Acyclic Distonic Acylium Ions: Dual Free Radical and Acylium Ion Reactivity in a Single Molecule

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Three gaseous acyclic distonic acylium ions: $\bullet CH_2$–CH_2–C^+=O, $\bullet CH_2$–CH_2–CH_2–C^+=O, and $\bullet CH_2$=C(CH_2)–C^+=O, are found to display dual free radical and acylium ion reactivity; with appropriate neutrals, they react selectively either as free radicals with inert charge sites, or (and more pronouncedly) as acylium ions with inert radical sites. The free radical reactivity of the ions is demonstrated via the Kenttämaa reaction: $CH_3S^\bullet$ abstraction with the spin trap dimethyl disulfide; their ion reactivity by two reactions most characteristic of acylium ions: transacetalization with 2-methyl-1,3-dioxolane and the gas-phase Meerwein reaction, that is, expansion of the three-membered epoxide ring of epichlorohydrin to the five-membered 1,3-dioxolanylium ion ring. In "one-pot" reactions with gaseous mixtures of epichlorohydrin and dimethyl disulfide, the ions react selectively at either site, but more readily at the acylium charge site, to form the two *mono*-derivatized ions. Further reaction at either the remaining free radical or acylium charge site forms a single *bi*-derivatized ion as the final product. Becke3LYP/6-31G(d) calculations predict the reactions at the acylium charge sites of the three distonic ions to be highly exothermic, and both the "hot" transacetalization and epoxide ring expansion products of $\bullet CH_2$–CH_2–CH_2–C^+=O to dissociate rapidly by H_2C=CH_2 loss in overall exothermic processes. The calculations also predict highly spatially separate odd spin and charge sites for the novel cyclic *distonic ketal ions* formed by the reactions at the acylium charge sites. (J Am Soc Mass Spectrom 2000, 11, 697–704) © 2000 American Society for Mass Spectrometry

Unique electronic structures impart to distonic ions [1, 2] a potentially rich reactivity—they may react either as free radicals or as charged species, or more fascinating, as both. But this dual chemical behavior is rare [3]; distonic ions display most frequently reactivity that is characteristic of either their radical or ion nature [2].

Recently [4], dual ion and free radical reactivity was reported for the distonic ions **1b** and **1c**. These isomeric and aromatic distonic acylium ions display σ-localized odd spin and π-delocalized charge densities placed in orbitals lying in different symmetry planes [5]; hence, they can be regarded as distonic ions with "orbital-separated" [4] radical and charge sites. Owing to this unique electronic structure, and their free radical and acylium charge sites, both chemically unsaturated and reactive, **1b** and **1c** react readily and selectively with appropriate neutrals either as free radicals with inert charge sites, or as acylium ions with inert radical sites. The distonic ions **1b** and **1c** display, therefore, in a single molecule, either free radical or acylium ion reactivity, or both.


1a   1b   1c
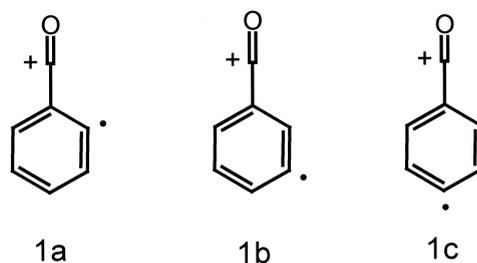
The *ortho*-isomer **1a** also displays similar electronic structure and the expected radical and acylium ion reactivity, but reactions at its acylium site either occur simultaneously with, or are followed by, H abstraction reactions promoted by its radical site [4]. For **1b** and **1c**, however, the rigid phenyl ring promotes effective spatial separation between the radical and the carbonyl charge site that prevents the neutral reagent from binding or reacting simultaneously at both sites.

The acyclic ions **2** [6], **3** [7], and **4** [8] are also potential candidates for distonic acylium ions with dual chemical behavior. Owing, however, to the flexible aliphatic chain and conformational equilibrium of **3** and the "ortho-like" position in **2** and **4**, their charge and radical sites are not efficiently separated; hence, both

sites could concurrently influence reactivity. In the reactions so far reported for **2**, **3**, and **4** [2, 9], both sites likely participate, but the acylium charge sites play a minor role since initial binding at the electrophilic CO$^+$ group just facilitates or catalyzes radical reactions. This subsidiary role of the charge site has therefore inspired conclusions that the reactivity of acylium distonic ions is governed by their radical sites [9b].

Most likely, however, the minor role observed for the
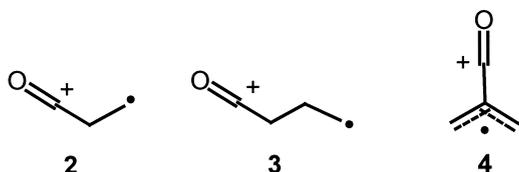
acylium charge site in the reactivity of **2**, **3**, and **4** is circumstantial because none of the reactions so far performed for the ions [2, 9] were those most characteristic of the often reactive acylium charge sites [10–14].

