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RADICAL IONS

XXVII *. RADICAL IONS OF TETRAKIS(TRIMETHYLSILYL)BUTATRIENE

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Summary

One-electron oxidation and one-electron reduction of the electron-rich acetylene derivative, hexakis(trimethylsilyl)-2-butyne $[(H_3C)_3Si]_3C—C{\equiv}C—C[Si(CH_3)_3]_3$, unexpectedly produce the persistent radical cation and radical anion of the hitherto unknown neutral compound, tetrakis(trimethylsilyl)butatriene $(R_3Si)_2C{=}C{=}C{=}C(SiR_3)_2$. The radical anion can also be generated from the corresponding diacetylene, bis(trimethylsilyl)-1,3-butadiyne $R_3Si—C{\equiv}C—C{\equiv}C—SiR_3$ and potassium metal, obviously via disproportionation. Photoelectron and electron spin resonance spectroscopic data permit the detection and characterization of the individual species. The stability of both the radical anion and the radical cation of the same molecule can be rationalized by the unique combination of the twofold butatriene π-system with 4 R_3Si substituents, which can act either as electron donors or electron acceptors and thus stabilize the ground state of either the cation or the anion.

Introduction

Trialkylsilyl groups SiR_3 are considered to behave as π-electron acceptors [3], but separation by a single carbon center in substituents $—\overset{|}{\underset{|}{C}}—SiR_3$ transforms them into strong electron donors [4—7]. Whereas the π-electron accepting effect may be treated by π-back-bonding models [3,8], the electron donation is best rationalized by σ_{CSi}/π-hyperconjugation [7,9]. As one consequence of this ambivalence, numerous silyl substituted cyclic or open-chain π-systems have been reported to yield persistent radical ions, i.e., radical anions [10—12] and

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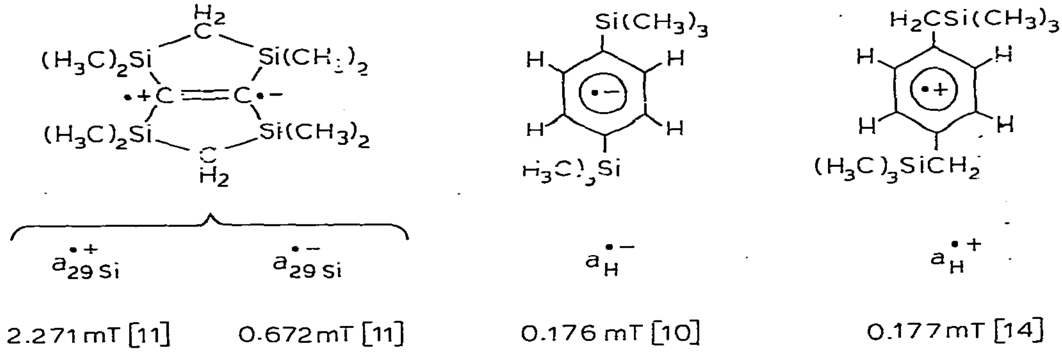
* For part XXVI see ref. 1.

** Part of dissertation [2].

[11]/or radical cations [2,13,14]:



(1)

For the novel radical cations, generated by means of the selective one-electron oxidation reagent $AlCl_3$ in H_2CCl_2 solution [2,11,13,14], extensive conformational studies have substantiated charge delocalizing stabilization as predicted by σ_{CSi}/π-hyperconjugation [15,16].

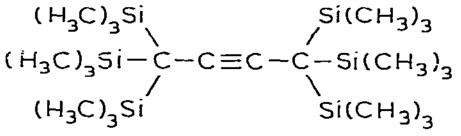
A molecule in which the two ambivalent substituent effects of SiR_3 groups should be able to exercise both types of electronic influence is the still unknown 1,1,4,4-tetrakis(trimethylsilyl)-1,2,3-butatriene (I) (2). Formally, butatrienes

(I)

(2)

contain two different π-systems, one butadiene moiety and the central ethylene bond, perpendicular to each other. Thus, the substituents SiR_3 should both act as π-electron acceptors to the butadiene π-system (increasing its electron affinity and thus enabling the reduction to a persistent radical anion) and simultaneously as hyperconjugative electron donors toward the ethylene π-system (lowering the first ionization potential and thus fulfilling one of the conditions for the oxidation to a persistent radical cation [13,14]).

Tetrakis(trimethylsilyl)butatriene, I, has not yet been synthesized. Therefore we investigated the one-electron oxidation and reduction behaviour of two closely related compounds, 1,1,1,4,4,4-hexakis(trimethylsilyl)2-butyne (II) [17] and 1,4-bis(trimethylsilyl)-1,3-butadiene (III) [17]. The reduction of III to its



(II)

$(H_3C)_3Si{-}C{\equiv}C{-}C{\equiv}C{-}Si(CH_3)_3$

(III)

(3)

radical anion $III^{\bullet-}$ has been reported in 1974 [18]; however, our ESR investigations, as discussed below, do not confirm the assumed assignment, and prove that both compounds II and III yield only the persistent radical ions of tetrakis(trimethylsilyl)butatriene $I^{\bullet+}$ and $I^{\bullet-}$.

