Synthesis of silicon heterocycles *via* gas-phase silylium ion reactions with cyclic acetals and ketals†

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Silylium cations react with a variety of cyclic acetals and ketals by initial *O*-silylation followed by ring-opening and then recyclization with elimination of an aldehyde or ketone, respectively. The reaction occurs with high efficiency and results in the replacement of C–O in the cyclic acetals and ketals by $Si–O^+$. The cyclic nature of the product ions was established by multiple-stage mass spectrometry (MS^2 and MS^3). For a series of silylium ions, $(CH_3O)_3Si^+$, $(CH_3O)_2Si^+CH_3$, $CH_3OSi^+(CH_3)_2$, and $Si^+(CH_3)_3$, increasing electron deficiency at silicon favors the formation of intact adducts; correspondingly, the highly oxygen-substituted silylium cations tend to undergo the recyclization reaction to form the replacement product ion. In the absence of oxygen in the reactant ion (*e.g.* $Si^+(CH_3)_3$) an acyclic product is generated and characterized by its collision-induced dissociation (CID) spectrum, which shows silicon-to-carbon methyl migration. The reactivity of silylium ions was further explored using thiazolidine and 1,3-oxazinane and the products of replacement of C–N, C–S and C–O by $Si–O^+$ were observed. The silylium ion reactions thus provide a general, structurally diagnostic, method for the gas-phase characterization of cyclic acetals and ketals.

Introduction

During the last few decades, exploration of the chemistry of silicon has increased rapidly, driven both by its intrinsic interest and by an increasing number of industrial applications. Organosilicon reagents have become major tools in organic synthesis, both as protecting groups and as regio- and stereochemical directing groups.[1] Modified silica is widely used as a support in liquid chromatography, providing high column efficiency and great mechanical stability.[2] Synthetic silicone polymers offer remarkable chemical and physical properties that have led to their extensive use in cosmetics and pharmacological formulations.[3] Silicon-containing compounds and polymers are excellent precursors to glasses and ceramics.[4] The ever-increasing technological applications of organic silicon compounds have led to growing attention being paid to their mass spectrometry and gas-phase ion chemistry, and a variety of gas-phase reactions of silicon-containing ions have been explored. Such studies may serve also as sources of information on the probable reactivity of silicon-containing ions in the condensed phase.

Gas-phase ion–molecule reactions of silicon-containing ions with various coordination numbers have been investigated.[5–8] The chemistry of ions with low coordination numbers (silicon centers with coordination numbers 1, 2, or 3) is dominated by the tendency of silicon to form strong bonds to oxygen, nitrogen, and sulfur.[6] For example, the atomic silicon cation $Si^{+\bullet}$ yields $SiO^{+\bullet}$ in reactions with oxygen-containing compounds such as N_2O; in subsequent reactions with the same reagent, $SiO^{+\bullet}$ is converted to the highly oxidized $SiO_4^{+\bullet}$ cation.[9] Silyl anions (R_3Si^-) react with CO_2, N_2O and CS_2 by oxygen or sulfur transfer to form R_3SiO^- (or R_3SiS^-).[10] The formation of hypercoordinate silicon species is observed in both the gas and condensed phase.[11,12] Of particular importance are pentacoordinate silicon anions. These species have been proposed as intermediates in nucleophilic substitution reactions at silicon.[13,14] Squires *et al.* employed pentacoordinate silicon hydrides, $RSiH_3(OR')^-$ (R, R′ = alkyl) to effect regiospecific reduction of carbonyl compounds.[15,16] The decomposition of the dialkoxysiliconate ions formed is sensitive to structure and thus useful for quantitative determination of the diastereomeric products. By a rigorous measurement of the threshold for collision-induced dissociation of pentacoordinate silicon hydrides, Squires and co-workers also carried out the first systematic measurements of hydride affinities (HA) of alkylsilanes.[17] In addition, this group reported a regiospecific synthetic method,[18] based on the fluoride-induced desilylation reaction first introduced by Depuy and co-workers,[19] which they used to produce structurally-defined negative ions of organic biradicals such as the benzyne anions and the trimethylenemethane anion. In work of great elegance, they subsequently used this procedure to prepare unprecedented biradical and distonic negative ions.[20–22]

Due to the pivotal importance of the carbenium ion in organic chemistry, its silicon analog, the tricoordinate silicon cation, *i.e.* the silylium (also known as the silylenium or silicenium) ion, has drawn much attention.[23,24] Considerable difficulties have been encountered in generating silylium ions in solution, either as stable species or as reactive intermediates, the primary impediment being the high affinity of silicon for Lewis bases, especially oxygen and halogens.[6,25] These constraints are lifted in the gas phase, which provides an environment free from possible interfering solvents. Appropriately, therefore, the chemistry and thermochemistry of the silylium ions have been studied in some detail in this medium. The most extensively studied silylium ion, the trimethylsilyl ion ($(CH_3)_3Si^+$), readily forms adducts with alcohols,[26] ethers,[27] ketones,[28] and carboxylic acids.[29] This reaction is proposed to occur by a two-step process and involves formation of strong Si–O bonds followed by radiative or collisional stabilization of the adduct.[30] Tetramethylsilane (TMS), the high pressure mass spectrum of which is dominated by the silylium ion $(CH_3)_3Si^+$, therefore proves to be a useful chemical ionization (CI) reagent gas.[31,32] It has been employed to differentiate neutral stereoisomers such as *cis*- and *trans*-pentane-1,2-diol based on different relative stabilities and dissociation behavior of the adduct ions.[33] Gas-phase trimethylsilylium cation ($(CH_3)_3Si^+$) affinities towards primary, secondary, and tertiary alkylamines have been measured by high pressure mass spectrometry and found to increase linearly with

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† Dedicated to the memory of Robert R. Squires, in respect and admiration.

the proton affinities of the corresponding amines.[30] In addition, Shin and Beauchamp[34] measured the hydride affinities of the methyl-substituted silylium ions, $(CH_3)_3Si^+$, $(CH_3)_2Si^+H$, and $CH_3Si^+H_2$, and observed that the hydride affinities of the silylium ions are generally about 30 kcal mol^{-1} lower than those of the corresponding carbenium ions.

