"d-Orbital Effects" in Silicon-Substituted π-Electron Systems. XI.[1] Syntheses and Properties of the Isomeric Bis(trimethylsilyl)-1,3-butadienes

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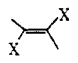
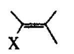
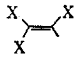
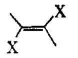
Abstract: The isomeric 1,2-, 1,3-, 1,4-, and 2,3-bis(trimethylsilyl)-1,3-butadienes have been synthesized, and their vertical ionization energies, characteristic vibrational frequencies, ^{1}H nmr signals, half-wave reduction potentials, radical-anion coupling constants, and electronic transitions have been determined. The different properties relative to those of the corresponding alkyl derivatives are discussed in terms of inductive polarization $+I_{SiR_3} > +I_{CR_3}$ and additional electron back donation $Si \leftarrow C_\pi$.

So-called "p_π-d_π" interactions are widely used to explain many of the discrepancies between analogous compounds of second- and third-row elements,[2] although very little is known about the energy differences[3] connected with them. In order to obtain such data, we compared silyl and alkyl derivatives of well-known linear and cyclic, alternant and nonalternant π-electron systems.[1,4] To determine the influences of R_3Si and R_3C groups on the individual molecular energy levels, the following quantities were measured:[4] vertical ionization energies, charge-transfer excitations, characteristic vibrational frequencies, and ^{1}H nmr signals for ground-state interactions, and half-wave reduction potentials and coupling constants of the corresponding radical anions for substituent interactions on the lowest antibonding orbital. The over-all differences should show up in the electronic transition energies. Thus, for ethylene, the smallest isoconjugate π-electron system, the collected data (Table I) may be interpreted in terms of inductive polarization, $+I_{SiR_3} > +I_{CH_2SiR_3} > +I_{CR_3}$ and additional $Si \leftarrow C_\pi$ electron back-donation.[5]

Table I. Vertical Ionization Energies (IE), ^{1}H Chemical Shifts (τ), $\pi \rightarrow \pi^*$ Transition Energies ($\nu_m^{\pi\rightarrow\pi^*}$) and Intensities ($\epsilon_m^{\pi\rightarrow\pi^*}$), C=C Stretching ($\nu_{C=C}$) and =CH$_2$ Wagging ($\delta_{=CH_2}$) Frequencies, Half-Wave Reduction Potentials ($E_{1/2}^{Red}$), and Radical-Anion Coupling Constants (a_H) for Alkyl- and Silylethylenes[15]

		X = H	SiR$_3$	CR$_3$	CH$_2$SiR$_3$
	IE, eV	10.54	9.32	8.99	7.95
	τ, ppm	4.65	3.44	4.73	4.81
	$\nu_m^{\pi\rightarrow\pi^*}$, cm^{-1}	61,000	51,150	54,650	48,800
	$\epsilon_m^{\pi\rightarrow\pi^*}$, l. mole^{-1} cm^{-1}	10,000	20,100	16,050	12,150
	$\nu_{C=C}$, cm^{-1}	1623	1598	1639	1634
	$\delta_{=CH_2}$, cm^{-1}		932	909	894
	$E_{1/2}^{Red}$, V	<−2.5	2.0	...	...
	a_H, G	(10.8)[a]	7.49	...[b]	...[b]

[a] Calculated using the McConnell equation, $a_H = c^2_{J\mu}|Q|$ with $|Q| = 20.8$. [b] No radical anions could be obtained with K-dimethoxyethane at −80°.

The assumptions involved, as well as the additional effects to be taken into account, will be discussed subsequently in connection with the properties of the isomeric disilylbutadienes. These compounds have been synthesized to avoid difficulties encountered in the case of the smaller ethylene π-electron system, *e.g.*, the unexpected long-wavelength shift of the $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ (?) mystery bands[6] due to upper σ or lower σ^* states or the inaccessible (with one exception) half-wave reduction potentials. On substituting different positions of the butadiene π-electron system with the R_3Si groups, further information was expected in correlating the data and served as a basis for MO calculations.[7]

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[1] Previous communication: H. Bock and H. Seidl, *Chem. Ber.*, 101, 2815 (1968).

[2] *Cf.*, for instance, F. G. A. Stone and G. Seyferth, *J. Inorg. Nucl. Chem.*, 1, 112 (1955); C. Eaborn, "Organosilicon Compounds," Butterworth & Co., Ltd., London, 1960; H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1964; R. F. Hudson, *Pure Appl. Chem.*, 9, 371 (1964); N. L. Paddock, *Quart. Rev.* (London), 168 (1964); H. Bürger, *Fortschr. Chem. Forsch.*, 9, 1 (1967); Abstracts of the First International Conference on Silicon Chemistry, *Pure Appl. Chem.*, 13, 1 (1967); Abstracts of the International Symposium on Valence and Reactivity, Oxford, Jan 9–11, 1968, The Chemical Society, London; as well as literature quotations given in these publications.

[3] R. West, *J. Organometal. Chem.*, 3, 314 (1965).

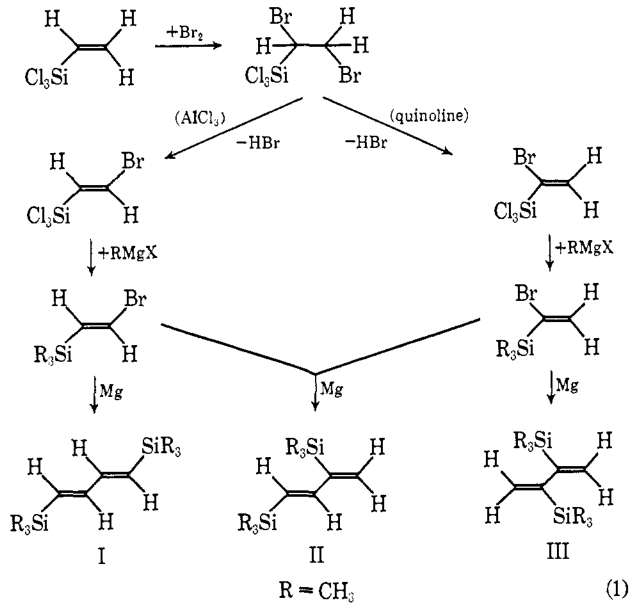
[4] H. Bock, H. Alt, H. Seidl, F. Gerson, and H. Heinzer, *Angew. Chem.*, 79, 932, 933, 934, 1106 (1967); *Angew. Chem. Intern. Ed. Engl.*, 6, 941, 942, 943, 1085 (1967); *Chem. Commun.*, 1299 (1967); *J. Organometal. Chem.*, 3, 87, 103 (1968); *Helv. Chim. Acta*, 51, 707 (1968).