Results

Ionization potentials

The photoelectron (PE) spectrum of hexakis(trimethylsilyl)-2-butyne, II (Fig. 1) exhibits the low first ionization energy of only IE_1^V = 7.60 eV, a value considerably smaller than the first ionization potentials of other acetylenic compounds (Table 1). The tremendous stabilization of the resulting radical cation ground state, i.e., the delocalization of the positive charge, is best explained by the multiple σ_{CSi}/π-hyperconjugative interaction between the acetylenic π-system and the six Si—C σ-bonds. The predominant σ-character of the hexakis(trimethylsilyl)-2-butyne radical cation ground state is supported by the fact, that the ionization energy of the unsubstituted acetylene π-system (Table 1, IE_1 = 11.40 eV) is higher than that for the σ_{SiC} bonds in tetramethylsilane (IE = 10.5 eV; cf. ref. 9b). Furthermore, the reactivity of II resembles that of an alkyl silane rather than that of an acetylene derivative [17], although this has to be attributed also to the steric shielding of the triple bond.

The first ionization potential of bis(trimethylsilyl)-butadiyne, III, has been determined both mass spectroscopically by the retarding potential difference (RPD) method ($IE_1 \sim$ 9.2 eV [5b]) and, more precisely, by photoelectron spectroscopy, IE_1^V = 8.85 eV [2].

One-electron oxidation

The first ionization potential of only 7.60 eV implies that it should be possible to generate the radical cation of hexakis(trimethylsilyl)-2-butyne, $II^{\cdot+}$ with $AlCl_3$ in H_2CCl_2 [2,13,14]. At temperatures below 210 K, an initial ESR spectrum is observed which consists of a doublet (Fig. 2, a = 0.738 mT) accompanied by isotope satellites from the ^{29}Si nuclei (I = 1/2, nat. abundance 4.7%). The considerable line width and the Gaussian lineshape suggest that hyperfine structure is hidden under the two broad peaks, but it was impossible to obtain a better resolution.

On warming of this sample to temperatures >220 K, the ESR spectrum (Fig. 2) decays rapidly and another radical is observed, which persists even at 300 K and gives rise to a temperature independent ESR spectrum (Fig. 3 (A)). The ESR spectrum of the secondary radical cation (Fig. 3 (A)) can be analysed by

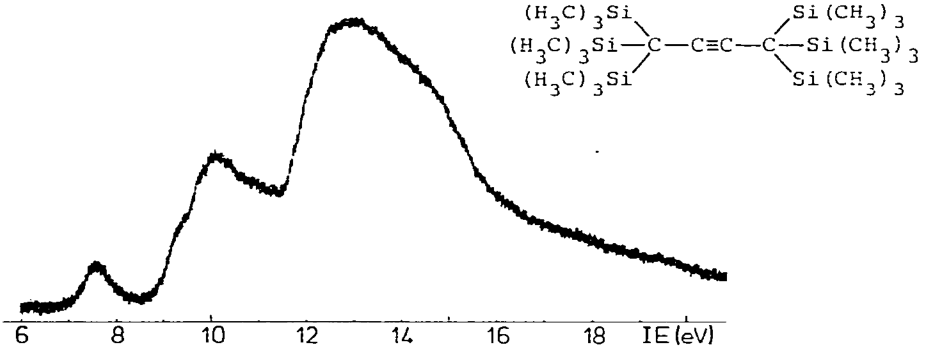


Fig. 1. He(I) photoelectron spectrum of hexakis(trimethylsilyl)-2-butyne, II.

TABLE 1

FIRST VERTICAL IONIZATION POTENTIALS IE_1^V (eV) OF ACETYLENE DERIVATIVES X—C≡C—X

X	IE_1^V (eV)
H [8,19]	11.40
SiH_3 [8]	10.46
CH_3 [8,19]	9.61
$Si(CH_3)_3$ [5b]	10.41 [a]
$C(CH_3)_3$ [5b]	9.19 [a]
$CH_2Si(CH_3)_3$ [5b]	8.85 [a]
$C(Si(CH_3)_3)_3$	7.60

[a] Measured by RPD mass spectrometry.

computer simulation (Fig. 3 (B)), taking into account 36 equivalent protons with a_H 0.033 mT and 4 equivalent Si nuclei with $a_{^{29}Si}$ 1.21 mT. The number of the nuclei and the magnitude of their hyperfine coupling constants (Table 2) suggest a radical cation containing only 4 equivalent trimethylsilyl substituents. Obviously, hexakis(trimethylsilyl)-2-butyne reacts easily with $AlCl_3$ splitting off at least two SiR_3 groups.

Bis(trimethylsilyl)butadiyne, III, also reacts immediately with $AlCl_3$ in CH_2Cl_2 at 190 K, but only a single unresolved line shows up in the ESR spectrum.

One-electron reduction

Hexakis(trimethylsilyl)-2-butyne, II, reacts very slowly with alkali metal in solvating ethers at room temperature. After ~100 h contact of a 1,2-dimethoxyethane solution of II with a potassium mirror at 293 K, the ESR spectrum shows the presence of a single very stable radical anion (Fig. 4 (A)). Prolonged contact with potassium metal seems to result in the formation of a dianion.