The starting point for the investigation undertaken in this paper is the ion–molecule transacetalization reaction which occurs when acylium ions react in the gas phase with cyclic acetals, ketals, and related heterocycles.[35,36] This process has become known as the Eberlin transacetalization. Analogous reactions have been observed with cations having amphoteric Lewis character, including sulfinyl ($R–S^+=O$),[37] borinium [$(RO)_2B^+$][38] and phosphonium ($R_2P^+=O$) ions.[39] In the prototype transacetalization reaction of five- and six-membered cyclic ketals with acylium ions, initial *O*-acylation is followed by a ring opening/recyclization process in which neutral carbonyl compounds are eliminated and 1,3-dioxanium or 1,3-dioxolanium ions are formed. In analogy to the protection of neutral ketones in the condensed phase, the resulting 1,3-dioxanium or 1,3-dioxolanium ions serve as "ionic ketals" to protect acylium ions in the gas phase. Also interesting is the fact that collision-induced dissociation of the cyclic "ionic ketals" reforms the acylium ions in high yield, a step that is comparable to the hydrolysis of neutral acetals and ketals in the condensed phase.[35,36] Experimental results and *ab initio* calculations show that the reaction enthalpy is predominantly governed by the Lewis acidity of the reactant cation.[38] To explore further the scope of the Eberlin transacetalization and related reactions, silylium ions were reacted with various acetals and ketals, and the products were subjected to detailed investigation by multiple-stage mass spectrometry. A highly efficient reaction channel generating cyclic tetracoordinate silicon ions from the acyclic tricoordinate reactants was observed. Sequential electrophilic addition, ring opening, and intramolecular nucleophilic recyclization is proposed.

Experimental

Tandem (MS^2) and triple stage (MS^3) mass spectrometric experiments were performed using a Finnigan TSQ 700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA) and a home-built pentaquadrupole mass spectrometer. The pentaquadrupole mass spectrometer consists of three mass-analyzing quadrupoles (Q1, Q3, Q5) and two reaction quadrupoles (Q2, Q4) and is described in detail elsewhere.[40] Ion–molecule reactions were performed by mass-selecting the reactant ion using Q1 and then allowing reaction with a dioxolane, thiazolidine or other compounds introduced into Q2. The product spectrum was recorded by scanning Q5, while operating Q3 in the rf-only mode. Ion–molecule products of interest were characterized by MS^3 experiments;[41] in this experiment the product of interest was mass-selected by Q3 and allowed to undergo collision-induced dissociation (CID) with argon in Q4, while Q5 was scanned to record the sequential product ion spectrum. The collision energy, given as the voltage difference between the ion source (grounded) and the collision quadrupole, was nominally 0 eV for ion–molecule reactions in Q2, and 10 eV for CID in Q4 which was performed under multiple collision conditions with 40% beam attenuation.

Competition experiments on substituted silylium ions with dioxolanes were performed using the TSQ 700, which has greater sensitivity. The reagents were mixed and a 1 μL aliquot of the mixture was introduced into the ion source on the rhenium wire filament of a direct insertion probe. The single-stage mass spectrometry experiments were performed by scanning the third quadrupole while keeping the first and second quadrupole in the rf-only mode to transmit all ions. In MS^2 experiments, the ions were mass selected in the first quadrupole and allowed to undergo CID with argon at a nominal pressure of 0.2 mtorr. The dissociation products were mass analyzed by scanning the third quadrupole.

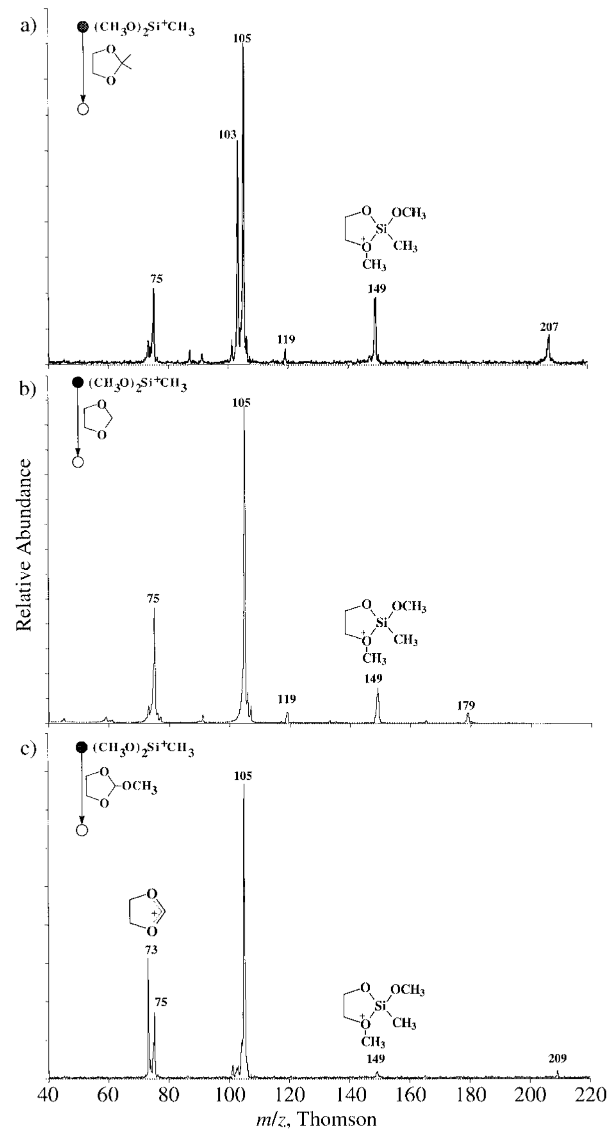


Fig. 1 Product ion (MS^2) spectra showing the ionic products of reaction of $CH_3Si^+(OCH_3)_2$ with a) 2,2-dimethyl-1,3-dioxolane; b) 1,3-dioxolane; c) 2-methoxy-1,3-dioxolane. In the terminology used to describe the scan mode employed, a filled circle shown in the figure represents a selected mass, an open circle, a scanned mass, while the neutral reagent or collision gas that causes the mass transitions is shown between the circles. See ref. 41 for details.