[5] H. Bock and H. Seidl, *J. Organometal. Chem.*, 13, 87 (1968).

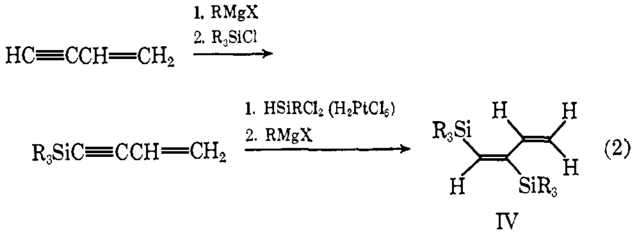
[6] M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, 44, 1803 (1966). For instance, in the case of tris(trimethylsilyl)ethylene,[5] the first absorption band is found at 35,700 cm^{-1} with a molar extinction coefficient of 350 l./mole^{-1} cm^{-1}.

Syntheses

The hitherto unknown 1,4-, 1,3-, and 2,3-bis(trimethylsilyl)-1,3-butadienes were synthesized by the routes shown in eq 1. The 1,2 derivative[8] was obtained in reasonably good yield from vinylacetylene.

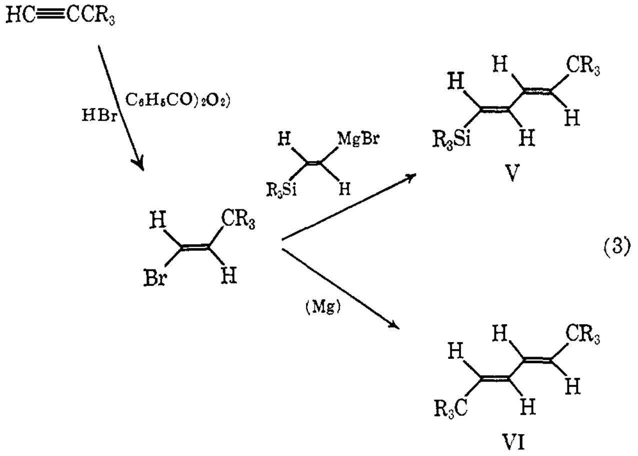


(1)

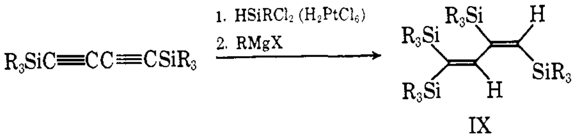


(2)

For the first-time preparations of 1-trimethylsilyl-4-*t*-butyl- and of 1,4-di(*t*-butyl)butadienes, the methods shown in eq 3 were chosen. For two other stable alkyl standards, 1,3-di(*t*-butyl)butadiene (VII) and 2,3-dimethylbutadiene (VIII), literature procedures[9,10] were available. The 2,3-di(*t*-butyl) derivative is known to be twisted[11] due to nonbonding interactions. The large interference radii of the bulky substituents might also be responsible for the fact that 1,1,3,4-tetrakis(trimethylsilyl)butadiene was obtained instead of the desired 1,1,4,4 derivative from the reaction shown in eq 4.

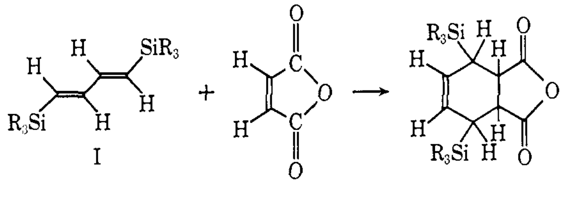


(3)



(4)

The trimethylsilylbutadienes I–V and IX are stable at room temperature; obviously the steric reason mentioned above prevents polymerization. Nevertheless, Diels–Alder additions are possible, for instance, with the 1,4 derivative I (eq 5) and also with the 1,2 derivative IV.[6]



(5)

Results and Discussion

A. Ionization Energies. The values for the silyl- and alkylbutadienes I–VIII were determined by mass spectrometry and correspond therefore (in contrast to the "adiabatic" ionization energies from electronic spectra) to a "vertical" excitation in the Franck–Condon scheme. For butadiene itself, the data obtained from different methods of measurement are consistent,[12] thus showing that in this case the vertical excitation might be approximately assigned to a 0 → 0 transition. According to Koopmans theorem,[13] the first ionization energies are generally correlated to the highest occupied SCF molecular energy level.[14] On the assumption involved which seems to be valid for all π systems investigated,[1] that the resulting butadiene radical cations are at least comparably stabilized, the vertical ionization potentials (Figure 1) represent the relative energies of the highest occupied molecular orbitals of dialkyl- and disilylbutadienes.

The substituent effects can be interpreted in a qualitative one-electron MO scheme as follows.

(1) Alkyl groups raise—corresponding to their positive inductive effects ($+I_{CR_3} > +I_{CH_3}$)—the highest occupied π-molecular orbital, ψ_2, of butadiene.