We now report that the acylium charge site plays a major role in the gas-phase reactivity of acyclic distonic acylium ions; that when appropriate neutral reagents are selected, these ions react either as radicals with inert charge sites or as acylium ions with inert radical sites thus displaying, in a single molecule, dual free radical and (more pronouncedly) acylium ion reactivity.

Methods

The gaseous ions were produced, reacted, and their products analyzed via double-(MS^2) and triple-stage (MS^3) mass spectrometric experiments [15] performed with an Extrel (Pittsburgh, PA) pentaquadrupole mass spectrometer [16]. The instrument, denoted $Q_1q_2Q_3q_4Q_5$, is composed of a sequential arrangement of three mass analyzing (Q1, Q3, Q5) and two "rf-only" ion-focusing reaction quadrupoles (q2, q4). The reactant ions were formed by either 70 eV EI-induced dissociation or rearrangement of appropriate precursors: **2** (γ-butyrolactone) [6], **3** (cyclobutanone) [7], and **4** (α-methylene-γ-butyrolactone) [8]. In the MS^2 ion/molecule reactions, Q1 was used to mass select the ion of interest for further reactions in q2 with a selected neutral reagent. Ion translational energies were set to near 0 eV as calibrated by the m/z 39:41 ratio in neutral ethylene/ionized ethylene reactions [17]. Product ion mass spectra were acquired by scanning Q5, while operating Q3 and q4 in the broad band rf-only mode. The target gas pressures in q2 caused typical beam attenuations of 50%–70%, viz., multiple collision conditions were used, which increase reaction yields and promote collisional quenching of both the reactant and product ions [15b].

For the MS^3 experiments [15], a q2-product ion of interest was mass selected by Q3 for further 15 eV collision dissociation with argon in q4, while scanning Q5 to record the spectrum. The 15 eV collision energy
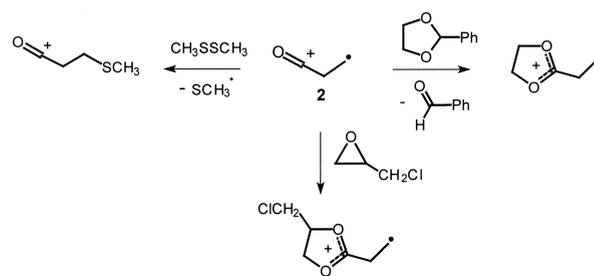
Scheme 1

was taken as the voltage difference between the ion source and the collision quadrupole. The indicated pressures in each differentially pumped region were typically 2×10^{-6} (ion source), 8×10^{-6} (q2) and 8×10^{-5} (q4) torr, respectively.

Optimized geometries and energies of idealized conformations were obtained by molecular orbital calculations using Becke3LYP [18] DFT/HF hybrid functionals and 6-31G(d) basis sets as implemented in Gaussian94 [19]. The geometry optimizations were performed without any symmetry constraint. Acceptable values (lower than 0.76) for spin contamination were obtained for the odd-electron species.

Results and Discussion

Scheme **1** summarizes for **2**, the sequence of structurally diagnostic reactions and expected products used to explore the dual reactivity of the ions.

Free radical reactivity has been already demonstrated for acyclic distonic acylium ions via the "Kenttämaa reaction" [20], that is, CH$_3$S$^\bullet$ abstraction [21] (or CH$_3$Se$^\bullet$ abstraction) [22] with dimethyl disulfide (or dimethyl diselenide) performed in ICR reaction cells; this reactivity was then further tested under the present quadrupole multiple-collision reaction conditions.

Acylium ion reactivity was tested via two reactions most characteristic of acylium ions: (a) transacetalization with cyclic acetals and ketals [11] (2-phenyl-1,3-dioxolane was selected); and (b) the gas-phase Meerwein reaction [13] with epoxides (epichlorohydrin was selected); that is, expansion of the three-membered epoxide ring to the five-membered 1,3-dioxolanylium ion ring promoted by acylium ions.

Free Radical Reactivity

CH$_3$S$^\bullet$ abstraction. Figure 1 collects the double-stage (MS^2) product ion mass spectra for reactions with dimethyl disulfide. Reaction conditions, adjusted to maximize product yields, were kept unchanged when reacting each of the three distonic ions. That **2** (Figure 1a), **3** (Figure 1b), and **4** (Figure 1c) react as free radicals (Scheme **1**) is demonstrated by the respective CH$_3$S$^\bullet$ abstraction products [21] of m/z 103, 117, and 115.

