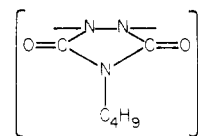


products of the oxidation, conditions under which dimer 7 dissociates very little. Workup of the reaction gives solid 1 contaminated with dimer 7. When 1 is purified by sublimation it dissociates at the higher temperatures (40–50 °C) into 2 which sublimes along with 1. The azo compound 1 is so soluble in organic solvents it must be crystallized at low temperatures, and as a result the higher molecular weight (and presumably less soluble) dimer cocrystallizes with the azo compound. When this mixture of 1 and 7 is in solution at room temperature and above, 7 dissociates into 2, which slowly changes to the thermodynamically more stable final radical 6. This radical is itself in equilibrium with dimer 8 as shown by the enhancement of the ESR signal as the temperature is raised.

In two cases, samples of triazolinodiones were obtained which were free of detectable radical. The first was a degassed ESR sample of 1a in ether that stood at room temperature for 18 h. This sample on warming to 55 °C gave the final radical 6. Apparently the dissociation of the dimer 8 into 6 is not as favorable in ether. Pirkle and Gravel² reported that the dimer of 3 was much less dissociated in nonpolar solvents than in polar solvents.

The second sample was a degassed ESR sample of 1b in glyme-THF which had been stored in the dark for 6 months. On photolysis of this sample in the ESR cavity with an ultraviolet lamp, the ESR signal reappeared almost instantly and then disappeared within about 1 h as the color of the azo compound disappeared. When this same sample stood at room temperature for 2 days, the color of the azo compound was regenerated. These results are consistent with the spectroscopic observations of Pirkle and Stickler,^{9,10} who studied the photopolymerization of 1c to give a nitrogen backbone polymer (10) with about 20 monomer units. Our results suggest that this polymerization may be initiated by radical 2, produced by dis-



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sociation of a dimer 7; i.e., the polymerization may not involve photolytically activated azo compound 1c at all.

Finally, it has been reported that 4-substituted 1,2,4-triazoline-3,5-diones add ethers photolytically to give 1-substituted urazoles. However, THF and dioxane give even better yields of the addition product thermally.¹ It seems quite clear that these thermal addition reactions are being initiated by the radical impurities in the triazolinodione.

Experimental Section

All ESR work was performed on an X-band Varian 4500 spectrometer using a single cavity or single cavity equipped with a variable-temperature Dewar container. All ESR samples were prepared on a high-vacuum line and carefully degassed to less than 10^{-4} torr by the standard freeze-thaw technique. The 4-substituted 1,2,4-triazoline-3,5-diones were prepared by standard methods using a variety of oxidizing agents.¹¹ They were purified by either sublimation and/or recrystallization from concentrated solutions in methylene chloride at -20 °C. All solvents were spectral grade and were used directly, except for the ethers, which were distilled from lithium aluminum hydride prior to use.

The spectra were analyzed by comparison of the line shapes, positions and intensities with those calculated by using ESRSPEC2.³

Registry No. 1a, 4233-33-4; 2a, 80540-38-1; 2d, 80540-39-2; 4d, 80540-40-5.

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(9) W. H. Pirkle and J. C. Stickler, *J. Am. Chem. Soc.*, **92**, 7497 (1970).

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α -Silicon-Substituted Vinyl Cations. A Theoretical ab Initio Investigation

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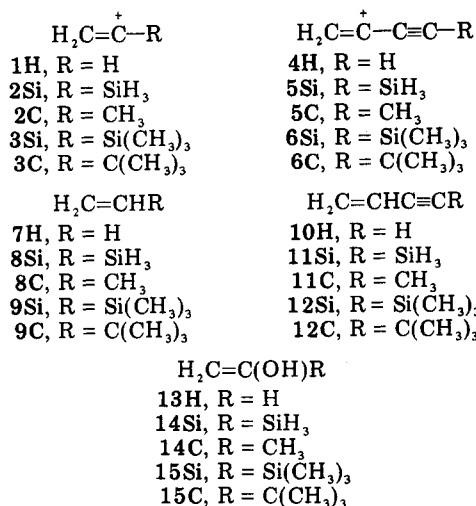
Received October 5, 1981

Ab initio calculations with the STO-3G, 3-21G, and 6-31G* basis sets were used to investigate several silyl- and alkyl-substituted vinyl cations, i.e., $H_2C=C^+-XR_3$ and $H_2C=C^+-C\equiv CXR_3$ where X = C, Si and R = H, CH_3 , α -Silyl and α -methyl substituents stabilize $H_2C=CH^+$ by 25 and 24 kcal mol⁻¹, respectively (6-31G*), so that $H_2C=CSiH_3^+$ and $H_2C=CCH_3^+$ [or $H_2C=CSi(CH_3)_3^+$ and $H_2C=CBu-t^+$] have comparable stabilities in a hydride-transfer process (eq 5 and 6). $H_2C=C(OH)SiH_3$ is destabilized by 4.5 kcal mol⁻¹ (6-31G*) relative to $H_2C=C(OH)CH_3$, so that the equation $[H_2C=C(OH)SiH_3 + H_2C=CCH_3^+ \rightarrow H_2C=CSiH_3^+ + H_2C=C(OH)CH_3]$ that models the solvolysis reactions of the corresponding triflates is exothermic by 5.6 kcal mol⁻¹ (6-31G*). $H_2C=CC=CH^+$ is less stable than $H_2C=CCH_3^+$ by 2.0 kcal mol⁻¹ (6-31G*). A triple bond transmits the electronic effects of alkyl substituents more effectively than that of silyl substituents. Thus, $H_2C=CC=CR^+$ where R = CH_3 and SiH_3 are more stable than the parent cation (R = H) by 15.5 and 8.7 kcal mol⁻¹, respectively (3-21G). Consequently, $H_2C=CCCR^+$ cations with R = alkyl are more stable than with R = silyl. The close agreement between the results of the calculations and the solvolysis rates suggests that the solvation energies of the alkyl- and silyl-substituted vinyl cations are comparable.

