Radiolytic Silylation of Alkenes and Alkynes by Gaseous R_3Si^+ Ions. Stereochemical Evidence for the β-Silyl Effect

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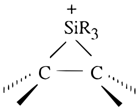
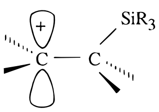
Abstract: Carbocation intermediates stabilized by a β silyl group have been characterized, using the silylation of alkenes by R_3Si^+ ions as a route of formation. Neutral silylated products have been obtained from the reaction of R_3Si^+ ions, generated in a gaseous medium at atmospheric pressure by a radiolytic technique, with selected alkenes, alkynes, and allene, thereby indicating the occurrence of electrophilic silylation. Notable features of the charged silylated intermediates emerge from the isomeric product distribution. The silylation of *cis*- and *trans*-2-butene shows a high degree of retention of configuration, as expected if a bridged species (**I**) were the reaction intermediate. Alternatively, the intermediacy of an open structure (**II**), whereby C−C bond rotation is inhibited by the hyperconjugative interaction between the β silyl group and the vacant p orbital, should be inferred. The charged intermediates from the silylation of alkenes and alkynes are found to be unreactive toward conceivable isomerizations to more stable species, such as the ones bearing the positive charge on silicon. Stereoelectronic factors affect the deprotonation of the silylated intermediates, which may involve loss of the proton from either the α or the γ position with respect to the silylated carbon. A comparison of the reactivity of alkenes and alkynes in the cationic silylation reaction is presented.

One of the salient features of organosilicon chemistry is the stabilizing effect exerted on a carbenium ion by a silyl group in a position β to the carbon bearing the formal charge, the so-called β effect.[1] A remarkable number of reactivity studies in solution, mainly focused on solvolytic processes, have reported on the stabilization of a positive charge by β silicon, which gives rise to low energy transition states and/or intermediates, causing rate enhancements of up to 10^{12} with respect to model systems.[2] An open question regards the structure of the postulated intermediate species. It may in fact be described either as a bridged structure (**I**), where the Si atom exploits the ability to expand its coordination, or as a β silylated carbenium ion (**II**). The magnitude of the developing β-silicon effect depends in a crucial way on the p-σ_{CSi} hyperconjugation, which is maximized when the 2p orbital developing on the cationic carbon and the C−Si σ bonding orbital are aligned in the same plane. However, the actual involvement of structure **I** vs **II** is hard to prove.[2e]



I



II

In principle, the study of naked ions in the gas phase should provide the most objective description of ion structures and energetics. Gaseous ions of the general formula $C_nH_{2n+3}Si^+$, that include species **I**/**II** as possible isomers, have been generated from different precursors, and their unimolecular and bimolecular reactivity has been investigated by mass spectrometric techniques. These experimental studies have been accompanied by MO calculations, providing a fairly comprehensive picture of the relative stabilities of isomeric structures and their interconversion pathways.[3] However, the question of whether **I** or **II** should be favored remains open. We have used the R_3Si^+ reaction with alkenes as an entry to **I**/**II** type species, because the reaction of Me_3Si^+ ions with alkenes was known to yield abundant adduct ions in a high-pressure ion source.[4] The equilibrium constants for the association reactions (eq 1) were studied as a function of temperature, and thermodynamic data were derived.

$$Me_3Si^+ + R_1R_2C{=}CR_3R_4 \rightarrow [Me_3Si{-}CR_1R_2CR_3R_4]^+ \quad (1)$$

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[1] (a) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83. (b) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (c) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; chapter 2. (d) Bassindale, A. R.; Taylor, P. G. *The Chemistry of Organic Silicon Compounds*; Chapter 14. (e) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1. (f) Nguyen, K. A.; Gordon, M. S.; Wang, G.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798.

[2] Recent examples include: (a) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (b) Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120. (c) Bausch, M. J.; Gong, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5963. (d) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3838. (e) Lambert, J. B.; Liu, X. *J. Organomet. Chem.* **1996**, *521*, 203. (f) Surya Prakash, G. K.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076. (g) Siehl, H.-U.; Kaufmann, F. P.; Apeloig, Y.; Braude, V.; Danovich, D.; Berndt, A.; Stamatis, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1479. (e) Siehl, H.-U.; Kaufmann, F. P.; Hori, K. *J. Am. Chem. Soc.* **1992**, *114*, 9343.

