Radical Ions. 37. Ionization and One-Electron Oxidation of Electron-Rich Silylalkyl Olefins[1-3]

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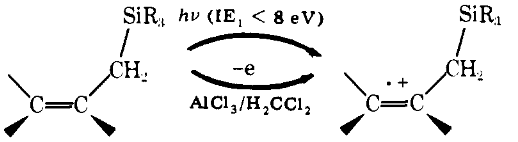
Abstract: Trialkylsilylalkyl substituents $(R_3Si)_nC-$ are powerful electron donors, which enormously modify the properties of parent π systems like ethylene, cyclopentadiene, or 1,4-cyclohexadiene. Owing to the destabilization of the molecular ground state and the charge delocalization in the corresponding radical cation, the vertical first ionization energies drop down to 7 eV (!) and selective one-electron oxidation with $AlCl_3$ in H_2CCl_2 produces novel silylalkyl radical cations like $(R_3SiCH_2)_2C{=}C(CH_2SiR_3)_2^{+\cdot}$, stable even at room temperature. The photoelectron and the electron spin resonance data reported are best interpreted by σ_{CSi}/π hyperconjugative interactions, assisted in the sterically overcrowded molecules by fixed optimum conformations with the σ_{CSi} bonds collinear to the π system. The ESR coupling constants provide evidence for a considerable spin population in the $(H_3C)_3Si$ groups and yield information on the structure in solution, and their temperature dependence reveals essential aspects of the dynamic behavior of the novel radical cations generated.

A useful criterion to predict the possible oxidation of a molecule M to a persistent[4] radical cation $M^{+\cdot}$ in solution is its first ionization potential determined, e.g., by photoelectron spectroscopy.[2,5,6] The key to the generation of numerous novel species $M^{+\cdot}$ containing heteroelements like B, Si, Ge, P, S, or Se[1,2,5-10] proved to be the selective one-electron oxidation with $AlCl_3$ in H_2CCl_2, the oxidation potential of which corresponds to a first ionization potential of ~8 eV. One of the principles to design compounds M easy to ionize—the multiple introduction of $(H_3C)_3Si$ groups in β position to π systems[2,6,8,10] or in α[1,7,8,10] or β[9] position to lone pairs—can also be extended



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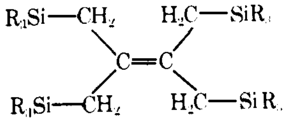
to olefins. The compounds investigated may be grouped into fully silylated prototype molecules (R = CH_3) (2) and partly substituted derivatives (3) which have been synthesized by the routes in eq 4-6 (cf. Experimental Section).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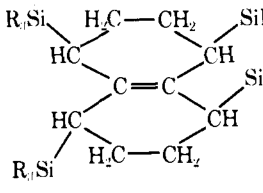
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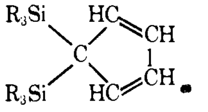
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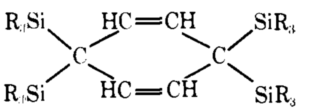
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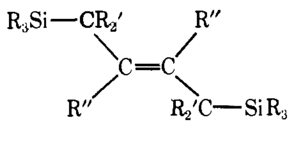
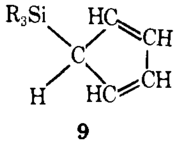


R' = H		CH_3	H
R'' = CH_3		H	H
(*E*)	(*Z*)	(*E*)	(*E*)
3	**4**	**5**	**6**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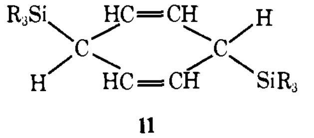
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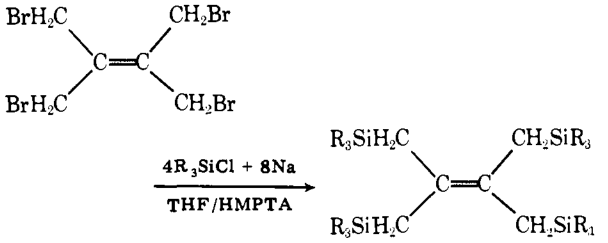

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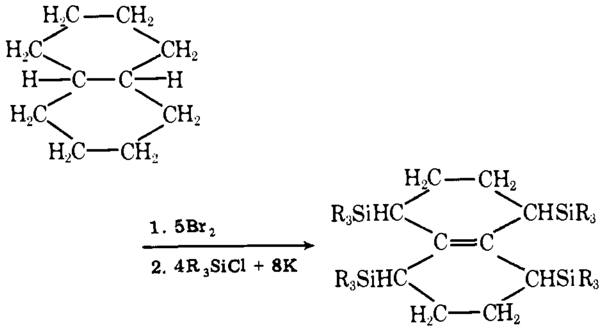

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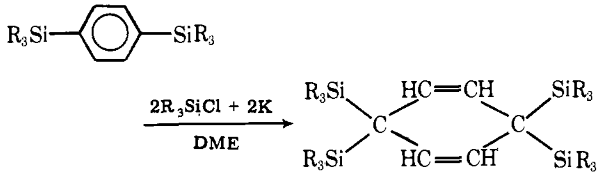

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The elegant procedures developed have also been used to generate some radical cations without even isolating the parent compounds by simply adding $AlCl_3$ to the reaction mixture; ESR spectra thus recorded comprise the tetrakis(triethylsilylmethyl)ethylene species $\mathbf{7}^{+\cdot}$, and the product from (6) starting with durene, $\mathbf{12}^{+\cdot}$, i.e., the tetramethyl derivative of $\mathbf{11}^{+\cdot}$ (cf. Experimental Section).

The silylated derivatives synthesized and the successful oxidation of the seven with first ionization energies below 7.9 eV to their radical cations, $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, $\mathbf{3}^{+\cdot}$, $\mathbf{7}^{+\cdot}$, $\mathbf{10}^{+\cdot}$, $\mathbf{11}^{+\cdot}$, and $\mathbf{12}^{+\cdot}$, displays several interesting facets:

(i) Stable radical cations of ethylene derivatives have been obtained so far only from dialkylamino[11,12] or alkylthio[13] substituted ones; the rather unstable tetraalkyl species could only be characterized in flow systems.[14]

(ii) Sterically overcrowded ethylenes have attracted much attention recently because of their unusual chemical[15] and spectroscopic[16] properties; prototype molecules are tris(*tert*-butyl)ethylene[15a] or tetrakis(neopentyl)ethylene,[16f] which is the carbon analogue to our silyl derivative **1** (2).

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(iii) Radical cations of heteroatom bridged 1,4-cyclohexadienes $X(HC{=}CH)_2X$ with $X = NR$[17] or $X = S$[18] have been known for a decade, and a comparison of their spin distributions with those of the silyl-substituted carbon analogues $\mathbf{10}^{+\cdot}$ to $\mathbf{12}^{+\cdot}$ is of interest.

More generally, the combination of PES and ESR measurements does not only allow us to predict and to detect species $M^{+\cdot}$ in solution, but yields interesting data to characterize the radical cation ground state: its vertical energy difference IE_1 to the molecular ground state and the coupling constants a_X provide information on the adiabatic relaxation of $M^{+\cdot}$ including structural changes, spin population, and dynamic behavior.

Experimental Section

The silylalkyl olefins were synthesized either by organometallic coupling reactions using alkali metals or magnesium in THF[19] or via reductive silylation of conjugated π systems.[20] All reactions were run under pure and dry nitrogen; THF and 1,2-dimethoxyethane (DME) had been freshly distilled from Na/K alloy. Routine spectra were taken on a Varian T-60 (^{1}H NMR) and on a Cary 14 spectrometer (UV-vis). Melting points are uncorrected.

Tetrakis(trimethylsilylmethyl)ethylene (1). Attempts to prepare **1** by Grignard reactions or by a Wurtz synthesis from tetrakis(bromomethyl)ethylene[21] and trimethylchlorosilane did not even yield a trace of the desired product; only the following modification proved to be successful.

A solution is prepared which contains tetrakis(bromomethyl)ethylene[21] (10.0 g, 25 mmol), trimethylchlorosilane (11.9 g, 110 mmol), and hexamethylphosphoric triamide (HMPTA, 20.5 g, 110 mmol) in 120 mL of THF. Clean-cut sodium (5.0 g, 220 mmol) and a trace of potassium are added, the mixture is kept for 2 h at room temperature under vigorous stirring, and then the solution is refluxed for another 2 h. The cooled reaction mixture may be filtered under air; the solvent is evaporated. Repeated extraction with *n*-hexane/water effectively removes the HMPTA. Finally the collected organic fractions are dried and distilled in vacuo to yield 1.9 g (20%) of a colorless oil which crystallizes on standing: bp 80 °C (0.001 mm); mp 32 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.03 (s, 36 H), 1.35 (s, 8 H) at room temperature; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 0.00 (12 C), 25.61 (4 C), 121.00 (2 C); Raman (neat) 2958, 2902, 1629, 1415, 1260, 1172, 1120 cm^{-1}; UV (*n*-hexane) λ_{max} 238 nm (ϵ 6000).