The effect of silicon substitution on the stability of carbenium ions is much less investigated and understood than simple alkyl substitution. The limited solvolytic data

available indicates that β -silicon substitution stabilizes alkyl carbenium ions while α -substitution causes destabilization.¹ Recently Schiavelli, Stang, and co-workers

Chart I



reported the first solvolytic study of α -silicon-substituted vinyl cations and concluded that the (CH₃)₃Si group is accelerating and hence stabilizing relative to hydrogen but destabilizing relative to a *t*-Bu group.² However, due to difficulties in the preparation of some of the solvolysis precursors a quantitative comparison of the relative stabilizing effects of silyl and alkyl groups was not attempted.² Furthermore, the use of solvolysis rates for measuring the relative stabilities of carbenium ions is complicated by ground-state and solvation effects. Solvation, for example, effects considerably the relative stabilities of charged species.³ The "inherent stabilities" of isolated α -silylvinyl cations free of solvation compared to α -alkylvinyl cations are not known, as the required gas-phase data (e.g., heats of formation) are not available. The lack of data in the gas phase, Schiavelli and Stang's solvolysis report,² the synthetic interest in such intermediates,⁴ and our interest in the effect of first vs. second row substituents on carbenium ions' stabilities⁵ have prompted us to study silicon-substituted vinyl cations theoretically. Numerous studies have established that molecular orbital theory and in particular ab initio methods reliably predict relative energies of carbenium ions.⁶

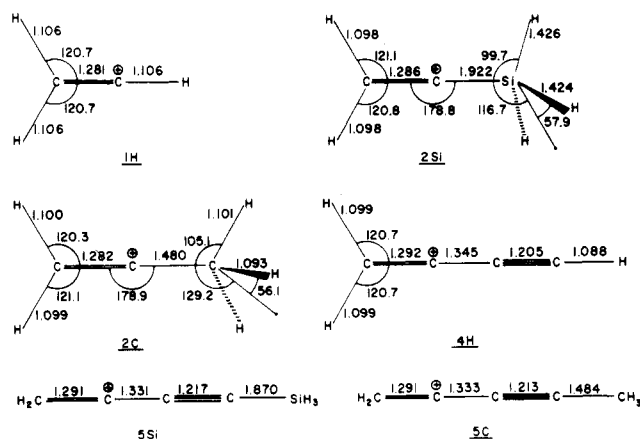
(1) (a) Eaborn, C.; Feichtmayr, F.; Horn, M.; Murrell, J. N. *J. Organomet. Chem.* **1974**, *77*, 39. (b) Traylor, T. G.; Hanstein, N.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. (c) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1971**, *29*, 389. (d) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153. (e) Cartledge, F. K.; Jones, J. P. *Tetrahedron Lett.* **1971**, 2193; *J. Organomet. Chem.* **1974**, *67*, 379.

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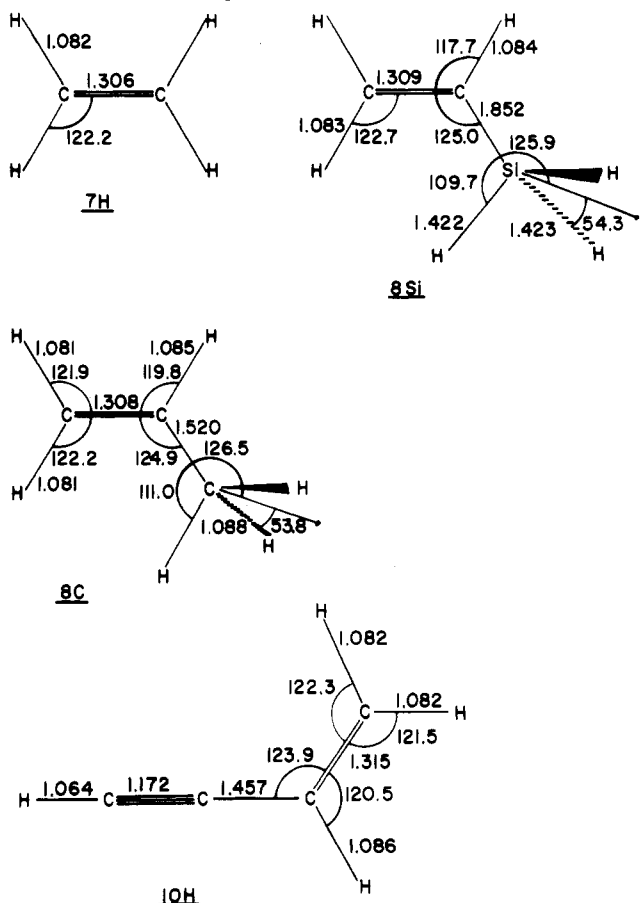
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Chart II. Optimized STO-36 Geometries^a

^a The "dummy atoms" (·) are located on the bisectors of the HSiH and HCH angles. Bond lengths in angstroms, bond angles in degrees.

Chart III. Optimized STO-3G Geometries^a

^a The "dummy atoms" (·) are located on the bisectors of the HSiH and HCH angles. Bond lengths in angstroms, bond angles in degrees.

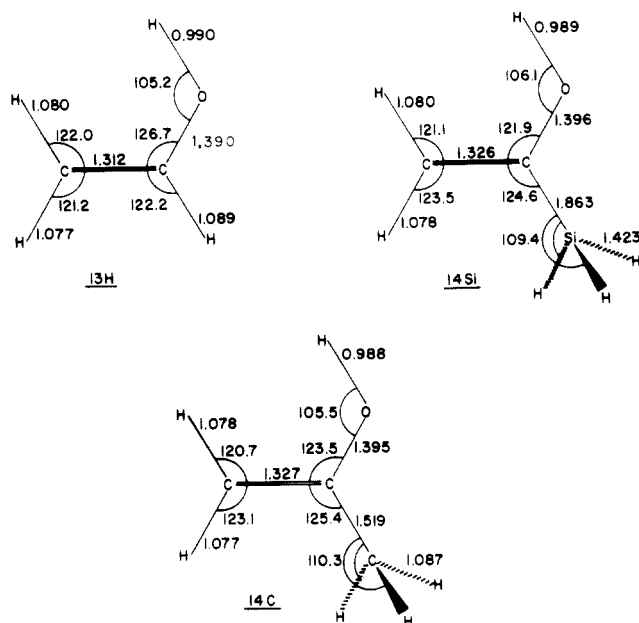
We study here by ab initio methods two representative α -silylvinyl cations, 2Si and 3Si (see Chart I). The effect of the insertion of a triple bond between the cationic center

(6) For reviews see: (a) Hehre, W. J. In "Application of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, pp 277-331. (b) Radom, L.; Poppinga, D.; Haddon, R. C. *Carbonium Ions*, **1976**, *5*, 2303-2426. Note also, for example, the excellent agreement between the calculations in ref 6c and the experimental gas phase results in ref 6d. (c) Apeloig, Y.; Collins, J. B.; Cremer, D.; Bally, T.; Haselbach, E.; Pople, J. A.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 3496. (d) Franke, W.; Schwarz, H.; Stahl, D. *Ibid.* **1980**, *45*, 3493.