[3] (a) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212. (b) Drewello, T.; Burgers, P. C.; Zummack, W.; Apeloig, Y.; Schwarz, H. *Organometallics* **1990**, *9*, 1161. (c) Bakhtiar, R.; Holznagel, C. M.; Jacobson, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 3227. (d) Ciommer, B.; Schwarz, H. *J. Organomet. Chem.* **1983**, *244*, 319. (e) Apeloig, Y.; Karni, M.; Stanger, A.; Schwarz, H.; Drewello, T.; Czekay, G. *J. Chem. Soc., Chem. Commun.* **1987**, 989. (f) Maerker, C.; Kapp, J.; Schleyer, P. v. R. In *Organosilicon Chemistry II*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996. (g) Angelini, G.; Keheyan, Y.; Laguzzi, G.; Lilla, G. *Tetrahedron Lett.* **1988**, *29*, 4159.

[4] Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.

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For example, the binding energy for the association of Me_3Si^+ to ethylene ($-\Delta H°_1$ for $R_1 = R_2 = R_3 = R_4 = H$) was found to be equal to 23.6 kcal mol^{-1}, in good agreement with a "corrected" theoretical value referred to **I** as the structure for the $[Me_3Si-C_2H_4]^+$ adduct ion.[3e] A high equilibrium concentration of the $[Me_3Si\text{-alkene}]^+$ adducts is expected at the conditions prevailing in the radiolytic experiments,[5] where the high bath gas pressure (ca. 700 Torr) allows collisional relaxation of possibly excited primary species and inhibits the occurrence of isomerization processes characterized by substantial activation energies. These features, combined with the identification of the neutral reaction products, offered to us the possibility to investigate the regio- and stereochemistry of the R_3Si^+ reaction with alkenes and alkynes and to obtain information on the relevant ionic intermediates.

Experimental Section

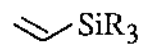
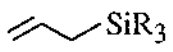
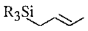
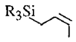
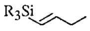
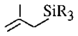
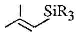
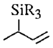
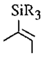
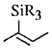
Materials. CH_4 and O_2 were high-purity (>99.9 mol %) gases from Matheson Co. The other chemicals to be used as substrates or additives or as GLC-MS standards were purchased from Aldrich Chemical Co. The silylated alkenes that were not commercially available were prepared from the Wurtz-Fittig reaction of R_3SiCl with the appropriate alkenyl bromide[6] and were purified by preparative GLC using a 4-m long, 4-mm i.d. stainless steel column, packed with 5% Carbowax 20M-KOH (2%) on Supelcoport. Their identity was verified by NMR spectrometry and MS.

Radiolytic Experiments. The gaseous mixtures were prepared in Pyrex vessels (135 mL) that were thoroughly outgassed and filled with the gaseous components in the selected ratio. Liquid components were introduced within weighted fragile glass ampules. The vessels were sealed, and gases and vapors were allowed to mix and then submitted to γ-radiation at 40 °C in a 220 Gammacell from Nuclear Canada Ltd for 2 h at the dose rate of 10^4 Gy h^{-1}. The radiolytic products were extracted by freezing the vessel at 77 K and careful washing of its inner surface with *n*-hexane. The final solution, containing the unreacted substrate as major component (conversion into products is kept to ca. 1%), was analyzed by GLC-MS using a Hewlett-Packard 5890 gas chromatograph in line with a Model 5989B quadrupole mass spectrometer. The following columns were used: (i) a 100 m long, 0.32-mm i.d. Petrocol DH fused silica capillary column and (ii) a 50 m long, 0.32-mm i.d. PONA fused silica capillary column. The radiolytic products were identified by comparisons of their retention times and EI mass spectra with those of authentic samples under the same operating conditions. Their yields were determined from the areas of the corresponding elution peaks using the internal standard calibration method. Blank experiments were performed to exclude any thermal contribution to the products of interest. To this end, gaseous mixtures, identical to the radiolytic samples, were submitted to the same experimental procedure except for the γ-irradiation.