Anal. Calcd for $C_{18}H_{44}Si_4$ (372.90): C, 58.0; H, 11.9. Found: C, 57.8; H, 11.8.

1,4,5,8-Tetrakis(trimethylsilyl)-$\Delta^{4a(8a)}$-octalin (2). Potassium (16.0 g, 400 mmol) is added to a solution of 1,4,5,8-tetrabromo-$\Delta^{4a(8a)}$-octalin[22] (18.0 g, 40 mmol) and trimethylchlorosilane (21.6 g, 200 mmol) in 150 mL of THF. The mixture is heated carefully and, after melting of the potassium metal, refluxed for 3 h. The blue alkali halogenides are filtered off and the solvent is evaporated in vacuo. The remaining liquid can be distilled at 130 °C (0.01 mm) to give a colorless, viscous oil. On cooling to 0 °C a solid precipitates from this liquid. Recrystallization from methanol affords 2.0 g (12%) of colorless crystals: mp 75 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.06 (s, 36 H), 1.54 (broad s, 4 H), 1.70 (broad s, 8 H).

Anal. Calcd for $C_{22}H_{48}Si_4$ (424.97): C, 62.2; H, 11.4. Found: C, 61.9; H, 11.2.

(*E*)-1,4-Bis(trimethylsilyl)-2,3-dimethyl-2-butene (3).[20a] A solution of (*E*)-2,3-bis(bromomethyl)-2-butene[23] (12.1 g, 50 mmol) in 50 mL of THF is run slowly into a mixture of magnesium turnings (2.4 g, 100 mmol), trimethylchlorosilane (10.8 g, 100 mmol), and 200 mL of THF. The reaction mixture is refluxed for 2 h; then the cooled solution may be carefully hydrolyzed. Extraction with $CHCl_3$, drying with Na_2SO_4, and fractionated distillation yields 2.3 g (20%) of a colorless liquid: bp 40 °C (0.1 mm); ^{1}H NMR (neat/Me_4Si) δ 0.00 (s, 18 H), 1.51 (s, 4 H), 1.56 (s, 6 H).

Anal. Calcd for $C_{12}H_{28}Si_2$ (228.53): C, 63.1; H, 12.3. Found: C, 62.9; H, 12.5.

(*Z*)-1,4-Bis(trimethylsilyl)-2,3-dimethyl-2-butene (4).[20a] Preparation by the recommended[20a] reductive silylation of 2,3-dimethyl-1,3-butadiene with sodium in THF yielded 51%: bp 95 °C (15 mm); ^{1}H NMR (neat/Me_4Si) δ 0.00 (s, 18 H), 1.45 (s, 4 H), 1.61 (s, 6 H).

Anal. Calcd for $C_{12}H_{28}Si_2$ (228.53): C, 63.1; H, 12.3. Found: C, 63.0; H, 12.3.

(*E*)-2,5-Bis(trimethylsilyl)-2,5-dimethyl-3-hexene (5).[20a] Preparation according to ref 20a yielded 40%: bp 55 °C (0.5 mm); mp 25 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ −0.03 (s, 18 H), 0.96 (s, 12 H), 5.10 (s, 2 H).

Anal. Calcd for $C_{14}H_{32}Si_2$ (256.58): C, 65.5; H, 12.6. Found: C, 65.4; H, 12.7.

(*E*)-1,4-Bis(trimethylsilyl)-2-butene (6)[20a,24] was prepared according to ref 24 by an "in situ" Grignard reaction:[19] yield 20%; bp 72 °C (15 mm); ^{1}H NMR (neat/Me_4Si) δ 0.00 (s, 18 H), 1.40 (m, 4 H), 5.15 (m, 2 H).

Anal. Calcd for $C_{10}H_{24}Si_2$ (200.47): C, 59.9; H, 12.1. Found: C, 59.6; H, 12.0.

Tetrakis(triethylsilylmethyl)ethylene (7). The procedure given for the preparation of **1** is repeated using triethylchlorosilane instead of the trimethyl compound. The reaction results in large quantities of hexaethyldisilane,[25] which may be removed by distillation, bp 58 °C (0.1 mm); only very little residue remains. It contains, besides several impurities, the desired product **7** as established by NMR and, most conclusive, by ESR. Treatment of a small quantity of this residue with $AlCl_3/CH_2Cl_2$ results in a quite persistent radical cation; its highly resolved ESR spectrum can be interpreted in perfect analogy to that of the permethyl compound $\mathbf{1}^{+\cdot}$ (cf. text). Attempts to isolate pure **7**, however, were unsuccessful because of the small quantity of **7** formed.

5,5-Bis(trimethylsilyl)-1,3-cyclopentadiene (8)[26b] **and 5-(trimethylsilyl)-1,3-cyclopentadiene (9)**[26a] were prepared according to ref 26 by reaction of KC_5H_5 with R_3SiCl.

8: yield 57%; bp 32 °C (0.5 mm); ^{1}H NMR (neat/Me_4Si) δ −0.06 (s, 18 H), 6.53 (m, 4 H).

9: yield 40%; bp 36 °C (15 mm); ^{1}H NMR (neat/Me_4Si) δ −0.06 (s, 9 H), 3.0 (m, 1 H), 6.6 (m, 4 H).

3,3,6,6-Tetrakis(trimethylsilyl)-1,4-cyclohexadiene (10).[27] Clean-cut potassium metal (3.4 g, 85 mmol) is molten in 30 mL of DME. The mixture is cooled down to −20 °C and a solution of 1,4-bis(trimethylsilyl)benzene[28] (8.9 g, 40 mmol) in 20 mL of DME is added carefully to yield the green color of the corresponding dianion. Trimethylchlorosilane (10.8 g, 100 mmol) in 50 mL of DME is run into this solution at −20 °C; the reaction mixture is then allowed to warm up. At 10 °C the KCl begins to precipitate; it may be filtered off after completing the reaction by stirring at room temperature for 1 h. The solvent is evaporated; fractionated distillation at 0.1 mm yields first sublimating 1,4-bis(trimethylsilyl)benzene (50 °C) and then liquid reaction products (bp ~75 °C), most probably unsymmetrical silylated cyclohexadienes (cf. ref 27). The residue of the distillation is purified by repeated sublimation and recrystallization from ethanol to yield 0.6 g (4%) of colorless needles: 105 °C (0.1 mm) (sublimes); mp 110 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.10 (s, 36 H), 5.10 (s, 4 H).

Anal. Calcd for $C_{18}H_{40}Si_4$ (368.86): C, 58.7; H, 10.9. Found: C, 58.7; H, 10.7.

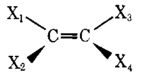
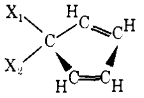
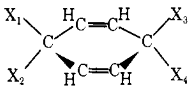
***trans*-3,6-Bis(trimethylsilyl)-1,4-cyclohexadiene (11).**[20b] During the preparation according to ref 20b the product **11** easily rearomatizes to form 1,4-bis(trimethylsilyl)benzene,[28] yielding only 31%: bp 75 °C (1 mm); mp 52 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.03 (s, 18 H), 2.16 (ps, 2 H), 5.41 (ps, 4 H).

Anal. Calcd for $C_{12}H_{24}Si_2$ (224.50): C, 64.2; H, 10.8. Found: C, 64.4; H, 10.7.

3,6-Bis(trimethylsilyl)-1,2,4,5-tetramethyl-1,4-cyclohexadiene (12). Potassium metal (9.6 g, 240 mmol) is added to a solution of durene (13.4 g, 100 mmol) and trimethylchlorosilane (26.0 g, 240 mmol) in 120 mL of THF. The mixture is refluxed for 1 day and, after cooling down to room temperature, the solids are filtered off. The solvent is evaporated in vacuo; NMR analysis of the dry residue exhibits mainly unreacted durene; the yield of **12** is less than 1%. This poor conversion is due to the very low electron affinity of durene, as exemplified further by the impossibility of obtaining a radical anion. Even addition of HMPTA (cf. **1**) did not improve the yield of **12**; however, it was again possible to obtain the corresponding radical cation $\mathbf{12}^{+\cdot}$ by reacting the crude product with $AlCl_3/CH_2Cl_2$. Although the broad ESR band of the durene-$AlCl_3$ complex interferes with the ESR spectrum of $\mathbf{12}^{+\cdot}$, it can be completely analyzed, showing all proton hyperfine couplings with the magnitude and the multiplicity as expected (cf. text).