Under the present quadrupole reaction conditions, however, CH$_3$S$^\bullet$ abstraction occurs not as effectively.
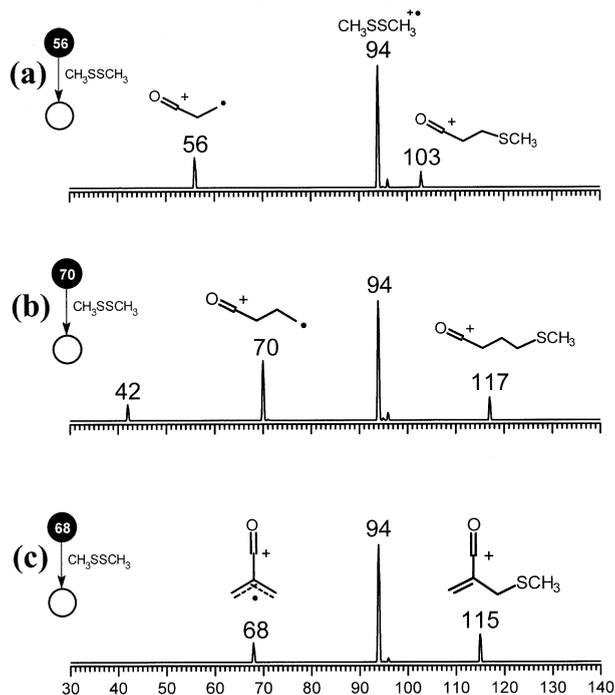
Figure 1. Double-stage (MS^2) product ion mass spectra for reactions with dimethyl disulfide of (**a**) **2**, (**b**) **3**, and (**c**) **4**.

For **2** (Figure 1a), the m/z 103 to m/z 94 abundance ratio (11% : 89%) is slightly greater than that reported under ICR reaction conditions (7 : 93) [21], but for **3** (16 : 88) and **4** (19 : 81), the relative yields of the CH$_3$S· abstraction product are considerably lower: **3** (55 : 43) [21] and **4** (69 : 6) [9b]. Under ICR conditions, **4** also reacts moderately with CH$_3$SSCH$_3$ (but not with CH$_3$SeSeCH$_3$) to form m/z 114 by CH$_3$S· abstraction accompanied by CH$_3$SH loss (a reaction likely promoted by intramolecular H atom transfer within the ion–molecule collision complex) [9b], but this certainly slower reaction is surpassed at the present quadrupole reaction conditions (Figure 1c).

Acylium Ion Reactivity

Transacetalization. Figure 2 collects the double-stage (MS^2) product ion mass spectra for reactions with the cyclic acetal 2-phenyl-1,3-dioxolane. Pronounced reactivity characteristic of an acylium ion is evident for the three acyclic distonic ions since transacetalization [11] occurs promptly and nearly exclusively.
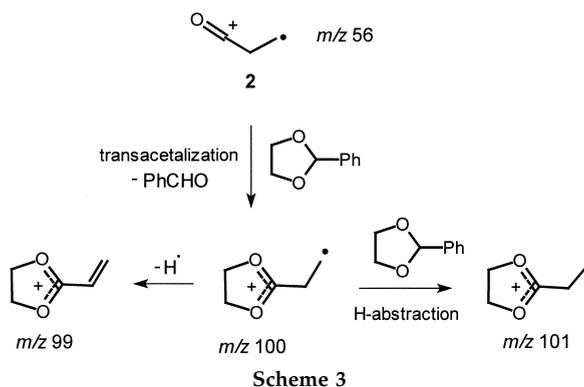
The intact transacetalization products of **2** (m/z 100, Figure 2a) and **4** (m/z 112, Figure 2c) are formed to great extents. That of **3** is, however, unique: transacetalization dominates for **3**, but its primary transacetalization product of m/z 114 is not observed (Figure 2b). Most likely, the CH$_2$CH$_2$CH$_2$· chain facilitates rapid dissociation of m/z 114 by H$_2$C=CH$_2$ loss (Scheme **2**) to form m/z 86, formally a ketal form of ionized ketene. Then, likely in a secondary reaction, m/z 86 abstracts an H atom from 2-phenyl-1,3-dioxolane to form its even-electron analog, that is, the cyclic "ionic ketal" [11b] of m/z 87.
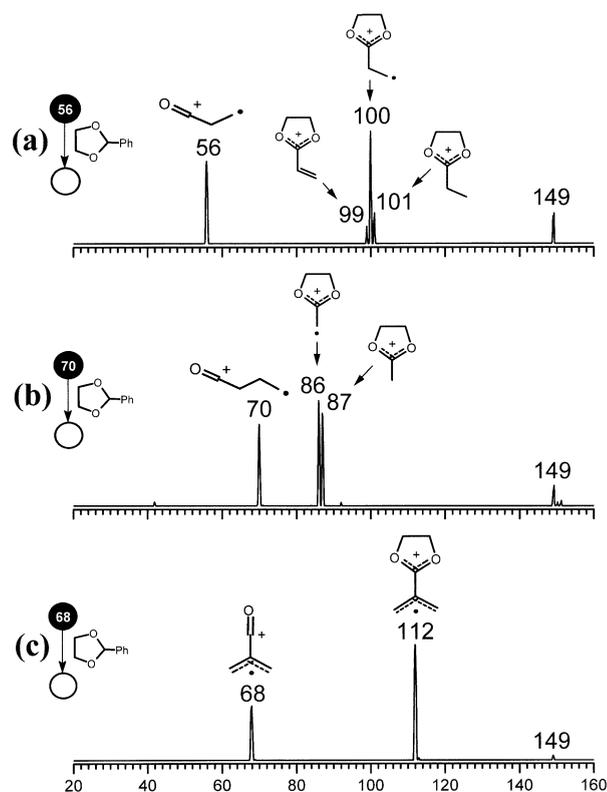
Figure 2. Double-stage (MS^2) product ion mass spectra for reactions with 2-phenyl-1,3-dioxolane of (**a**) **2**, (**b**) **3**, and (**c**) **4**.