All compounds except 1,3-oxazinane were commercially available and used without further purification. 1,3-Oxazinane was synthesized according to a previously reported procedure.[42] Mass/charge ratios (*m*/*z*) were reported using the Thomson unit (1 Th = 1 atomic mass per unit positive charge).[43]

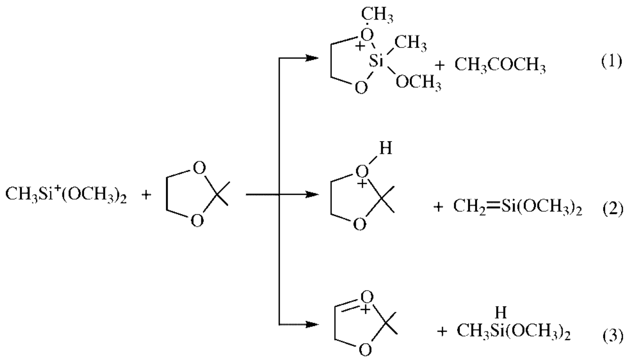
Results and discussion

The tricoordinate silylium ions, $(CH_3O)_3Si^+$ (*m*/*z* 121) and $CH_3Si^+(OCH_3)_2$ (*m*/*z* 105) were generated by standard 70 eV electron ionization of methyltrimethoxysilane, mass-selected, and allowed to react with a series of substituted dioxolanes, dioxane, thiazolidine, and 1,3-oxazinane. Major ionic products are listed in Table 1 and a typical MS^2 product ion spectrum illustrating the reaction of $CH_3Si^+(OCH_3)_2$ with 2,2-dimethyl-1,3-dioxolane is shown in Fig. 1a. Note that the abundant product ion of *m*/*z* 149 is likely produced *via* elimination of acetone from the intact adduct (*m*/*z* 207) by net replacement of C–O by Si–O$^+$ in the cyclic ketal [eqn. (1)]. Simple proton transfer [eqn. (2)] and hydride abstraction [eqn. (3)] are major

Table 1 Major ionic products of ion–molecule reactions of silylium ions $(CH_3O)_3Si^+$ and $CH_3Si^+(OCH_3)_2$ with dioxolanes, dioxane, and thiazolidine[a]

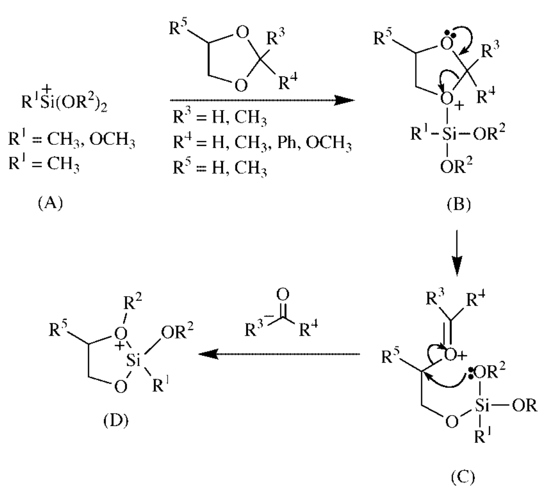
			Products *m/z* (relative abundance)[b]		
Reactant ion (*m/z*)	Neutral reagent	Adduct	Replacement product	Proton transfer	Hydride abstraction
$(CH_3O)_3Si^+$ (121)	1,3-Dioxolane	195(20)	165(100)	N/A[e]	73(90)
	2-Methyl-1,3-dioxolane	209(18)	165(100)	89(25)	87(40)
	2,2-Dimethyl-1,3-dioxolane	223(14)	165(42)	103(100)	101(18)
	2-Phenyl-1,3-dioxolane	271(12)	165(100)	151(95)	149(35)
	2-Methoxy-1,3-dioxolane	225(15)	165(20)	N/A	N/A
	4-Methyl-1,3-dioxolane	209(60)	179(100)	89(15)	87(80)
	1,3-Dioxane	209(80)	179(100)	89(10)	87(70)
	Thiazolidine	210(18)	181(41),[c] 164(38)[d]	90(35)	88(20)
	1,3-Oxazinane	208(12)	179(2),[c] 178(12)	88(81)	86(100)
$CH_3Si^+(OCH_3)_2$ (105)	1,3-Dioxolane	179(30)	149(100)	N/A	73(20)
	2-Methyl-1,3-dioxolane	193(15)	149(100)	89(25)	87(33)
	2,2-Dimethyl-1,3-dioxolane	207(18)	149(34)	103(100)	101(13)
	2-Phenyl-1,3-dioxolane	255(15)	149(100)	151(90)	149(30)
	2-Methoxy-1,3-dioxolane	209(18)	149(20)	N/A	N/A
	4-Methyl-1,3-dioxolane	193(70)	163(100)	89(15)	87(90)
	1,3-Dioxane	193(80)	163(100)	N/A	87(75)
	Thiazolidine	194(55)	165(30),[c] 148(25)[d]	90(100)	88(60)
	1,3-Oxazinane	192(18)	163(3),[c] 162(17)	88(74)	86(100)

[a] All data are for MS^2 product ion spectra using mass-selected silylium ions. [b] Relative to the base peak, excluding the reactant ion, as a percentage. [c] Replacement of C–N by Si–O^+. [d] Replacement of C–S by Si–O^+. [e] Ratio cannot be determined due to the interference from the fragment of the reactant ion.



competing reactions which form ions of *m/z* 101 and *m/z* 103, respectively, while fragmentation of the reactant ion by loss of neutral formaldehyde, to give the peak at *m/z* 75, is also observed.

A general mechanism for the replacement of C–O by Si–O^+ in cyclic acetals and ketals is proposed in Scheme 1. This mechanism is analogous to that proposed for the Eberlin transacetalization of acylium ions.[35,36] The reaction proceeds by initial electrophilic addition of the silylium ion (A) to form an adduct (B), followed by ring opening to form an oxonium ion (C), and subsequent intramolecular nucleophilic attack by the methoxy oxygen in (C) leads to the loss of an aldehyde or ketone with ring closure to form the final 1,3,2-dioxasilacycloalkyl cation (D).



Scheme 1

Evidence for the proposed mechanism was obtained by recording the MS^3 sequential product ion spectra of the intact adducts and comparing them with the MS^3 sequential product spectra of the replacement products (Table 2). (One remarkable feature of the behavior of the silylium ions, in contrast to the previously reported acylium, borinium, and phosphonium ion reactions, is that the intact adducts of the silylium ion with cyclic acetals or ketals are abundant enough to allow MS^3 experiments to be performed.) These two sets of MS^3 spectra are similar and they support the conclusion that the Eberlin replacement reaction proceeds *via* intact adducts of the type shown in eqn. (1). In general, the adduct ions dissociate upon collision at low energy to form the 1,3,2-dioxasilacyclopentane cation replacement products in high yield; further dissociation then re-forms the reactant silylium ion as well as other fragment ions. For example, the intact adduct of *m/z* 195 formed by the reaction of $(CH_3O)_3Si^+$ with 1,3-dioxolane dissociates upon CID to generate the replacement product ion of *m/z* 165 and silylium ion of *m/z* 121. The MS^3 spectrum shows that the product ion (*m/z* 165) is the precursor of the reactant silylium ion, *m/z* 121, and that it also dissociates to yield *m/z* 135, by loss of neutral CH_2O.