(2) Silyl groups lower—despite of the expected larger inductive effect ($+I_{SiR_3} > +I_{CR_3}$)—the energy of the butadiene molecular orbital, ψ_2, relative to that of the *t*-butyl derivatives as is indicated by the higher ionization potentials of the former. The same result is found in the case of alkyl- and silylethylenes (Table I), where the value for the *trans*-1,4-bis(trimethylsilyl)butene-2 (IE = 7.95 eV) allows a crude estimate of the $+I_{CH_2SiR_3}$ effect. Compared with butene-2 (IE = 9.3 eV[12]) substitution of two hydrogen atoms by SiR$_3$ groups lowers the ionization energy by about 1.3 eV. Assum-

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(7) J. Kroner and H. Bock, *Theor. Chim. Acta*, in press.

(8) M. D. Stadnichuk and A. A. Petrov, *J. Gen. Chem. USSR*, 32, 3449 (1962).

(9) H. J. Backer and J. Strating, *Rec. Trav. Chim.*, 56, 1069 (1937).

(10) C. F. Allen and A. Bell, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 312.

(11) H. Wynberg, A. de Groot, and D. W. Davies, *Tetrahedron Letters*, 1083 (1963).

(12) R. I. Reed, "Ion Production by Electron Impact," Academic Press, New York, N. Y., 1962.

(13) T. Koopmans, *Physica*, 1, 104 (1934).

(14) A. Streitwieser, Jr., "Molecular Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 188–201.

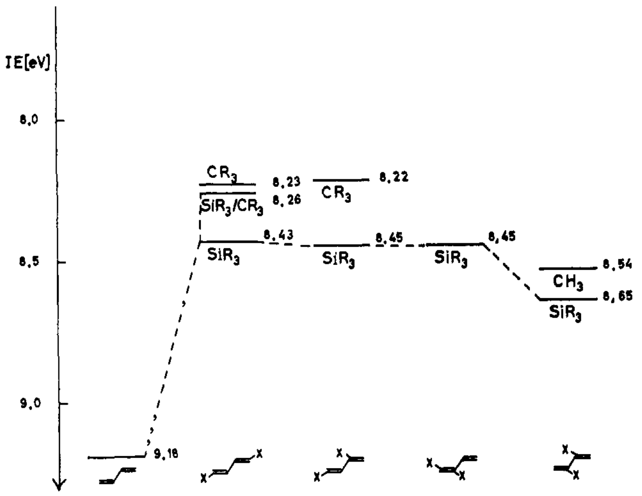
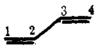


Figure 1. Vertical ionization potentials (IE, eV) of dialkyl- and disilylbutadienes.

Table II. Characteristic Vibrational Frequencies (cm^{-1}) of Alkyl- and Silylbutadienes

No.	Substituents	 $\nu_{C=C}$	δ_{-CH}	δ_{-CH_2}	$2\delta_{-CH_2}$
I	1,4-SiR$_3$	1552 m	1008 vs		
V	1-SiR$_3$-4-CR$_3$	1644 w 1584 m	1002 vs		
VI	1,4-CR$_3$	1626 w	990 vs		
II	1,3-SiR$_3$	1587 m 1565 w	988 s	923 s	1845 w
VII	1,3-CR$_3$	1642 w 1613 m	972 s	890 s	1786 w
III	2,3-SiR$_3$	1572 w		922 s	1848 w
VIII	2,3-CH$_3$	1597 w			
IV	1,2-SiR$_3$	1610 m 1517 m	975 s 988 m	907 s	1818 w
IX	1,1,3,4-SiR$_3$	1564 m 1522 m			

ing that the tetrahedral carbon insulates the silicon atoms from the π-electron system, and with a weakening factor for inductive effects in α and β positions, I_β: $I_\alpha \sim 0.6$,[15] the energy difference due to the $+I_{SiR_3}$ effect of α-silyl groups should be about 2.2 eV. On the other hand, the ionization energies of butadiene and 1,4-disilylbutadiene (Figure 1) differ only by about 0.7 eV. Therefore an additional conjugative interaction lowering the highest occupied molecular energy level has to be taken into account. Extending the π model used here, such an electron back-donation (Si←C$_\pi$) can be described as d-π interaction.

(3) First-order perturbation in a one-electron MO scheme predicts a lowering of the highest occupied molecular orbital, ψ_2, of disilylbutadienes (coefficients $c_{21} = c_{24} > c_{22} = c_{23}$) in the following sequence of derivatives: 1,4 > 1,3 = 1,2 > 2,3. This expectation is qualitatively met by the observed ionization energies (Figure 1).

(4) The ionization energy of the 2,3-disilylbutadiene seems to be too high relative to the 2,3-dimethyl compound (ΔIE = 0.11 eV), when compared with the differences between the corresponding ethylene derivatives.[5] This may be due to steric effects of the bulky R$_3$Si groups; these effects are found to be still greater in the 2,3-di(*t*-butyl)butadiene.[11]

Calculations using the Pariser–Parr–Pople method[7] confirm the foregoing qualitative interpretation which will serve as a basis for the following discussions of other ground-state properties.

B. Characteristic Vibrational Frequencies. The infrared spectra of the silyl- and the alkylbutadienes show characteristic vibrations, whose values in reciprocal centimeters are given in Table II. In butadiene itself, the mean value of the symmetric $\nu^{s}_{C=C}$ and antisymmetric $\nu^{as}_{C=C}$ stretching frequencies[16] ($\bar{\nu}_{C=C}$ = (1635 + 1590)/2 = 1613 cm^{-1}) is found at longer wavelengths than those of monoalkylethylenes[5] ($\nu_{C=C} \sim$ 1630 – 1650 cm^{-1}). This is usually explained by a lowering of the force constant, $k_{C=C}$, due to a strengthening of the bond C$_2$–C$_3$. In unsymmetrically substituted butadienes, both C=C stretching frequencies are observed, whereas only the $\nu^{as}_{C=C}$ will be symmetry allowed in symmetrically substituted butadienes. The energies of the two C=C stretching vibrations are determined by the π coupling between the two double bonds as well as by inductive and conjugative effects of the substituents attached to butadiene. If SiR$_3$ substituents will exert an acceptor function on the butadiene π-electron system, then the C=C stretching frequencies should be shifted to longer wavelengths corresponding to a lowering of the force constants. Mass effects on replacing CR$_3$ groups by SiR$_3$ groups are expected to be almost negligible.[5] Thus the collected data may be interpreted as follows.