Computer simulation of the ESR spectrum recorded after reduction of II can only be completed by again assuming 4 equivalent Si atoms and 36 equivalent protons. In addition, an isotope hyperfine splitting from 12 equivalent ^{13}C nuclei (I 1/2, natural abundance 1.1%) has to be included into the calculation (Fig. 4 (B)). All three coupling parameters obtained (Table 2) are slightly temperature dependent. The striking similarity of the ESR coupling constants for the radical

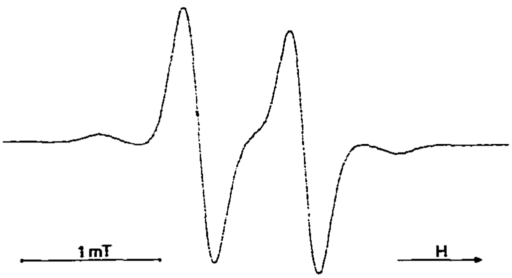


Fig. 2. ESR spectrum of the first observable paramagnetic species from the reaction of hexakis(trimethylsilyl)-2-butyne, II, with $AlCl_3$ in CH_2Cl_2.

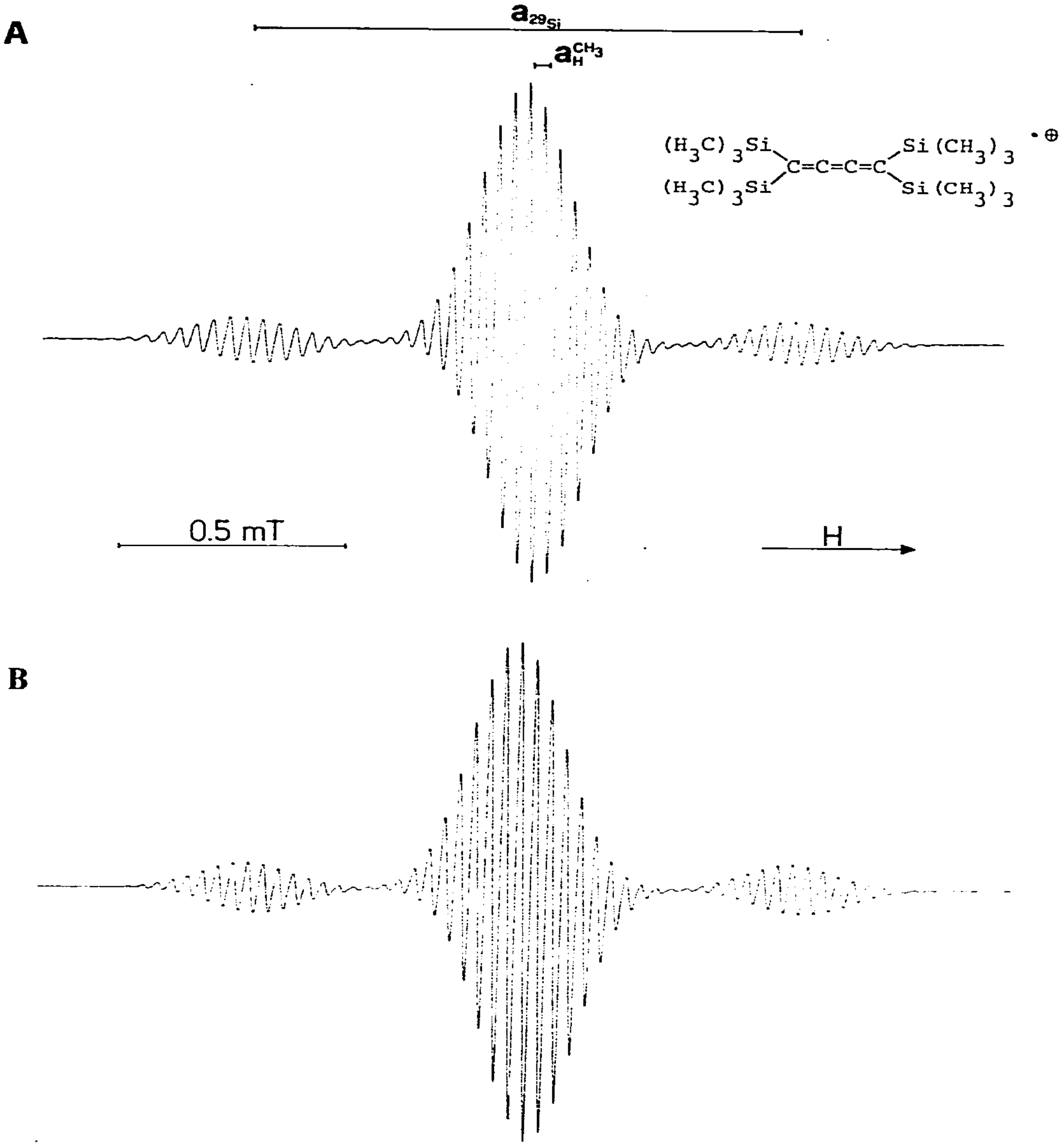


Fig. 3. ESR spectrum of the persistent radical cation $I^{\cdot+}$ formed on reaction of hexakis(trimethylsilyl)-2-butyne, II, with $AlCl_3/CH_2Cl_2$ above 220 K (A), and its computer simulation (B).

anion $I^{\cdot-}$ (Fig. 4) and for the radical anion of bis(trimethylsilyl)butadiyne, $III^{\cdot-}$, as reported by Evans et al. [18] prompted us to repeat these experiments. In fact, the ESR spectra for the radical anion obtained on reduction of III with sodium or potassium in 1,2-dimethoxyethane (DME) or in tetrahydrofuran (THF) were completely identical with that displayed in Fig. 4. In order to confirm or correct the assignments published [18], further experiments were performed.