Table I. Total Energies (Hartrees) of Substituted Vinyl Cations and of the Corresponding Olefins and Alcohols^a

compd	energy			compd	energy		
	STO-3G// STO-3G	3-21G// STO-3G	6-31G*// STO-3G		STO-3G// STO-3G	3-21G// STO-3G	6-31G*// STO-3G
1H	-76.165 40 ^b	-76.655 77 ^d	-77.086 73	9Si	-479.647 20 ^c		
2Si	-363.017 96	-365.252 19	-367.201 50 ^f	9C	-231.395 26 ^c		
2C	-114.792 96 ^b	-115.516 47 ^g	-116.164 50 ^h	10H	-151.806 29 ^b	-152.856 22 ^d	-153.706 61 ⁿ
3Si	-478.817 10 ^c			11Si	-438.623 45 ^c	-441.427 90 ^c	
3C	-230.545 19 ^{c,i}			11C	-190.398 53 ^c	-191.682 47 ^c	
4H	-150.942 15 ^j	-151.943 96	-152.796 76	12Si	-554.399 12 ^c		
5Si	-437.772 94 ^c	-440.529 57 ^c		12C	-306.137 28 ^c		
5C	-189.555 20 ^c	-190.794 93 ^c		13H	-150.916 68 ^b	-152.041 76 ^d	-152.888 88 ^e
6Si	-553.564 92 ^c			14Si	-437.704 80	-440.591 54	-442.954 83
6C	-305.301 53 ^c			14C	-189.503 62	-190.864 06	-191.926 74
7H	-77.073 95 ^c	-77.600 99 ^d	-78.031 45 ^k	15Si	-553.489 53 ^c		
8Si	-363.863 30	-366.155 57	-368.106 32 ^l	15C	-305.237 73 ^c		
8C	-115.660 38 ^b	-116.424 01 ^d	-117.071 11 ^m				

^a We use Pople's notation, e.g., 3-21G//STO-3G indicates that the energy is calculated at 3-21G by using the STO-3G optimized geometry. ^b Carnegie-Mellon University Quantum Chemistry Archive. ^c Partially optimized; see text for details. ^d 3-21G//3-21G. ^e 6-31G*//6-31G*. ^f $E = -367.201$ 13 hartrees by using Gordon's basis set. ^g $E = -115.518$ 73 hartrees. ^h $E = -116.164$ 64 hartrees. ⁱ $E = -230.543$ 41 hartrees was reported by: Radom, L. *Aust. J. Chem.* 1975, 28, 1. ^j From ref 16. ^k $E = -78.031$ 72 hartrees. ^l $E = -368.11$ 11 hartrees at 6-31G*/3-21G; see ref 8e. ^m From ref 8d. At 6-31G*//6-31G*, $E = -117.071$ 47 hartrees. ⁿ Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1975, 97, 6941.

Chart IV. Optimized STO-3G Geometries^a

^a Bond lengths in angstroms, bond angles in degrees.

and the silyl substituent was also studied (i.e., 5Si, 6Si) in order to allow a direct comparison with the available solvolysis rates.² The corresponding alkyl and alkynylvinyl cations (2C, 3C, 5C, 6C) were calculated for comparison.

Computational Methods

Calculations were carried out with the Gaussian 76 series of programs.⁷ The structures of the silyl and the alkylvinyl cations (2 and 5) of vinylsilane (8Si) and of the 1-silyl- and 1-methylvinyl alcohols (14Si and 14C) were fully optimized by using the minimal STO-3G basis set,^{8a} except that in

Table II. Calculated Energies for the Isodesmic Eq 1-16^{a,b}

eq	calculated energies, kcal mol ⁻¹		
	STO-3G	3-21G	6-31G*
1	25.9	23.6	23.9
2	39.7	26.3	25.0
3	10.8		
4	9.6		
5	13.8	2.6	1.1
6	12.5		-0.2 ^c
7	23.4		10.7 ^c
8	0.4	-0.5	-1.1
9	-0.8	-3.0	-5.6
10	-1.1	-2.6	-4.5
11	-15.0	-5.2	-5.6
12	-12.6		-3.2 ^d
13	-2.0		2.0
14a	-13.1	-15.5	
14b	-14.8	-8.7	
15a	-17.8	-20.2 ^e	
15b	-18.8	-12.7 ^f	
16a	1.8	-6.8	
16b	1.0	-7.6 ^g	

^a Using the energies in Table I. ^b A negative sign indicates that the reaction as written is exothermic.

^c Estimated value. The correction is based on the STO-3G vs. 6-31G* calculated energies of eq 2. ^d Estimated value. The correction is based on the STO-3G vs. 6-31G* calculated energies of eq 11. ^e Estimated value. The correction is based on eq 14a. ^f Estimated value. The correction is based on eq 14b. ^g Estimated value. The correction is based on eq 16a.