(1) The antisymmetric C=C stretching frequency of 1,4-disilylbutadiene is lowered 74 cm^{-1} relative to that of the di(*t*-butyl) derivative (Table II). Assuming the $\nu^{as}_{C=C}/\nu^{s}_{C=C}$ splitting remains approximately constant, this long-wavelength shift can be interpreted by an electron withdrawal due to Si←C$_\pi$ back bonding. The C=C stretching vibration of monosubstituted ethylenes (Table I) is influenced similarly on replacing the CR$_3$ by the SiR$_3$ groups. The underlying assumption that the $\nu^{as}_{C=C}/\nu^{s}_{C=C}$ splitting should be nearly constant, *i.e.*, that the amount of π coupling between the two double bonds should be comparable, is further strengthened by the following finding: the mean value of the asymmetric stretching frequencies of 1,4-di(*t*-butyl)- and 1,4-disilylbutadiene ($\nu^{as}_{C=C}$ = (1626 + 1552)/2 = 1589 cm^{-1}) is in fairly good agreement with the asymmetric stretching frequency of 1-trimethylsilyl-4-*t*-butylbutadiene ($\nu^{as}_{C=C}$ = 1584 cm^{-1}).

(2) Twisting of the butadiene system due to bulky substituents in the 2 or 3 positions (indicated by the ionization potentials) reduces the $\nu^{as}_{C=C}/\nu^{s}_{C=C}$ splitting[17] (Table II: V → II, VII). Electron-withdrawing effects Si←C$_\pi$ might also be smaller in the 2 or 3 positions. Thus one expects a long-wavelength shift of the asymmetric stretching frequencies in the sequence 2,3 < 1,3 < 1,4 which is confirmed experimentally (Table II). The largest shift is expected and found for the tetrasilyl derivative IX.

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(15) O. Exner and J. Jonas, *Collection Czech. Chem. Commun.*, 27, 2296 (1962).

(16) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., Princeton, N. J., 1966.

(17) The large splitting ($\nu^{s}_{C=C}/\nu^{as}_{C=C}$ = 93/cm) in 1,2-disilylbutadiene (IV) can be partly attributed to the differences in the vibrational energy levels of the two unequally substituted C=C fragments.

(3) The out-of-plane deformation vibrations, $\delta_{=CH}$ (proving by their intensities and positions the *s-trans* configuration[18]), are shifted to shorter wavelengths in the silylbutadienes. The same shift is found for the wagging deformation frequencies, $\delta_{=CH_2}$, which are considered to reproduce the over-all electronic effects of substituents,[19] and which thus will lend additional evidence to the electron withdrawal by SiR_3 groups, *i.e.*, $Si \leftarrow C_\pi$ interactions in the ground state of silylbutadienes.

C. ¹H Nmr Signals. In the case of *trans*-disubstituted ethylenes (Table I), the ¹H nmr signals of the ethylenic protons are shifted downfield with increasing vertical ionization energies in the sequence of substituents $CH_2SiR_3 < CR_3 < SiR_3$. This finding suggests that the electron withdrawal by SiR_3 relative to CR_3 groups in the ground state should lead to deshielding. Furthermore, in monosubstituted ethylenes,[5] the differences in the downfield shift, Δ, of the ethylenic protons increase in the order $H^{(1)}_{vic} < H^{(2)}_{cis} < H^{(3)}_{trans}$. These differences in the chemical shifts indicate that, as, for example, in acrylonitrile,[20] effects other than the electron withdrawal by R_3Si relative to R_3C groups also have to be taken into account, *e.g.*, dipole-induced permanent electric fields and changes in diamagnetic anisotropy.[21]

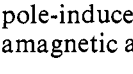
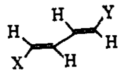
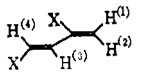
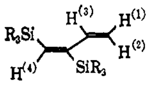
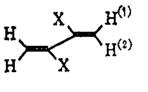
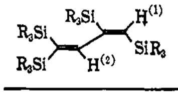
		τ, ppm		
	X	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$
	CR_3	4.13	5.09	5.18
	SiR_3	3.90	4.38	4.19
	Δ	0.23	0.71	0.99

Table III. ¹H Nmr Signals of Alkyl- and Silylbutadienes

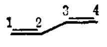
	X	CR_3	SiR_3	SiR_3
	Y	CR_3	CR_3	SiR_3
	τ, ppm	4.29	3.93	3.87
	X		CR_3	SiR_3
	τ, ppm	$H^{(1)}$	5.09	4.57
		$H^{(2)}$	5.29	4.27
		$H^{(3)}$	3.90	3.37
		$H^{(4)}$	4.22	4.17
	J, Hz	J_{12}	1.7	3.2
		J_{13}	0.7	0.8
		J_{24}	0.3	0.5
		J_{34}	15.5	19.1
	τ, ppm	$H^{(1)}$ 5.06	J, Hz	J_{12} 1.6
		$H^{(2)}$ 5.02		J_{13} 10.5
		$H^{(3)}$ 3.51		J_{23} 17.7
		$H^{(4)}$ 4.01		J_{34} 1.1
	X	CH_3[23]	CR_3[11]	SiR_3
	τ, ppm	$H^{(1)}$ 5.00	4.9	4.59
		$H^{(2)}$ 5.10	5.3	
	τ, ppm	$H^{(1)}$ 4.03	J_{12}, Hz	2.5
		$H^{(2)}$ 2.57		

Concerning the alkyl- and silylbutadienes, the situation is still more complicated: AA′BB′ and ABCD systems generally must be solved by computer calculations, so Table III[22] contains only the centered values of those derivatives. Furthermore, in the isomeric butadienes, diamagnetic anisotropy plays an important role. In butadiene itself the difference in the chemical shift of the protons in 1,4 and 2,3 positions has been explained this way.[23] Nevertheless, the data (Table III) reflect the same substituent effects as described for the ethylene derivatives; R_3Si groups always cause downfield shifts of equivalent protons relative to those in the alkyl derivatives. Also, the order of differences, Δ, is the same ($H_{vic} < H_{cis} < H_{trans}$). Thus the largest downfield shift is found for the ²H proton in 1,1,3,4-tetrasilylbutadiene.

