Eberlin reaction of arenesulfenylium cations with cyclic acetals and ketals: ring contraction and cycloreversion

Xubin Zheng, W. Andy Tao and R. Graham Cooks*

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA

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Arenesulfenylium ions (ArS^+), elusive species in the condensed phase, are readily generated in the gas phase by electron ionization of sulfur-containing compounds and here their reactions with cyclic acetals and ketals are studied in a pentaquadrupole mass spectrometer. As a strong electrophile, the arenesulfenylium ion (ArS^+) reacts with five-membered cyclic acetals and ketals by hydride abstraction and electrophilic addition followed by ketone or aldehyde elimination. This latter process is ascribed to an oxygen-assisted ring-opening process in the adduct, followed by intramolecular nucleophilic substitution at carbon by the neutral arylthio group (ArS). This latter recyclization step generates a four-membered 2-aryl-1,2-oxathietan-2-ium ion. *Ab initio* calculations at the Becke3LYP/6-31G(d) level are performed to obtain the optimized structure of the ring contraction product and they predict the overall reaction to be highly exothermic. Collision-induced dissociation of the elimination product is consistent with its being the four-membered ring contraction product and this provides evidence for the gas-phase cycloreversion. Similarly, reaction with six-membered cyclic acetals and ketals forms a five-membered 2-aryl-1,2-oxathiolan-2-ium product ion. The overall reaction is of the Eberlin reaction type, the prototype of which is the transacetalization of acylium ions (M. N. Eberlin and R. G. Cooks, *Org. Mass. Spectrom*., 1993, **28**, 679). Substituents at the *para*-position of the arenesulfenylium cation have a significant influence on reactivity; the *p*-fluorobenzenesulfenylium cation displays similar reactivity to the unsubstituted arenesulfenylium cation, while the Eberlin product is not observed for the electron-donating amino (NH_2) or methoxy (CH_3O) substituted ions.

Introduction

Sulfenylium ions (RS^+), expected to be very strong electrophiles, are elusive species and their existence as free ions in the condensed phase has been debated for decades.[1–4] Two approaches have been proposed to prepare sulfenylium cations. The first is unimolecular sulfur–heteroatom (S–X, X = electronegative heteroatoms) bond fission of "cationoid" complexes or "carriers" of sulfenated compounds, a process usually attempted in the presence of strong Lewis acids.[5–8] Another approach involves the single electron oxidation of disulfides.[1,3,9–11] Although the existence of sulfenylium cation equivalents[12–14] and even the isolation of the sulfenylium cation salts[15] have been reported, no direct evidence of the presence of free sulfenylium cations (RS^+) has been reported for studies made in the condensed phase.[16]

Mass spectrometry is the method of choice to generate and study elusive species.[17] High abundances of sulfenylium cations can be readily produced in the gas phase, simply by electron or chemical ionization of sulfides or other sulfur-containing compounds. However, the generation of simple alkanesulfenylium cations (RS^+, R = alkyl) in the gas phase seems unlikely due to the ease of hydrogen or alkyl migration to form the more stable thiocarbonyl ions.[18] *Ab initio* MO calculations for the species $[CH_3S]^+$ predict that the singlet methanesulfenylium cation, CH_3S^+, which lies significantly lower in energy than the triplet cation, can easily rearrange to the more stable mercaptomethyl cation, $CH_2{=}SH^+$, without an energy barrier.[19,20] Experimental studies by collision-induced dissociation,[21,22] ion/molecule reactions[23] and photoionization mass spectrometry[24] of the isomeric mercaptomethyl cation, $CH_2{=}SH^+$, and the methanesulfenylium cation, CH_3S^+, are consistent with the *ab initio* calculation results. On the other hand, similar 1,2-H rearrangements are impossible for arenesulfenylium ions, which makes them good candidates to begin a study of the structure, energetics, and reactivity of gas-phase sulfenylium cations. Benzenesulfenylium cations (as prototypes of arenesulfenylium cations) have been generated in high abundance by ionization of different precursors and aspects of their gas-phase reactivity have been reported.[25–27] The arylthio group (ArS) is of intrinsic interest and has long been incorporated into organic molecules as building blocks in organic synthesis.[28–30] Incorporation of arylthio substituents (ArS) into peptides provides a series of highly potent HIV inhibitors.[31,32]

Unlike the phenoxylium cation (PhO^+), in which the positive charge is preferentially located at the *para*- and *ortho*-positions rather than at the oxygen atom, molecular orbital calculations reveal that the positive charge resides on the sulfur atom rather than the phenyl group in the arenesulfenylium cation (ArS^+).[8] Thus, nucleophilic attack will preferentially occur on the sulfur atom of the arenesulfenylium cation. In addition, other calculations show that the singlet state of the PhS^+ is 15 kcal mol^{-1} more stable than the triplet state due to the interaction of the reciprocally orthogonal p orbitals on sulfur with the orbitals of the aromatic ring.[27] Experimental studies on the gas-phase reactivity of the PhS^+ ion toward ethylene, carbon monoxide and nitrogen nucleophiles suggest that addition occurs at the sulfur atom,[27] as predicted by calculation.[8] The current study employs triple-stage mass spectrometry (MS^3) to gain insights into the structure, reactivity and mechanism of reaction of arenesulfenylium cations with cyclic acetals and ketals.