We reduced III with K in DME adding an excess of dicyclohexyl-18-crown-6, which effectively complexes K^+ ions during alkali metal reduction [20,21]. At

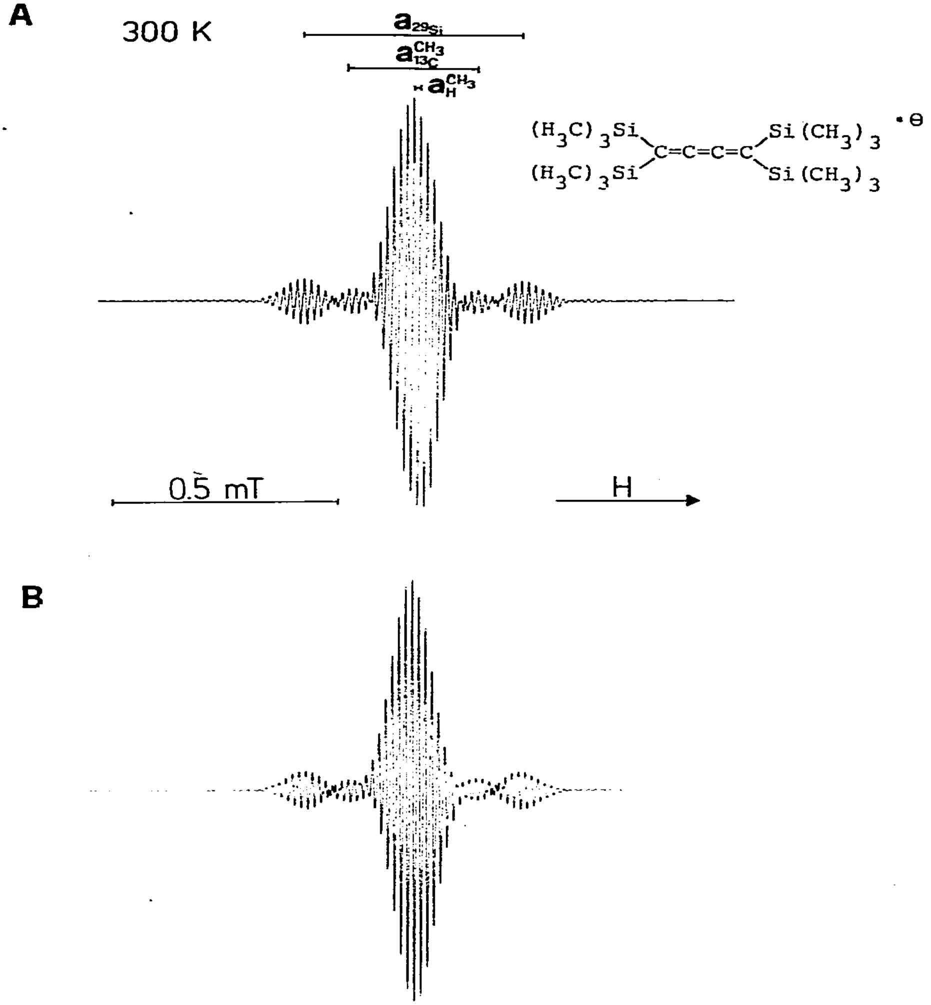


Fig. 4. ESR spectrum of the persistent radical anion $I^{\bullet-}$ formed on reaction of hexakis(trimethylsilyl)-2-butyne, II, or bis(trimethylsilyl)-1,3-butadiyne, III, with Na or K in DME or THF at 300 K (A), and its computer simulation (B).

TABLE 2

ESR COUPLING CONSTANTS a_x (mT) OF THE ONE-ELECTRON OXIDATION AND REDUCTION PRODUCTS FROM II (YIELDING $I^{\bullet+}$ AND $I^{\bullet-}$) AND FROM III [18] (FOR ASSIGNMENT TO $I^{\bullet-}$ SEE TEXT)

Radical ion	T_{ESR} (K)	$a_{^{29}Si}$	$a_H^{SiR_3}$	$a_{^{13}C}$
$I^{\bullet+}$	300	1.210 (4 Si)	0.033 (36 H)	[a]
$I^{\bullet-}$	193	0.515 (4 Si)	0.0155 (36 H)	0.297 (12 C) [b]
	300	0.485 (4 Si)	0.0151 (36 H)	0.290 (12 C) [b]
$III^{\bullet-}$ [18]	193	0.495 (2 Si)	0.016 (18 H) [c]	0.463 (6 C)

[a] Not observed. [b] Another $^{13}C'$ coupling constant a 0.78 mT (2 C′) can be extracted from the ESR spectrum (Fig. 5). [c] Additional potassium hyperfine coupling a 0.030 mT has been included in ref. 18.