Summarizing, the substituent effects of R_3Si groups on ground-state properties like ¹H nmr signals or characteristic vibrational frequencies, though not directly linked to the ionization energies, can be interpreted on the basis of an electron back-donation $Si \leftarrow C_\pi$, conceivably a d–π interaction.

D. Half-Wave Reduction Potentials. The interactions in excited states of silyl-substituted π-electron systems are not accessible by direct measurements. Nevertheless, numerous correlations support the assumption that reversible half-wave reduction potentials should reflect the relative energies of the lowest unoccupied molecular orbitals in neutral π-electron systems.[24] Table IV contains the values for the reversible one-electron redox equilibria of alkyl- and silylbutadienes, measured in DMF *vs.* the mercury pool anode and fulfilling the criterion $E_{3/4} - E_{1/4} \sim -0.6$ V from the Ilkovič equation.[25]

Table IV. Half-Wave Reduction Potentials (V) of Alkyl- and Silylbutadienes



	1,4	1,3	1,2	2,3
SiR_3, SiR_3	−1.80	−1.85	−1.90	−2.13
SiR_3, CR_3	−2.10	...	... .	...
CR_3, CR_3	<−2.4	<−2.4	...	−2.18 (R = H)

Relative to butadiene [$E_{1/2}^{Red} \sim -2.1$ V (estimated from the potential $E_{1/2}^{Red} = -2.63$ V *vs.* a saturated calomel electrode according to ref 24)] itself, alkyl substitution raises the negative potential in the sequence $CH_3 < CR_3$, the *t*-butyl derivatives not being reduced within the range of measurement conditions. On the other hand, the negative potentials in silylbutadienes are lowered despite of the large $+I_{SiR_3}$ effect, which dominates in the ground state as is shown by the ionization potentials. Therefore, in the singly occupied molecular orbital of the radical anion, the inductive effect of silyl groups must be overcome by the electron back-donation. This would confirm the expectation[3] that due to better energy matching the d–π* interac-

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(18) P. Kurtz, H. Schwarz, and H. Disselschötter, *Ann.*, 631, 21 (1960).

(19) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, 15, 679 (1955).

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1965.

(21) F. Schraml and V. Chvalovsky, *Collection Czech. Chem. Commun.*, 31, 503 (1966).

(22) Values for chemical shifts and coupling constants have been taken directly from the spectra. A more detailed discussion including C^{13}–H coupling constants is intended to be published later.

(23) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, 12, 76 (1964).

(24) Reference 14, pp 173–185.

(25) D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 82, 2617 (1960).

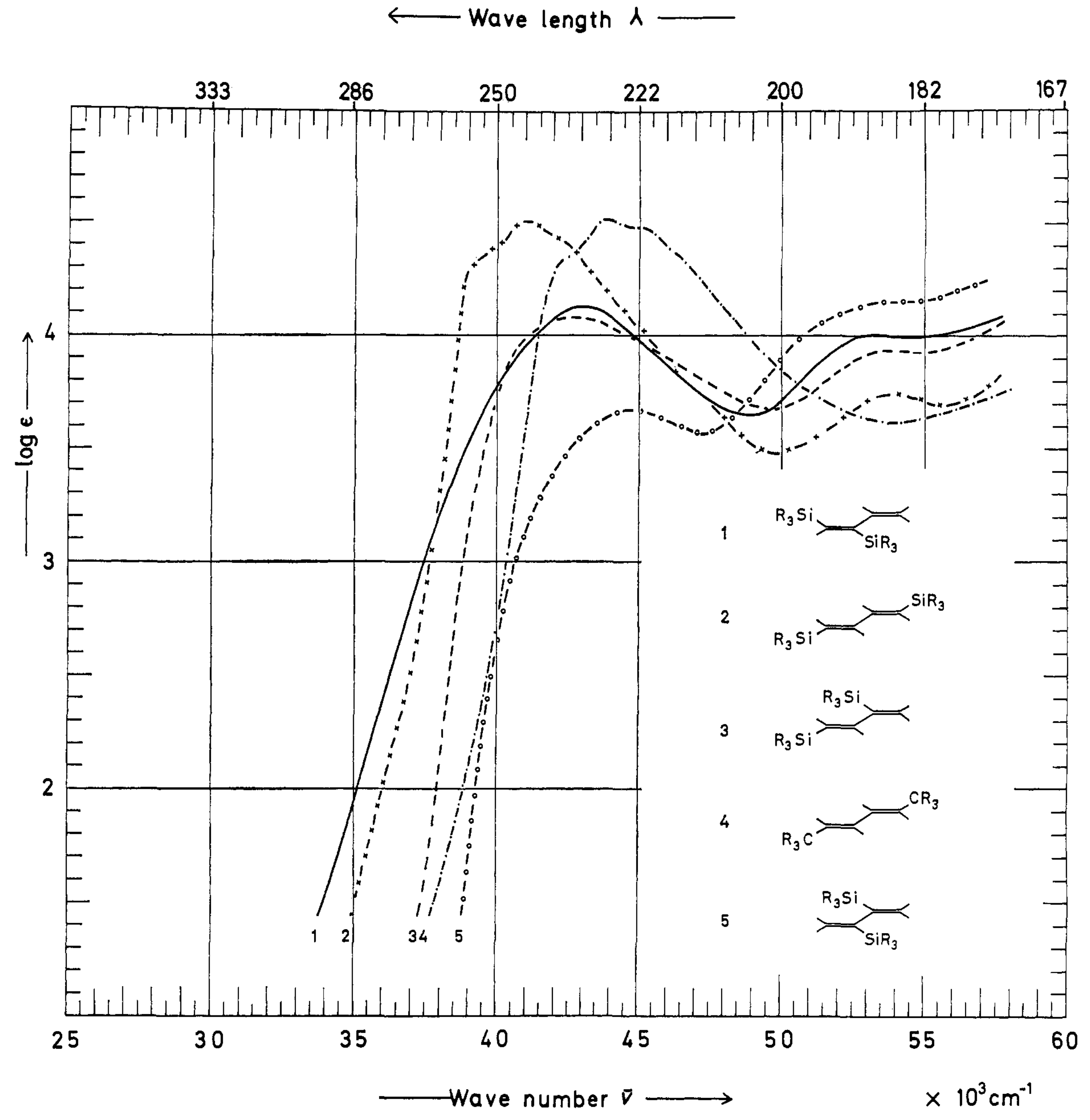
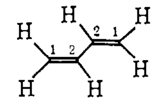