5 the geometry of the H₂C= fragment was assumed to be identical with that of 4H. In 11, the structure was assumed to be the same as in vinylacetylene (10H), but the C-R bond lengths were optimized (i.e., to 1.486 and 1.813 Å in 11C and 11Si, respectively). Single-point calculations at the STO-3G-optimized geometries were performed with the split valence 3-21G^{8b} (33-21G for Si^{8c}) basis set and for 2 and 5 with the augmented 6-31G*^{8d} (66-31G* for Si^{8e,f}) basis set which includes a set of *d* functions on all non-hydrogen atoms. For the larger molecules 3, 6, 9, 12, and 15 we have used the STO-3G-optimized geometries of the corresponding parent systems (e.g., 2 for 3) and substituted the allylic silyl or methyl hydrogens by "standard" methyl groups (i.e., C-H = 1.09 Å, ∠HCH = 109.47°, Si-CH₃ = 1.86 Å, and C-CH₃ = 1.54 Å; all the methyl hydrogens were

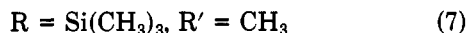
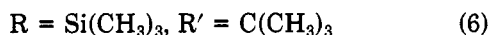
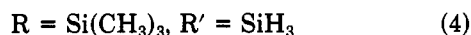
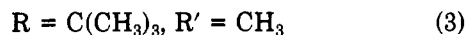
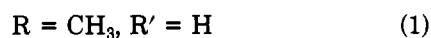
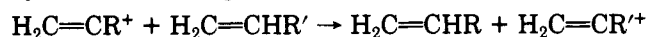
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staggered to the adjacent CC or CSi bonds). The optimized geometries of the cations and of the corresponding neutral molecules are presented in Charts II-IV and the total energies are given in Table I.

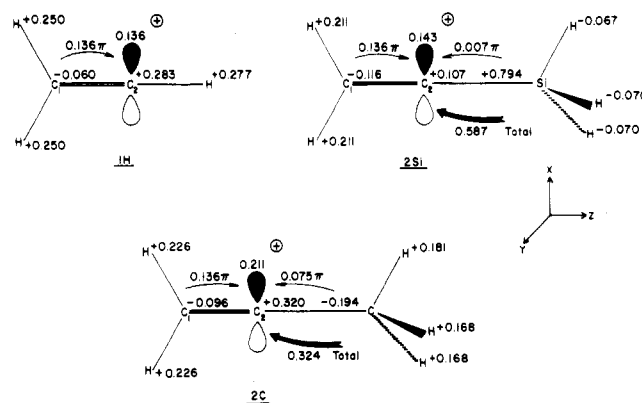
Results and Discussion

(a) α -Silyl- and α -Alkylvinyl Cations. The stabilities of the α -silylvinyl cations are evaluated in the isodesmic hydride transfer equations (eq 1-6; Table II).



Both methyl and silyl substitutions stabilize the vinyl cation substantially (Table II, eq 1 and 2). However, while the calculated stabilization energy of methyl is insensitive to the basis set (eq 1), the stabilization by silyl drops considerably on going from STO-3G to 3-21G (eq 2). The addition of polarization functions (i.e., at 6-31G*) has little additional effect on the energy of eq 2. The calculated relative stability of **2Si** and **2C** (eq 5) is necessarily also basis set dependent. At STO-3G, H_3Si is substantially more stabilizing than CH_3 , while at 3-21G and 6-31G* their effects are comparable. We⁵ and others⁹ have found similar basis set dependencies of the relative stabilities of H_2CX^+ vs. H_2CY^+ cations, where X and Y are first and second row substituents (including those for X = CH_3 and Y = SiH_3). In all these cases the minimal basis set overestimates the stabilization by the second row substituents (e.g., H_3Si , PH_2 , SH , Cl),⁵ so that a basis set with at least split-valence quality must be used for a reliable prediction of silicon stabilization energies. We therefore conclude that in the gas phase **2Si** and **2C** have comparable stabilities. Compared to hydrogen, both silyl and methyl substitution are highly stabilizing, by ca. 25 and 24 kcal mol⁻¹, respectively. In similar isodesmic comparisons where only STO-3G calculations are available, corrections (based on the calculated STO-3G vs. 6-31G* energies of eq 2 and 5) of 14.7 (for eq 4) and 12.7 kcal mol⁻¹ (for eq 6 and 7) should be applied.^{10a} The substitution of the silyl and the methyl substituents by $\text{Si}(\text{CH}_3)_3$ and *t*-Bu, respectively, stabilizes the cations to a similar extent, i.e., by 9.6 and 10.8 kcal mol⁻¹, respectively (STO-3G).^{10b} Thus, **3C** and **3Si** also have comparable stabilities (Table II, eq 6, corrected value), in contrast to the conclusions which were based on solvolysis rates.^{2,10c} Note that in the gas phase $\text{Si}(\text{CH}_3)_3$

Chart V. Orbital Populations and Total Charges in α -Silyl and α -Alkyl Vinyl Cations



is more stabilizing than CH_3 by ~ 9 kcal mol⁻¹ (eq 7 corrected for the STO-3G deficiencies).

Why is an α - SiH_3 substituent not more stabilizing than methyl, although silicon is more electropositive than carbon (Pauling's electronegativities: Si, 1.8; C, 2.5^{11a}), and although a $\text{Si}(\text{CH}_3)_3$ substituent is a stronger σ donor than *t*-Bu (σ_I values are -0.11 and -0.01, respectively)?^{11b} We believe that this is due primarily to a weaker hyperconjugation in **2Si** than in **2C** and to an electrostatic repulsion between the positively charged cationic carbon and the α -silicon atom. Both effects counterbalance the stronger inductive effect of SiH_3 (See Chart V). Thus, the population of the $2p(\text{C}^+)$ orbital in **2Si** (0.143 electrons) is lower than that in **2C** (0.211 electrons), indicating a greater hyperconjugative electron donation by the CH_3 than by the SiH_3 group. The inductive σ donation by the α - SiH_3 group is, however, much higher (0.587 vs. 0.324 for SiH_3 and CH_3 , respectively, Chart V). Due to this strong inductive donation the silicon atom in **2Si** bears a high positive charge (Chart V). Upon ionization the electrostatic repulsion between the silicon atom and the adjacent cationic carbon causes a considerable weakening of the C-Si bond which is 0.07 Å longer in the cation **2Si** than in **8Si** (Charts II and III). This bond weakening destabilizes the α -silyl cation **2Si**. In **2C**, on the other hand, the methyl carbon is negatively charged (Chart V), and the C- CH_3 bond is 0.04 Å shorter in the cation than in 2-propene.^{12a} The strengthening of the C- CH_3 bond upon ionization stabilizes the cation reinforcing the stabilizing inductive and hyperconjugative effects of the methyl group. Overall, α -methyl and α -silyl substituents stabilize vinyl cations to a similar degree, but this conclusion is not general. In other cations (e.g., CH_3CH_2^+ vs. $\text{H}_3\text{SiCH}_2^+$), H_3Si is considerably less stabilizing than CH_3 .^{5d,9}