Based on the proposed mechanism, substituents at the 2-position of cyclic acetals and ketals are expected to affect the extent of the Eberlin replacement reaction through their effect on the ring-opening process. As seen in Table 1 and Fig. 1a and 1b, the results for 2-substituted 1,3-dioxolanes show that 2-alkyl groups increase the efficiency of the replacement reaction. This result can be explained by the fact that alkyl groups in the 2-position stabilize the charge and thus facilitate ring opening. A methoxy group at the 2-position, on the other hand, substantially decreases the extent of Eberlin replacement as shown in Fig. 1c. The lone pair of electrons on the oxygen of the methoxy group allows resonance structures which distribute the charge in the oxonium ion, inhibiting intramolecular nucleophilic ring closure. Alternatively, the initial silylium ion addition may occur at the exocyclic oxygen and the resulting adduct then undergoes dissociation by loss of methoxy-

Table 2 MS^3 sequential products of intact adducts and of the replacement products[a]

Reactant ion (*m*/*z*)	Neutral reagent	Adduct	Fragments, *m*/*z* (relative abundance)[b]	Eberlin product	Fragments, *m*/*z* (relative abundance)[b]
$(CH_3O)_3Si^+$ (121)	1,3-Dioxolane	195	165(100), 121(80)	165	125(20), 121(100)
	2-Methyl-1,3-dioxolane	209	165(100), 121(65)	165	125(45), 121(100)
	2,2-Dimethyl-1,3-dioxolane	223	165(100), 121(90), 135(20)	165	135(35), 121(100), 91(6)
	2-Phenyl-1,3-dioxolane	271	165(100), 121(75), 135(15)	165	135(33), 121(100)
	2-Methoxy-1,3-dioxolane	225	—[c]	165	—[c]
	4-Methyl-1,3-dioxolane	209	179(100), 121(20)	179	121(100), 91(25)
	1,3-Dioxane	209	179(100), 151(60), 121(80)	179	121(100), 151(66)
	Thiazolidine	210	181(50), 178(80), 164(25),	181	151(10), 121(100)
			150(45), 148(28), 121(100)	164	134(85), 121(100)
	1,3-Oxazinane	208	176(100), 179(1), 178(6),	179	151(100), 121(65), 91(32)
			151(26), 150(38), 121(12)	178	149(100), 148(29), 121(15)
$CH_3Si^+(OCH_3)_2$ (105)	1,3-Dioxolane	179	149(80), 135(100), 105(80)	149	105(100), 119(30)
	2-Methyl-1,3-dioxolane	193	149(100), 105(80)	149	105(100), 75(20)
	2,2-Dimethyl-1,3-dioxolane	207	149(100), 105(35), 119(15)	149	119(100), 105(75)
	2-Phenyl-1,3-dioxolane	255	149(100), 105(24)	149	105(100), 119(33)
	2-Methoxy-1,3-dioxolane	209	—[c]	149	—[c]
	4-Methyl-1,3-dioxolane	193	163(100), 105(95)	163	105(100), 75(33)
	1,3-Dioxane	193	163(100), 135(50), 105(60)	163	135(40), 105(100), 75(15)
	Thiazolidine	194	165(60), 162(100), 148(5),	165	105(100), 135(10)
			134(35), 105(55)	148	105(30), 118(100)
	1,3-Oxazinane	192	160(100), 163(3), 162(16),	163	135(100), 105(65), 75(18)
			135(24), 134(41), 105(18)	162	133(100), 132(33), 105(25)

[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 in sequence while the third mass-analyzer was scanned. [b] Relative to the base peak, excluding the reactant ion, as a percentage. [c] MS^3 experiments could not be carried out due to the low ion abundance.

silane instead of undergoing the Eberlin replacement reaction. Furthermore, substituents at the 4-position of 1,3-dioxolane seem to inhibit the replacement process due to steric effects (Table 1), suggesting that the ring-closure process is rate determining. Further evidence for this is found in the effects of substituents on Si, as discussed later. Similar conclusions were suggested by theoretical calculations on the corresponding reactions of borinium and phosphonium ions.[38]

The observed reactivity of silylium ions is useful, to some extent, in differentiating isomeric cyclic acetals and ketals by revealing the substituent position on the ring (Table 2). In particular, it is possible to determine whether the substituent is located at the 2-position or another site. For instance, both 4-methyl-1,3-dioxolane and its 2-methyl isomer form adducts of *m*/*z* 193 upon reaction with $CH_3Si^+(OCH_3)_2$ (*m*/*z* 105). However, in the 4-methyl-1,3-dioxolane case, replacement occurs *via* loss of neutral formaldehyde to form a product ion of *m*/*z* 163. For 2-methyl-1,3-dioxolane, the result of the replacement process is the loss of the 2-methyl group which is incorporated into the released neutral aldehyde. This process results in a product ion 14 Da lower in mass (*m*/*z* 149). In the more difficult case of the isomers 4-methyl-1,3-dioxolane and 1,3-dioxane, both of which give an intact adduct ion having *m*/*z* 193 and a dissociation product ion having *m*/*z* 163, isomer differentiation is also achieved. The sequential product ion spectrum of the intact adduct ion (*m*/*z* 193) formed by the reaction of $CH_3Si^+(OCH_3)_2$ with 4-methyl-1,3-dioxolane is shown in Table 2 and Fig. 2a. The spectrum displays two fragment ions: the silylium ion (*m*/*z* 105) and the Eberlin replacement product (*m*/*z* 163). For the adduct ion (*m*/*z* 193) formed by the reaction of $CH_3Si^+(OCH_3)_2$ with the isomer 1,3-dioxane, the sequential product ion spectrum (Fig. 2b) displays three fragment ions. In addition to the two product ions observed for the 4-methyl-1,3-dioxolane case, a unique fragment of *m*/*z* 135, formed by cycloreversion of the replacement product with loss of neutral ethylene, is observed. The distinctive dissociation patterns of the isobaric adducts *m*/*z* 193 generated from 4-methyl-1,3-dioxolane and 1,3-dioxane are summarized in Scheme 2.