The three ions also react competitively (but modestly) with 2-phenyl-1,3-dioxolane by formal hydride abstraction to form m/z 149. To minor extents, the


Scheme 2
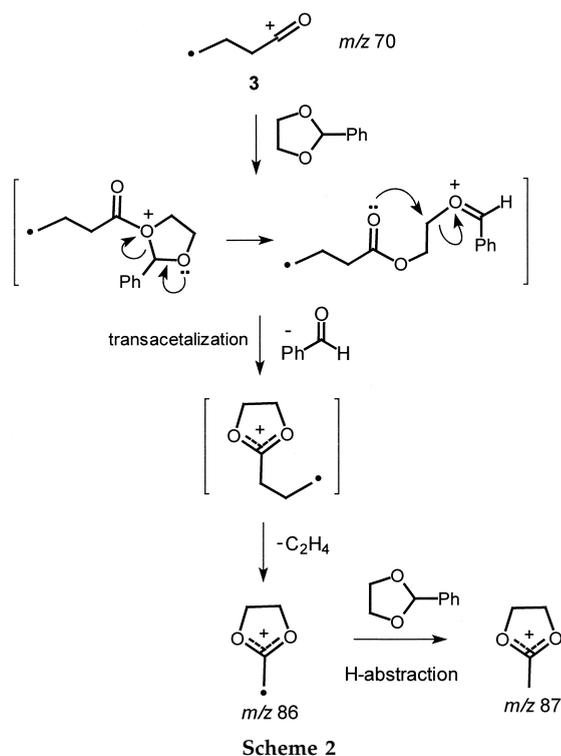
Scheme 3

Scheme 4

transacetalization product of **2** (*m/z* 100) either abstracts an H atom from 2-phenyl-1,3-dioxolane to form its respective even-electron cyclic "ionic ketal" [11b] of *m/z* 101 or dissociates by H loss to form *m/z* 99 (Figure 2a, Scheme **3**).
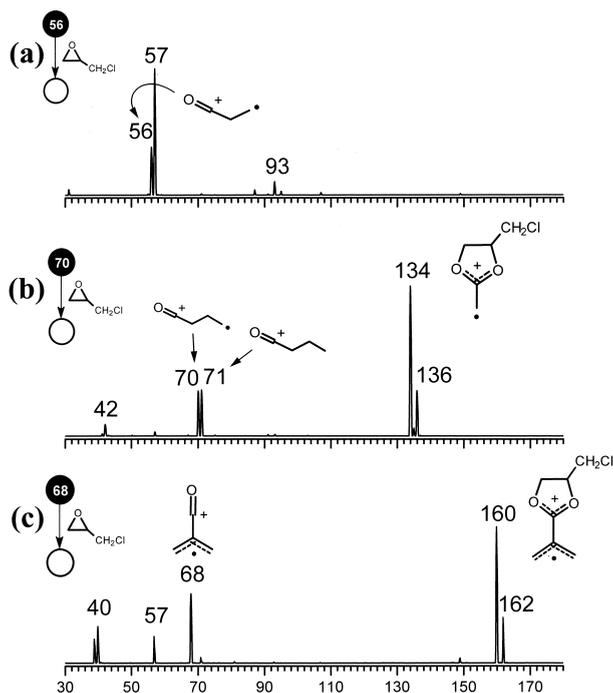
The gas-phase Meerwein reaction.   Figure 3 collects the product ion mass spectra for reactions of **2**, **3**, and **4** with epichlorohydrin. Ion **4** (Figure 3c) shows pronounced acylium ion reactivity; it yields mainly the Meerwein products [23] of *m/z* 160/162 (the two ^{35}Cl/^{37}Cl isotopomers).