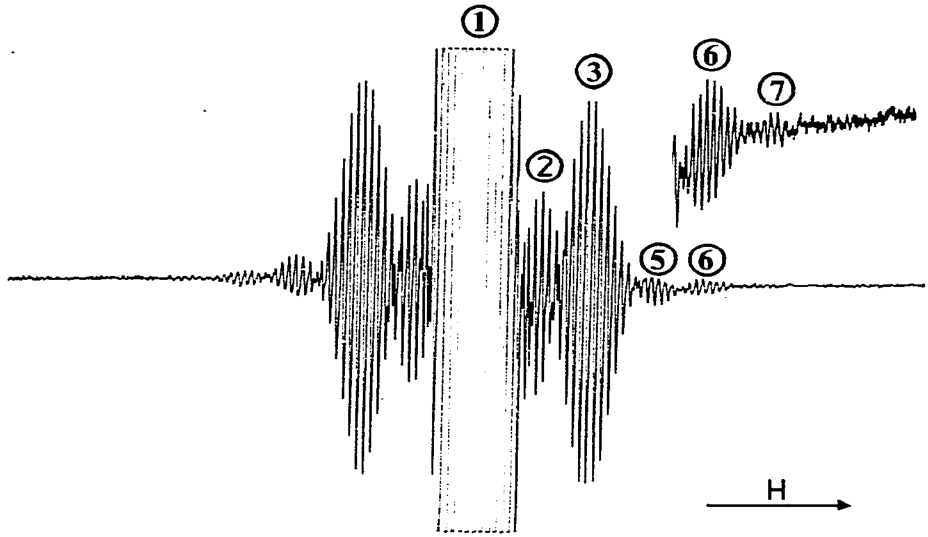


Fig. 5. Amplified ESR spectrum of $I^{\cdot-}$ exhibiting several satellite line groups from ^{29}Si and ^{13}C isotope combinations (cf. Table 3).

first, an intermediate radical is formed (ESR: doublet of doublets), which can also be generated by electrolytic reduction of III. After some hours, however, the ESR spectrum of Fig. 4 appears. This experiment, together with the variation of alkali metal, of solvent and of temperature, excludes additional coupling due to alkali metal ion pairing, which had been assumed [18] to account for the observed 36 H multiplet by superposing an 18 H multiplet with an appropriate alkali metal coupling. The Me_3Si cleavage from hexakis(trimethylsilyl)-2-butyne with K in DME under addition of dicyclohexyl-18-crown-6 is a very slow reaction, and only after some weeks of contact with the potassium mirror at am-

TABLE 3

$^{29}Si/^{13}C$ ISOTOPE COMBINATIONS OBSERVED IN THE AMPLIFIED ESR SPECTRUM OF THE RADICAL ANION $I^{\cdot-}$ (cf. Fig. 5)

Line group (Fig. 5)	Number of spin-bearing isotopes		Line group position (mT)	Probability $W_{m,n}$	Calculated intensity (%)	Observed intensity (%)
	^{29}Si	^{13}C				
1	0	0	0	0.7223	100.00	100.00
2	0	1	$0.145 = a_C/2$	0.0964	6.60	6.7
3	1	0	$0.242 = a_{Si}/2$	0.1425	9.76	12.5
4	0	2		0.0059	0.21	[a]
5	1	1	$0.387 = a_{Si}/2 + a_C/2$	0.0190	0.66	
	0	0 [b]	$= a_{C'}/2$ [b]		1.10 [b]	1.2
6	2	0	$0.485 = a_{Si}$	0.0105	0.36	0.5
7	2	1	$0.630 = a_{Si} + a_C/2$	0.0014	0.024	
	1	0 [b]	$= a_{Si}/2 + a_{C'}/2$ [b]		0.107 [b]	0.13

[a] Not observed because of overlapping. [b] With inclusion of an additional ^{13}C coupling $a_{C'}$ 0.78 mT for two carbon nuclei.

bient temperature is the radical anion $I^{\cdot-}$ detected by ESR spectroscopy.

Amplification (Fig. 5) of the 300 K ESR spectrum (Fig. 4) exhibits additional line groups from various isotope combinations.

Calculation of line intensities for the individual isotope combinations (Table 3) is based on the equation [2]:

$$W_{m,n} = \prod_{1}^{r} p_r^n (1 - p_r)^{m-n} \binom{m}{n} \tag{4}$$

where	W	probability of the isotope combination
	r	number of the different groups of nuclei
	p_r	relative abundance of the isotope
	m	total number of equivalent nuclei in one group
	n	number of isotopes with the relative abundance p_r

Comparison of observed and calculated intensities (Table 3) shows good agreement except for the too intense first ^{29}Si satellite group. Moreover, it reveals an additional hyperfine splitting from two other carbon nuclei (Table 3 (b)), for which a coupling constant $a = 0.78$ mT is determined. The alternative assignment for the ^{29}Si/^{13}C-satellite coupling constants can be ruled out as follows: A superposition of the ^{29}Si and the ^{13}C splitting was assumed [18] in order to obtain the correct magnitude of the satellite lines (the addition of two ^{29}Si and six ^{13}C nuclei almost yields the value expected for 4 equivalent Si atoms). However, the actual ^{13}C splitting due to 12 equivalent nuclei is clearly observed in the high-resolution ESR spectrum at 300 K (Fig. 4 (A)). Amplification exhibits further line groups in the spectrum as a result of different isotope combinations (Fig. 5).

