$  have a different chain length separating the charge and the radical site, they abstract methylene from ketene at a similar efficiency (0.1–0.2) which does not support a strong involvement of the charge site. An electrostatic rather than covalent interaction between the charge site of the distonic ion and the  $\pi$ -system of neutral ketene is more likely and may help orient ketene for bond formation (Scheme XIII).<sup>28</sup>

As discussed earlier, there appears to be a limit to the number of methylene groups which can be transferred to an ion, and this limit depends on the reactant ion. For example, transfer of one  $\text{CH}_2$  group occurs to ionized dimethyl sulfide while three  $\text{CH}_2$  groups are transferred to the ion  $\cdot\text{CH}_2\text{OCH}_2^+$ . Note that as the separation between the radical and charge sites increases in the reactant distonic ion, the exothermicity of the methylene transfer reaction becomes smaller. For example,  $\cdot\text{CH}_2\text{OH}_2^+$  has a heat of formation of 195 kcal/mol while that of the higher homologs,  $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$  and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+$ , is 175 kcal/mol for both.<sup>2,29</sup> Thus, transfer of  $\text{CH}_2$  from ketene to  $\cdot\text{CH}_2\text{OH}_2^+$  is thermodynamically more favorable than transfer of a  $\text{CH}_2$  group to  $\cdot\text{CH}_2\text{CH}_2\text{OH}_2^+$ , the former reaction being exothermic by about 35 kcal/mol and the latter reaction only by 15 kcal/mol.

The enthalpy change for the abstraction of  $\text{CH}_2$  from ketene was estimated for a few of the ions studied (Scheme XIV).<sup>4,12,16</sup> The numbers obtained suggest a correlation between the exothermicity of methylene abstraction and the number of methylene

groups abstracted by the ion. For example, ionized dimethyl sulfide abstracts only one methylene in a reaction with  $\Delta H_{\text{reaction}} \approx -12$  kcal/mol; the reaction is significantly more exothermic ( $\Delta H_{\text{reaction}} \approx -19$  kcal/mol) for ionized acetone which abstracts two methylenes, and even more so for  $\cdot\text{CH}_2\text{OCH}_2^+$  ( $\Delta H_{\text{reaction}} \approx -25$  kcal/mol) which abstracts three methylene groups. All the methylene abstraction reactions proceed at a rate lower than the collision rate, suggesting that there is a relatively high energy barrier on the reaction coordinate and that this barrier must be close to the "solvation energy" provided by neutral ketene to the ions. The well depth corresponding to the collision complex with neutral ketene is approximately 13 kcal/mol for all the ions studied here.<sup>30</sup>

## Conclusions

A promising approach is described for the gas-phase synthesis of distonic radical cations. Neutral ketene can be used to transfer one to three methylene groups to radical cations, including distonic ions. All the product ions whose structures were examined proved to be stable distonic radical cations. There is a limit to the maximum number of methylenes that can be added to an ion. This seems to be attributable to a decrease in the reaction exothermicity as the hydrocarbon chain length in the reactant ion increases. Only reactions which are exothermic by at least 12 kcal/mol were found to take place, suggesting a sizable barrier on the reaction coordinate. The current evidence points to a simple radical addition/elimination mechanism involving the terminal carbon of ketene and leading to bond formation at the radical site in the ion. Hence, this approach allows the homologation of distonic ions with the odd spin on a primary carbon.

**Acknowledgment** for financial support is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (CHE-9107121), the Lubrizol Corp., and Eli Lilly and Co. Dr. Leonard Chyall is thanked for useful discussions.

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