Ion **3** shows, again, unique reactivity with epichlorohydrin (Figure 3b). Most likely, it reacts promptly as an acylium ion by the gas-phase Meerwein reaction, but the nascent ring-expanded dioxolanylium product ions of *m/z* 162/164 dissociate rapidly. Again, the $CH_2CH_2CH_2^{\bullet}$ chain facilitates $H_2C=CH_2$ loss (Scheme **4**)
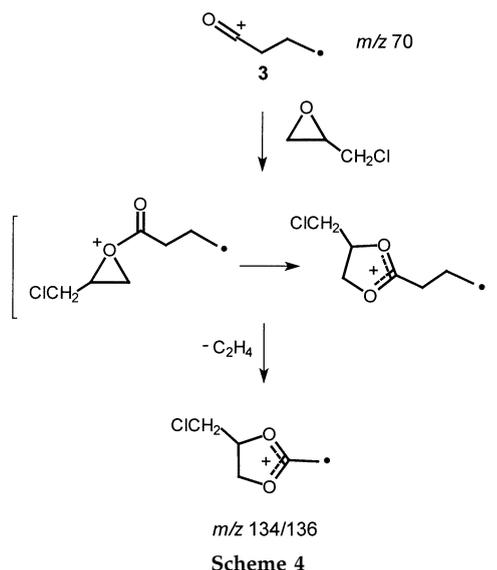
and the isotopomeric products of *m/z* 134/136 are formed to great extents (Figure 3b). Ion **3** also abstracts an H atom from epichlorohydrin to form to a moderate extent its even-electron analog, the acylium ion of *m/z* 71.

With epichlorohydrin, however, **2** (Figure 3a) fails to show the reactivity expected for an acylium ion. For this particular case, either electron transfer followed by fast Cl$^{\bullet}$ loss or H-abstraction (or both) are favored forming *m/z* 57; this ion apparently reacts in turn with epichlorohydrin by proton transfer to form the minor product of *m/z* 93.

Dual Free Radical and Acylium Ion Reactivity

"One-pot" reactions.   To test further the dual reactivity of the ions, that is, their abilities to react selectively at either the radical or charge site and then to react further at the remaining reactive site; "one-pot" reactions were performed with gaseous mixtures of dimethyl disulfide and epichlorohydrin.

Figure 4 exemplifies for **4** the resulting product ion mass spectrum. When the two neutral reactants are present in the collision quadrupole (q2), **4** reacts selec-

Figure 3. Double-stage (MS^2) product ion mass spectra for reactions with epichlorohydrin of (**a**) **2**, (**b**) **3**, and (**c**) **4**.
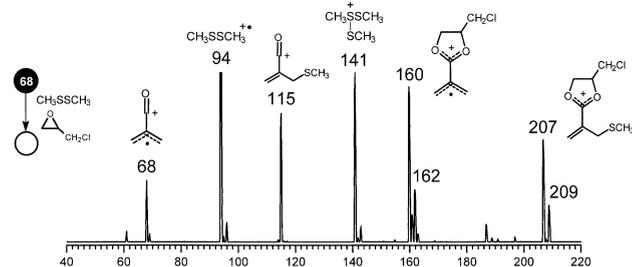
Figure 4. Double-stage (MS^2) product ion mass spectra for "one-pot" reactions of **4** with a gaseous mixture of neutral epichlorohydrin and dimethyl disulfide. The *m/z* 94 peak is off scale.
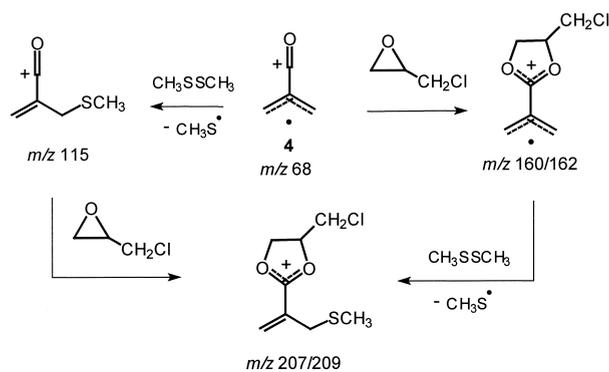
Scheme 5

Scheme 7

tively at either of its reactive sites to yield the two *mono*-derivatized ions of *m/z* 115 and *m/z* 160/162; and then the *bi*-derivatized ions of *m/z* 207/209 (Scheme **5**). In the *mono*-derivatized products of *m/z* 160/162, the C^+=O site is chemically saturated, that is, protected as a cyclic *ionic ketal* [11–13], but the radical site remains free and reactive; hence, these still distonic ions further abstract CH$_3$S· from dimethyl disulfide to yield the *bi*-derivatized products of *m/z* 207/209.

Similarly, primary radical reactions of **4** with CH$_3$SSCH$_3$ yield the *mono*-derivatized CH$_3$S· abstraction product of *m/z* 115, an even-electron acylium ion that reacts further with epichlorohydrin by the gas-phase Meerwein reaction at its free and reactive acylium site to form the same *bi*-derivatized products of *m/z* 207/209 (Scheme **5**).