Ground-state effects should be taken into consideration for a meaningful comparison between the calculations and the solvolysis rates.² Accurate ab initio calculations of vinyl triflates are impractical at present. The best model compounds which are accessible computationally are the corresponding vinyl alcohols (i.e., **13H**, **14**, and **15**).^{12b} The major electronic effects which are associated with the

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(10) (a) The basis set corrections exhibited by eq 2 and 5 correct the poor description of the $^+\text{C-Si}$ bond by the minimal STO-3G basis set. In eq 4, 6, and 7 a β -Si-H bond is substituted by a β -Si- CH_3 bond, but the $^+\text{C-Si}$ bond remains intact. Computational experience shows that the calculated energies of such isodesmic reactions, where only a remote position from the "problematic" center is substituted, are not sensitive to the applied basis set.^{9a,b} We therefore assume that the corrections of eq 2 and 5 can be applied to eq 4 and to eq 6 and 7, respectively. (b) The only relevant data in the gas phase to which these calculations can be compared is that $\text{H}_2\text{C}=\text{C}^+-\text{Pr}-i$ is more stable than **2c** by 14.5 kcal mol⁻¹, relative to hydride transfer. See: Aue, D. H. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9. (c) These conclusions are based primarily on the solvolysis rates of α -alkynyl vinyl triflates (e.g., $\text{CH}_2=\text{C}(\text{OTf})\text{C}\equiv\text{CR}$; R = *t*-Bu, $\text{Si}(\text{CH}_3)_3$). Calculations show, however (see below), that the $\text{H}_2\text{C}=\text{CCCR}^+$ cations are poor models for the corresponding $\text{H}_2\text{C}=\text{CR}^+$ cations (see also footnote 14b).

(11) (a) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93. (b) Charton, M. *Prog. Phys. Org. Chem.* 1981, 13, 119.

(12) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1973, 95, 6531. (b) The same approach was used in ref 12a. (c) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965. (d) This assumption, which is probably valid for $\text{H}_2\text{C}=\text{C}(\text{OTf})\text{R}$, may be incorrect for the more crowded $(\text{CH}_3)_2\text{C}=\text{C}(\text{OTf})\text{R}$ systems where ground-state interactions between the leaving group and the *cis*- β -methyl group may be significant. See for example: Cheng, P.-T.; Nyburg, S. C.; Thankachan, C.; Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 654.

presence of the C–O bond and which affect the ground-state energies of the vinyl triflates are reflected also in the energies of the corresponding vinyl alcohols (but not in those of the corresponding ethylenes). Sterically the OH and the OSO₂CF₃ groups are expected to be rather similar, as exemplified by the almost identical axial ⇌ equatorial equilibrium of cyclohexenyl-X derivatives, where X = OH, OCH₃, or OSO₂C₆H₅-*p*-CH₃.^{12c,d} The bond-separation energies (eq 8 and 9, Table II) which measure the interaction between the hydroxyl and the geminal methyl and silyl groups are significantly different. The interaction between CH₃ and OH is minor but the interaction between H₃Si and OH is *destabilizing* by 5.6 kcal/mol⁻¹ (6-31G*, Table II). Thus, the ground state of H₂C=C(OH)SiH₃ is 4.5 kcal/mol⁻¹ (eq 10 at 6-31G*) *higher* than that of H₂C=C(OH)CH₃. We have found an even larger ground-state destabilization in H₂C(OH)SiH₃,^{5d} and recent experimental studies¹³ support these conclusions. We attribute this destabilization to a repulsive four-electron hyperconjugative interaction between the oxygen's lone pair and the high-lying C–Si bond electrons.^{5d}

The OH⁻-transfer equations (eq 11 and 12) model the H₂C=CH₂ + H₂C=C(OH)CH₃ →
H₂C=CHOH + H₂C=CHCH₃ (8)

H₂C=CH₂ + H₂C=C(OH)SiH₃ →
H₂C=CHOH + H₂C=CHSiH₃ (9)

H₂C=C(OH)SiH₃ + H₂C=CHCH₃ →
H₂C=C(OH)CH₃ + H₂C=CHSiH₃ (10)

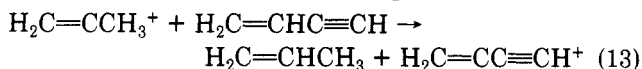
H₂C=C(OH)SiR₃ + H₂C=CCR₃⁺ →
H₂C=CSiR₃⁺ + H₂C=C(OH)CR₃
R = H (11)

R = CH₃ (12)

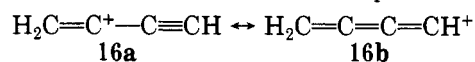
solvolysis reactions² more accurately than eq 5 or 6 because they take into account both the relative stabilities of the cations and the ground-state effects. Thus, although H₂C=CSiH₃⁺ is only 1.1 kcal/mol⁻¹ more stable than H₂C=CCH₃⁺ (eq 5), the ionization of H₂C=C(OH)SiH₃ (which models H₂C=C(OTf)SiH₃) is predicted to be by 5.6 kcal/mol⁻¹ more exothermic than the ionization of H₂C=C(OH)CH₃ (eq 11). Unfortunately, a direct comparison between the solvolysis rates of CH₂=C(OTf)SiR₃ and of CH₂=C(OTf)CR₃ (R = H, CH₃) is not available because H₂C=C(OTf)Si(CH₃)₃ solvolyses in 50% ethanol by an E2 mechanism.² However, we estimate that the S_N1 reactivity of CH₂=C(OTf)Si(CH₃)₃^{14a} is ca. 10 times faster

than that of (CH₃)₂C=C(OTf)-*t*-Bu,^{14b} in reasonable agreement with the calculations (i.e., eq 12, after basis set corrections, is exothermic by ca. 3.2 kcal/mol⁻¹). We emphasize, however, that such comparisons must be done with great caution due to the important role of solvation, which often narrows considerably the energy differences between gaseous ions and occasionally even reverses the stability order.^{3a,15} The agreement between the calculations and the solvolysis rates suggests that the solvation energies of the silyl- and the methyl-substituted vinyl cations are comparable.