Results and Discussion

Silyl cations are easily generated in the gas phase from many different neutral precursors.[7] In particular, the reaction of Me_4Si or Et_3SiH with the CH_5^+ and $C_2H_5^+$ ions from the primary ionization of CH_4 is an efficient source of R_3Si^+ ions (R = Me, Et) which can be generated by this route both by mass spectrometric techniques[8] and by γ-radiolysis.[9]

Table 1. Trialkylsilylation of Alkenes by Gaseous R_3Si^+ Ions

System composition[a] (Torr)		Ionic reagent R_3Si^+	Product distribution[b] (%)			Yield of products ($G_M \times 10^2$)[c]
Substrate	Additive					
						
1 (5)	TEA (0.66)	R = Me	100			1.8
						
2 (5)	TEA (0.71)	R = Me	91	9		2.0
						
3 (5)	TEA (0.67)	R = Me	47	40	13	1.0
3 (5)	TEA (1.2)	R = Et	57	32	11	5.3
						
4 (5)	TEA (0.72)	R = Me	99.5	0.5		2.2
						
5 (5)[d]	TEA (0.27)	R = Me	88	9.5	2.5	1.2
5 (5)[d]	TEA (0.64)	R = Me	92	7.0	1.0	1.2
5 (5)[d]	TEA (1.1)	R = Me	88	9.5	2.5	2.4
5 (5)[d]	TEA (1.7)	R = Me	90	8.5	1.5	1.9
5 (5)[d]	PPD (0.62)	R = Me	62	37	1.0	0.39
5 (5)[d]	PEA (0.72)	R = Me	98	2.0	n.d.	1.5
5 (5)[d]	TEA (0.60)	R = Et	91.5	8.5	n.d.	1.2
5 (5)[d]	PPD (0.59)	R = Et	51	49	n.d.	0.49
6 (5)[d]	TEA (0.72)	R = Me	85	2	13	2.0
6 (5)[d]	PPD (0.61)	R = Me	94	0.5	5.5	0.64
6 (5)[d]	PPD (0.55)	R = Et	100	n.d.	n.d.	0.60

[a] All systems contained CH_4 (500−600 Torr), a radical scavenger (O_2 at 10 Torr), and the neutral precursor of R_3Si^+ (20 Torr of Me_4Si, R = Me, or Et_3SiH, R = Et). [b] Average error ± 1%. [c] The radiochemical yield, G_M, is given in units of μmol J^{-1}. In the absence of added amine, the formation of silylated products is below the detection limit. [d] The unreacted substrate does not show any evidence of *cis*−*trans* isomerization.

Silylation of Alkenes. Table 1 summarizes the pattern of products from the reaction of R_3Si^+ with some representative alkenes: ethylene (**1**), propene (**2**), 1-butene (**3**), *iso*-butene (**4**), *cis*-2-butene (**5**), and *trans*-2-butene (**6**). The R_3Si-substituted products are indicative of the formation of covalent $[R_3Si\text{-alkene}]^+$ adducts, which are subsequently neutralized by proton transfer to a base. The ionic origin of the observed products is ensured by the presence of O_2 in the medium, as an effective silyl radical scavenger,[10] and also by the negligible yield of silylated products recovered in the absence of a strong nitrogen base, typically triethylamine (TEA). As pointed out previously,[9] the base performs the critical role of deprotonating the cationic silylated intermediates, which are otherwise prone to evolve by a desilylation process effected by oxygen nucleophiles. Oxygen nucleophiles such as H_2O, MeOH, and Me_2CO are present in trace amounts in the radiolytic systems, as unavoidable impurities or radiolytic side products. The silylation of alkenes appears then to conform to a general scheme similar to the one describing the silylation of aromatics (Scheme 1).[9] In particular, the ionic intermediate from R_3Si^+ attack at the alkene double bond undergoes competition between desilylation by oxygen nucleophiles and deprotonation (possibly accompanied by desilylation) by an added base. This reaction pattern explains why no neutral silylation products are obtained in the absence of an amine. Because the proton affinity (PA) of the silylated alkene is expected to be high (a PA value of 199 kcal mol^{-1} has been derived for $Me_3SiCHCH_2$),[3a] strong bases have been selected, namely TEA (PA = 232 kcal mol^{-1}),[11] piperidine