In the "one-pot" reactions (Figure 4), the yield of the final *bi*-derivatized products of *m/z* 207/209 was limited by the low reactivity of the radical site and then the need to use relatively higher pressures of dimethyl disulfide than those of epichlorohydrin. As shown in Figure 1c, **4** reacts with CH$_3$SSCH$_3$ to form a minor CH$_3$S· abstraction product of *m/z* 115 and a major electron transfer product of *m/z* 94. Relatively higher pressures of dimethyl disulfide also favor a secondary reaction: ionized dimethyl disulfide of *m/z* 94 abstracts CH$_3$S· from neutral dimethyl disulfide to form, most likely, the S-methylated dimethyl trisulfide cation: CH$_3$SS(SCH$_3$)CH$_3^+$ of *m/z* 141.

MS^3 Structural Characterization

The structures of the major product ions were examined via triple stage (MS^3) collision-induced dissociation


Scheme 6
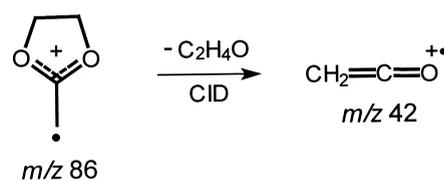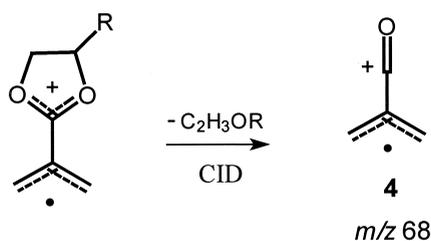
(CID) experiments. As exemplified in Figure 5a for the novel cyclic *distonic ketal* ion formed when **4** reacts with epichlorohydrin, all the cyclic ionic ketals, both the odd- and even-electron ones, display the expected and characteristic dissociation behavior: upon CID, they reform exclusively the protected acylium ion (Scheme **6**). Just as condensed-phase hydrolysis releases aldehydes or ketones from acetals and ketals, so gas-phase CID releases acylium ions from cyclic ionic ketals [11–13].

Figure 5b shows that, similarly to "ketal-protected" acylium ions, the *m/z* 86 product (formed from **3** by transacetalization followed by the loss of ethylene, Figure 2b) dissociates by C$_2$H$_4$O loss to form exclusively, and most likely, ionized ketene of *m/z* 42 (Scheme **7**). The authentic *m/z* 86 ion, formed by 70 eV EI-induced dissociation of 2-pentamethylene-1,3-dioxolane [24], displays a nearly identical low-energy CID spectrum (not shown).

MO Calculations

Cyclic distonic ketals: charge and odd spin densities.   Four novel cyclic *distonic ketal* ions (**5a,b** and **6a,b**) have been formed by the acylium ion reactions. Figure 6 shows the Becke3LYP/6-31G(*d*) charge and odd-spin densities of two model ions: **5a** and **6a**, and for comparison, those of neutral 2-methyl-1,3-dioxolane.