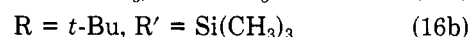
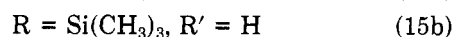
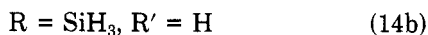
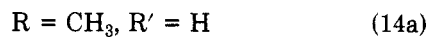
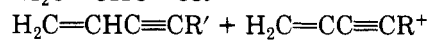
(b) *α*-Silyl- and *α*-Alkylalkynylvinyl Cations. The insertion of an acetylenic bond between the positive center and the *α*-substituent is expected to attenuate its electronic effect. Is this attenuation effect the same for alkyl and silyl substituents? This question is discussed below. Theoretical (eq 13)¹⁶ as well as experimental data^{2,17} in-



dicates that the substitution of an *α*-methyl by a triple bond destabilizes the vinyl cation. This has been ascribed to the greater inductive withdrawing effect of the triple bond compared to its resonance-stabilizing effect (i.e., 16a ↔ 16b). Suitable substitution of the triple bond should



increase the contribution of the resonance form 16b and stabilize the cation. This is indeed the case for both alkyl and silyl substitution, as exemplified by the exothermicities of eq 14 and 15. Thus, 5C and 5Si are more stable than H₂C=CC≡CR'⁺ + H₂C=CHC≡CR →



4H by 15.5 and 8.7 kcal/mol⁻¹, respectively (eq 14a and 14b at 3-21G). Both, 5C and 5Si are more stable than the corresponding *α*-substituted cations 2Si and 2C. Substitution in 5 of SiH₃ by Si(CH₃)₃ and of CH₃ by *t*-Bu stabilizes the cations comparably, by 4.0 and 4.7 kcal/mol⁻¹, respectively (STO-3G). We estimate that at 3-21G (see above), 6C and 6Si are more stable than 4H by 20.2 and 12.7 kcal/mol⁻¹, respectively (eq 15a and 15b, Table II). In contrast, alkyl and silyl substituents which are attached directly to the cationic center stabilize the vinyl cation to a similar degree (eq 1 and 2). The acetylenic bond transmits the electronic effects of alkyl substituents more effectively than that of silyl substituents (compare eq 1 and 2 with eq 14a and 14b, respectively). This probably reflects the fact that *π*-conjugation effects are transmitted

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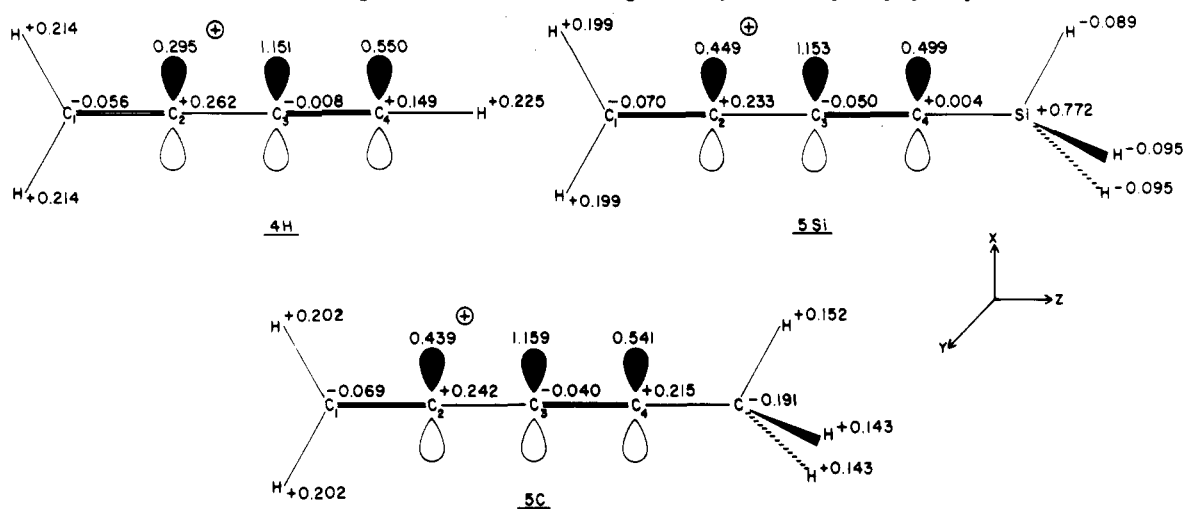
(14) (a) H₂C=C(OTf)Si(CH₃)₃ may solvolyse by an S_N1 mechanism in better ionizing and less nucleophilic solvents than 50% ethanol such as trifluoroethanol. (b) (CH₃)₂C=C(OTf)Si(CH₃)₃ solvolyzes 24 times faster than CH₂=C(OTf)-*t*-Bu.² We estimate that the S_N1 reactivities of CH₂=C(OTf)Si(CH₃)₃ and of (CH₃)₂C=C(OTf)Si(CH₃)₃ are comparable. This assumption is based on the following reasoning. (1) In noncrowded systems a *β*-methyl substituent has little effect on solvolysis rates, e.g., *k*[(CH₃)₂C=C(OTf)CH₃]/*k*[CH₂=C(OTf)CH₃] = 0.75.² (2) Relief of ground-state steric repulsions between the *cis* CH₃ and Si(CH₃)₃ groups is probably of only minor importance in determining the solvolysis rate of (CH₃)₂C=C(OTf)Si(CH₃)₃ because C–Si bond lengths are relatively long (ca. 1.86 Å, Chart IV). Schiavelli, Stang, et al. arrived at the opposite conclusion, namely, that “an *α*-Si(CH₃)₃ is deactivating compared to *t*-Bu”,² by comparing the solvolysis rates of (CH₃)₂C=C(OTf)-*i*-Pr and of (CH₃)₂C=C(OTf)Si(CH₃)₃ (relative rate 0.75). However, the solvolysis of (CH₃)₂C=C(OTf)-*i*-Pr is accelerated by ground-state steric crowding. Thus, H₂C=C(OTf)-*t*-Bu solvolyzes only 3.7 times faster than H₂C=C(OTf)CH₃, but (CH₃)₂C=C(OTf)-*i*-Pr solvolyzes 160 times faster than (CH₃)₂C=C(OTf)CH₃. If this ground-state effect is taken into account, then the solvolytic data, in our opinion, strongly supports our conclusion that the Si(CH₃)₃ group is “inherently” more activating in solvolysis than *t*-Bu. Note that the stabilities of the corresponding cations 3C and 3Si are comparable.^{10c}