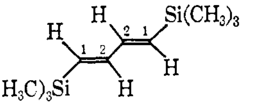
Figure 2. Electronic spectra of some dialkyl- and disilylbutadienes in *n*-hexane.

tions should be substantially stronger. Furthermore, the sequence of negative potentials of the isomeric bis(trimethylsilyl)butadienes 1,4 < 1,3 ~ 1,2 < 2,3 deduced from first-order perturbation in the HMO model is met by the experimental data.

Additional evidence that radical anions are stabilized by silyl substituents, in other words, that their large positive inductive effect might be exceeded by their acceptor property, is obtained from esr investigations.[26] Thus the radical anion of 1,4-bis(trimethylsilyl)butadiene may be warmed up to room temperature without immediate decomposition. The coupling constants (compared with those of butadiene[27] itself) clearly indicate that some spin density is transferred to the $(CH_3)_3Si$ group. For the smaller π-electron system of ethylene[26] (Table I), this transfer is even greater.



$a_H^{(1)} = 7.62$ G
$a_H^{(2)} = 2.79$ G



$a_H^{(1)} = 6.71$ G $a_{^{29}Si} = 5.73$ G
$a_H^{(2)} = 3.22$ G $a_H^{(CH_3)} = 0.24$ G

E. Electronic Transitions. The ionization potentials (section A) which reflect the ground-state energies increase from alkyl- to disilylbutadienes and in the isomers of the latter according to the order 1,4 < 1,3 ~ 1,2 < 2,3. The foregoing half-wave reduction potentials (section D), which are correlatable with the substituent influence on the lowest unoccupied molecular orbital, decrease in the sequence dialkyl ≫ disilyl 2,3 > 1,2 > 1,3 > 1,4. Thus for the over-all effect of R_3C and R_3Si groups on the π → π* transitions of the substituted butadienes described here, one would expect the following observations.

(1) Alkylbutadienes should have larger π → π* transition energies than the corresponding silyl com-

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[26] F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, 51, 707 (1968).

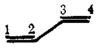
[27] D. H. Levy and R. J. Myers, *J. Chem. Phys.*, 41, 1062 (1964).

pounds with mixed derivatives showing intermediate values.

(2) The $\pi \rightarrow \pi^*$ absorption of the isomeric disilylbutadienes should be shifted to longer wavelengths in the order 1,4 > 1,3 > 1,2 > 2,3.

The electronic spectra of representative dialkyl- and disilylbutadienes (Figure 2) as well as the data in Table V are in agreement with the foregoing predictions, thus giving additional credit to the assumptions serving as a basis in interpreting the ionization energies and half-wave reduction potentials.

Table V. $\pi \rightarrow \pi^*$ Absorption Maxima (ν_m, cm^{-1}), Molar Extinctions (ϵ_m, l. mole^{-1} cm^{-1}) and Oscillator Strengths (f) of Alkyl- and Silylbutadienes



No.	Substituents	ν_m, cm^{-1}	ϵ_m, l. mol^{-1} cm^{-1}	f
I	1,4-SiR_3	40,810	32,100	0.74
V	1-SiR_3-4-CR_3	42,100	30,100	0.65
VI	1,4-CR_3	43,860	32,300	0.79
a	1,4-CH_3	44,100		0.74
II	1,3-SiR_3	42,550	12,200	0.35
VII	1,3-CR_3	44,840	6,650	0.30
b	1,3-CH_3	43,860	22,400	
IV	1,2-SiR_3	43,010	12,800	0.36
III	2,3-SiR_3	44,640	4,670	0.11
VIII	2,3-CH_3	44,050	23,000	0.52
IX	1,1,3,4-SiR_3	$(40{,}000)_{sh}$	$(3{,}400)_{sh}$	

[a] P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955). [b] J. N. Nazarov and M. V. Mavrov, *Bull. Acad. Sci. USSR*, 446 (1959).

The uv data (Table V) of butadienes with *t*-butyl or trimethylsilyl groups in 2 or 3 positions again indicate twisting distortions due to the large interference radii of the bulky substituents. Whereas the high oscillator strengths of 1,4 derivatives (I, V, VI) are almost constant, the lower value for 2,3-bis(trimethylsilyl)butadiene (III) relative to the sterically unhindered 2,3-dimethyl compound VIII must be interpreted this way. In contrast to all other isomeric alkyl and silyl pairs of compounds, the methyl compound also absorbs at longer wavelengths. From the 1,3-di(*t*-butyl)- and 1,3-dimethylbutadienes, a maximum value $\Delta_m \sim 1000$ cm^{-1} may be estimated for the blue shift due to steric nonbonding interactions, which should be minor for R_3Si groups because of the larger distance $d_{SiC} > d_{CC}$. For the 1,1,3,4-tetra(trimethylsilyl) derivative IX the Stuart-Briegleb model suggests a skew conformation which was found as well in the 2,3-di(*t*-butyl) compound,[11] thus explaining why no distinct absorption maximum is observed.

Independent of steric interferences, R_3Si groups will act as strong acceptors in excited states. In terms of 3d-orbital participation, this may be discussed as follows: due to better energy matching, d–π^* interactions are substantially larger than d–π interactions in the ground state. This becomes evident when the ionization potentials and the transition energies are combined to a molecular orbital scheme (Figure 3) on the basis of the underlying assumptions.