Radical cations have been generated in the ESR glass capillary (d_i = 2 mm) under N_2 by the following procedure:[3] 1 mg of the compound is dissolved in 0.1 mL of oxygen-free methylene chloride (CH_2Cl_2),

Table I. Vertical π Ionization Energies of β-Trimethylsilyl Substituted Alkyl Olefins and of Some Reference Compounds

compd ($R = CH_3$)	no.	X_1	X_2	X_3	X_4	$IE_{\pi,1}$, eV	$IE_{\pi,2}$, eV
	**1**	R_3SiCH_2	R_3SiCH_2	R_3SiCH_2	R_3SiCH_2	7.15	
	2	H_2C R_3SiCH	H_2C R_3SiCH	H_2C R_3SiCH	H_2C R_3SiCH	6.98	
	3	R_3SiCH_2	H_3C	H_3C	R_3SiCH_2	7.70	
	4	R_3SiCH_2	H_3C	R_3SiCH_2	H_3C	7.70	
	5	R_3SiCR_2	H	H	R_3SiCR_2	7.90	
	6	R_3SiCH_2	H	H	R_3SiCH_2	8.30	
		R	R	R	R	8.41	
	**8**	R_3Si	R_3Si			8.05	9.10
	9	R_3Si	H			8.30	9.10
		H	H			8.61	10.70
	**10**	R_3Si	R_3Si	R_3Si	R_3Si	7.00	9.05
	11	R_3Si	H	H	R_3Si	7.70	9.30
		H	H	H	H	8.82	9.88

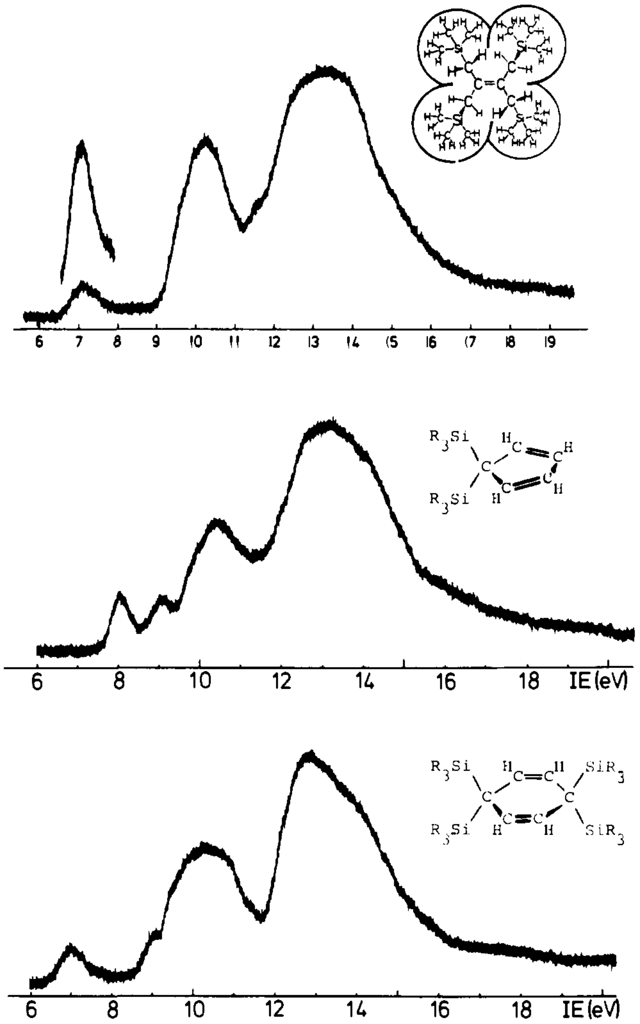


Figure 1. He(I) photoelectron spectra of tetrakis(trimethylsilylmethyl)ethene (**1**), of 5,5-bis(trimethylsilyl)-1,3-cyclopentadiene (**8**), and of 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (**10**).

which is kept dry over $AlCl_3$; ~5 mg of $AlCl_3$ are added to this solution. In case of less stable radical cations this procedure has to be performed in a cooling bath.

Charge-transfer (CT) complexes were obtained by reacting sublimed tetracyanoethylene (TCNE) with the compound in CH_2Cl_2 (Uvasol).

Photoelectron spectra have been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system and are calibrated using the $Xe(^2P_{3/2}) = 12.13$ eV and $Ar(^2P_{3/2}) = 15.76$ eV peaks.

Electron spin resonance spectra have been recorded using a Varian E 9 spectrometer with a variable-temperature equipment E 257. The spectra have been recorded at 9.5-GHz frequency, 330-mT magnetic field, and with a field modulation of 100 kHz. The coupling constants are assumed to be correct within ±1%; calibration was performed with Fremy's salt ($2a_N = 2.618$ mT) and with perylene radical anion in DME.[29]

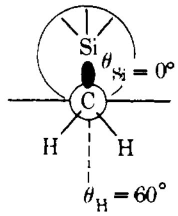
Low-temperature ^1H NMR spectra of **1** have been kindly measured by Dr. A. Walter and Professor H. Kessler; the Bruker HX 90/4-15 spectrometer was also used to record the ^{13}C NMR of **1**. The Raman spectrum of **1** was kindly provided by Dr. H. J. Zehnder and Professor W. Sterzel.

ESR spectra simulation could be achieved using the program ESPLOT;[3] it contains some subroutines from the optimization program ESOP,[30] which has been kindly provided to us by Professor A. v. Zelewsky of the University Fribourg. Because of the unusual requirements for trimethylsilyl-containing radical cations, the program capacity has been extended to incorporate up to 10^4 theoretical lines from up to 10^2 equivalent nuclei of eight different sorts or isotopes. The calculations were performed on the Univac 1108 of the Hochschul-Rechenzentrum Frankfurt.

Results and Discussion

Photoelectron spectra of three fully silylated prototype olefins (**1**, **8**, and **10**) are displayed in Figure 1. Their π ionization energies are listed together with those of **2**, of the partly silylated derivatives (2), and of some reference compounds in Table I. The ionization patterns (Figure 1) of silylalkyl-substituted π systems can be subdivided rather generally into four regions: isolated π ionization bands below 10 eV, the ionizations σ_{SiC} followed by and usually overlapping with σ_{CC} ionizations between 10 and 12 eV, the big multiple ionization hill around 13–14 eV, and the sometimes only indicated $3s_{Si}$-type ionizations above 16 eV.[31] Of foremost interest in our context are the π ionizations, which on comparison show some regularities within the individual classes of compounds.

i. Ethylene derivatives containing the smallest π subunit exhibit the largest $(H_3C)_3SiCH_2$– substituent effect. Relative to ethylene ($IE_1 = 10.52$ eV[32]), the lowering amounts to $\Delta IE_1 = 3.37$ eV (!) and relative to the tetramethyl derivative (Table I) still to $\Delta IE_1 = 1.26$ eV. For a rationalization of this enormous shift, two MO arguments may be emphasized: steric overcrowdedness leads to the preferred conformation (7) in which σ_{CSi} bonds collinear to the π system guarantee maxi-



(7)

mum hyperconjugative interaction.[33] The latter is also energetically favored, because the two basis orbitals π_{CC} (10.52 eV[32]) and σ_{SiC} (~10.6 eV[31]) match almost perfectly and according to second-order perturbation[33] a maximum split should result. The considerable hyperconjugative destabilization of the molecular ground state also affects other spectroscopic properties, e.g., the $\pi \rightarrow \pi^*$ excitation at ν_m 42 000 cm^{-1} with ϵ_m 6000 in *n*-hexane is bathochromically shifted by ~1 eV relative to other tetraalkylethylenes,[34] and in contrast to other silylalkylethylenes (**3**-**6**), which form in H_2CCl_2 solution with TCNE blue CT complexes (ν_m^{CT}-14 400 cm^{-1}), the tetrasubstituted **1** is oxidized by TCNE as verified by the ESR spectroscopically characterized $TCNE^{+\cdot}$ radical anion formed. The tetrasilaoctalin derivative **2** with its R_3Si groups in optimum position for hyperconjugative interactions possesses a record-low first ionization potential of only 6.98 eV (Table I).

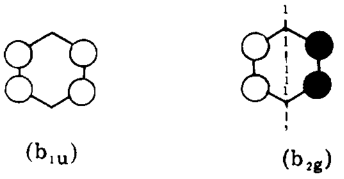
ii. 1,3-Cyclopentadiene derivatives also show a considerable overlap between σ_{CSi} bonds and the system: according to ab initio calculations,[35] and in close analogy to other partly delocalized five-center/6π-electron heteroring systems,[36] strong σ_{SiC}/π interactions are expected. This is in accord with the widely recognized NMR result, that the R_3Si group fluctuates around the cyclopentadiene ring[26] with a barrier of about 15 kcal/mol.[37] As far as the π radical cation states are concerned (Table I), they can be assigned via Koopmans' theorem in correspondence to the two occupied π orbitals of *cis*-butadiene[32,36] (8). Trimethylsilyl substitution in position 5 therefore should affect the two π ionizations differently: because of the nodal plane through the substitution center in a_2, the lowering ΔIE_1 is predicted and found to be rather small relative to ΔIE_2 (Table I: $\Delta IE_1 = 0.56$, $\Delta IE_2 = 1.60$ eV). A comparison with the π ionizations of heterocyclopentadienes[36] (9) further confirms the assignment (8) and discloses in addition that the effect of $(R_3Si)_nC$ moieties resembles that of amino groups.[8b] Owing to the relatively high first ionization potentials IE_1 >7.9 eV, no radical cations could be generated with $AlCl_3$ in H_2CCl_2 solution (1).