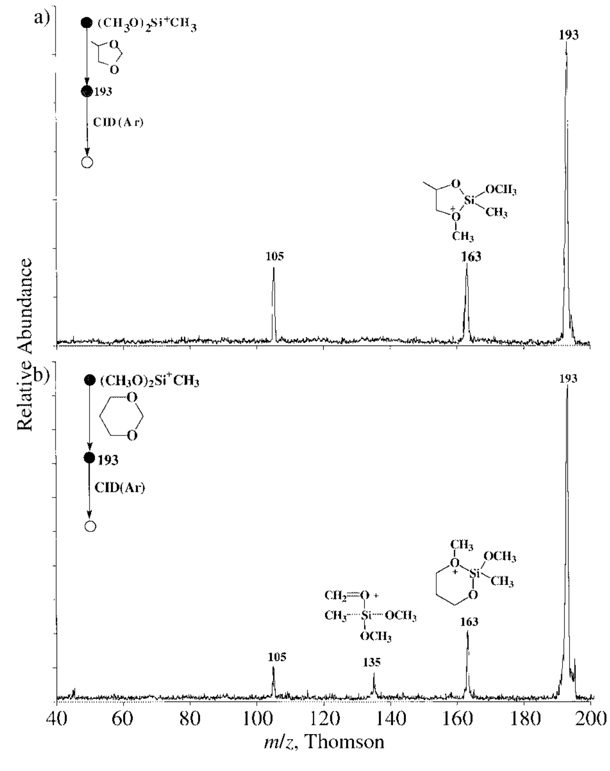


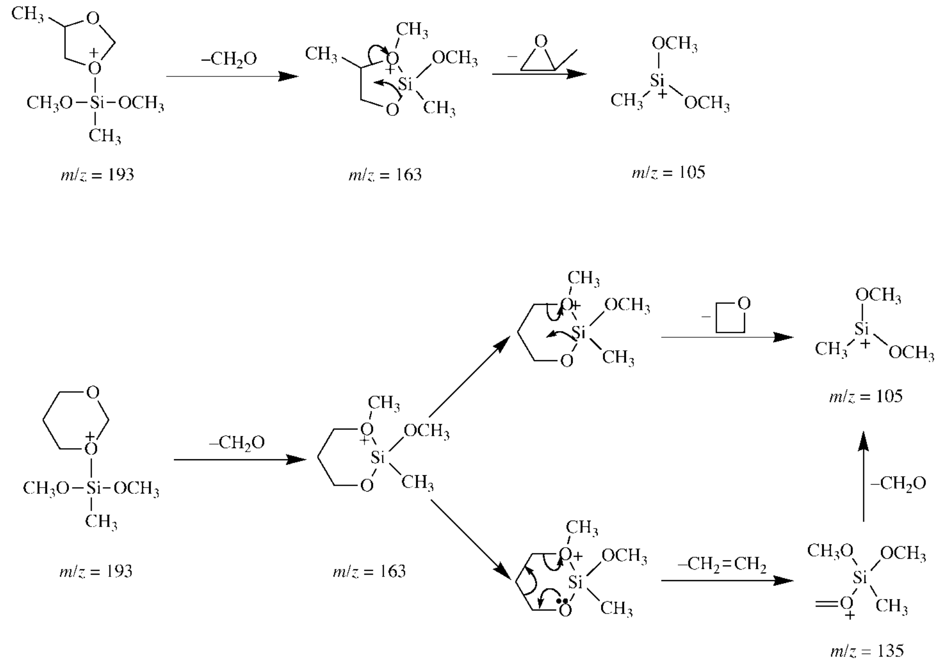
Fig. 2 Sequential product ion (MS^3) spectra of the proposed replacement products of $CH_3Si^+(OCH_3)_2$ with a) 4-methyl-1,3-dioxolane; b) 1,3-dioxane.

The reactivity of silylium ions, and hence the efficiency of the replacement process, is sensitive also to the nature of the substituents at the silicon center. Silylium ions $(CH_3)_2Si^+OCH_3$ (*m*/*z* 89) and $(CH_3)_3Si^+$ (*m*/*z* 73), which are generated from 70 eV electron impact of $CH_3Si(OCH_3)_2$ and $(CH_3)_4Si$, respectively, together with $(CH_3O)_3Si^+$ and $CH_3Si^+(OCH_3)_2$ generated from $CH_3Si(OCH_3)_3$, were chosen to probe the role of substituents on the silylium ion in the course of ion–molecule reaction with dioxolanes. Equivalent amounts of the three precursors were mixed with 1,3-dioxolane or 2,2-dimethyl-1,3-dioxolane. The mixture was deposited on the probe tip and allowed to evaporate into the ion source, where the ion–molecule reactions of interest occur. The relative abundances of intact adducts of

Table 3 Relative abundance of adducts and the Eberlin replacement products in competitive reactions of silylium ions with 1,3-dioxolane and 2,2-dimethyl-1,3-dioxolane[a]

Reactant ion (*m*/*z*)	Neutral reagent	Adduct, *m*/*z* (relative abundance)[a]	Replacement product, *m*/*z* (relative abundance)[b]
$(CH_3O)_3Si^+$(121)	1,3-Dioxolane	195(0.9)	165(100)
$CH_3Si^+(OCH_3)_2$(105)		179(1.8)	149(77)
$(CH_3)_2Si^+OCH_3$(89)		163(4.9)	133(31)
$(CH_3)_3Si^+$(73)		147(24)	117(9)
$(CH_3O)_3Si^+$(121)	2,2-Dimethyl-1,3-dioxolane	223(1.3)	165(100)
$CH_3Si^+(OCH_3)_2$(105)		207(1.7)	149(85)
$(CH_3)_2Si^+OCH_3$(89)		191(5.6)	133(33)
$(CH_3)_3Si^+$(73)		175(25)	117(10)

[a] All data are for mass spectra and refer to reactions occurring in the ion source. [b] Relative to the base peak, excluding the reactant ion, as a percentage.



Scheme 2

the silylium ions and 1,3-dioxolanes, and those of the replacement products, are listed in Table 3. Relative abundances of the intact adducts increase in the order $(CH_3O)_3Si^+ < (CH_3O)_2Si^+CH_3 < CH_3OSi^+(CH_3)_2 < Si^+(CH_3)_3$, which corresponds to the order of increasing electron deficiency at the silicon center. The MS^2 product ion spectrum showing the ion–molecule reactions of the silylium ion $(CH_3)_3Si^+$ with 2,2-dimethyl-1,3-dioxolane is reproduced in Fig. 3a. Note the abundance of the intact adduct of *m*/*z* 175, compared to the intact adduct ion of *m*/*z* 223 in Fig. 3b in the case of $(CH_3O)_3Si^+$. The ionic product of *m*/*z* 117, which is formed *via* elimination of acetone from the intact adduct, is still observed but at relatively lower abundance. Ions of *m*/*z* 101 and *m*/*z* 103 are product ions from proton transfer and hydride abstraction reactions, respectively.