According to Figure 3 the difference $\Delta E_{\pi}{}^*$ is about three times the difference ΔE_{π}. Thus in the excited state, the large positive inductive effect of SiR_3 groups is almost compensated by the electron back-donation $Si \leftarrow C_{\pi}{}^*$. Pariser–Parr–Pople calculations[7] reproducing the numerical values support the underlying assumption of a first excited state composed of a nearly pure $\chi_1{}^{-1}$ configuration, whereas the second excited state contains contributions from several configurations. As a further indication of the relative energies of the lowest antibonding molecular orbitals the half-wave reduction potentials (section D) might be considered showing that in the radical anions the $+I_{SiR_3}$ effect is even overcompensated by the electron back-donation.

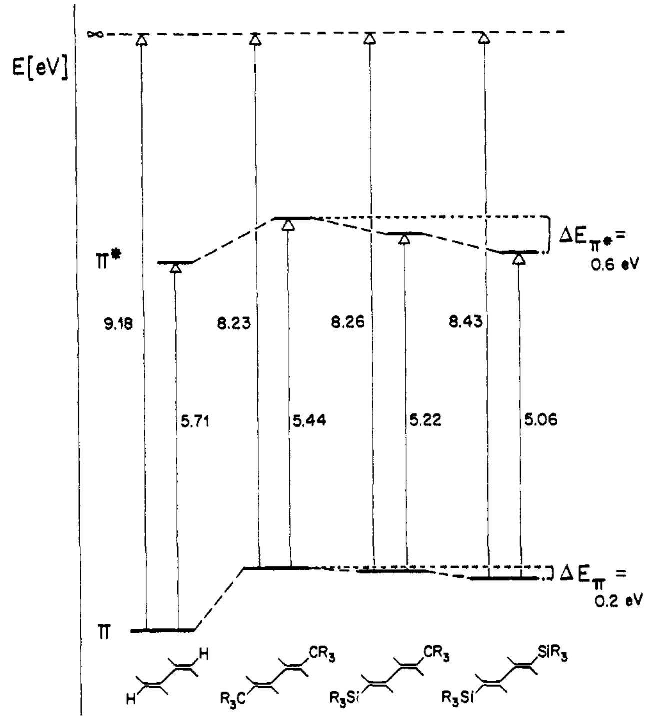


Figure 3. MO scheme for 1,4-disubstituted butadienes from ionization potentials and $\pi \rightarrow \pi^*$ transition energies.

Summary

Combined methods of measurements (evaluation of vertical ionization potentials, characteristic vibrational frequencies, ^1H nmr signals, half-wave reduction potentials, esr coupling constants, and electronic transition energies) are used to distinguish between inductive and conjugative effects of alkyl and silyl substituents on the butadiene π-electron system. The observed electron back-donation $Si \leftarrow C_{\pi}$ might be interpreted on the basis of σ–π separation in terms of d–π and d–π^* interactions, the latter being substantially larger due to better energy matching. Nevertheless, participation of empty silicon 3d orbitals is only assumed to rationalize the acceptor property of silyl substituents which must be of π symmetry.

Experimental Section

All compounds were purified by gas chromatography using a Varian Model A-700 instrument, equipped with a 6-m silicon oil column SE 30. Ionization energies were determined using a Krupp MAT CH 4 mass spectrometer equipped with a Fox ion source.[12] In the series studied, the individual values deviated at most by ±0.04 eV on repeating each measurement four times. The infrared spectra of capillary films were recorded on a Perkin-Elmer Model 21 spectrometer with a NaCl prism. ^1H nmr spectra were obtained from 10% solutions in carbon tetrachloride using a Varian Model A-60 spectrometer. Chemical shifts are given in parts per million relative to TMS as an internal standard. The ultraviolet spectra were recorded on a Cary N 14 spectrometer using Merck Uvasol *n*-hexane as a solvent. For measurements in the vacuum uv region, a self-recording double-beam spectrograph, McPherson 225 with a Hinteregger hydrogen lamp, was employed. Half-wave reduction potentials were measured with the friendly permission of Professor E. Heilbronner at the Eidgenössische Technische Hochschule, Zürich, using a Metrohm Polarecord E 261 R in a 0.2 *M* solution of tetrabutylammonium iodide in dimethylformamide at 23° with the Hg pool as reference. Esr spectra were recorded by D. F. Gerson and J. Heinzer (Eidgenössische Technische Hochschule, Zürich).

Hydrolyzable compounds were synthesized under dry nitrogen. The intermediate compounds needed in the butadiene syntheses, 1-bromo-1-trimethylsilylethylene ($n^{20}\mathrm{D}$ 1.4592) and *trans*-1-bromo-2-trimethylsilylethylene ($n^{20}\mathrm{D}$ 1.4668), have been obtained according to ref 28. The ^{1}H nmr spectrum for *trans*-1-bromo-2-trimethylsilylethylene shows only one singlet for the ethylenic protons at 3.45 ppm.

***s-trans*-1,4-Bis(trimethylsilyl)-1,3-butadiene** (I). To 0.94 g (0.039 g-atom) of magnesium in 15 ml of THF a solution of 7 g (0.039 mole) of *trans*-1-bromo-2-trimethylsilylethylene in 10 ml of THF was slowly added and the mixture stirred until the magnesium almost disappeared. Then to the Grignard solution another 7 g (0.039 mole) of 1-bromo-2-trimethylsilylethylene was added. After refluxing for 20 hr and hydrolysis with dilute HCl, the product was extracted with ether. The solution was dried with $CaCl_2$ and fractionally distilled to give 4.0 g (51%) of I, bp 46–49° (15 mm), $n^{20}\mathrm{D}$ 1.4679.

Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.70; H, 11.10.