(8)

X	IE_1, eV	IE_2, eV
O	8.89	10.42
S	8.80	9.44
NH	8.22	9.22

(9)

iii. 1,4-Cyclohexadiene derivatives exhibit in their photoelectron spectra two still discernible π bands (Figure 1), the assignment of which can be based straightforwardly on the one for the parent compound,[38,39] i.e., assuming D_{2h} symmetry, to the occupied π orbitals (10) with b_{1u} destabilized by hyperconjugative interaction to climb above b_{2g}. Perturbation arguments based on the nodal plane through the substitution centers suggest—opposite to cyclopentadiene (8)—that this time the first ionization energy should be more strongly shifted (Table I: $\Delta IE_1 = 1.82$, $\Delta IE_2 = 0.83$ eV). The value for the fully 3,3,6,6-tetrasilylated **10**, IE_1 = 7,00 eV, deserves a special notation: like the one for **2**, it is even as low as, e.g., the IE_1 of perylene (!).[40] This rather large reduction below the 7.9-eV limit (1) allowed us to predict the existence of a radical cation $10^{+\cdot}$, which subsequently could be selectively generated with $AlCl_3$ in H_2CCl_2.



(10)

Electron spin resonance spectra have been obtained for radical cations from all silylalkyl olefins with first ionization potentials below 7.9 eV (Table I), i.e., the species $1^{+\cdot}$, $2^{+\cdot}$, $3^{+\cdot}$, $4^{+\cdot}$, $10^{+\cdot}$, and $11^{+\cdot}$. In addition, radical cations $7^{+\cdot}$ and $12^{+\cdot}$ could be generated without isolating the parent compounds **7** and **12** by simply adding the selective oxidizing agent $AlCl_3$ to the synthesis product solution in H_2CCl_2 (cf. Experimental Section). The electron-rich 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (**10**) can transfer an electron also to TCNE reducing it to $TCNE^{-\cdot}$. For an illustration, the following ESR spectra have been selected: $1^{+\cdot}$ for computer simulation and to demonstrate the temperature dependence (Figure 2), $2^{+\cdot}$ for the largest number of signals—theoretically 13 875 (!)—as well as for its dynamic behavior (Figures 3 and 6), and $10^{+\cdot}$ as an example for the cyclohexadiene radical cations generated (Figure 4). The ESR spectrum of $3^{+\cdot}$ has been published previously.[2] All coupling constants observed and assigned are summarized in Table II. To begin with, first the ESR details for the individual compounds will be reported.

i. Tetrakis(trimethylsilylmethyl)ethylene radical cation ($1^{+\cdot}$) exhibits a strongly temperature dependent ESR spectrum (Figure 2): the dominating two quintets of the two different methylene protons change their ratio. Also the ^{29}Si coupling ($I = \frac{1}{2}$, natural abundance 4.70%) of the labeled species, which adds 2 × 925 lines to the total of 2775 and is needed for the simulation (Figures 2B, D), decreases with increasing temperature (Table II, footnotes *a* and *b*).

ii. Tetrakis(triethylsilylmethyl)ethylene radical cation ($7^{+\cdot}$) could be generated in situ by adding $AlCl_3$ to the synthesis product mixture (cf. Experimental Section). Its ESR spectrum closely resembles that of $1^{+\cdot}$, also showing two different methylene proton quintets (Table II). On high resolution another multiplet with $a = 0.013$ mT is observed, which according to attempted computer simulation cannot result from 24 equivalent ethyl CH_2 protons.

iii. 1,4,5,8-Tetrakis(trimethylsilyl)-$\Delta^{4a(8a)}$-octalin radical cation ($2^{+\cdot}$) is expected to yield a rather complex ESR spectrum because of the fluxional behavior of the neutral molecule as detected by NMR spectroscopy (cf. Experimental Section and Figure 5A). The ESR spectrum (Figure 3) can be interpreted based on conformation (7) with an angle $\Delta\theta$ ~10° as discussed below; for the two species $M^{+\cdot}$ with four equivalent $(H_3C)_3Si$ groups, which are either unlabeled or contain one nucleus ^{29}Si, altogether 4625 + (2 × 4625) = 13 875 lines are predicted. All the coupling has been resolved, partly by temperature variation (Figure 6 and Table II), and partly due to the stability of $2^{+\cdot}$ even at room temperature, allowing us to prepare highly concentrated solutions. The geometry of $2^{+\cdot}$ and its dynamic behavior as deduced from the ESR coupling constants and their temperature dependence (Table II and Figure 6) will be discussed subsequently.

iv. Radical Cation from the (*E,Z*)-1,4-Bis(trimethylsilyl)-2,3-dimethyl-2-butenes $3^{+\cdot}$ ($4^{+\cdot}$). The ESR spectra[2] of the species $M^{+\cdot}$ generated from **3** or **4** with $AlCl_3$ are identical. The coupling pattern can be simulated perfectly[2] with sets of each 8, 2, and 18 equivalent protons. This indicates, in analogy to

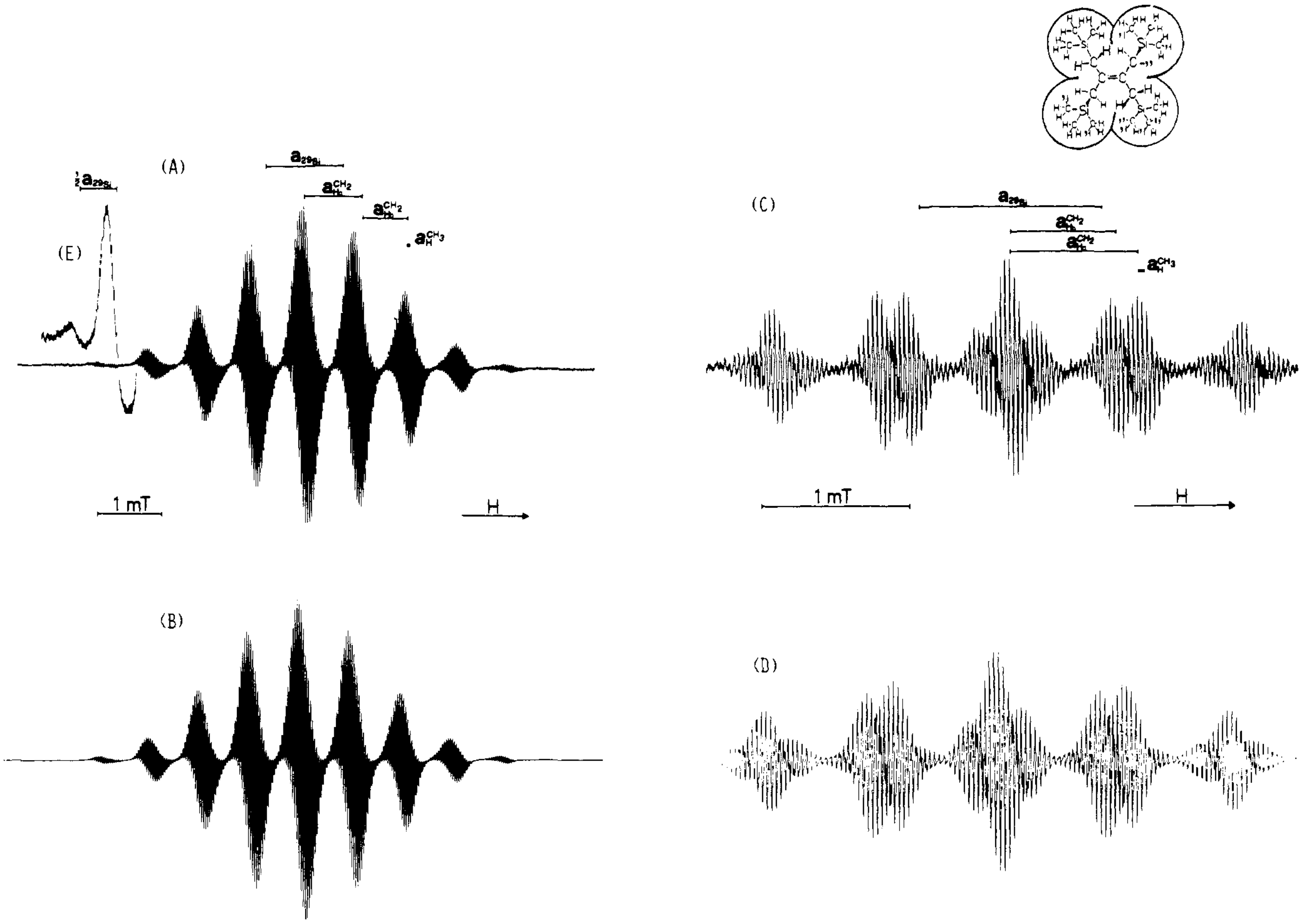
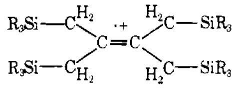
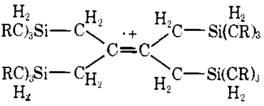
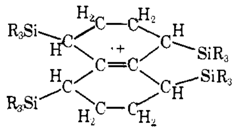
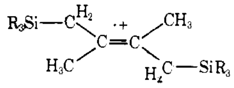
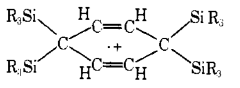
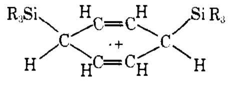
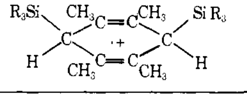


Figure 2. ESR spectrum of tetrakis(trimethylsilylmethyl)ethene radical cation at 200 K (A) and a section of it at 290 K (C) with the respective computer simulations (B and D) based on the coupling constants listed in Table II. The ^{29}Si satellite line (E) has been enlarged.