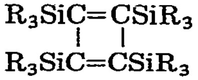
Discussion

Hexakis(trimethylsilyl)-2-butyne, II, although of low chemical reactivities [17], yields on one-electron oxidation or reduction radical ions of different structrues. The ESR spectra show that the resulting stable paramagnetic species $I^{\cdot+}$ and $I^{\cdot-}$ contain 4 equivalent trimethylsilyl groups; only one further ^{13}C coupling constant is observed in case of the radical anion $I^{\cdot-}$. This anion can also be generated from bis(trimethylsilyl)butadiyne, III, on reduction with alkali metals, although not electrolytically.

Reasonable structures for both persistent radical ions, $I^{\cdot+}$ and $I^{\cdot-}$, can be constructed only from carbon π-systems with 4 equivalent SiR$_3$ groups such as

$(R_3Si)_2C{=}C(SiR_3)_2$

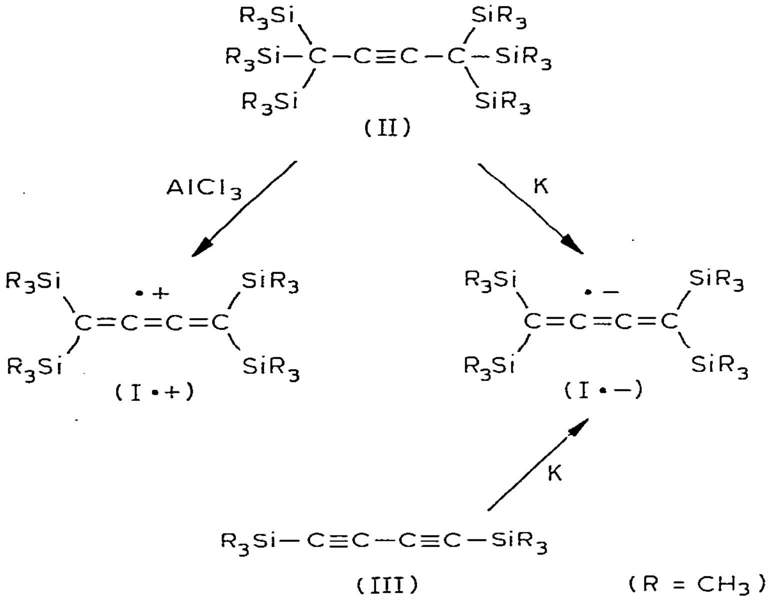
$(R_3Si)_2C{=}C{=}C(SiR_3)_2$



$$\begin{array}{c} R_3SiC{=}CSiR_3 \\ |\quad\ \ | \\ R_3SiC{=}CSiR_3 \end{array} \tag{5}$$

$(R_3Si)_2C{=}C{=}C{=}C(SiR_3)_2$

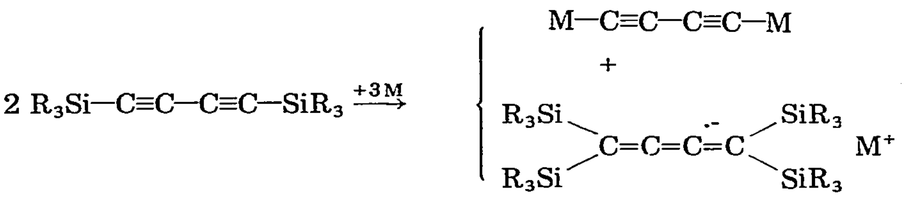
Of these molecules, tetrakis(trimethylsilyl)ethylene is unknown, probably for steric reasons [17,22]. Tetrakis(trimethylsilyl)allene, although easily synthesized in various ways [17], can be disregarded for the following reasons: one-electron reduction with potassium in DME yields the radical anion of 1,4-bis(trimethylsilyl)benzene [10], and its ionization potential is too high for the generation of a persistent radical cation with $AlCl_3/CH_2Cl_2$ [2]. The cyclobutadiene structure can be ruled out at least for the anion radical $I^{\cdot -}$ because two equivalent carbon atoms are observed (Table 3). Of the remaining alternatives, the tetrakis(trimethylsilyl)butatriene skeleton is the most probable for both the radical anion $I^{\cdot -}$ and the radical cation $I^{\cdot +}$.



(6)

The evidence from the reactivity, the stability, and from the ESR parameters can be summarized as follows.

During the generation of the butatriene radical ions $I^{\cdot +}$ and $I^{\cdot -}$ from the trimethylsilyl substituted butyne II and butadiyne III, the central C_4 chain is maintained. The easy cleavage of SiR_3 groups in β-position to π-systems by nucleophiles is a well-known [23] and still investigated reaction [24]. The rapid oxidation of the butyne II with $AlCl_3$ proceeds presumably via the radical cation intermediate $II^{\cdot +}$. The alkali metal reduction of bis(trimethylsilyl)butadiyne III may be a disproportionation and is slowed down considerably by



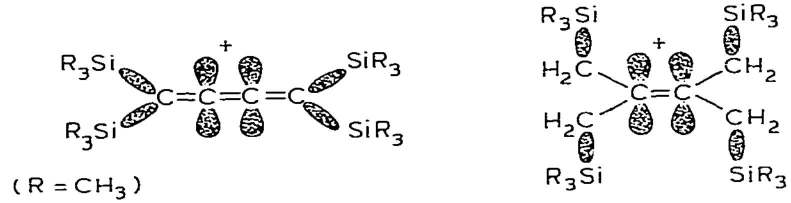
$$2\,R_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiR_3 \xrightarrow{+3M} \left\{ \begin{array}{c} M{-}C{\equiv}C{-}C{\equiv}C{-}M \\ + \\ (R_3Si)_2C{=}C{=}C{=}C(SiR_3)_2^{\cdot -}\quad M^+ \end{array} \right. \qquad (7)$$

complexation of the metal ions M^+ after addition of a crown ether, so that intermediate radicals can be observed. The electrolytic reduction of III does not yield any anion radical $I^{\cdot -}$.

