CHEMISTRY LETTERS, pp. 1845-1848, 1985.

ESR STUDY OF ALLYLSILANE CATION RADICALS1)

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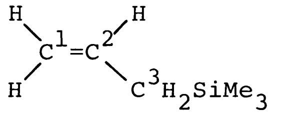
An ESR study of cation radicals of allyltrimethylsilane and derivatives generated by ^{60}Co γ-irradiation in frozen trichlorofluoromethane revealed the large polarization of the SOMO as a consequence of the enhanced σ-π conjugation.

Allylsilanes have been recognized as useful synthetic reagents undergoing regiospecific allyl transfer reactions with a variety of electrophiles.2) The high reactivity and regiospecificity are mainly attributed to the enhanced σ(Si-C)-π conjugation,3,4) which causes the exaltation of the energy level and large polarization of the highest occupied molecular orbital (HOMO). Experimentally, the former consequence of the σ-π conjugation has been actually demonstrated by photoelectron spectroscopy:5) the first ionization potential of allyltrimethylsilane is about 0.7 eV lower than that of propene. The latter point that the atomic coefficient at the γ-carbon in HOMO should be much larger than that at the β-carbon, may be proved by the magnitude of the hyperfine splitting (hfs) constants of the olefinic hydrogens of the cation radicals as studied by ESR spectroscopy.

Accordingly, we report herein ESR spectra of cation radicals of allyltrimethylsilane (**1**) and the derivatives **2**-**5** generated by ^{60}Co γ-irradiation of the substrates in frozen trichlorofluoromethane at 77 K.6) Whereas the ESR spectra of some cation radicals of allylsilanes such as tetrakis(trimethylsilylmethyl)ethylene have been investigated in dichloromethane solution,7) the present report provides the first study of allylsilane cation radicals which bear olefinic hydrogens, shedding light on the electronic structure of the π systems.



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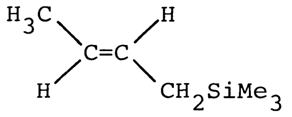

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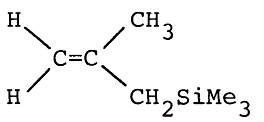

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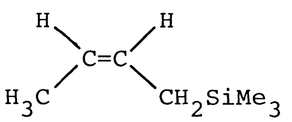

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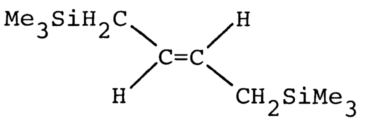

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Table 1. ESR Parameters of Allylsilane Cation Radicals [a)]

Allylsilane	T/K	Hfs/mT	g
1	133	1.61 (1H), 1.13 (1H)	2.0031
2	133	1.90 (1H), 1.35 (1H)	2.0030
3	133	2.3 (1H), 1.7 (3H)	2.0035
4	133	2.2 (1H), 1.75 (3H), 0.75[b)]	
5	133	unresolved	
$H_3CCH{=}CH_2$ [c)]	130	0.90 (2H), 1.60 (1H), 2.40 (3H)	
$(H_3C)_2C{=}CH_2$ [d)]	130	1.40 (2H), 1.65 (6H)	
$H_3CCH{=}CHCH_3$ [d)]	130	0.98 (2H), 1.39 (6H)	

a) Hfs values of **1**-**4** were determined by simulation. b) The splitting corresponds to 1H but it may possibly be a super-hyperfine splitting due to a fluorine.[12c)] c) Ref. 12c. The hfs values have been reported to depend on matrix and temperatures.[12)] d) Ref. 6.