Table II. ESR Coupling Constants a_X and Their Temperature Dependence (See Footnotes) for Silylalkyl-Substituted Olefins

compd	no.	$a_{H(\beta)}^{CH_2}$	$a_{H(\beta)}^{CH_2}$	$a_H^{CH_3}$	$a_{H(\gamma)}^{CH}$	$a_{^{29}Si}$	$a_H^{SiCH_3}$
	$1^{+\cdot}$	0.855	0.72[a]			1.25[b]	0.031
	$7^{+\cdot}$	0.83[c]	0.71[c]			1.0[d]	e
	$2^{+\cdot}$	1.38[f]			0.08 0.013[g]	1.3[h]	0.027
	$3^{+\cdot}$	1.072	0.762	1.072		1.4	0.046
	$10^{+\cdot}$	0.303[j]				2.093	0.018
	$11^{+\cdot}$	0.32[j]	1.7			[i]	0.055
	$12^{+\cdot}$	0.314[j]	1.98	0.314		[i]	0.047

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[a] Temperature dependent (310 K, 0.710 mT; 190 K, 0.729 mT). [b] Temperature dependent (310 K, 1.23 mT; 190 K, 1.27 m T). [c] Temperature dependent. [d] Temperature dependent (310 K, 0.95 mT; 190 K, 1.05 mT). [e] Not analyzed (cf. text). [f] Temperature dependent (310 K, 1.380 mT; 190 K, 1.375 mT). [g] $a_H^{axial} > a_H^{equatorial}$, at higher temperature equilibration. [h] Temperature dependent (310 K, 1.30 mT; 190 K, 1.34 mT). [i] Not observed. [j] $a_{H(\alpha)}^{CH}$.

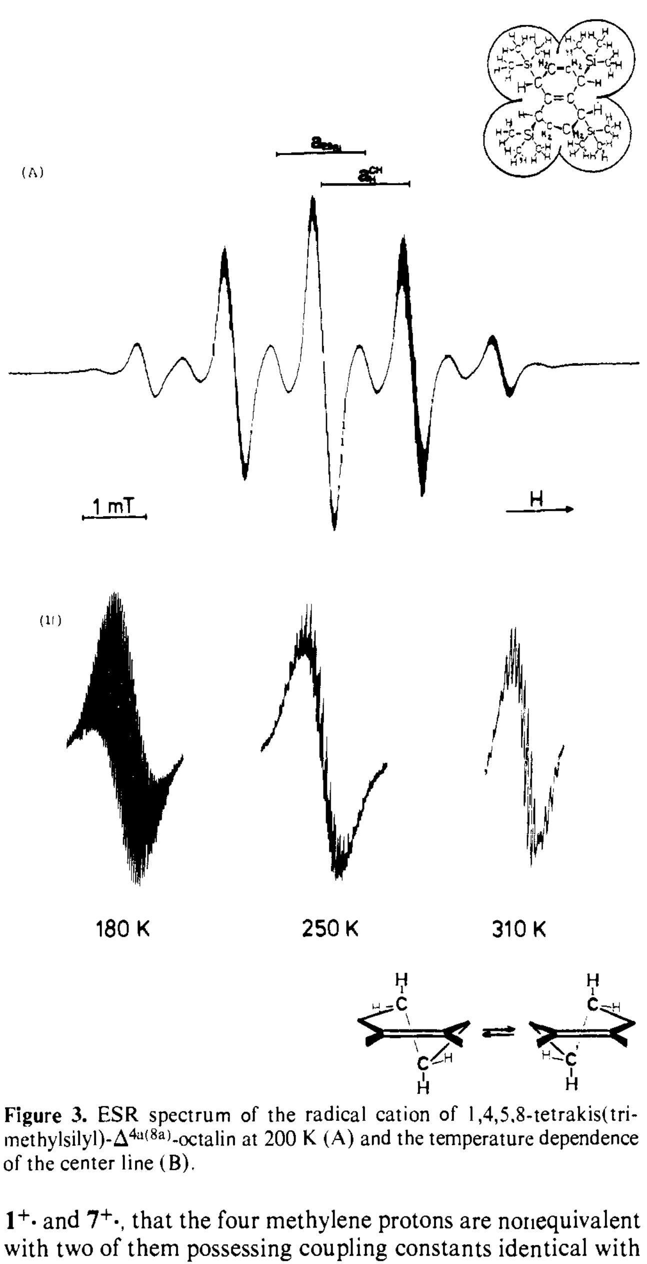


Figure 3. ESR spectrum of the radical cation of 1,4,5,8-tetrakis(trimethylsilyl)-$\Delta^{4a(8a)}$-octalin at 200 K (A) and the temperature dependence of the center line (B).

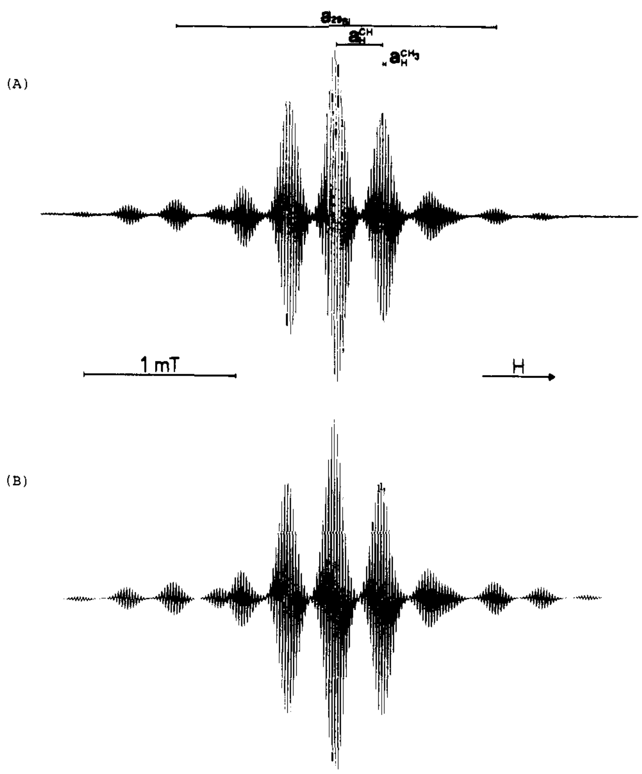


Figure 4. ESR spectrum of the radical cation of 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene at 223 K (A) and its computer simulation (B).

$1^{+\cdot}$ and $7^{+\cdot}$, that the four methylene protons are nonequivalent with two of them possessing coupling constants identical with those of the six CCH_3 protons. The cation $3^{+\cdot}$ ($4^{+\cdot}$) is stable up to 230 K and its ESR spectrum is temperature independent between 180 and 230 K. Because both isomers 3 and 4 each still contain traces (1-2%) of the other one, because their π ionizations are both below 7.9 eV (Table I), and with respect to the sensitivity of ESR detection, no definite assignment to either $3^{+\cdot}$ and/or $4^{+\cdot}$ can be made. The assumption of a radical cation $3^{+\cdot}$ with E-configuration may be supported by the similar observation for stilbene radical anion: both isomers yield the species $M^{+\cdot}$ with E configuration,[41] whereas the ESR spectrum of the Z isomer can be recorded only under extreme precautions.[42]

v. 3,3,6,6-Tetrakis(trimethylsilyl)-1,4-cyclohexadiene Radical Cation ($10^{+\cdot}$). Generated with $AlCl_3$ in H_2CCl_2 from **10** (cf. Experimental Section), it is stable only below 240 K—possibly due to steric strain. The temperature-independent ESR spectrum (Figure 4) shows the ethylene proton quintet, fine structured by the multiplet of the 36 $Si(CH_3)_3$ protons. In addition, one recognizes the large ^{29}Si coupling of a species $M^{+\cdot}$ labeled at one of the four equivalent Si centers. Owing to the enormous split $a_{^{29}Si} = 2.093$ mT (Table II) and the small line width of only 0.005 mT, a second-order effect[43] becomes manifest: relative to the ESR spectrum of unlabeled $10^{+\cdot}$, the center of the satellite spectrum is shifted to lower field by $\Delta H = a_{^{29}Si}^2 I_{^{29}Si}/2H_0 = (2.039^2)(\frac{1}{2})/2 \times 330 = 0.0033$ mT (H_0: external magnetic field). Only if this shift $a_{^{29}Si}^{sim.} = a_{^{29}Si} \pm 2\Delta H$ is taken into account, a perfect computer simulation of the overlapping ESR spectra can be obtained (Figure 4).

