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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXXIX*. EVIDENCE FOR FORMATION OF FREE SILYL RADICALS IN THE PHOTOLYSIS OF ARYLDISILANES

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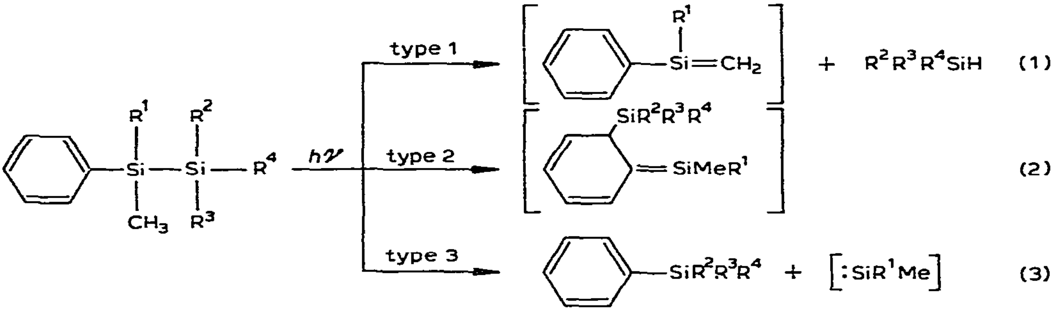
Summary

Free silyl radicals formed in the photolysis of aryldisilanes have been detected by a spin-trapping technique. A possible free-radical mechanism of the photolysis is presented.

Photolysis of organopolysilanes has been of interest for some time. For aryldisilanes, Boudjouk, Roberts, Golino and Sommer [2] reported first the type 1 reaction, while later Ishikawa, Fuchikami, Sugaya and Kumada [3] reported another type of reaction in which a rather unusual silicon—carbon double bonded species was postulated as a key intermediate. Production of a silylene has also been noted [3]**, and the peculiar solvent effect of DMSO on the photolysis has been reported [5].



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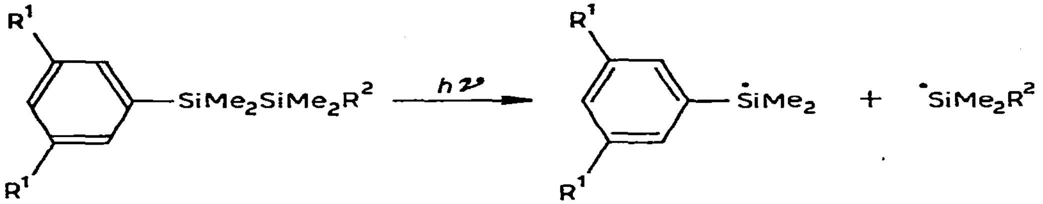
[*] For part CXXVIII, see ref. 1.

[**] Although, the extent of the formation of the silylene is only 1% for phenylpentamethyldisilane [3], it becomes 7% for $PhSiMe_2SiMe_2F$ (Ic) [4].

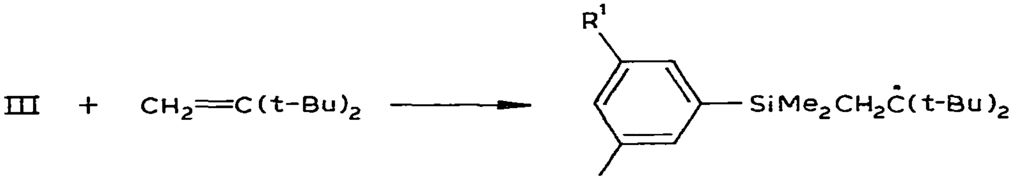
We have been interested in the photolysis of aryldisilanes in connection with the photochemistry of related organodisilanes [6], as well as in relation to the spectroscopic studies on aryldisilanes [7]. It is now disclosed that one of the primary steps of the photolysis of aryldisilanes (I) is the generation of silyl radicals which are successfully trapped with 1,1-di-t-butylethylene (II) to give relatively long-lived adduct radicals.



(4)

(I) (III) (IV)

a; R^1 = H, R^2 = Me
b; R^1 = t-Bu, R^2 = Me
c; R^1 = H, R^2 = F
d; R^1 = H, R^2 = O-t-Bu



(5)

(II) (V)

$$\text{IV} + \text{II} \longrightarrow R^2Me_2SiCH_2\dot{C}(t\text{-}Bu)_2 \qquad (6)$$

(VI).