Recently, a highly-efficient gas-phase reaction involving a cation with amphiphilic character [such as acylium ($R–C^+{=}O$),[33] sulfinyl ($R–S^+{=}O$),[34] silanylium ($(RO)_3Si^+$),[35] phosphinoylium ($R_2P^+{=}O$),[36] dimethoxyboranylium ($CH_3OB^+{-}OCH_3$)[37] and dimethylaminoboranylium ($(CH_3)_2NB^+N{-}(CH_3)_2$)[38] ions], and a cyclic acetal or ketal was discovered. The reaction is analogous to solution-phase transacetalization, and has become known as the Eberlin reaction.[39] For instance, upon reaction with a cyclic acetal and ketal, the acylium ion is incorporated into the ring with elimination of a neutral aldehyde or ketone to generate a 1,3-dioxanylium or

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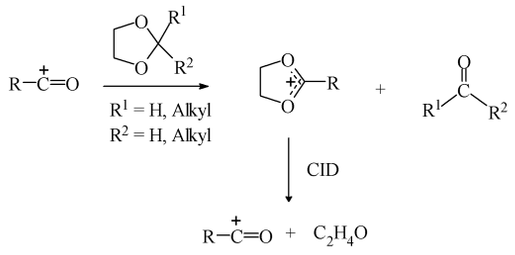


Scheme 1

1,3-dioxolanylium ion (Scheme 1). The product serves as an "ionic ketal" to protect the acylium ion in the gas phase in the same way as 1,2- or 1,3-diols protect the neutral aldehyde or ketone in the condensed phase through ketal formation. The acylium ion can be recovered in high yield by collision-induced dissociation (CID) of the 1,3-dioxanylium or 1,3-dioxolanylium ion, a process which is comparable to the hydrolysis of neutral acetals and ketals in the condensed phase. The high efficiency and characteristic nature of the reaction facilitate the study of particular ions. For example, the reaction was used to examine the cation reactivity of a distonic ion, dehydrobenzoyl cation:[40] similarly its transacetalization-like reactivity with 2-methyl-1,3-dioxolane allows the isomeric 2-, 3-, and 4-pyridyl cations to be distinguished easily by CID.[41]

Here, the Eberlin reaction is employed to study the gas-phase chemistry of sulfenylium ions. The arylthio group (ArS) shows amphiphilic character by displaying both electrophilic addition and intramolecular nucleophilic substitution during the course of the reaction. Net replacement of C–O by S^+ yields a characteristic ring contraction product, the 2-aryl-1,2-oxathietan-2-ium ion. 1,2-Oxathietane is an interesting intermediate in the condensed phase, since its analog 1,2-dioxetane is involved in a variety of biologically relevant processes including spontaneous mutations[42] and oxidative DNA damage.[43] Low energy CID of the 2-aryl-1,2-oxathietan-2-ium ion led to a gas-phase cycloreversion process. In addition, *ab initio* calculations were performed to study the electronic structures and gain insights into the mechanism of the proposed Eberlin-type ring contraction reaction.

Experimental

All experiments were conducted using a home-built pentaquadrupole mass spectrometer consisting of three mass-analyzing quadrupoles (Q1, Q3, Q5) and two reaction quadrupoles (Q2, Q4).[44] For MS^2 experiments, the reagent ions were generated by 70 eV electron ionization, mass-selected in Q1 and allowed to undergo ion/molecule reactions with neutral 1,3-dioxolanes or 1,3-dioxanes in Q2. The resulting spectra were recorded by scanning Q5 with both Q3 and Q4 set in the rf-only mode. For MS^3 experiments, the desired ions were generated in the ion source, mass selected in Q1 and then allowed to undergo ion/molecule reactions with neutral reagents in Q2. The desired ion/molecule product ion was mass-selected in Q3 and made to undergo collision-induced dissociation (CID) with argon in Q4. Sequential MS^3 spectra were recorded by scanning Q5.[45] The collision energy, given as the voltage difference between the ion source and the collision quadrupole, was nominally 0 eV for ion/molecule reactions in Q2, and 15 eV for CID in Q4, the latter being performed under multiple collision conditions using argon with 40% beam attenuation.