Both radical ions of tetrakis(trimethylsilyl)butatriene $I^{\cdot +}$ and $I^{\cdot -}$ should be quite stable. By analogy, the radical anions of SiR_3-substituted ethylenes and butadienes [10] as well as of tetraphenylbutatriene [25] have been reported as rather persistent paramagnetic species. As for the radical cation $I^{\cdot +}$, substituted butatrienes $R_2C{=}C{=}C{=}CR_2$ generally exhibit low first ionization potentials [26], and should thus possess energetically favorable radical cation ground states. Although SiR_3 substituents are easily cleaved from π-systems by electrophiles [23], this effect may well be outbalanced by the strong hyperconjugative σ_{SiC}/π-stabilization in a tetrasilyl substituted butatriene.

Comparison with the ESR data of other persistent silyl-substituted radical cations and anions also supports the proposed assignment for the tetrakis(trimethylsilyl)butatriene radical ions $I^{\cdot +}$ and $I^{\cdot -}$. Thus the ^{29}Si coupling constant of $I^{\cdot -}$ (Table 2: $a_{Si} \sim 0.5$ mT) is of the same magnitude as the one of 1,4-bis(trimethylsilyl)-1,3-butadiene radical anion (a_{Si} 0.574 mT [10]). Furthermore, the relative high ratio of the coupling constants $a^{29}{}_{Si}/a_H^{SiR_3}$, amounting to 33 for $I^{\cdot -}$ (Table 2), reveals [10] a considerable steric interference of the bulky $(H_3C)_3Si$ substituent groups. A butatriene structure for $I^{\cdot -}$ is also in good agreement with the observed $^{13}C'$ coupling constant $a_{C'}$ 0.78 mT (Table 2 (b)) for 2 carbon nuclei: for the 1,4-carbon atoms in the unsubstittued 1,3-butadiene radical anion a coupling constant $a_{^{13}C}$ 1.10 mT is calculated [27] *; however, the spin density in 1,4-position should be considerably lowered by SiR_3 substitution [10,28].

The ESR assignment for $I^{\cdot +}$ is strongly supported by comparison with the coupling constants for the tetrakis(trimethylsilylmethyl)ethylene radical cation



(8)

$a_{^{29}Si}$	1.21 mT	1.25 mT
$a_H^{SiR_3}$	0.033 mT	0.031 mT

[13]. Both ethylene π-systems are surrounded by 4 approximately coplanar σ_{SiC} bonds, and therefore, according to the Heller—McConnell equation [29] $a_x = B\rho_x^{\pi} \cos^2\theta$ should exhibit about the same ^{29}Si coupling constant (8).

The spin distribution in the butatriene radical cation $I^{\cdot +}$ should correspond to the highest occupied molecular orbital of the neutral compound. By comparison of the ionization potentials of 1,4-bis(trimethylsilyl)-1,3-butadiene (IE_1 8.43 eV [5a]) and E-1,4-bis(trimethylsilyl)-2-butene (IE_1 8.30 eV [2]) one may already assume that the singly occupied orbital will be characterized by a large σ_{SiC}/π_{CC} contribution analogous to the one shown in (8).

A comparison of the ^{29}Si hyperfine splittings between the cation $I^{\cdot +}$ and the anion $I^{\cdot -}$ suggests that the structures for both radical ions are actually identical:

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* The calculation is based on the parameters Q_C +3.56 mT and $Q_{C'C}$ −1.39 mT [27].

the ratio $a_{Si^{\cdot +}}/a_{Si^{\cdot -}} = 2.5$ is similar to that of 3.3 reported for a bicyclic tetrasilylethylene [11] (1).

The difference between the radical anion $I^{\cdot -}$, represented by the butadiene π-system (2) substituted with electron accepting R_3Si groups, and the radical cation $I^{\cdot +\prime}$ represented by the ethylene π system (2) and stabilized by $\sigma(SiC)/\pi$ hyperconjugation (8), is strikingly illustrated by the ^{13}C satellites due to the Si methyl groups: whereas the 12 methyl carbons in the anion $I^{\cdot -}$ give rise to a relatively large coupling constant, no corresponding hyperfine splitting is observed in the cation $I^{\cdot +}$ (Table 2). This result can be straightforwardly rationalized by the differing methyl group positions: in $I^{\cdot +}$ only γ to the ethylene π-system while β to the butadiene π-system in $I^{\cdot -}$, i.e., allowing an effective hyperconjugative spin delocalization to the carbon atoms only in the tetrakis(trimethylsilyl)butatriene radical anion.