Diels–Alder Addition of Maleic Anhydride. I, 400 mg (0.2 mmole), was refluxed with 200 mg (0.2 mmole) of maleic anhydride in 1 ml of benzene for 5 min. On cooling 500 mg (83%) of the Diels–Alder addition product crystallized in long white needles of mp 167–168° after recrystallization from ethanol.

Anal. Calcd for $C_{14}H_{24}O_3Si_2$: C, 56.71; H, 8.16. Found: C, 56.58; H, 8.39.

***trans*-1,3-Bis(trimethylsilyl)-1,3-butadiene** (II). According to the procedure described above, 0.94 g (0.039 g-atom) of magnesium in 15 ml of THF was slowly added to a solution of 7 g (0.039 mole) of 1-bromo-1-trimethylsilylethylene in 10 ml of THF. To the Grignard solution, 7 g (0.039 mole) of 1-bromo-2-trimethylsilylethylene was added, and the mixture was refluxed for 24 hr. After hydrolysis, fractional distillation yielded 5.9 g (75%) of II, bp 72–77° (34 mm), $n^{20}\mathrm{D}$ 1.4569.

Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.77; H, 11.21.

***trans*-2,3-Bis(trimethylsilyl)-1,3-butadiene** (III). The synthesis followed the procedure described for I, thus coupling 1-bromo-1-trimethylsilylethylene to 4.0 g (51%) of III, bp 54–58° (15 mm), $n^{20}\mathrm{D}$ 1.4520.

Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.44; H, 10.82.

***trans*-1,2-Bis(trimethylsilyl)-1,3-butadiene** (IV). This compound was prepared by the method of Stadnichuk and Petrov[8] by addition of methyldichlorosilane to trimethylsilylvinylacetylene in the presence of H_2PtCl_6 as a catalyst. Following the addition of the Grignard reagent, IV was obtained in 30% yield, bp 63–66° (10 mm), $n^{20}\mathrm{D}$ 1.4643, lit.[8] $n^{20}\mathrm{D}$ 1.4650.

Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.22; H, 11.09.

1-Bromo-2-*t*-butylethylene, needed for the syntheses of the alkylbutadienes V and VI, was prepared as follows. Through a mixture of 50 g (0.61 mole) of *t*-butylacetylene and 1.2 g of dibenzoyl peroxide at 0°, a slow stream of dry HBr was passed until the absorption stopped. The resulting solution was washed with sodium bicarbonate and water and finally extracted with ether. After the solution was dried with $CaCl_2$, fractional distillation yielded 66.5 g (66%) of 1-bromo-2-*t*-butylethylene, bp 127–129° (720 mm).

Anal. Calcd for $C_6H_{11}Br$: C, 44.20; H, 6.80. Found: C, 44.40; H, 7.05. The ^{1}H nmr spectrum shows two doublets for the ethylenic protons at 4.08 and 3.76 ppm with $J = 16.2$ Hz.

***s-trans*-1-Trimethylsilyl-4-*t*-butyl-1,3-butadiene** (V). To 0.06 mole of the Grignard compound, prepared from 1.46 g (0.06 g-atom) of magnesium and 10.7 g (0.06 mole) of 1-bromo-2-trimethylsilylethylene in 40 ml of THF, 10 g (0.06 mole) of 1-bromo-2-*t*-butylethylene was added slowly. The mixture was heated for 2 hr, hydrolyzed, and extracted with ether. The ether layer was dried with $CaCl_2$, and yielded upon fractional distillation 8.0 g (73.3%) of V, bp 87–89° (136 mm), $n^{20}\mathrm{D}$ 1.4651.

Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.37; H, 11.90.

***s-trans*-1,4-Di(*t*-butyl)-1,3-butadiene (VI).** To a solution of 0.06 mole of Grignard reagent prepared from 1.46 g (0.06 g-atom) of magnesium and 10 g (0.06 mole) of 1-bromo-2-*t*-butylethylene in 40 ml of THF, 10 g (0.06 mole) of 1-bromo-2-*t*-butylethylene was added slowly. The mixture was heated for 24 hr, hydrolyzed, and extracted with ether; the ether layer was dried with $CaCl_2$. Fractional distillation yielded 5.1 g (52%) of VI, bp 114–118° (136 mm), mp 66–68°.

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.33. Found: C, 87.03; H, 13.06.

1,3-Di(*t*-butyl)butadiene (VII). The synthesis is achieved by dimerization of pinacoline[9] with sodium followed by dehydration with oxalic acid: bp 170–172° (720 mm), $n^{20}\mathrm{D}$ 1.4447.

2,3-Dimethylbutadiene (VIII) was obtained by dehydration of pinacol hexahydrate:[10] bp 69–70° (720 mm), $n^{20}\mathrm{D}$ 1.4387.

1,1,3,4-Tetrakis(trimethylsilyl)-1,3-butadiene (IX). To a solution of 5 g (0.023 mole) of bis(trimethylsilyl)diacetylene[29] in 15 ml of *n*-hexane and 0.6 mole of 0.1 *M* hexachloroplatinic acid in 2-propanol 8 g (0.2 mole) of methyldichlorosilane was slowly added. The solution was stirred for 30 min at room temperature and then refluxed for 3 hr. After adding 0.5 mole of methylmagnesium iodide in ether and warming for 30 min, the solution was hydrolyzed and extracted with ether; the ether layer was dried with $CaCl_2$. Fractional distillation yielded 3.1 g (40%) of IX, bp 70–72° (0.1 mm), $n^{20}\mathrm{D}$ 1.4766.

Anal. Calcd for $C_{16}H_{38}Si_4$: C, 56.05; H, 11.17. Found: C, 56.05; H, 10.94.

Acknowledgments. The investigations have been financially supported by the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk. We are also indebted to Mr. M. Fochler for measuring the appearance potentials and Dr. H. Tom Dieck for his remarks on ir and ^{1}H nmr spectra.

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(29) J. A. Shikhiev, M. F. Shostakovski, and L. A. Kayutenko, *Dokl. Akad. Nauk SSSR*, **15**, 21 (1959); *Chem. Abstr.*, **53**, 15957 (1959).