When compared with those of neutral dioxolane, the

a ; R = H
b ; R= CH$_2$Cl
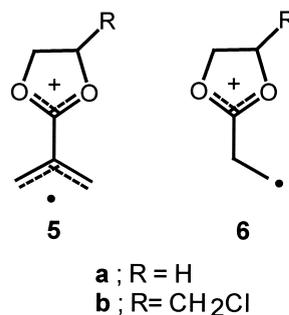
positive charges on the C2 carbon and on the two methylene ring groups of **5a** and **6a** increase considerably whereas those on the ring oxygens become less negative. These distributions suggest that the charge is delocalized mainly over the dioxolane ring.
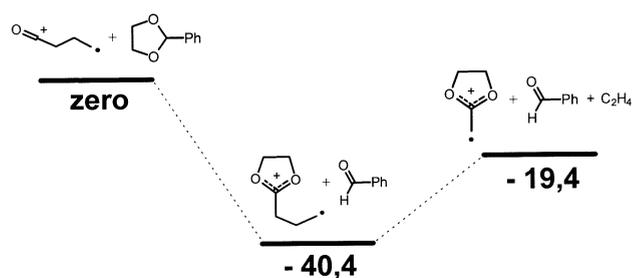
For the cyclic β-distonic ketal ion **6a**, the odd spin density is mainly on the β-methylene group (1.085); hence, **6a** displays, as expected, a highly localized odd spin site. The electronic structure of **5a** is unique. Most
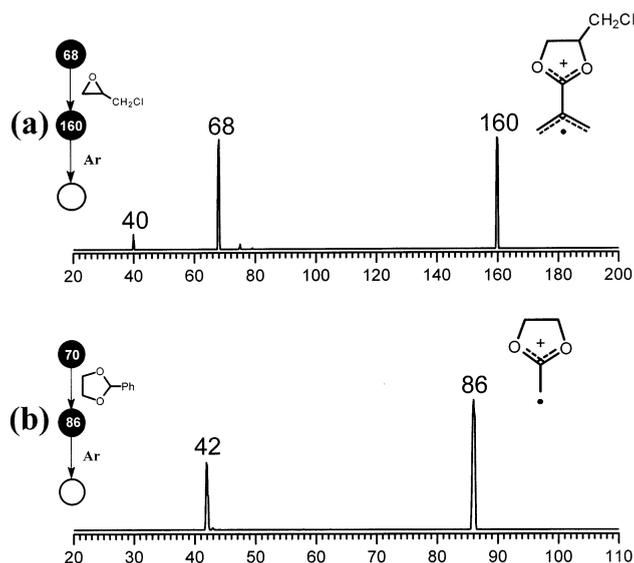
Figure 5. Triple-stage (MS³) CID sequential ion product ion mass spectra for (**a**) the cyclic *distonic ketals* formed by the gas-phase Meerwein reaction of **4** with epichlorohydrin and (**b**) of the product formed from **3** by transacetalization with 2-phenyl-1,3-dioxolane followed by rapid ethylene loss.
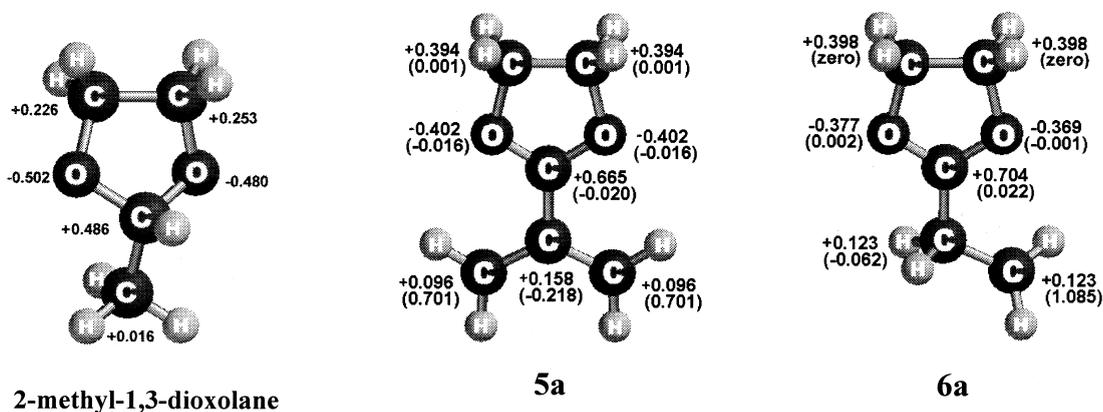

Figure 7. Becke3LYP/6-31G(*d*) potential energy surface diagram for transacetalization of **3** with 2-phenyl-1,3-dioxolane followed by ethylene loss. Energies are given in kcal/mol. Energy barriers were not estimated, and are not indicated. The electronic energies of the species are (in hartrees): **3** (−230.88928), 2-phenyl-1,3-dioxolane (−499.40132), the intact transacetalization product (−384.78148), benzaldehyde (−345.57345), the final product (−306.16060), and $CH_2=CH_2$ (−78.58746).

of the odd spin density is evenly delocalized over the two terminal methylene groups (0.701) thus characterizing an allylic radical system. Hence, as charge is mainly on the ring (+0.65), the structure of **5a** can be represented with "spatially" separated sites, that is, by a distonic structure in which both sites are delocalized by resonance: the spin site is delocalized over an allylic radical π-system and the charge site over a 1,3-dioxolanylium ion π-system (see representation for **5** above).

Reaction energetics. Figure 7 presents a Becke3LYP/6-31G(*d*) potential energy surface diagram for transacetalization of **3** with 2-phenyl-1,3-dioxolane. Transacetalization leading to the intact cyclic distonic ketal ion is predicted to be highly exothermic (−40.4 kcal/mol). Then, further dissociation of the "hot" primary product

by C_2H_4 loss to form the observed product of *m/z* 86 (Figure 2b) is also, overall, exothermic by −19.4 kcal/mol. Note that C_2H_4 loss is assumed because the acylium site is protected in the transacetalization product; hence the alternative CO loss is unlikely. These energy trends explain therefore both the favored transacetalization of **3** and the rapid dissociation by C_2H_4 loss of the nascent primary transacetalization product; hence its absence in the product ion mass spectrum.

Similarly, as for transacetalization followed by C_2H_4 loss, the Becke3LYP/6-31G(*d*) potential energy surface diagram of Figure 8 also presents the gas-phase Meerwein reaction of **3** followed by C_2H_4 loss (see Figure 4b) as a thermodynamically favored process, overall highly exothermic by −43.7 kcal/mol.

Becke3LYP/6-31G(*d*) calculations also predicts a highly favored, exothermic by −67.3 kcal/mol gas-phase Meerwein reaction of **4** with epichlorohydrin (Figure 9). But then no facile dissociation pathways are available; hence the intact primary isotopomeric ions of *m/z* 160/162 are observed as the main reaction products (Figure 3c).