Finally, chemical evidence for the butatriene anion radical intermediate $I^{\cdot -}$ can be presented from the reaction of bis(trimethysilyl)-1,3-butadiene, III, with an excess of potassium in DME and subsequent addition of trimethylchlorosilane $(CH_3)_3SiCl$. Work-up of the reaction mixture yields bis(trimethylsilyl)-1,3-butadiyne, III, as well as hexakis(trimethylsilyl)-2-butyne, II (cf. Experimental), which agrees with the proposed reaction scheme:

$$\begin{array}{c}
R_3SiC{\equiv}C{-}C{\equiv}CSiR_3 \\
\downarrow \scriptstyle 4\ K \\
[(R_3Si)_2C{=}C{=}C{=}C(SiR_3)_2]^{\cdot -}\ 2\ K^+ + KC{\equiv}C{-}C{\equiv}CK \\
\downarrow \scriptstyle 4\ R_3SiCl \\
(R_3Si)_3C{-}C{\equiv}C{-}C(SiR_3)_3 \quad + \quad R_3SiC{\equiv}C{-}C{\equiv}CSiR_3
\end{array} \tag{9}$$

The reductive silylation of 1,3-dienes is a well known reaction [30], 1,4-addition has also been observed on methylation of the tetraphenylbutatriene dianion [25].

A concluding comment

ESR spectroscopy is an advantageous technique to detect and to characterize paramagnetic intermediates, as demonstrated once more for the one-electron oxidation and the one-electron reduction of trimethylsilyl-substituted acetylene derivatives. Both compounds, the 1,1,1,4,4,4-hexakis(trimethylsilyl)-2-butyne, II, and the 1,4-bis(trimethylsilyl)-1,3-butadiyne, III, on change of their number of valence electrons undergo an easy conversion to secondary radical ions of different structure. Strong evidence is presented that the resulting persistent radical ions $I^{\cdot +}$ and $I^{\cdot -}$ are both paramagnetic species from the hitherto unknown 1,1,4,4-tetrakis(trimethylsilyl)-1,2,3-butatriene, I.

So far, only a few molecules have been both reduced to their radical anion and oxidized to their radical cation [31]. The unusual stability of $I^{\cdot +}$ as well as of $I^{\cdot -}$ can be rationalized in terms of the unique combination of the butatriene π-system with 4 trimethylsilyl substituents, which, depending on their relative positions, can either donate or accept electrons, and thus stabilize the ground states of either cationic or anionic molecular species.

Experimental

Compounds II and III were prepared by published methods [17].

Hexakis(trimethylsilyl)-2-butyne, II. M.p. 275°C; sbl. p. 140°C/0.01 mmHg; ^{1}H NMR (CDCl$_3$/TMS): $\delta = 0.19$ ppm. Found: C, 54.0; H, 11.4. $C_{22}H_{54}Si_6$ (487.19) calcd.: C, 54.2; H, 11.2%.

Bis(trimethylsilyl)-1,3-butadiyne, III. M.p. 110°C; sbl. p. 40°C/0.01 mmHg; ^{1}H NMR (CDCl$_3$/TMS): $\delta = 0.19$ ppm. Found: C, 61.8; H, 9.2. $C_{10}H_{18}Si_2$ (194.43) calcd.: C, 61.8; H, 9.3%.

Photoelectron spectroscopy. Spectra were recorded on a Perkin—Elmer PS 16 equipped with a heated inlet and are calibrated with Xe ($^2P_{3/2}$ 12.13 eV) and Ar ($^2P_{3/2}$ 15.76 eV).

Radical cations were conveniently generated by treating 1 mg of the compound with 5 mg $AlCl_3$ in 0.1 ml oxygen-free and dry methylene chloride [2,15].

Radical anion generation was carried out by the standard procedure using sublimed alkali metal under high vacuum; for the electrolytic reduction intra muros the apparatus described in ref. 21 was used.

Electron spin resonance spectra were recorded with a Varian E 9 equipment (frequency 9.5 GHz, 330 mT magnetic field and field modulation 100 kHz) and are calibrated with perylene radical anion in DME: $a_H = 0.04503, 0.30473$ and 0.34934 mT [32].

ESR spectra simulation used the program ESPLOT, a double precision version of ESOP, which was kindly provided by Prof. A. v. Zelewsky, University Fribourg. Because of the particular requirements for trimethylsilyl-substituted radical ions, the program capacity was extended to incorporate up to 10^4 theoretical lines from up to 10^2 equivalent nuclei of 8 different sorts or isotopes. The calculations were performed on the Univac 1108 of the Hochschul-Rechenzentrum Frankfurt.

Reductive silylation has been carried out by melting 0.6 g (15 mmol) potassium in 25 ml THF in an atmosphere of dry N_2. After addition of 0.6 g (3 mmol) bis(trimethylsilyl)-1,3-butadiyne, III, in 20 ml THF to the solution cooled down to 0°C and after subsequent stirring for 1 h the dark mixture is treated with 1.3 g (12 mmol) of trimethylchlorosilane in 15 ml THF. Finally the solution is filtered and the solvent distilled off; fractional sublimation at 0.01 mmHg yields first bis(trimethylsilyl)-1,3-butadiyne, III (40°C) and then hexakis(trimethylsilyl)-2-butyne, II (140°C), as established by mass spectra and melting points.

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