All compounds were commercially available and used without further purification. The mass/charge ratio (*m*/*z*) is reported using the Thomson unit (1 Th = 1 atomic mass per unit positive charge).[46]

Ab initio molecular orbital calculations were carried out with the Gaussian 98 program[47] package at the Purdue University Computing Center (PUCC). Optimized geometries and energies were obtained using Becke3LYP DFT and 6-31G(d) basis sets. Harmonic vibrational frequencies were calculated at the Becke3LYP/6-31G(d) level to characterize the stationary points and to obtain the zero-point vibrational energies, which were scaled by a factor of 0.96 and incorporated in the final total energy calculations.[48] Complete structural parameters, total energies, and lists of vibrational frequencies for all Becke3LYP/6-31G(d)-optimized structures are available upon request.

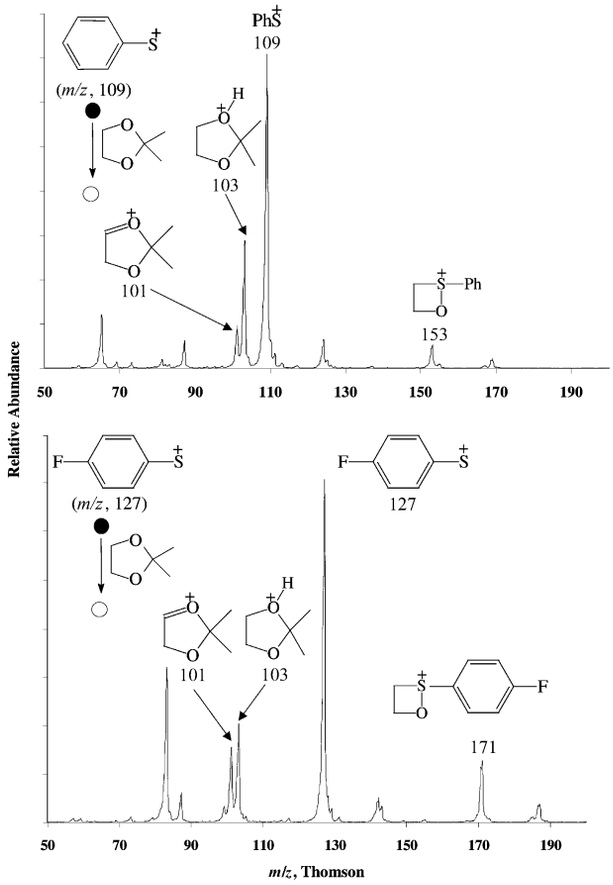


Fig. 1 Product ion (MS^2) spectra showing ion/molecule reactions of (a) benzenesulfenylium cation (PhS^+) and (b) *p*-fluorobenzenesulfenylium cation (*p*-F-PhS^+) with 2,2-dimethyl-1,3-dioxolane.

Results and discussion

Ion/molecule chemistry

The benzenesulfenylium cation (PhS^+) and the *p*-fluorobenzenesulfenylium cation (*p*-F-PhS^+) were readily generated in high abundance by electron ionization of thioanisole and *p*-fluorothioanisole, respectively. After mass selection, these ions were allowed to react with selected cyclic acetals and ketals. A typical MS^2 spectrum showing the products of ion/molecule reaction of benzenesulfenylium cation (*m*/*z* 109) with 2,2-dimethyl-1,3-dioxolane is displayed in Fig. 1a. The product ion with *m*/*z* 153 is tentatively assigned as the O,S-containing heterocyclic 2-phenyl-1,2-oxathietan-2-ium ion, generated *via* elimination of neutral acetone from the intact ion/molecule adduct. The reaction involves net replacement of C–O by S^+ in the cyclic ketals and is proposed to lead to a characteristic ring contraction product [eqn. (1)].

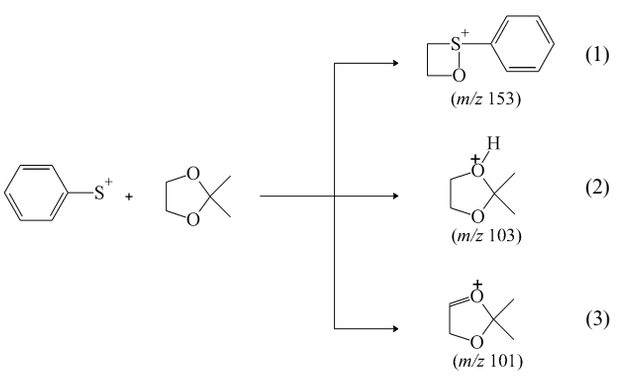
The product ion of *m*/*z* 101 arises *via* hydride abstraction [eqn. (3)]. A proton transfer product, *m*/*z* 103, [eqn. (2)] is most likely generated *via* a secondary reaction between the hydride abstraction product and 2,2-dimethyl-1,3-dioxolane.