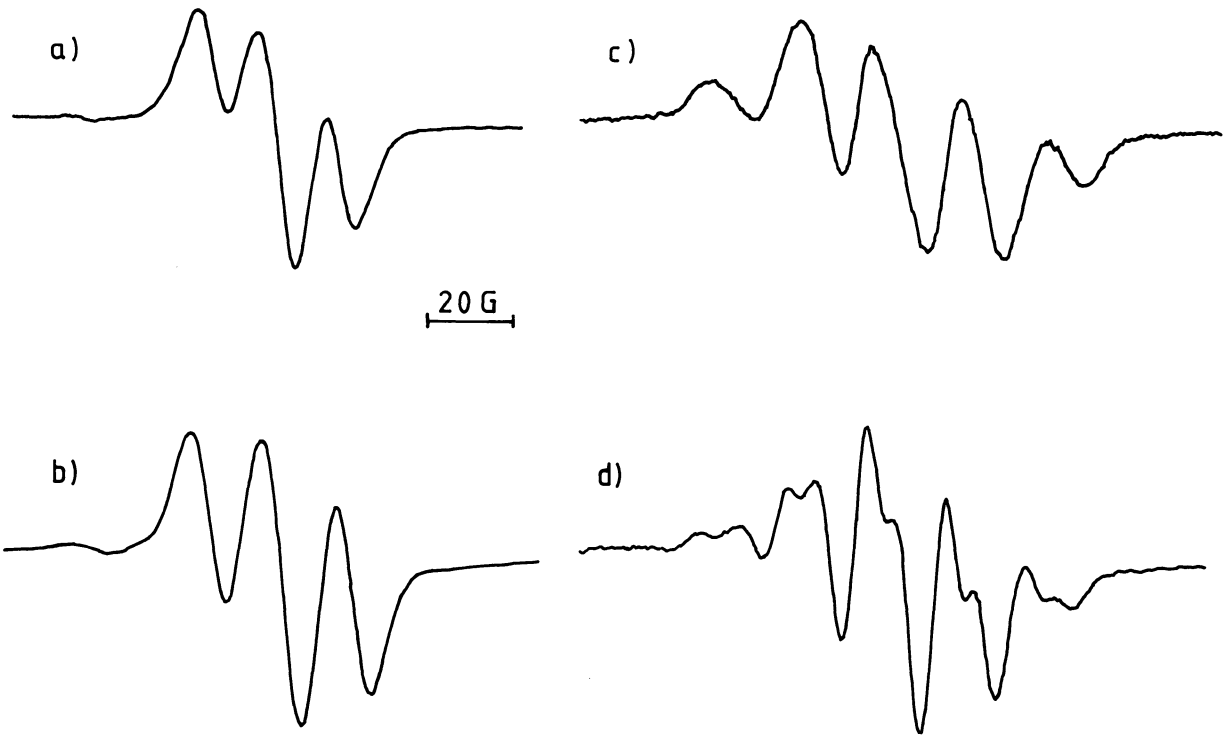


Fig. 1. ESR spectra of (a) $\mathbf{1}^{+\cdot}$ at 123 K; (b) $\mathbf{2}^{+\cdot}$ at 107 K; (c) $\mathbf{3}^{+\cdot}$ at 133 K; (d) $\mathbf{4}^{+\cdot}$ at 133 K in frozen $CFCl_3$.

The ESR spectra and the parameters determined by computer simulation are shown in Fig. 1 and Table 1, respectively. The spectrum of $\mathbf{1}^{+\cdot}$ was analyzed into a doublet of doublets whose hfs values were 1.61 and 1.13 mT. Interestingly, we have observed no other splitting, whereas there are five hydrogens in $\mathbf{1}^{+\cdot}$ expected to afford large hfs values; namely, three olefinic and two allylic hydrogens. Since $\mathbf{2}^{+\cdot}$ afforded apparently a triplet spectrum similar to $\mathbf{1}^{+\cdot}$ and since a doublet in $\mathbf{1}^{+\cdot}$ was replaced by a quartet in the spectra of $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ where one of the γ-hydrogens of $\mathbf{1}^{+\cdot}$ was substituted by a methyl group, the two hfs values in $\mathbf{1}^{+\cdot}$ should be assigned to the two hydrogens on C^1. Thus, the π spin densities at C^1 and C^2 were estimated to be ca. 0.50 and less than 0.1, respectively, according to the McConnell relationship[8] (Eq. 1), where a_i and ρ_i are the hydrogen hfs and the spin

$$a_i = Q_H \rho_i \qquad (1)$$

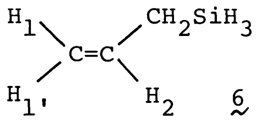
density at position i in the radical, respectively; the Q_H value may be taken to be around 2.7 mT, since the proton hfs value of the benzene cation radical has been observed as 0.44 mT.[9] Such a π spin distribution is indicative of the large polarization of the HOMO of allyltrimethylsilane ($\mathbf{1}$) in the first-order approximation. One may expect much larger hfs due to allylic hydrogens than the observed since the limiting structure $[H_2\overline{C\text{-}\dot{C}H\text{-}CH}_2\ {}^{+}SiMe_3]$ may be of major importance in $\mathbf{1}^{+\cdot}$ as a consequence of the enhanced σ-π conjugation. Actually, the averaged a_1 value of $\mathbf{1}^{+\cdot}$ is comparable to that of the propene cation radical, being suggestive of a significant amount of spin density on C^3.

We can imagine, however, that in the pyramidal configuration around the allylic carbon the spin polarization effect may be compensated by the direct spin delocalization on the hydrogens attached just as observed in a pyramidal radical such as cyclopropyl.[10] Hyperconjugative spin delocalization to the allylic hydrogens may also be small because of the small spin density at C^2 as well as of the eclipsed conformation between C^3-Si σ bond and π orbital.

The INDO-UHF calculation[11] for the cation radical of allylsilane ($\mathbf{6}$) gave a strong support for the idea that the large polarization is a consequence of the enhanced σ-π conjugation between σ(C-Si) and π orbitals (Table 2). The calculated hfs values due to β-hydrogen (a_2) depend significantly on the dihedral angle θ. When θ = 0° a_2 was calculated to be -0.16 mT, while the absolute value was much larger (-0.67 mT) when no σ(Si-C)-π conjugation exists (θ = 90°). The latter hfs value is almost the same as the corresponding experimental hfs for propene cation radical (0.90 mT).[12]

Table 2. Hfs values of allylsilane with different σ-π dihedral angles calculated by INDO-UHF method.

θ/deg	$a(H_1)$/mT	$a(H_{1'})$/mT	$a(H_2)$/mT
0	-1.22	-1.16	-0.16
90	-1.23	-1.20	-0.67



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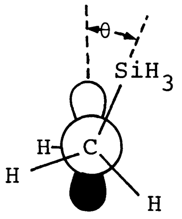

In accord with our present results, recent studies on the reactions of allylsilane cation radicals showed facile cleavage of the C^3-Si bond affording an allyl radical and a silyl cation.13)

Although the above discussion is based on the assumption of the planar π system of the cation radicals, several authors12b-d) have discussed on the possibility of twisting even in methyl-substituted ethylene cation radicals after our demonstration of twisting in the trimethylsilyl-substituted ethylenes.14) Whereas several unusual feature of the spectra of the methyl-substituted ethylene cation radicals does not permit decisive conclusion, we feel methyl-substitution may favor the planar π structure more than the twisted as shown by MNDO calculation,15) because of the homohyperconjugative stabilization of the former.16)

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(Received September 13, 1985)