Figure 6. Becke3LYP/6-31G(*d*) charge and odd-spin distributions of neutral 2-methyl-1,3-dioxolane and the cyclic *distonic ketals* **5a** and **6a**. For simplicity, the values for the hydrogen atoms were summed into those for the carbon atoms.
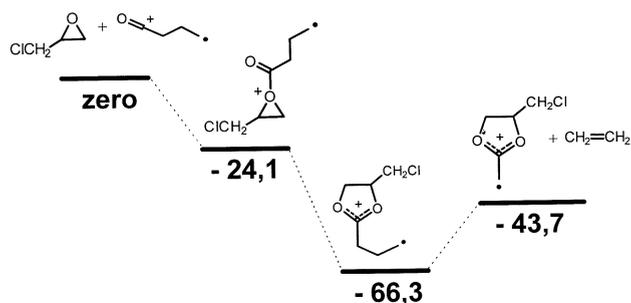
Figure 8. Becke3LYP/6-31G(d) potential energy surface diagram for **3** in gas-phase Meerwein reaction with epichlorohydrin followed by ethylene loss. Energies are given in kcal/mol. Energy barriers were not estimated, and are not indicated. The electronic energies of the species are (in hartrees): **3** (-230.88928), epichlorohydrin (-652.70055), O-acylated epichlorohydrin (-883.63039), the intact ring-expanded product (-883.69551), the final product (-883.65953), and $CH_2=CH_2$ (-78.58746).

Conclusion

Previously, acyclic distonic acylium ions were believed to display a predominant (therefore limited) radical reactivity with their charge acylium sites just promoting or catalyzing reactions at the radical site. Using appropriate neutral reactants, however, we have shown that acyclic distonic acylium ions display a rich, dual reactivity; that they react selectively as either free radicals with inert charge sites, or (and more pronouncedly) as acylium ions with inert radical sites. As demonstrated for **2** and **4**, both transacetalization and the gas-phase Meerwein reaction of acyclic distonic acylium ions form novel distonic ions: cyclic *distonic ketals*. As demonstrated for **3**, aliphatic $CH_2CH_2CH_2^{\bullet}$ chains facilitate fast ethylene loss from the nascent cyclic *distonic ketal ions* formed upon both transacetalization and the gas-phase Meerwein reaction.
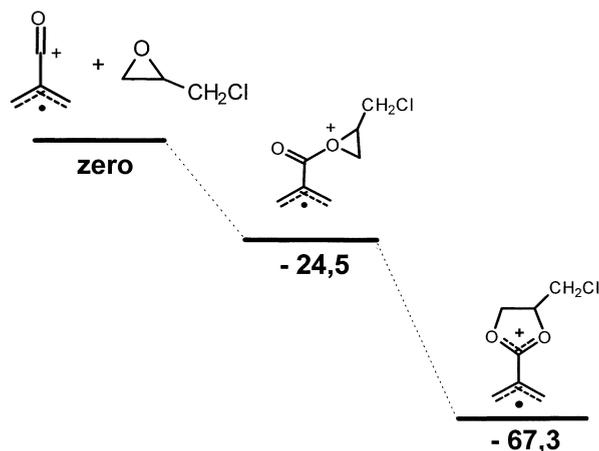
Figure 9. Becke3LYP/6-31G(d) potential energy surface diagram for **4** in gas-phase Meerwein reactions with epichlorohydrin. Energies are given in kcal/mol. Energy barriers were not estimated, and are not indicated. The electronic energies of the species are (in hartrees): **4** (-229.67990), epichlorohydrin (-652.70055), O-acylated epichlorohydrin (-882.41943), the Meerwein product (-882.48775).

Hence, acyclic distonic acylium ions display, in a single molecule, dual free radical and ion reactivity; under the experimental conditions used here, more pronounced acylium ion reactivity.

Note added in Proof: An alternative mechanism (to that shown in Scheme 2) can be proposed for the formation of *m/z* 87; it assumes C_2H_4 loss and a [1,4-H] shift prior to the ring-opening and recyclization steps of transacetalization:
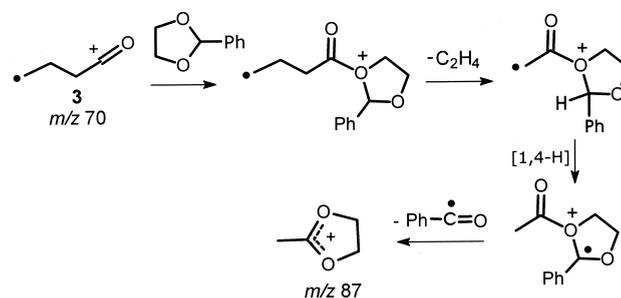
Scheme 8

Acknowledgments

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