Similar results were obtained using other neutral reagents, for example the six-membered 1,3-dioxane, and the results are summarized in Table 1. Besides these primary ion/molecule reaction products, simple fragmentation products of the

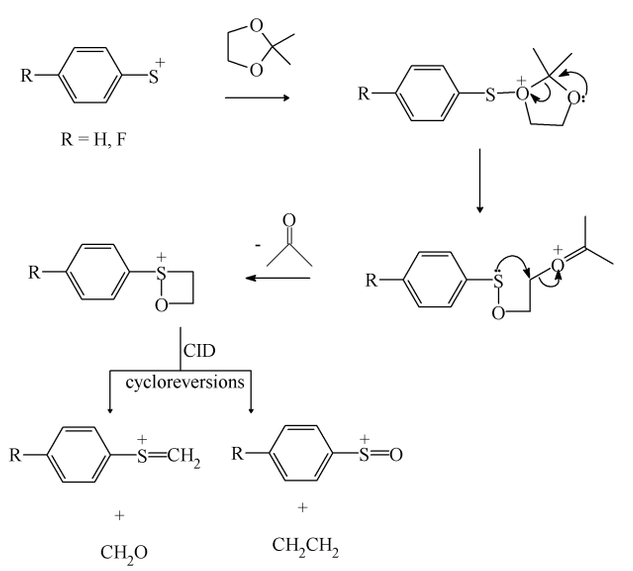
Table 1 Major ionic products of ion/molecule reactions of arenesulfenylium ions with 1,3-dioxolanes, 1,3-dioxane and thiazolidine

Reactant ion (*m/z*)	Neutral reagent	Products *m/z* (fractional ion abundance)[a]		
		Eberlin product	Proton transfer and hydride abstraction	Other ions
$C_6H_5S^+$ (*m/z* 109)	2,2-Dimethyl-1,3-dioxolane	153(8)	103(46), 101(15)	169(2), 87(10), 65(19)
	2-Methyl-1,3-dioxolane	153(6)	89(23), 87(40)	169(<1), 65(31)
	1,3-Dioxolane	153(<1)	75(<1), 73(28)	183(13), 65(59)
	1,3-Dioxane	167(22)	89(4), 87(12)	177(18) 65(43)
	Thiazolidine	169(3)	90(60), 88(24)	198(5), 65(8)
p-F-$C_6H_4S^+$ (*m/z* 127)	2,2-Dimethyl-1,3-dioxolane	171(14)	103(23), 101(18)	187(4), 87(6), 83(35)
	2-Methyl-1,3-dioxolane	171(6)	89(20), 87(37)	187(1), 83(36)
	1,3-Dioxolane	171(<1)	75(1<1), 73(25)	83(75)
	1,3-Dioxane	185(8)	89(8), 87(38)	177(5), 83(42)
	Thiazolidine	187(1)	90(56), 88(25)	83(16)
p-NH_2-$C_6H_4S^+$ (*m/z* 124)	2,2-Dimethyl-1,3-dioxolane	—[b]	103(17), 101(34)	80(49)
p-CH_3O-$C_6H_4S^+$ (*m/z* 139)	2,2-Dimethyl-1,3-dioxolane	—[b]	103(18), 101(44)	95(38)

[a] Relative to the total ion abundance, excluding the reactant ion, as a percentage. [b] Not observed.



reagents are observed, *e.g. m/z* 65 which is generated by the loss of neutral carbon sulfide (CS) from the reagent ion (PhS^+) and correspondingly, *m/z* 83 generated by fragmentation of *p*-F-PhS^+, and they are also listed in Table 1. A general mechanism for the Eberlin reaction of arenesulfenylium cations with cyclic acetals and ketals is proposed in Scheme 2: initial electrophilic



Scheme 2

addition occurs at the sulfur center of the benzenesulfenylium cation, followed by ring opening to generate an intermediate carbocation stabilized by neighboring-group participation. Subsequent recyclization occurs in the course of a nucleophilic substitution of the sulfur at the 4-position, accompanied by the elimination of a neutral aldehyde or ketone to generate the characteristic ring contraction Eberlin product.