vi. 3,6-Bis(trimethylsilyl)-1,4-cyclohexadiene radical cation ($11^{+\cdot}$) generated by $AlCl_3$ oxidation of **11** is contaminated by $10^{+\cdot}$ according to the recorded ESR spectrum. This finding may be traced back to the synthesis procedure (cf. Experimental Section): on reductive silylation of benzene to **11** also 1,4-bis(trimethylsilyl)benzene has been observed,[20b] which in return can be reductively silylated to form **10**. Alternatively, the direct R_3Si group transfer from **11** to **10** by $AlCl_3$ may be discussed, an assumption supported by the time-dependent intensity increase of the ESR signals of $10^{+\cdot}$ recorded. Nevertheless, the ESR spectrum of $11^{+\cdot}$ can be analyzed and assigned analogous to those of $10^{+\cdot}$ and $12^{+\cdot}$ (Table II): it is dominated by a large proton triplet due to the hydrogens in 3,6 positions of the 1,4-cyclohexadiene ring. Comparison with the ESR spectra of the 9,10-dihydroanthracene radical cations[8c] suggests a cis configuration of $11^{+\cdot}$ caused either by isomerization of the trans[44] isomer **11** on $AlCl_3$ oxidation or by traces of the cis isomer, already produced in the synthesis of **11** as discussed above.

vii. 3,6-Bis(trimethylsilyl)-1,2,4,5-tetramethyl-1,4-cyclohexadiene radical cation ($12^{+\cdot}$) has been generated by dissolving the residue from the reductive silylation (6) of durene in H_2CCl_2 and adding $AlCl_3$ (cf. Experimental Section). The ESR spectrum recorded is slightly unsymmetric and displays a broad and unresolved resonance line,[45] which can be attributed to unreacted durene. The dominating radical cation, which gives rise to a large proton triplet, however, must be the cis isomer $12^{+\cdot}$: the coupling constants are quite similar to those observed for the unmethylated $11^{+\cdot}$, and allow computer simulation of the essential part of the ESR spectrum.

ESR Coupling Constants and Spin Population. Only few π-type radical ions supply unequivocal information about the spin delocalization into the substituent groups like 1,2-disubstituted ethylenes: inserting the ethylene proton coupling constants $a_{H(\alpha)}{}^{\pi}$ into the McConnell equation[43]

$$\rho_C{}^{\pi} = a_{H(\alpha)}{}^{\pi}/|Q| \tag{11}$$

yields the π spin densities $\rho_C{}^{\pi}$, which allow us to approximate the spin densities $\rho_X{}^{\pi}$ in the substituents X:

$$\rho_X{}^{\pi} = 1 - \sum \rho_C{}^{\pi} \tag{12}$$

For, e.g., the radical anion of (*E*)-1,2-bis(trimethylsilyl)ethylene $R_3SiHC{=}CHSiR_3{}^{-}\cdot$, the π spin delocalization into the R_3Si group has been determined by (11) and (12) using the Q value $|Q| = 2.1$ mT from butadiene radical anion to amount to $\rho_{SiR_3}{}^{\pi} = 0.16$;[46] i.e., still more than ⅔ of the extra electron formally remains in the ethylene π system.

For β protons in methyl-substituted ethylene radical cations like $\mathbf{3}^{+}\cdot$ (Table II), the π spin population $\rho_C{}^{\pi}$ has to be calculated from the Heller-McConnell equation[47a]

$$a_{H(\beta)} = (B_0 + B_2 \cos^2\theta)\,\rho_C{}^{\pi} \approx (B_2 \cos^2\theta)\,\rho_C{}^{\pi} \tag{13}$$

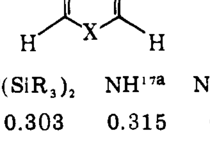
in which the smaller constant B_0 may be neglected.[8b] B_2 can be approximated using tetrasubstituted ethylene derivatives; thus from the tetramethyl derivative $(H_3C)_2C{=}C(CH_3)_2{}^{+}\cdot$ one obtains by substituting $a_H(\beta) = 1.66$ mT,[48] $\rho_C{}^{\pi} = 0.5$, and $\cos^2\theta = 0.5$ for free rotation[49] into (13) a value $B_2 \approx 6.64$ mT, or from the tetrasilylated species $\mathbf{1}^{+}\cdot$ with $a_{H(\beta)} = 0.79$ mT (Table II), $\rho_C{}^{\pi} = 0.5$ and $\cos^2\theta = 0.25$ for the blocked[49] structure ((7): $\theta = 60°$); in satisfying agreement $B_2 \approx 6.32$ mT. With the average value, $B_2 \approx 6.5$ mT, the methyl proton coupling constant $a_{H(\beta)} \equiv a_H{}^{CH_3} = 1.072$ mT of $\mathbf{3}^{+}\cdot$ (Table II) and assuming free rotation ($\cos^2\theta = 0.5$[49]) for the methyl groups, one calculates from (13) a total π spin density $2\rho_C{}^{\pi} \approx 0.66$ mT. In the twofold methylated species (cf. (3): **3**) $R_3SiH_2C(H_3C)C{=}C(CH_3)CH_2SiR_3{}^{+}\cdot$, the spin delocalization into the R_3SiCH_2 substituents, $\rho_{CH_2SiR_3}{}^{\pi} = 0.17$ mT, approximated by the difference (12), accordingly is much smaller than in the dimethylamino derivative $R_2NHC{=}CHNR_2{}^{+}\cdot$, for which $\rho_C{}^{\pi} = 0.16$ and $\rho_N{}^{\pi} = 0.34$ result.[50]

Analogous to the "hyperconjugation" parameter B_2 for proton coupling (13) one for ^{29}Si coupling can be defined

$$a_{^{29}Si} \approx (B_2{}^{Si} \cos^2\theta)\,\rho_C{}^{\pi} \tag{14}$$

$B_2{}^{Si} \approx 2.5$ mT is determined from $\mathbf{1}^{+}\cdot$ (Table II $a_{^{29}Si} = 1.25$ mT) assuming the geometry (7) with $\cos^2\theta = 1$, i.e., $\theta = 0°$. The value obtained is somewhat smaller than the one for R_3SiCH_2-substituted benzenes, $B_2 \approx 3$ mT.[8a]

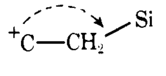
The silylated 1,4-cyclohexadiene derivatives $\mathbf{10}^{+}\cdot$, $\mathbf{11}^{+}\cdot$, and $\mathbf{12}^{+}\cdot$ (Table II) exhibit a spin distribution similar to those of heterosubstituted ones (15). Obviously, the σ donor group



(15)

X =	$C(SiR_3)_2$	NH[17a]	NCH_3[17b]	S[18]
$a_{H(\alpha)}{}^{CH}$, mT	0.303	0.315	0.285	0.282

$>C(SiR_3)_2$ does not change significantly the π spin distribution relative to species with n_X donor centers. On the other hand, the π spin densities $\rho_C{}^{\pi} \approx 0.12$ calculated from (11) using an average value for radical cations, $\overline{Q} \approx -3$ mT, and $\rho_X{}^{\pi} \approx 0.6$ obtained from (12), suggest that more than half the spin must be located in the $>C(SiR_3)_2$ moieties. The pronounced hyperconjugative π delocalization



may also be rationalized by the different effective nuclear charges $Z_{eff}(C) \gg Z_{eff}(Si)$.

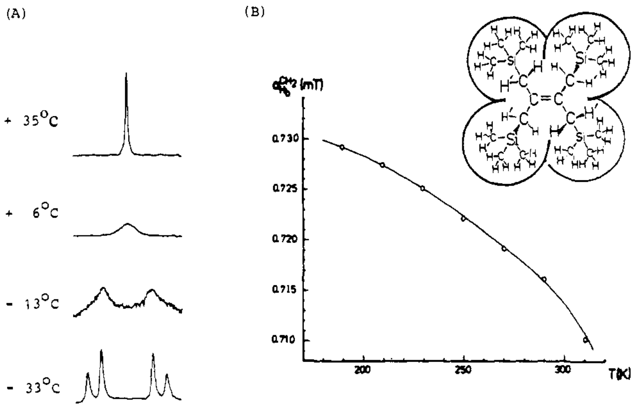
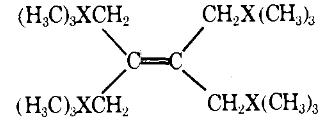


Figure 5. Temperature-dependent processes in tetrakis(trimethylsilyl)ethene (**1**) and its radical cation $\mathbf{1}^{+}\cdot$: (A) ^1H NMR coalescence AB → A_2 of the two different geminally coupled methylene protons; (B) one ESR methylene proton coupling constant $a_H{}^{CH_2}$ and its decrease with increasing temperature, i.e., increasing vibrational deformation of the angle CCSi.

Steric Hindrance in Silylalkyl Olefins and Their Radical Cations

As pointed out in the introduction, sterically overcrowded alkylethylenes recently have attracted much attention because of their unusual properties.[15,16] Two further aspects will be added in this chapter: the comparison of isosteric carbon and silicon compounds $((H_3C)_3XCH_2)_2C{=}C(CH_2X(CH_3)_3)_2$ and of the molecular and radical cation ground states of the same organosilicon compounds.