(15) (a) Wolf, J. F.; Harch, P. G.; Taft, R. W. *J. Am. Chem. Soc.* 1975, 97, 2904. (b) Arnett and Pienta have shown, however, that for carbenium ions which do not differ dramatically in their sizes or charge delocalization, the differential solvation energies in nonnucleophilic solvents (e.g., superacid media) are small.^{3d} (c) Contradicting cases are, however, well-known. For example, in the gas phase CH₃CH=CCH₃⁺ is 7.9 kcal/mol⁻¹ more stable than H₂C=CCH₃⁺, but the solvolysis rates of their derivatives are comparable (for references see footnote 19 of ref 6c).

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(17) (a) Hassdenteufel, J. R.; Hanack, M. *Tetrahedron Lett.* 1980, 503. (b) Kobayashi, S.; Nishi, T.; Koyama, I.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* 1980, 103.

Chart VI. Orbital Populations and Total Charges in Silyl and Alkylalkynylvinyl Cations



through a triple bond more effectively than σ -inductive effects.^{11b} As shown above, hyperconjugation, a π -conjugative effect, is more important for alkyl groups, while the inductive effect is the principal stabilizing mechanism for silyl substituents. An important consequence of these different "transmission factors" is that the silyl-substituted cations **5Si** and **6Si** are less stable than their alkyl analogues **5C** and **6C** by 6.8 (eq 16a, 3-21G) and ca. 8 kcal mol⁻¹ (eq 16b, corrected). Note the contrast with the parent vinyl cations, where **2C** and **2Si** (or **3C** and **3Si**) have comparable stabilities (eq 5 and 6). We emphasize, therefore, that conclusions regarding the stabilizing effects of α -silyl and α -alkyl groups may be misleading if they are based, as suggested,² on the solvolysis rates of the corresponding acetylenic derivatives. The calculations are in agreement with the solvolysis data.^{2,18} Thus, $\text{H}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CSiMe}_3$ solvolyses 30 times faster than $\text{H}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CH}$ (compare with eq 15b) but 50 times slower than $\text{H}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CBu-}t$ (compare with eq 16b).² The large difference in the "transmission factor" through a triple bond for silyl and alkyl substituents is clearly demonstrated by the following solvolysis rate ratios:² $k(\text{Me}_2\text{C}=\text{C}(\text{OTf})\text{SiMe}_3)/k(\text{Me}_2\text{C}=\text{C}(\text{OTf})\text{Bu-}t) \simeq 30$,¹⁴ $k(\text{Me}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CSiMe}_3)/k(\text{Me}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CBu-}t) = 0.021$.

Alkynyl carbenium ions have recently attracted considerable interest, and therefore a special effort was made to elucidate their structures and charge distributions.^{19,20} We therefore briefly discuss the geometries and the charge distributions in the analogous alkynylvinyl carbenium ions **5**, in order to evaluate the effect of silyl and alkyl substitutions on the relative importance of the mesomeric forms **16a** and **16b**. The parent α -ethynylvinyl cation **4H** was analyzed previously.¹⁶ The effect of methyl or silyl substitutions on the geometry of the carbenium ion is small but consistent with a greater contribution of the cumulenonic form **16b**. Thus in both **5C** and **5Si** the C_2C_3 bond lengths

are shorter and the C_3C_4 bond lengths are longer than in the parent **4H** (Chart II). Similar changes in the geometry were found in the analogous $\text{H}_2\text{CC}\equiv\text{CCH}_3^+$ and $\text{H}_2\text{CC}\equiv\text{CH}^+$ cations.^{20b} The charge distribution in **4H** changes substantially upon substitution (Chart VI), emphasizing the increasing importance of the allylic-type resonance form **16b**. In **4H** the cationic $2p_x(\text{C}_2^+)$ orbital contains 0.295 electrons. In **5C** and **5Si** the population of this orbital increases to 0.439 and 0.449 electrons, respectively, so that the positive charge is divided more equally between the $p_x(\text{C}_2)$ and the $p_x(\text{C}_4)$ orbitals. The population of the $p_x(\text{C}_4)$ orbital is higher in **5C** than in **5Si**, reflecting the stronger hyperconjugative effect of methyl. As noted for **4H**, in **5C** and **5Si** the ethylenic C_1C_2 π bond is also highly polarized, pointing to contributions from resonance forms $\text{H}_2\text{C}^+-\text{C}\equiv\text{C}\equiv\text{CR}$. The total charges reflect both the inductive effect and the π donation by the substituent. The total charges at C_2 are smaller in **5C** and **5Si** than in **4H**, but the changes are much smaller than in the $p_x(\text{C}_2)$ orbital. The large inductive donation of the H_3Si group is reflected in the much higher total charge at C_4 in **5Si** compared to that for **5C**.