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(5) (a) Cacace, F. *Acc. Chem. Res* **1988**, *21*, 215. (b) Speranza, M. *Mass Spectrom. Rev.* **1992**, *11*, 73. (c) Cacace, F. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987.

(6) Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877.

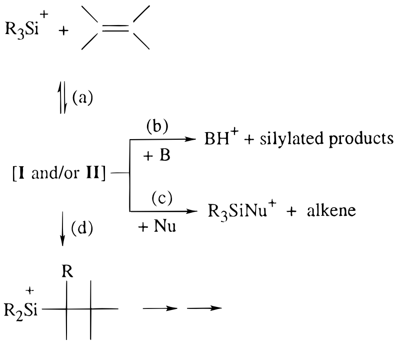
(7) Schwarz, H. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 7.

(8) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 59.

(9) (a) Cacace, F.; Crestoni, M. E.; Fornarini, S.; Gabrielli, R. *Int. J. Mass Spectrom. Ion Processes* **1988**, *84*, 17. (b) Fornarini, S. *J. Org. Chem.* **1988**, *53*, 1314. (c) Cacace, F.; Attinà, M.; Fornarini, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 654.

(10) Niiranen, J. T.; Gutman, D. *J. Phys. Chem.* **1993**, *97*, 4106.

Scheme 1



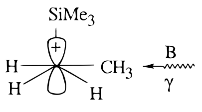
(PPD, PA = 226 kcal mol^{-1}), and *N,N*-diisopropylethylamine (PEA, PA = 232 kcal mol^{-1}). Their basicities are expected to significantly exceed those of the silylated alkenes. Therefore the changes in the absolute yield of products (G_M) when the amine is varied and other factors are kept constant are assigned to structural factors. An increased yield of products is observed in the reaction of Me_3Si^+ with *cis*-2-butene on going from PPD to PEA and in the reaction with *trans*-2-butene on going from PPD to TEA. In both cases an increasing steric bulk of the base favors the formation of the neutral silylated products, a result that may reflect a reduced extent of an unproductive desilylation process effected by the increasingly hindered nitrogen base.

A feature that is common to all the silylated products is that the entering silyl group appears to bind to one of the carbon atoms formerly involved in the double bond, while the carbon skeleton of the olefin is retained. Within the framework of Scheme 1, this finding implies that the primary ionic intermediate, either **I** or **II**, does not undergo rearrangement processes (e.g., path d in Scheme 1) but is efficiently deprotonated by the base B. Thus, the unambiguous structural assignment of the isomeric silylation products definitely confirms the conclusions of mass spectrometric and computational studies, ascribing a high activation barrier to the isomerization of **I**/**II**, especially if compared to the energy required for the dissociation to R_3Si^+ and alkene (the reverse of step a in Scheme 1).[3]

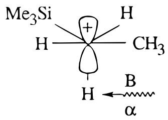
The deprotonation step may occur with different regioselectivity because the base can remove the proton from either the α or the γ position with respect to the silyl bearing carbon, to an extent that depends on the branching at the double bond, on the electrophile, and on the structure of the base. However, the most relevant result from the stereochemistry is the α deprotonation pathway, yielding the silylated alkene. In fact, the isomeric *cis*- and *trans*-2-butenes yield silylated butenes retaining the original stereochemistry to a noticeable extent, namely ca. 80% for the *cis*-isomer and ca. 90% for the *trans*-isomer when TEA is the base. The lack of stereoconvergence from the silylation of the two geometric isomers points to the effective role of the entering silyl group in preventing C−C bond rotation prior to deprotonation by the base. The most straightforward way to explain this effect suggests the formation of a cyclic structure (**I**) from the electrophilic attack of R_3Si^+ at the C−C double bond. Even though the alternative possibility of an open structure (**II**) cannot a priori be excluded, the present results do exclude that the formerly double C−C bond may freely rotate, following the R_3Si^+ addition.[12]