Fundamentally, alkyl and silylalkyl substituted π systems differ sterically due to the different bond lengths $d_{C\text{-}C} = 154$ pm $\ll d_{C\text{-}Si} = 188$ pm, and therefore the organosilicon compounds must be less dense or more flexible (16). The Raman



$$((H_3C)_3XCH_2)_2C{=}C(CH_2X(CH_3)_3)_2$$

(16)

	$\nu_{C=C}$, cm^{-1}	δ ^{13}C, ppm	$\Delta G^{\ddagger}$ kcal/mol
X = Si	1629	121.00	14.0
X = C[16g]	1607	136.56	21.7

stretching frequency of the tetrakis(silylmethyl)ethylene **1** fits into the normal olefinic region, while the one of the carbon analogue exhibits a rather low frequency,[16g] exceeded only by sterically more strained[51] derivatives like $((H_3C)_3X)_2C{=}CHX(CH_3)_3$ with X = C,[15c] Si.[52] The large ^{13}C NMR chemical shift also indicates some skeletal distortion for the neopentyl derivative,[16g] whereas the relatively strong shielding in the organosilicon compound may be attributed partly to the donor effect of β SiR_3 substituents.[53] The greater flexibility of the organosilicon compound[2b] is strikingly demonstrated by the NMR coalescence AB → A_2 of the methylene proton signals observed already at room temperature (Figure 5A), corresponding to a much lower barrier (16) than has been determined for the carbon analogue, which equilibrates only on heating above 145 °C.[16g]

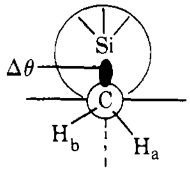
A comparable difference in rotational barriers has been determined for 1,1,2,2-tetrasubstituted ethanes $((H_3C)_3X)_2HCCH(X(CH_3)_3)$:[54] expectedly, the value for X = Si ($\Delta G^{\ddagger} = 18.8$ kcal/mol[54]) is considerably smaller than for X = C ($\Delta G^{\ddagger} > 23$ kcal/mol[54]). The origin of the rotational barriers can be further illustrated by estimating the distance between adjacent substituents from standard bond lengths and angles; thus for conformation (7) of tetrakis(trimethylsilylmethyl)ethylene (Figure 5), the centers in 1,1 position are ~513 pm apart and in 1,2 position only ~495 pm.

What happens during the oxidation of the silylalkyl olefins, i.e., what kind of structural information on the ground state of radical cations is supplied by the ESR spectra? The rather small difference between the two individual coupling constants $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH_2}}$ (Table II), e.g., for $\mathbf{1}^{+}\cdot$, supports the assumption of a preferred conformation (7). This conformation is more or less "blocked", i.e., the individual R_3SiCH_2 groups are hardly rotating any more as confirmed by the R values defined by[49]

$$R = a_{\mathrm{H}}{}^{\mathrm{CH_2X}}/a_{\mathrm{H}}{}^{\mathrm{CH_3}} = \langle\cos^2\theta\rangle/0.5 \qquad (17)$$

Comparison of the tetramethyl and the tetrakis(trimethylsilylmethyl) radical cations yields a ratio R = 0.48 ($(H_3C)_2C{=}C(CH_3)_2{}^{+}\cdot$, $a_{\mathrm{H}}{}^{\mathrm{CH_3}}$ = 1.66 mT; $(R_3SiCH_2)_2C{=}C(CH_2SiR_3)_2{}^{+}\cdot$, $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH_2}}$ ~0.80 mT (Table II)). The ethyl homologue $\mathbf{7}^{+}\cdot$ leads to R = 0.46. Both R values provide evidence that any internal rotation around C_α–C_β is completely frozen within the ESR time scale of 10^{-6}–10^{-8} s.

The differing coupling constants $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH_2}}$ observed for $\mathbf{1}^{+}\cdot$, $\mathbf{3}^{+}\cdot$, and $\mathbf{7}^{+}\cdot$ (Table II) result obviously from different twist angles $\Delta\theta$ of the R_3SiCH_2 group deviating from the idealized conformation (7) and are caused by the different steric interference between the R_3Si groups in 1,1 and 1,2 positions mentioned above. The deviation $\Delta\theta$ (18) can be estimated from

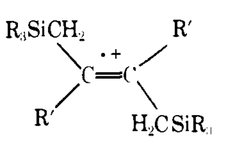


(18)

an expanded[8a] Heller-McConnell equation:

$$\sin(2\Delta\theta) = \frac{a_1 - a_2}{B_2\rho_{\mathrm{C}}{}^{\pi}(\sin 2\theta)} \qquad (19)$$

Inserting the tested constant $B_2 \approx 6.5$ mT, $\rho_{\mathrm{C}}{}^{\pi} = 0.5$, $\theta = 60°$ (7), and $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH_2}}$ from Table II, the following twist angles $\Delta\theta$ result (20). Obviously, the higher substituted the ethylene with



R′	$CH_2Si(C_2H_5)_3$	$CH_2Si(CH_3)_3$	CH_3
R	C_2H_5	CH_3	CH_3
Δθ	1.0	1.5	3.0

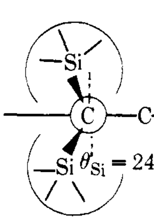
(20)

sterically demanding groups R′ and R, the more the twist angle $\Delta\theta$ will be reduced owing to more pronounced substituent staggering analogous to silylalkyldurenes.[8a] A similar argument suggests that $\mathbf{3}^{+}\cdot$, which displays a rather large twist angle $\Delta\theta$ = 3.0° (20), must be present in the less strained E configuration—with the $Z \rightarrow E$ isomerization being facilitated by a reduced C=C bond order in the radical cation. The largest deviation ($\Delta\theta$ ~10°) is found for the octalin derivative $\mathbf{2}^{+}\cdot$ applying the Heller-McConnell equation (13):

$$\cos^2\theta \approx a_{\mathrm{H}}/B_2\rho_{\mathrm{C}}{}^{\pi} = 1.38/(6.5 \times 0.5) = 0.425;\ \theta \approx 50° \qquad (21)$$

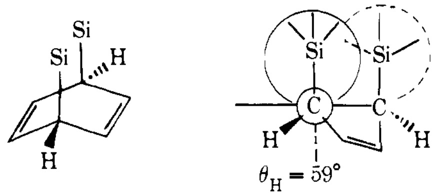
For a rationalization, one has to take into account that the staggered conformation of the H_2C-CH_2 linkages enforces a larger twist angle $\Delta\theta$ = 60° − 50° = 10°. The H_2C-CH_2 staggered conformation is also in accord with the ratio for axial:equatorial coupling constants $a_{\mathrm{H}(\gamma)}{}^{\mathrm{CH_2}}$ of 6:1 (Table II), which is similar to the 4.9:1 ratio reported for the γ hydrogen coupling in bicyclo[2.2.1]heptane radical.[55]

In tetrasilyl-substituted 1,4-cyclohexadiene radical cation $\mathbf{10}^{+}\cdot$ the steric overcrowding alone should lead to a planar ring skeleton.[56] The angle θ between the π system and the σ_{CSi} bond can be approximated by inserting $a_{^{29}\mathrm{Si}}$ = 2.093 mT (Table II), the constant $B_2{}^{\mathrm{Si}} \approx 2.5$ mT deduced above from $\mathbf{1}^{+}\cdot$, and the total π spin density $4\rho_{\mathrm{C}}{}^{\pi}$ = 1,[57] into (14); the value θ = 24° obtained corresponds to a widened angle SiCSi (22). For the



(22)

cis-bis(trimethylsilyl) derivative $\mathbf{11}^{+}\cdot$ one estimates from the Heller-McConnell equation (13) with $B_2 \approx 6.5$ mT, $4\rho_{\mathrm{C}}{}^{\pi}$ = 1,[57] and $a_{\mathrm{H}}{}^{\mathrm{CH}}$ = 1.7 mT (Table II) an angle $\theta \sim 60°$ between π system and σ_{CH} bond in the boat conformation[8c] (23). Accordingly, the σ_{SiC} bond must occupy an almost axial position, and, because of the optimum arrangement for hyperconjugative interaction, a large ^{29}Si coupling is expected. Unfortunately, the low radical cation concentrations achievable do not permit an experimental determination, but eq 14 allows us to predict $a_{^{29}\mathrm{Si}} \approx (B_2{}^{\mathrm{Si}}\cos^2 0°)\rho_{\mathrm{C}}{}^{\pi} = (2.5\ \mathrm{mT} \times 1)1 = 2.5$ mT. Another estimate can be based on the ratio $a_{^{29}\mathrm{Si}}/a_{\mathrm{H}}{}^{\mathrm{SiR_3}}$ ~ 40–50 observed for silyalkyl-substituted radical cations of benzene[8] or ethylene (Table II): from the average ratio and $a_{\mathrm{H}}{}^{\mathrm{SiR_3}}$ = 0.55 (Table II), a coupling constant $a_{^{29}\mathrm{Si}} \approx 45 \times 0.055$ = 2.5 mT results in good agreement. For the sterically overcrowded $\mathbf{10}^{+}\cdot$, the ratio $a_{^{29}\mathrm{Si}}/a_{\mathrm{H}}{}^{\mathrm{SiR_3}}$ ~ 2.093/0.018 = 116 deviates considerably, and thus indicates structural distortions like (22) as have been exemplified before for trimethylsilylnaphthalene radical anion.[46] Methyl substitution of $\mathbf{11}^{+}\cdot$ to $\mathbf{12}^{+}\cdot$ especially causes an increase in the proton coupling in 3,6 positions (Table II, $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH}}$). Applying again relation (13), an angle θ = 57° results, which corresponds to a flattening of the boat conformation (23) caused presumably by the additional steric interaction between the methyl groups inside the boat.