Substituents at the *para*-position of the benzene ring are expected and observed to affect the reactivity of the arenesulfenylium cation. While *p*-fluorobenzenesulfenylium cation displays a similar reactivity compared to the unsubstituted arenesulfenylium cation, no Eberlin product is observed when an electron-donating group is substituted at the *para*-position of the benzene ring, although the hydride abstraction and proton transfer reactions do occur. Upon fluorine substitution, the reactivity and hydride affinity of *p*-fluorobenzenesulfenylium cation are probably not much affected due to the opposing π-donor and inductive effects. The experimental results demonstrate that the Eberlin product of *p*-fluorobenzenesulfenylium cation with cyclic acetals and ketals displays similar fractional ion abundance (defined as the ratio of the product ion abundance relative to the total ion abundance, excluding the reactant ion) to that of unsubstituted benzenesulfenylium cation (Table 1).

Eberlin products are not observed when *p*-aminobenzenesulfenylium cation (*p*-NH_2-$C_6H_4S^+$ *m/z* 124) or *p*-methoxybenzenesulfenylium cation (*p*-CH_3O-$C_6H_4S^+$ *m/z* 139) is treated with 2,2-dimethyl-1,3-dioxolane (Table 1). Instead, hydride abstraction and proton transfer lead to the two major products observed. In addition, abundant fragment ions, 2-NH_2-$C_5H_4^+$ having *m/z* 80 or 2-CH_3O-$C_5H_4^+$ having *m/z* 95, generated by elimination of neutral carbon sulfide (CS) from the corresponding *p*-aminobenzenesulfenylium cation (*p*-NH_2-$C_6H_4S^+$ *m/z* 124) or *p*-methoxybenzenesulfenylium cation (*p*-CH_3O-$C_6H_4S^+$ *m/z* 139), are also observed. A possible explanation is the fact that amino (NH_2) or methoxy (CH_3O) at the *para*-position delocalizes the positive charge and stabilizes the arenesulfenylium cation making it less reactive. Amino (NH_2) and methoxy (CH_3O) *para*-substituents also decrease the hydride affinity (defined as the enthalpy change for the reaction $RSH \rightarrow RS^+ + H^-$ at 298 K) of the corresponding arenesulfenylium cation. However, these effects may have more effect on the Eberlin reaction process than on the hydride abstraction process.

Initial efforts to generate the methanesulfenylium cation (CH_3S^+) by electron ionization of dimethyl sulfide, proved to be unfruitful due to the ready 1,2-H rearrangement discussed earlier. As a result, no reaction product was observed when the reagent ion, *m/z* 47, with the structure of mercaptomethyl cation, $CH_2{=}SH^+$, was treated with neutral cyclic acetals and ketals.

Collision-induced dissociation chemistry

Additional evidence for the cyclic structure of the Eberlin product was obtained by performing MS^3 sequential product ion scans on the 2-aryl-1,2-oxathietan-2-ium ions generated by the ion/molecule reactions. A typical MS^3 spectrum, illustrating

Table 2 MS^3 sequential products generated from the Eberlin products[a]

Reactant ion (*m/z*)	Neutral reagent	Products *m/z* (relative abundance)[b]	
		Eberlin product	Fragments, *m/z* (relative abundance)
$C_6H_5S^+$ (*m/z* 109)	2,2-Dimethyl-1,3-dioxolane	153(100)	125(21), 123(6)
	2-Methyl-1,3-dioxolane	153(100)	125(23), 123(8)
	1,3-Dioxane	167(100)	125(4), 109(10)
	Thiazolidine	169(100)	141(20), 109(34)
p-F-$C_6H_4S^+$ (*m/z* 127)	2,2-Dimethyl-1,3-dioxolane	171(100)	143(48), 141(12), 127(5)
	2-Methyl-1,3-dioxolane	171(100)	143(34), 141(15), 127(4)
	1,3-Dioxane	185(100)	143(6), 127(17)

[a] All data are for MS^3 experiments in which the reactant ion and either the adduct or the replacement product ion were mass-selected while the third mass-analyzer was scanned. [b] Relative to the base peak, excluding the reactant ion, as a percentage.