Calculations on $[H_3Si-CH_2-CH-CH_3]^+$ as a model to evaluate the β silicon effect on secondary carbenium ions predict the corresponding open structure **II** to be more stable than the cyclic species (**I**) by only 4 kcal mol^{-1}.[13] The barrier to C−C bond rotation in this model system is evaluated as 22 kcal mol^{-1} and arises from the increase in energy due to the attainment of an orthogonal relationship between the vacant p and σ_{CSi} orbitals. It may be considered that the Me_3Si^+ addition to *trans*-2-butene is an exothermic process releasing 31 kcal mol^{-1} in the primary adduct ions;[4] therefore, C−C bond rotation might occur within excited $[Me_3Si-MeCHCHMe]^{+*}$ ions, if the related barrier is indeed around 22 kcal mol^{-1}. Thus, the observed high degree of retention of stereochemistry at the double bond is remarkable and suggests that in the high-pressure environment of the radiolytic systems fast collisional quenching of the excited intermediates has taken place.

Although the α-deprotonation products, namely the silylated alkenes retaining the double bond position, have provided valuable mechanistic information, nevertheless they are accompanied by noticeable yields of γ deprotonation products. Because of the scant thermochemical information on silicon compounds,[14] it cannot be stated whether this finding may reflect the relative thermodynamic stabilities of the two types of products. A major structural difference is that the alkenes formed by α deprotonation bear a silyl group as substituent of the double bond, at variance with the ones arising from γ deprotonation. However, the dependence on the structural features of the base suggests that the product distribution is governed by kinetic effects. The formation of γ deprotonation products can be assigned to the contribution of stereoelectronic factors at the transition state for the deprotonation which can be viewed in the Newman projections of **II**, a similar reasoning applying to **I** as the ionic intermediate. For example, species **IIa**, deriving from Me_3Si^+ attack to propene, is best suited to p-σ_{CSi} hyperconjugation, allowed by the parallel orbital alignment. Deprotonation at the γ position may occur maintaining the full advantage of the favorable orbital interaction. However, in the transition state for deprotonation at the α carbon p-σ_{CSi} hyperconjugation is at least partially lost (**IIb**), which may account for the typically lower yields of α deprotonation products.



IIa



IIb

Silylation of Alkynes. Table 2 summarizes the pattern of products from the reaction of Me_3Si^+ with selected alkynes (acetylene (**7**), propyne (**8**), 2-butyne (**10**), and 1-pentyne (**11**)) and allene (**9**). Once again, the formation of neutral silylated products is in favor of an ionic silylated intermediate which can be depicted either as a bridged species or as a $\beta-$silyl substitued vinyl cation. The formation of the silylation product of acetylene itself, the parent alkyne, is remarkable, in view of

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(11) Unless stated otherwise, all thermodynamic data is taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D; Mallard, N G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, 17.

(12) The ambiguity between a symmetrical cyclic intermediate and an open structure, whereby the electronic interaction of a neighboring group with the vacant orbital of a β positive site inhibits C−C bond rotation, is frequently met in solution chemistry and is also found in gas-phase reactions, for example: (a) Fornarini, S.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *110*, 34. (b) Fornarini, S.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *110*, 42.