The relative abundance of the Eberlin replacement products for the reactions of $(CH_3O)_3Si^+$, $(CH_3O)_2Si^+CH_3$, $CH_3OSi^+(CH_3)_2$, and $Si^+(CH_3)_3$ with dioxolanes shows the opposite behavior with methoxy substitution to that of the adducts (Table 3 and Fig. 3). This is further evidence for the recyclization step being rate forming (see above). Product ion spectra (MS^2) of the ionic products (*m*/*z* 165, *m*/*z* 149, *m*/*z* 133, and *m*/*z* 117), formed from the reactions of 2,2-dimethyl-1,3-dioxolane with the reactant ions $(CH_3O)_3Si^+$, $(CH_3O)_2Si^+CH_3$, $CH_3OSi^+(CH_3)_2$, and $Si^+(CH_3)_3$, respectively, are shown in Fig. 4. Product ions of *m*/*z* 165 and *m*/*z* 149 from the silylium ions $(CH_3O)_3Si^+$ and $CH_3Si^+(OCH_3)_2$, respectively, give two major fragments upon CID. They are silylium ions (*m*/*z* 121 and 105, respectively) and ions formed by loss of neutral formaldehyde (*m*/*z* 135 and 119, respectively) (Fig. 4a and 4b). In the case of $(CH_3)_2Si^+OCH_3$, the CID spectrum of the Eberlin replacement product ion (*m*/*z* 133) gives similar fragments (*m*/*z* 89 and 103, respectively) but at much lower abundance. Other fragments such as the methyl transfer product $CH_3Si^+(OH)OCH_3$ (*m*/*z* 91) are also observed (Fig. 4c). For the ion–molecule products (*m*/*z* 117) generated from the reaction of $(CH_3)_3Si^+$ with 2,2-dimethyl-1,3-dioxolane, dissociation leading to the reactant silylium ion and loss of neutral formaldehyde (*m*/*z* 73 and *m*/*z* 97) are barely seen, but peaks at *m*/*z* 59 and *m*/*z* 75 are observed in fair abundance (Fig. 4d). These two peaks, which correspond to silylium ions $(CH_3)_2SiH^+$ (*m*/*z* 59) and $(CH_3)_2SiOH^+$ (*m*/*z* 75), are observed in the dissociation of alkoxydimethylsilylium ions where they can be generated *via* the methyl migration.[44] The ion of *m*/*z* 117 has a distinctive dissociation pattern, which is consistent with an acyclic structure. While the Eberlin replacement products of $(CH_3O)_3Si^+$ and $CH_3Si^+(OCH_3)_2$ exhibit characteristics of a cyclic ionic structure, the product ion *m*/*z* 133 formed from $(CH_3)_2Si^+OCH_3$ seems to be a mixture of cyclic and acyclic ionic structures.

The above observations demonstrate that the oxygen atom in the reactant silylium ion plays an essential role in the Eberlin replacement process. The electron lone pair on oxygen provides the driving force for the nucleophilic recyclization step. Because of the lack of an oxygen atom in $(CH_3)_3Si^+$, ring closure to form a cyclic ionic structure cannot take place. In the case of

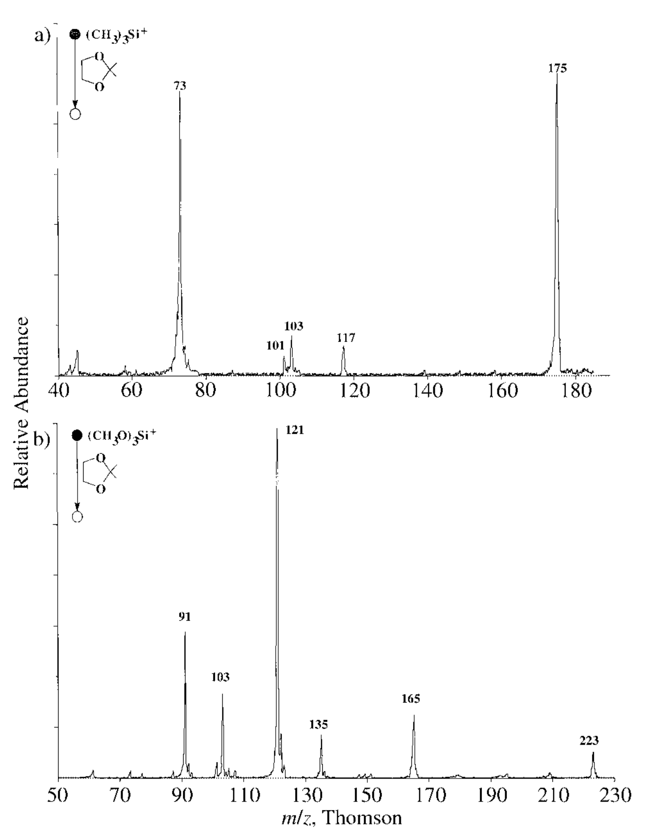


Fig. 3 Product ion (MS^2) spectrum showing the ionic products of reaction of 2,2-dimethyl-1,3-dioxolane with a) $(CH_3)_3Si^+$; b) $(CH_3O)_3Si^+$.

$(CH_3)_2Si^+OCH_3$, nucleophilic ring closure to form the final cyclic product can still occur. Steric hindrance, however, inhibits nucleophilic attack and thus results in a much lower efficiency, and an alternative mechanism involving methyl migration from silicon to carbon takes place instead.

The Eberlin replacement process also occurs for thiazolidine and 1,3-oxazinane, which can be considered as sulfur/nitrogen and nitrogen/oxygen cyclic acetals, respectively. With the presence of two nucleophilic sites, N and S, thiazolidine can form two cyclic product ions *via* reaction with silylium ions: the 1-oxa-3-thia-2-silacyclopentane ion (*m*/*z* 181) and the 1-aza-3-oxa-2-silacyclopentane ion (*m*/*z* 164). These two species are formed by initial silylation at sulfur and nitrogen, respectively. The MS^2 product ion spectrum displaying $(CH_3O)_3Si^+$ reactions with thiazolidine and the MS^3 sequential product ion spectrum of the intact adduct ion of *m*/*z* 210 are shown in Fig. 5a and 5b, respectively. Note that the abundances of the two replacement products (*m*/*z* 164 and *m*/*z* 181) are nearly equal. The product ions with *m*/*z* 148, 150 and 178 result from initial attack at the nitrogen site. No other product ion resulting from initial attack at sulfur is observed. The silylium ion is expected to preferentially attack at nitrogen because of its higher basicity compared to that of sulfur.[38,39] Due to competing dissociation channels of the N-attached silylium–thiazolidine adduct, the relative abundances of the replacement products (*m*/*z* 164 and *m*/*z* 181) are not suitable for the measurement of reaction efficiencies. The product ion (MS^3) mass spectra of *m*/*z* 181 and *m*/*z* 164 are shown in Fig. 6. Not surprisingly, these ions dissociate to yield the reactant ion, $(CH_3O)_3Si^+$, and ions of *m*/*z* 151 and 134, respectively, by loss of neutral formaldehyde. A detailed mechanism for the Eberlin replacement process in thiazolidine is shown in Scheme 3.