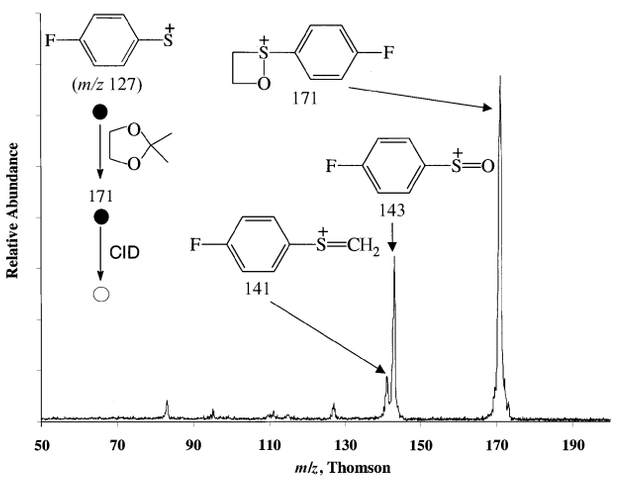
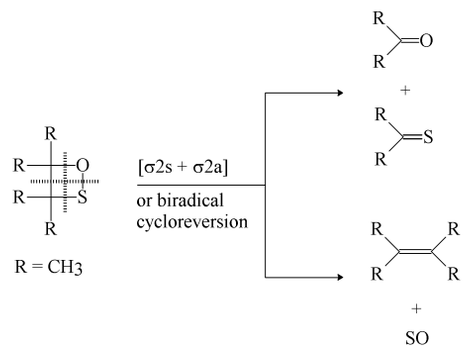


Fig. 2 Sequential product ion (MS^3) spectra of the proposed Eberlin reaction product of *p*-fluorobenzenesulfenylium cation (*p*-F-PhS^+) with 2,2-dimethyl-1,3-dioxolane.

the CID behavior of the product of reaction of 2,2-dimethyl-1,3-dioxolane with *p*-fluorobenzenesulfenylium cation, is shown in Fig. 2. The ionic four-membered 2-aryl-1,2-oxathietan-2-ium ion shows a characteristic gas-phase cycloreversion with the elimination of either a neutral ethylene or neutral formaldehyde to form *p*-fluorophenylsulfinyl cation (*p*-F-C_6H_4-S^+=O, *m/z* 143) or *p*-fluorophenylmethylenesulfonium cation (*p*-F-C_6H_4-S^+=CH_2, *m/z* 141), respectively. Similar CID behavior was observed when the benzenesulfenylium cation (PhS^+) was treated with 2,2-dimethyl-1,3-dioxolane and 2-methyl-1,3-dioxolane, though to a smaller extent. The data showing the dissociation of 2-aryl-1,2-oxathietan-2-ium ions generated from arenesulfenylium cations with various cyclic acetals and ketals are summarized in Table 2. A condensed-phase cycloreversion reaction involving heterocyclic intermediate 1,2-oxathietanes has previously been reported by Lown and co-workers[49,50] to give fragmentation products acetone and thioacetone and, to a much smaller extent, the alternative products but-2-ene and sulfur monoxide. The reaction might occur either *via* a [σ2s + σ2a] cycloreversion or by a biradical mechanism, as shown in Scheme 3.[49,50] However, the major products of the reaction of the neutral compound in solution are the S–O bond fission products, while cycloreversion of the ionic Eberlin product in the gas phase favors the sulfinyl cation product (*e.g.*, *p*-F-C_6H_4-S^+=O, *m/z* 143). This difference can probably be attributed to the fact that the single S–O bond is the weakest bond in the neutral 1,2-oxathietane, while this is not the case for the 2-aryl-1,2-oxathietan-2-ium ions. Neighboring group participation by the oxygen atom stabilizes the positive charge on sulfur, and gives the S^+–O bond partial double bond character (resonance structure S=O^+). *Ab initio* calculations confirm this feature as discussed further below.

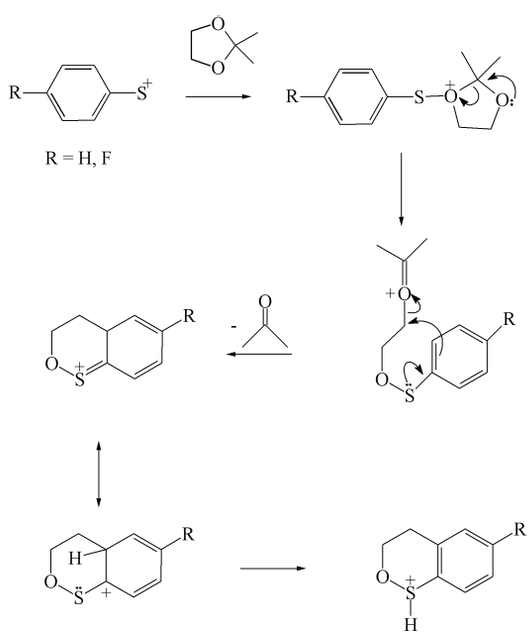
Interestingly, examination of Fig. 1a and 1b shows evidence that dissociation of the Eberlin products *m/z* 153 and 171 has