(13) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

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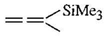
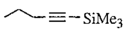
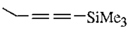
Table 2. Trialkylsilylation of Alkynes and Allene by Gaseous Me_3Si^+ Ions

System composition[a] (Torr)		Product distribution[b] (%)			Yield of products ($G_M \times 10^2$)[c]
Substrate	Additive				
		≡−$SiMe_3$			
7 (8)	TEA (1.1)	100			2.8
		−≡−$SiMe_3$	==−$SiMe_3$	Others[d]	
8 (5)	TEA (0.80)	40	26	34	1.9
8 (10)	TEA (0.77)	39	21	40	3.0
8 (10)	PPD (1.0)	52	22	25	6.3
8 (10)	PEA (1.1)	45	35	20	5.4
			==−$SiMe_3$		
9 (7)	PEA (0.91)	62	38		3.7
					
10 (10)	TEA (1.0)	100			8.1
				Others[d]	
11 (10)	TEA (0.84)	48	19	33	9.9
11 (10)	PEA (1.1)	51	16	33	9.8

[a] See note (a) of Table 1. [b] See note (b) of Table 1. [c] See note (c) of Table 1. [d] Other products contain two substrate units, probably deriving from addition of a primary $[\text{substrateSiMe}_3]^+$ ionic intermediate to a second substrate molecule, followed by deprotonation.

the inability to observe the silylated adduct ion in high-pressure mass spectrometry.[15] This contrasting behavior is probably the result of the different pressure range used by the two techniques.

The Me_3Si^+ addition to triple bonds is less exothermic than the reaction with similarly substituted alkenes.[15] For example, a binding energy of only 18 kcal mol^{-1} was estimated for the association of Me_3Si^+ to acetylene (eq 2).[15,16]

$$Me_3Si^+ + CHCH \rightarrow [Me_3Si{-}CHCH]^+ \qquad (2)$$

This finding parallels the somewhat smaller intrinsic stability of vinyl cations compared to alkyl cations,[11] whereas the β stabilization due to a silyl group is large and comparable in magnitude for both vinyl and alkyl cations.[17] An additional feature emerging from the R_3Si^+ reaction with alkenes and alkynes is the higher tendency of the $[R_3Si\text{-alkyne}]^+$ adduct to attack a second alkyne molecule yielding dimeric products, as shown both by the radiolytic reactions and by high-pressure mass spectrometric experiments.[15]

The silylation of alkynes and allene does not provide the stereochemical insight on the structure of the ionic intermediates as in the case of the alkene reactions. Once again, all silylated products retain the carbon skeleton of the substrate, and the silyl group is attached to the unsubstituted end of the triple bond of the products, whenever such a choice is possible. In particular, no products are found that may derive from a 1-silaallyl cation.[18,19]

Having excluded skeletal rearrangements, the possibility also exists of a propenyl ion → allyl ion isomerization which may follow the Me_3Si^+ attack to propyne and higher homologues. This process is exemplified in the following propyne reaction (eq 3).

$$Me_3Si^+ + CH_3CCH \rightarrow [Me_3Si{-}CHCCH_3]^+ \rightarrow [Me_3Si{-}CHCHCH_2]^+ \qquad (3)$$

However, the occurrence of the propenyl ion → allyl ion rearrangement can be disproved on the following basis: (i) the direct deprotonation of an allyl type ion should lead exclusively to an allene, e.g., $Me_3SiCH{=}C{=}CH_2$ from the propyne reaction, whereas this product is accompanied by major amounts of 1-Me_3Si-1-propyne; (ii) the propenyl ion → allyl ion rearrangement involves substantial activation barriers, even when it is markedly exothermic, as in the $CH_3C{=}CH_2^+ \rightarrow CH_2CHCH_2^+$ process;[11,20] (iii) the allyl product ion loses the hyperconjugative contribution of β silyl stabilization since no formal positive charge is placed in a position β to the silyl group. A direct proof that the propenyl ion → allyl ion rearrangement does not occur, or at least is by no means complete, can be seen from the products formed from the Me_3Si^+ reaction with allene. The Me_3Si^+ reaction with allene yields an ionic intermediate that may rearrange to the same allyl ion (eq 4) that can be obtained from the propyne reaction.

$$Me_3Si^+ + CH_2{=}C{=}CH_2 \rightarrow [Me_3Si{-}CH_2CCH_2]^+ \rightarrow [Me_3Si{-}CHCHCH_2]^+ \qquad (4)$$

However, the two C_3H_4 isomers yield a different pattern of silylated products, whose formation is accounted for by retention of both the carbon and the hydrogen framework in the primary intermediates.