In the case of 1,3-oxazinane which also has two nucleophilic sites, N and O, initial silylation occurs mainly at the expected nitrogen site. This is demonstrated by the dominant product ions (*m*/*z* = 176, 150, 178) seen in the reaction spectrum of $(CH_3O)_3Si^+$ with 1,3-oxazinane. The replacement product ion *m*/*z* 178, resulting from initial attack at nitrogen, has much higher relative abundance than that of the ion at *m*/*z* 179 which is a replacement product resulting from initial attack at oxygen (Table 1).

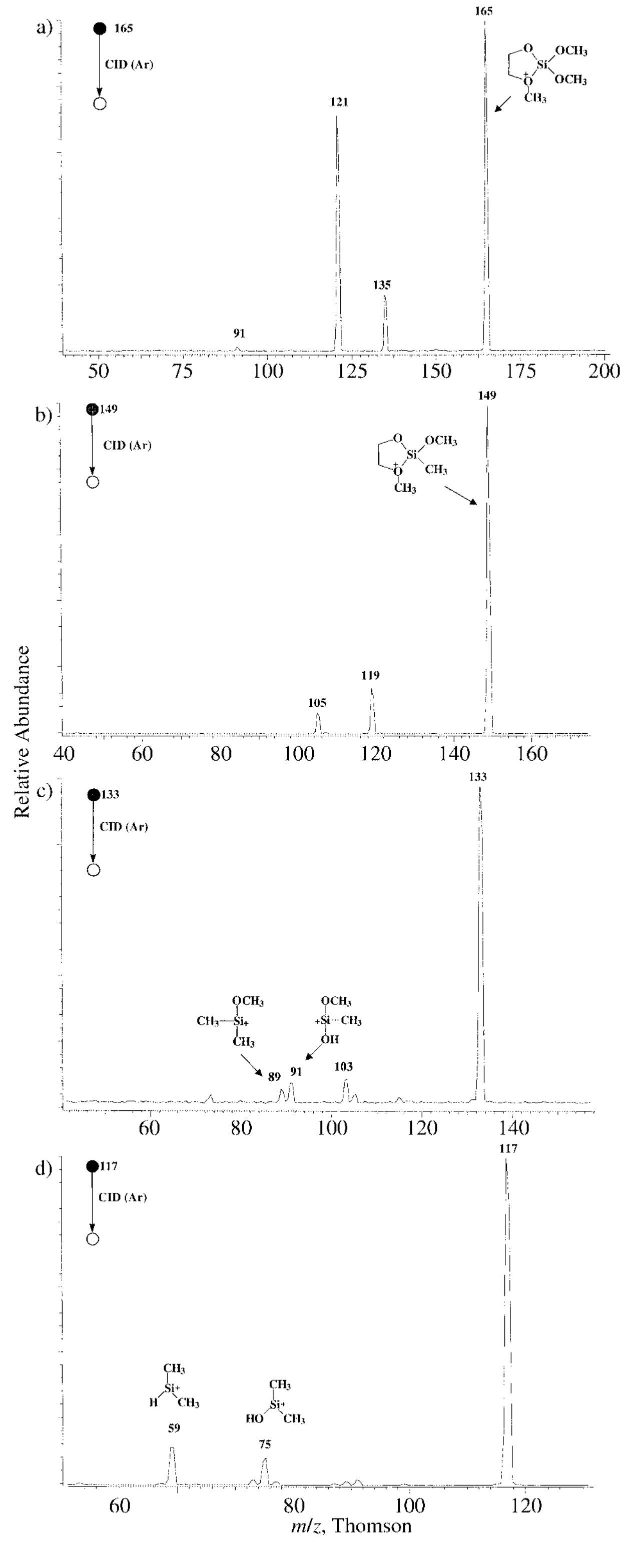
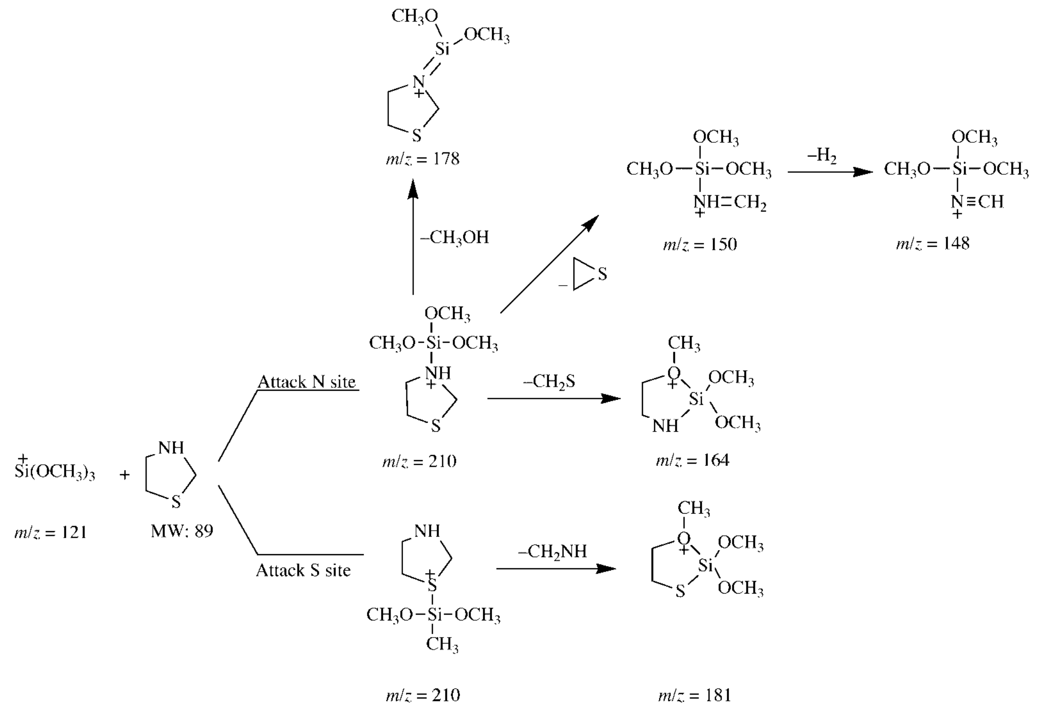


Fig. 4 Product ion (MS2) spectrum showing collision-induced dissociation of the proposed Eberlin replacement products of dimethyl-1,3-dioxolane with a) $(CH_3O)_3Si^+$; b) $CH_3Si^+(OCH_3)_2$; c) $(CH_3)_2Si$-$^+OCH_3$; d) $(CH_3)_3Si^+$.