Scheme 3

already occurred to some extent in the reaction quadrupole, thus forming the phenylsulfinyl cation (C_6H_4-S^+=O, *m/z* 125) and *p*-fluorophenylsulfinyl cation (*p*-F-C_6H_4-S^+=O, *m/z* 143) respectively. These ions will likely undergo further ion/molecule reaction with neutral acetals and ketals to generate the secondary Eberlin products of *m/z* 169 and 187, as reported earlier by Eberlin and co-workers (Table 1).[51]

An alternative to the ring contraction pathway can be proposed for the reaction of arenesulfenylium cation with cyclic acetals and ketals, as shown in Scheme 4: after initial formation

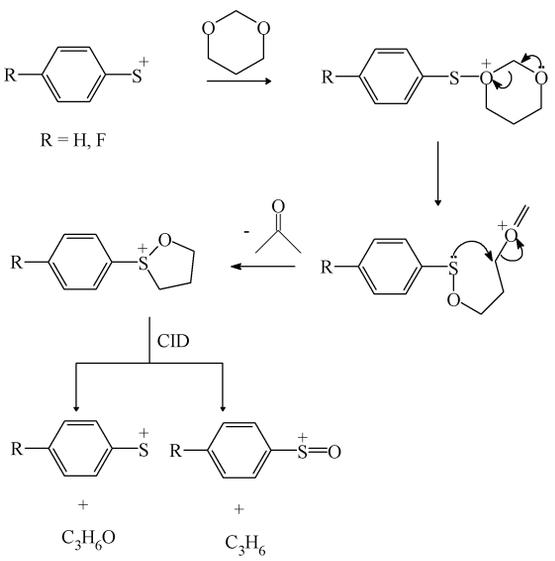


Scheme 4

of the adduct by electrophilic addition at the sulfur atom and subsequent ring opening, the nucleophilic displacement reaction by the elimination of a neutral acetone could possibly involve de-aromatization of the phenyl ring assisted by the lone

pair electrons on the sulfur atom, thus forming a bicyclic 4,4a-dihydro-3*H*-benzo[*c*][1,2]oxathiin-1-ylium ion, with the charge located at sulfur. Subsequently, the bicyclic ion could undergo intramolecular proton transfer followed by re-aromatization to generate a favored 3,4-dihydrobenzo[*c*][1,2]oxathiin-1-ium ion. This ion, like the proposed ring-contraction product, may dissociate upon CID to form the same *m*/*z* product ions associated with loss of both C_2H_2 and CH_2O. At present, we are unable to distinguish the bicyclic ion formed *via* the alternative reaction pathway from the Eberlin ring contraction product. However, the observed *higher* reactivity of PhS^+ toward the six-membered acetal (1,3-dioxane) (below) contrasts with the expectation of *decreased* reactivity by this alternative pathway to generate the less favorable seven-membered bicyclic product ion.

Compared to the Eberlin reaction with 1,3-dioxolanes, the arenesulfenylium ions react with 1,3-dioxane to give products of higher fractional ion abundance (compare *m*/*z* 153 and 171 in Table 2, with *m*/*z* 167 and 185, respectively, in Table 1). This reaction is proposed to generate ring-contracted O,S-containing 2-aryl-1,2-oxathiolan-2-ium ions. The reaction mechanism proposed in the case of the six-membered acetal is illustrated in Scheme 5. The high fractional ion abundance



Scheme 5

can be attributed to the formation of favorable, unstrained five-membered 2-aryl-1,2-oxathiolan-2-ium product ions. Unlike the cycloreversion of the four-membered 2-aryl-1,2-oxathietan-2-ium ions, CID of the resulting five-membered 2-aryl-1,2-oxathiolan-2-ium ions mainly gives the recovered reagent ion of PhS^+ or *p*-F-PhS^+.

Thiazolidine (C_3H_7NS) has two nucleophilic sites and might therefore form two isomeric ring contraction product ions, following initial addition at the sulfur or nitrogen site, respectively. However, only one product, that due to initial nucleophilic attack at the sulfur atom of the benzenesulfenylium or *p*-fluorobenzenesulfenylium cation, followed by elimination of neutral methanimine (CH_2=NH), was observed (Table 1). The higher nucleophilicity of sulfur is the expected result and parallels observations made in earlier Eberlin reactions with thiazolidine.[33,36] The CID behavior of the resulting Eberlin product, *m*/*z* 169, is analogous to that of the 1,3-dioxolane products (Table 2). Proton transfer led to the major reaction product, consistent with the expected high proton affinity of thiazolidine.