Relative Reactivity of Alkenes and Alkynes. The absolute values of radiochemical yields (G_M) are fairly high, accounting for a large fraction of the primary CH_5^+ and $C_2H_5^+$ ions produced from the radiolysis of CH_4.[21] This finding testifies that the observed reaction products account for the most important, if not the exclusive, ionic pathways taking place within the gaseous medium. It is therefore tempting to relate the yields to the activation of the individual alkynes and alkenes toward electrophilic attack, though this reasoning is undermined by the complex character of the silylation reaction (Scheme 1), where the R_3Si^+ attack is followed by competing routes, one of them (the desilylation route) leading to the unreacted substrate. Each step is likely to be affected to an unknown extent by the alkyl substituents at the multiple bond, by the features of the base, and by the attacking electrophile. It is known, for example, that the presence of Et_3Si in the place of Me_3Si as β substituent makes the cationic intermediate more resistant to nucleophilic desilylation.[22] This fact is confirmed by the reactivity of 1-butene (**3**), whose reaction with Et_3Si^+ in the presence of TEA gives the highest yield of silylated alkenes. Within these limitations, absolute yields were obtained that suggest alkynes to be moderately more reactive than alkenes. This indication is confirmed by competition experiments where accurately known concentrations of alkyne and alkene were allowed to react with Me_3Si^+ in the presence of PEA. The ensuing product yields gave an apparent reactivity ratio $k_{\text{alkyne}}/$

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(21) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *93*, 4010. It is important to remind that the silylation reaction follows from a stepwise pattern where both the $CH_5^+/C_2H_5^+$ reaction with Me_4Si to form the reactant Me_3Si^+ ion and the Me_3Si^+ reaction with the unsaturated substrates face competition with an unproductive reaction channell with the added base. In this view, the observed G_M values compare well with the G_M value of ca. 0.3 μmol J^{-1} of the $CH_5^+/C_2H_5^+$ ions in methane.

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k_{alkene} equal to 7 from the 1-pentyne/1-pentene pair and equal to 20 from the propyne/propene pair.

Conclusions

The investigation of the R_3Si^+ reaction with alkenes and alkynes using a radiolytic approach has yielded valuable information on the following issues. In the first place, an electrophilic silylation forming neutral silylated alkenes, alkynes, and allene has been achieved, taking advantage of the ready availability of R_3Si^+ ions in the gas phase and of selected reaction conditions. In particular, a stringent requirement for obtaining silylated products lies in the presence of a strong and preferably hindered nitrogen base, able to perform fast deprotonation of the charged silylated intermediates, which are otherwise prone to evolve by a desilylation channel. This behavior resembles the reactivity pattern typical of aromatic silylation. In the second place, the foremost role of the β silyl group has clearly emerged from the outcome of the R_3Si^+ reaction with *cis*- and *trans*-2-butene, which shows a remarkable degree of retention of stereochemistry at the double bond. This result is accounted for by a cyclic silyl-bridged species (**I**) as reaction intermediate, though the alternative possiblity of an open structure (**II**), whereby a strong hyperconjugative interaction between the σ_{CSi} bond and the vacant p orbital on the β carbon is established, may not be excluded. In any event, the lack of stereoconvergence from the silylation of *cis*- and *trans*-2-butene shows that the rotation about the former C−C double bond is largely inhibited. In this context, the behavior of silyl radicals in the addition reaction to double bonds marks a striking contrast. The $(Me_3Si)_3Si^{\cdot}$ radical is in fact found to *promote* the *cis*−*trans* interconversion of alkenes by an addition−elimination sequence, where the key step is the facile rotation about the C−C bond of the β silyl substituted alkyl radical intermediate.[23] In the third place, the characterization of the end silylation products has demonstrated that neither $[R_3Si\text{-alkene}]^+$ nor $[R_3Si\text{-alkyne}]^+$ adducts show any tendency to isomerize in the high-pressure environment, though their deprotonation may involve the α or γ site, yielding isomeric neutral products.

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