(23)

Finally, ESR information on the dynamic behavior of the organosilicon radical cations investigated will be discussed. No rotational barrier like the one detected by ^{1}H NMR for the molecular ground state (16) can be measured: the ESR time scale of 10^{-6}–10^{-8} s is too short, and barriers in hyperconjugatively stabilized species $M^{+}\cdot$ even should be enhanced relative to M. Thus, a high rotational barrier has been observed for $(R_2N)_2C{=}C(NR_2)_2{}^{+}\cdot$,[58] while the RS groups in $(RS)_2C{=}C(SR)_2{}^{+}\cdot$ at room temperature still rotate freely within the ESR time scale.[14] The measured temperature dependence of the coupling constants $a_{\mathrm{H}(\beta)}{}^{\mathrm{CH}}$ and $a_{^{29}\mathrm{Si}}$ of $\mathbf{1}^{+}\cdot$ (Figure 5B and Table II), therefore, rather can be traced back to the deformation vibration within the trimethylsilylmethyl group[8b] (24). The average angle γ increases with temperature,

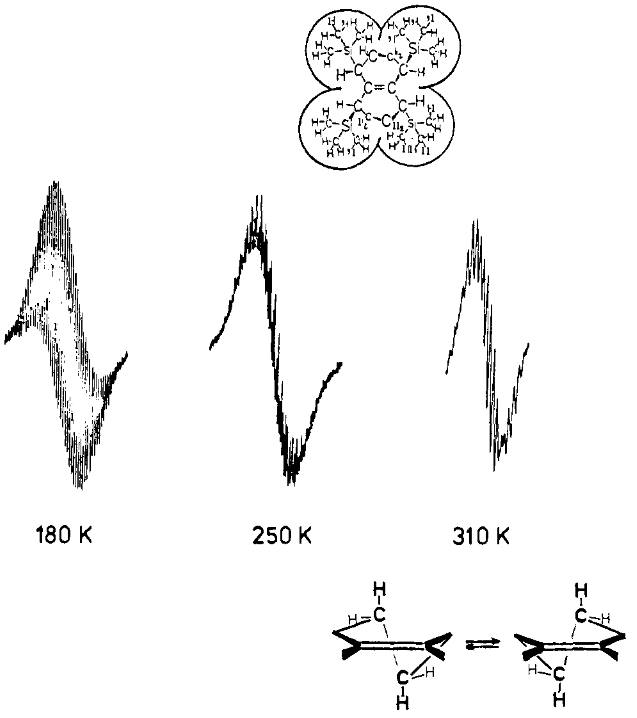
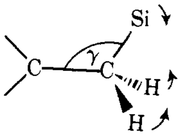


Figure 6. Center line of the ESR spectrum of 1,4,5,8-tetrakis(trimethylsilyl)-$\Delta^{4a(8a)}$-octalin cation $2^{+\cdot}$ and its temperature dependence.



(24)

and with decreasing hyperconjugative interactions both the CH_2 and the ^{29}Si coupling should be reduced.

Another dynamic process is noticeable by the temperature dependence of the ESR spectrum of the tetrasilyloctalin radical cation $2^{+\cdot}$: a flipping of its H_2C-CH_2 bridges. The full ESR spectrum (Figure 3) shows a dominating proton quintet, which overlaps with the ^{29}Si satellite lines. Magnifying, e.g., the center line, from the total of $5 \times 5 \times 37 = 925$ lines theoretically predicted, about 50 become distinguishable at low temperature (Figure 6, 180 K). Without confirmation by ENDOR, the equidistant signals can only be tentatively assigned to $a_H^{\text{axial}} \sim 3a_H^{\text{SiR}_3} \sim 6a_a^{\text{equatorial}}$ by the following arguments: the smallest coupling of only 0.013 mT must be due to the equatorial γ protons, and the 0.027-mT coupling by analogy to $1^{+\cdot}$ (Table II) to the 36 $Si(CH_3)_3$ protons. A trial and error simulation and subsequent fit to the measured intensities allow with some caution the assignment of the axial γ proton coupling. With increasing temperature all lines should broaden and finally vanish, which arise from transitions between spin states exhibiting different spin components of the geminal γ protons. Finally, only the multiplet of the 36 $Si(CH_3)_3$ protons is expected to remain—a situation almost achieved for $2^{+\cdot}$ at room temperature (Figure 6, 310 K). The conformational change, to which this γ-proton averaging has to be attributed, is the ring inversion of the cyclohexene rings. For the analogous process in cyclohexene radical, recently an inversion barrier of $\Delta G^{\ddagger} = 6.82$ kcal/mol has been established.[59]

Concluding Remarks

The selective oxidation of molecules to their radical cations by $AlCl_3$ in H_2CCl_2 opens an elegant route to the generation of numerous novel radical cations.[1-3,5-10] In addition, the existence of these species $M^{+\cdot}$—if persistent[4]—can be straightforwardly predicted by the first ionization potential of the parent molecule M, considerably facilitating the design of appropriate compounds. Novel radical cations are not just satisfying curiosity; investigation using the sensitive ESR method yields valuable information on their ground-state properties including structure, spin distribution, and in some cases even the dynamic behavior. Hopefully, the organosilicon example reported in detail will stimulate further investigation, especially of organometallic radical cations containing main-group elements.

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Organic Tellurium and Selenium Chemistry. Reduction of Tellurides, Selenides, and Selenoacetals with Triphenyltin Hydride

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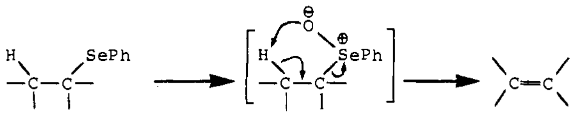
Abstract: Preparative and mechanistic details are described for the conversion of selenides into hydrocarbons [RSePh → RH] by heating with triphenyltin hydride at about 120 °C. The process has been extended to selenoacetals in a form that constitutes a reduction method for carbonyl compounds [$RR'C{=}O \rightarrow RR'C(SePh)_2 \rightarrow RR'CH_2$]. Selective reduction of selenoacetals in the presence of thioacetals is possible. Cold-labeled species can be prepared by using triphenyltin deuteride. Tellurides [RTePh] are available easily without problems arising from exposure to air provided that the work is done in a photographic darkroom equipped with a red safety light. These tellurides, as well as the corresponding dichlorides [$RTe(Cl_2)Ph$], are reduced under very mild conditions (25–80 °C) by triphenyltin hydride. The selenium- and tellurium-based chemistry has been used for the unusual process of reducing an epoxide in the presence of a ketone carbonyl.

Reduction of Selenium Compounds

Introduction. The recognition that selenoxide fragmentation (eq 1) constitutes a powerful method for generating double bonds,[1] particularly those conjugated with a carbonyl group, made it necessary to devise a variety of procedures for introducing selenium, usually as PhSe–, into organic molecules.[2] The more useful of these methods accomplish, at the same time, some additional elaboration of the molecular framework and two such processes are known: the formation of C-C bonds with selenium-stabilized carbanions[2a,3] and the process of *cyclofunctionalization.*[4,5]


(1)

The general utility of these reactions obviously increases as the range of functional group interconversions involving the unit C-SePh is extended. During our[6] work on cyclofunctionalization we needed to remove the benzeneseleno group from a number of compounds and replace it by hydrogen [⩾C-SePh → ⩾C-H], this step being required for structure proof of the selenium-containing species. Two methods were explicitly available for reducing selenides: the carbon-selenium bond can be cleaved by lithium in ethylamine and by the use of Raney nickel[7] (eq 2). However, the dissolving metal reduction was not likely to be applicable to compounds having an aromatic ring, besides that attached to the selenium atom.[8] Raney nickel also was unsuitable for our purpose because there is evidence[7] that the reaction can proceed, in certain cases, via an olefin.[9] In many of our compounds the carbon atom adjacent to that carrying the benzeneseleno group is an asymmetric center and olefin formation might result in alteration of stereochemistry at that point. We looked, therefore, for an unambiguous method of reduction and found[10] that triphenyltin hydride is an excellent general reagent for this purpose (eq 3).

$$\begin{tikzcd} \mathrm{RSePh} \arrow[r, bend left, "\mathrm{Li,\ EtNH_2}"] \arrow[r, bend right, "\mathrm{Raney\ nickel}"'] & \mathrm{RH} \end{tikzcd} \qquad (2)$$

$$\mathrm{RSePh} \xrightarrow[\sim 120°]{\mathrm{Ph_3SnH}} \mathrm{RH} \qquad (3)$$

Reduction of Selenides. Our results are listed in Table I, which shows most of the compounds we have studied and gives also the nature and yield of each product, the conditions used, and the scale on which the work was done. Experiments 1–18

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