Ab initio calculations

It is difficult to calculate accurately the singlet and triplet states of the PhS^+ cation. Previous *ab initio* calculations show that the

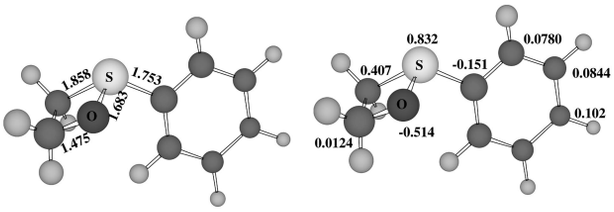


Fig. 3 Optimized geometries and natural atomic charges (Becke3LYP/6-31 G(d)//Becke3LYP/6-31 G(d)) of 2-phenyl-1,2-oxathietan-2-ium ion.

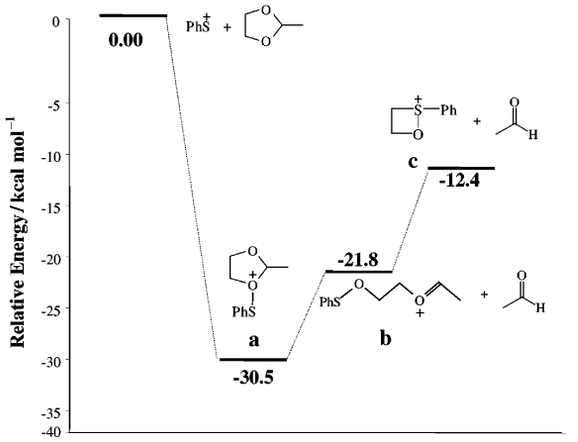


Fig. 4 Intrinsic reaction coordinate for the reactions of benzenesulfenylium cation (PhS^+) with 2-methyl-1,3-dioxolane.

singlet state is 15 kcal mol^{-1} more stable than the triplet state at the MP2/6-31G(d)//MP2/6-31G(d) level, while at the MP2/6-31G(d)//RHF/6-31G(d) level the triplet state is more stable than the singlet state. The present study employed *ab initio* calculations at the Becke3LYP/6-31G(d)//Becke3LYP/6-31G(d) level and found that the two states are essentially equal in energy—the singlet state is more stable than the triplet by only 0.34 kcal mol^{-1}. The Becke3LYP/6-31G(d)-optimized structure of the ring contraction product, 2-phenyl-1,2-oxathietan-2-ium ion, with net atomic charges, is presented in Fig. 3. The structure is characterized, with respect to neutral 1,2-oxathietane, by a shorter S–O bond length and by greater charge localization on sulfur. It is these features that also rationalize the CID behavior of the ion: in agreement with the location of the charge site, cycloreversion upon CID occurs to form products with charge on the sulfur side in both channels. This result is also consistent with the partial double-bond character of the S–O bond. The CID results show that the cleavage of the S–O σ bond is the less favorable pathway and as a result, ArS^+=O is the main CID product.

Referring to the proposed mechanism shown in Scheme 2, the calculated intrinsic reaction coordinate for reaction of benzenesulfenylium cation (PhS^+) with a typical cyclic acetal (2-methyl-1,3-dioxolane) is shown in Fig. 4. The diagram shows that formation of the intact adduct **a** by initial nucleophilic attack of the oxygen atom on the sulfur atom of the benzenesulfenylium cation is exothermic by −30.5 kcal mol^{-1}. Subsequent ring opening generates the resonance stabilized carbocation **b** and requires an energy input of 8.7 kcal mol^{-1} relative to the adduct **a**. Further dissociation of **b** by nucleophilic attack by the original sulfur atom to form a four-membered 2-phenyl-1,2-oxathietan-2-ium ion **c** is endothermic by 9.4 kcal mol^{-1}. This makes the overall Eberlin reaction exothermic by −12.4 kcal mol^{-1}.

Conclusion

Arenesulfenylium ions undergo highly efficient reactions with cyclic acetals and ketals to generate characteristic ring contrac-

tion products. The arylthio (ArS) group displays amphiphilic character as shown by its being involved in both electrophilic addition and intramolecular nucleophilic substitution steps during the reaction sequence. Evidence of gas-phase cycloreversion is found in the low energy collision-induced dissociation of the proposed 2-aryl-1,2-oxathietan-2-ium product ions, as shown by pentaquadrupole triple-stage (MS^3) mass spectrometry. While the *p*-fluorobenzenesulfenylium cation (*m*/*z* 127) displayed a similar reactivity toward the neutral cyclic acetals and ketals compared to the unsubstituted benzenesulfenylium cation (*m*/*z* 109), amino (NH_2) or methoxy (CH_3O) substituents stabilized the corresponding arenesulfenylium cation and lowered its hydride affinity. As a result, no Eberlin product was observed in these cases. Further studies might include the structure and reactivity of the analogous phenoxylium cation (PhO^+), and possible application of the ring contraction experiment in ion/surface reactions at interfaces.

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