Conclusions

Silylium cations, like acylium ions, react in high yield with a variety of cyclic acetals, ketals and related heterocycles, *i.e.* five- and six-membered 1,3-O,O-, 1,3-N,O- and 1,3-N,S-hetero-



Scheme 3

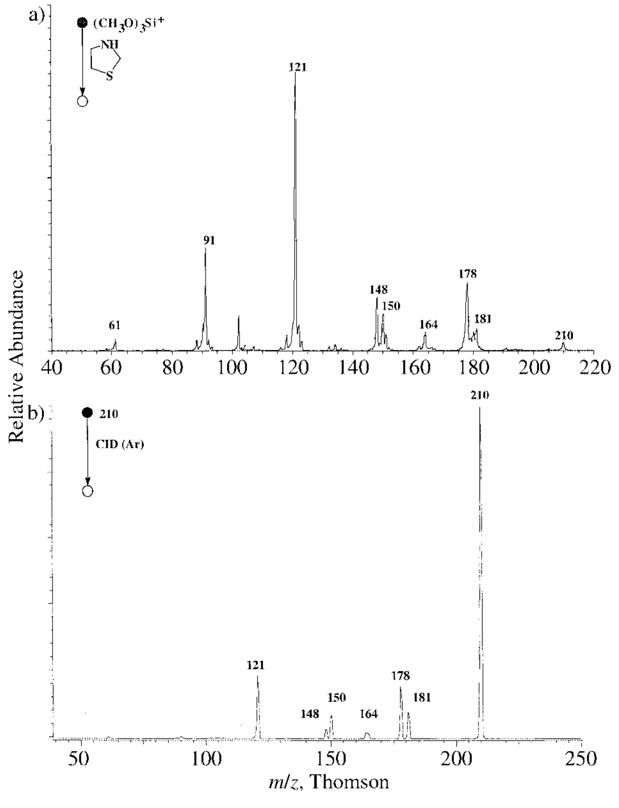


Fig. 5 a) Product ion (MS^2) spectrum for the ionic products of reaction of $(CH_3O)_3Si^+$ with thiazolidine; b) sequential product ion (MS^3) spectrum of the intact adduct, *m*/*z* 210. See text for details.

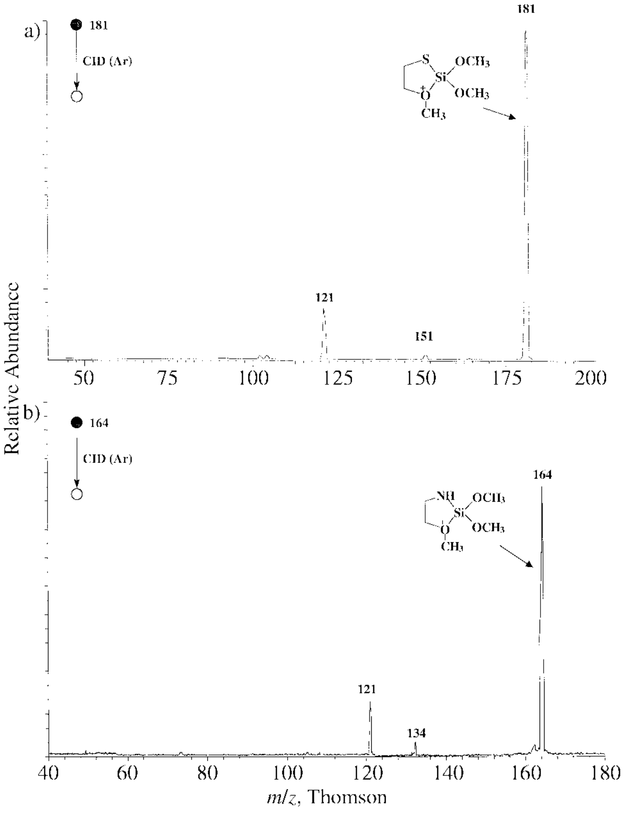


Fig. 6 Product ion (MS^2) spectra of the Eberlin replacement products of $(CH_3O)_3Si^+$ attack on thiazolidine at the a) N site; b) S site.

cycles. The process of replacing C–O (or C–S or C–N) by $Si–O^+$ in the cyclic acetals and ketals is proposed to occur *via* a mechanism which resembles the gas-phase Eberlin transacetalization.[35,36] Cyclic 1,3,2-dioxasilacyclopentane ions are formed, as characterized by triple-stage mass spectrometry. All cyclic product ions dissociate under low-energy collision conditions to regenerate the original reactant ions. Competition MS^2 experiments allowed the reactivity of silylium ions with different substituents, *viz.*, $(CH_3O)_3Si^+$, $(CH_3O)_2Si^+CH_3$, $CH_3OSi^+(CH_3)_2$, and $Si^+(CH_3)_3$, to be compared. The tendency towards electrophilic addition of silylium ions at the oxygen atom of cyclic acetals or ketals increases with the electron deficiency at silicon, as demonstrated by the increasing abundance of the intact adducts. However, the occurrence of the replacement reaction increases in the opposite order, suggesting that the recyclization step is rate determining. A Lewis base atom in the reactant ion, in this case oxygen, is necessary for the intramolecular nucleophilic ring closure that generates the Eberlin replacement product (*e.g.* the 1,3,2-dioxasilacyclopentane ion). The reactivity observed also provides a structurally diagnostic method for the gas-phase characterization of neutral cyclic acetals and ketals with respect to at least some substituent positions and ring size. Compared to the acylium ion, the silylium ion forms intact adducts of apparently higher stability and lower regio-selectivity, as exemplified by the reactions with thiazolidine.

The properties of many silicon-based industrial materials, such as thermal stability, durability, and insulating properties, are generally superior to those of their carbon analogs. This study reports on a method with the potential to generate alkoxysilanes from acetals and ketals. Furthermore, silicon-based reagents are used to protect alcohols and carbonyl compounds in the condensed phase, and we have described an alternative route to investigate the nature of deprotecting silicon-containing compounds without interference from solvent effects. Further investigations are ongoing to gain insight into the solvation of the silylium ion by alcohols.

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