In summary, calculations show that α -silyl and α -alkyl substituents stabilize the parent vinyl cation to a similar degree. However, a destabilizing interaction between the geminate silicon and oxygen atoms raises the ground-state energies of a α -silylvinyl triflates relative to that of the corresponding α -alkylvinyl triflates, so that the α -silyl derivatives are predicted to solvolyze faster. A triple bond transmits the stabilizing effect of an alkyl group more effectively than that of a silyl group. Consequently, the alkyl-substituted α -alkynylvinyl cations (e.g., $\text{H}_2\text{C}=\text{C}^+-\text{C}\equiv\text{C}-\text{alkyl}$) are more stable than the corresponding silyl substituted cations (e.g., $\text{H}_2\text{C}=\text{C}^+-\text{C}\equiv\text{C}-\text{silyl}$). The close agreement between the results of the calculations, which describe isolated molecules in the gas phase, and the solvolysis rates suggests that the solvation energies of the alkyl- and silyl-substituted vinyl cations are comparable. We hope that our study will prompt further studies, particularly in the gas phase, of the electronic nature of silyl substituents.

Acknowledgment. We thank Professor J. A. Pople for providing us with the 33-21G and the 66-31G* basis sets for silicon prior to publication and for valuable discussions. Professors P. J. Stang and M. D. Schiavelli are acknowledged for communicating their solvolytic data prior to publication and for valuable discussions. This research was partially supported by a grant from the United

(18) The differential ground-state effects between $\text{H}_2\text{C}=\text{C}(\text{OH})\text{C}\equiv\text{CSiR}_3$ and $\text{H}_2\text{C}=\text{C}(\text{OH})\text{C}\equiv\text{CCR}_3$ is probably small in contrast to the large difference between **14Si** and **14C**. This is because in $\text{H}_2\text{C}=\text{C}(\text{OH})\text{C}\equiv\text{CSiR}_3$ the silyl and the hydroxy groups are not bonded to the same carbon, and the destabilizing hyperconjugative interaction cannot occur.

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States-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

Registry No. 1H, 14604-48-9; 2Si, 80631-00-1; 2C, 50457-57-3; 3Si, 80631-01-2; 3C, 80631-02-3; 4H, 62698-25-3; 5Si, 80631-03-4; 5C,

80631-04-5; 6Si, 80631-05-6; 6C, 80631-06-7; 7H, 74-85-1; 8Si, 7291-09-0; 8C, 115-07-1; 9Si, 754-05-2; 9C, 558-37-2; 10H, 689-97-4; 11Si, 59923-57-8; 11C, 646-05-9; 12Si, 2696-32-4; 12C, 4911-58-4; 13H, 557-75-5; 14Si, 80631-07-8; 14C, 29456-04-0; 15Si, 80631-08-9; 15C, 79144-28-8.

Reaction of 2,4-Dinitrobenzenesulfonyl Chloride with Quadricyclene

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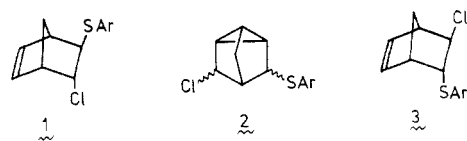
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Received December 15, 1981

The treatment of quadricyclene with 2,4-dinitrobenzenesulfonyl chloride has been reinvestigated and chloro adducts 1-A and 2b-A as well as acetates 4a-A, 4b-A, 6, and 7 have been obtained. Establishing 2b-A with *endo*-chloride led to the important conclusion that *endo*-chloride attack occurs by collapse of an ion pair. Monitoring changes in the proportions of acetates, especially with added LiClO₄, has allowed conclusions about the degree of development of the carbocation intermediates. These conclusions were proposed on the basis of the previously published ideas of stereocontrol by an ion pair.

The addition of sulfonyl chlorides to norbornadiene has received considerable attention.¹⁻⁸ These studies may be summarized as follows (despite differences in opinion on the stereochemistry of one addition product and thus the attendant mechanism). First, the relative proportions of products are extremely sensitive to the polarity of the solvent used. Second, products have been observed with stereochemistry that may be surprising to some. Third, the second double bond can interact with the incipient carbocation center, possibly stabilizing the intermediate and in many cases clearly allowing rearrangement to nortricyclic-structure adducts. These combined observations have led to important mechanistic conclusions^{4,9,10} for 2,4-dinitrobenzenesulfonyl chloride (DNBSC) additions.

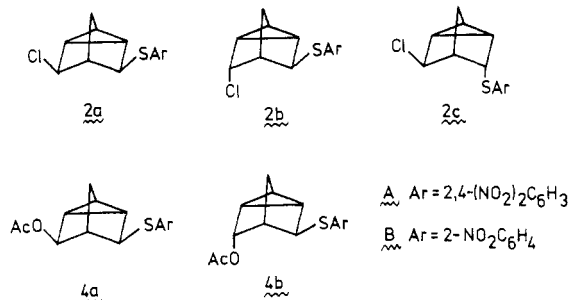
Let us expand upon these observations. Early papers described the formation in nonpolar solvents of *trans*-chloro sulfides (type 1, *endo*-Cl) mixed with minor



A Ar = 2,4-(NO₂)₂C₆H₃; B Ar = 2-NO₂C₆H₄

amounts of isomeric adducts with nortricyclic skeletons.

Chart I



More recently, the reports by the research groups of Zefirov and Morrill⁴ and of Garratt⁵ revealed a more complex picture. First, additions carried out in carbon tetrachloride and in dichloromethane solvents yield three major products, specifically adducts 1 and 2 as well as olefinic *trans*-chloro sulfide 3 with the SAr and Cl groups in a configuration opposite that of 1. The structure of 3-B has been established by X-ray diffraction.⁶ Adduct 3 indicates that the diene has been attacked by electrophilic sulfur on the *endo* side.

Second, yields of nortricyclic chloro sulfides 2 increase sharply with an increase in solvent polarity, and type-2 adducts predominate in acetic acid^{4,11} and in liquid sulfur dioxide.⁸ Garratt and Beaulieu⁵ have assigned configuration 2a (*exo*-chlorine, *exo*-thioether, Chart I) to their product on the basis of ¹³C NMR data. More recently Zefirov and Morrill⁴ published results leading to a different structure for this product; configuration 2b was assigned (*exo*-thioether, *endo*-chlorine) on the basis of single-crystal X-ray studies of 2b-A.^{4,7}

Formation of adduct 2b-A has been interpreted in terms of an ion-pair mechanism; this has evolved from the concept of "stereocontrol of addition" by ion pairs.^{4,9,12} Under "doping" conditions^{9,10,13} (LiClO₄ in the acetic acid), the

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