A solution of cyclopropane, I and II (1/1/1 in volume) was irradiated with a 500 W super-high-pressure mercury arc lamp in an ESR (a Varian E-12) cavity at −60~20°C. From Ia, a well-resolved ESR spectrum, which is shown in Fig. 1, was obtained. The spectrum appeared immediately after irradiation and stronger signals were obtained at higher temperatures up to +20°C. The spectrum can be expected as a composite of V (R^1 = H) and VI (R^2 = Me). However, the spectral parameters being almost identical, these possibly two spectra were not resolved on the chart. The same situation was obtained in the case of Ib. From Ic, a spectrum with a hyperfine coupling of ^{19}F was obtained, so that it is clear that the $FMe_2Si^{\bullet}$ radical was trapped by II to give VI (R^2 = F), but in this case the radical V (R^1 = H) was not detected explicitly. Finally, irradiation of Id in the presence of II

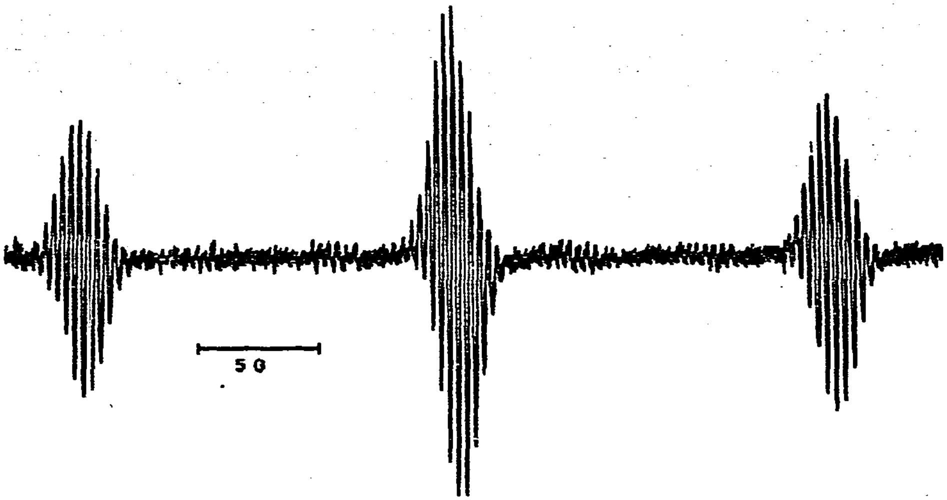


Fig. 1. ESR spectrum of adduct radical(s) derived from phenylpentamethyldisilane and 1,1-di-t-butylethylene.

gave a composite spectrum of V (R^1 = H) and VI (R^2 = t-BuO) as shown in Fig. 2a. The relative abundance of V/IV was about 1/3 as determined by computer simulation shown in Fig. 2b. The spectral parameters of these radicals as well as of some authentic radicals are shown in Table 1. A possible route to V and/or VI by the reaction of II with hydrosilanes, products of the type 1 photoreaction, was excluded by independent experiments. Without an initiator, hydrosilanes did not generate silyl radicals on photolysis, at least in detectable amounts.

The present results indicate unequivocally the involvement of free silyl radicals in the photoreaction of aryldisilanes. Although the result does not necessarily warrant that all the reaction proceeds by the free radical process, it is possible to explain the type 1, 2, and 3 reactions in terms of free silyl radicals in a unifying manner as shown below*.

TABLE 1

HYPERFINE COUPLING CONSTANTS OF $(t\text{-Bu})_2\dot{C}CH_2SiMe_2$ X RADICALS

X	Source	T/°C	hfcc/G			
			β-H	γ-H	$^{13}C(\gamma)$	^{29}Si
Me and/or Ph[a]	(Ia)	0	15.60	0.36	10.33	35.03
Me and/or Ar[a,b]	(Ib)	0	15.60	0.36	10.43	35.11
F	(Ic)	0	15.76	0.36	(^{19}F=2.98)	
Ph	(Id)	20	15.61	0.36		
O-t-Bu	(Id)	20	15.76	0.36		
Me [10]	Me_3SiH	25	15.76	0.36	10.23	35.02
Ph	$PhMe_2SiH$	0	15.59	0.36	10.25	35.10

[a] A possible composite spectrum, see text. [b] Ar = 3,5-di-t-butylphenyl.

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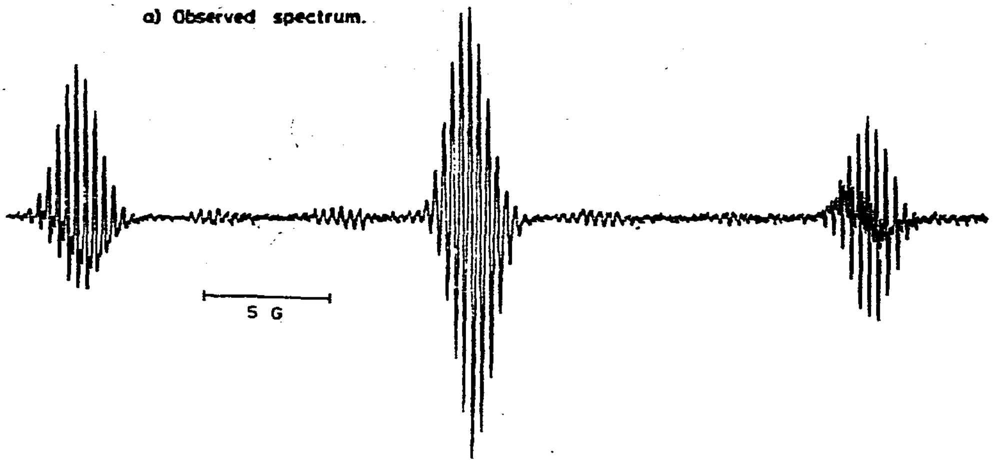
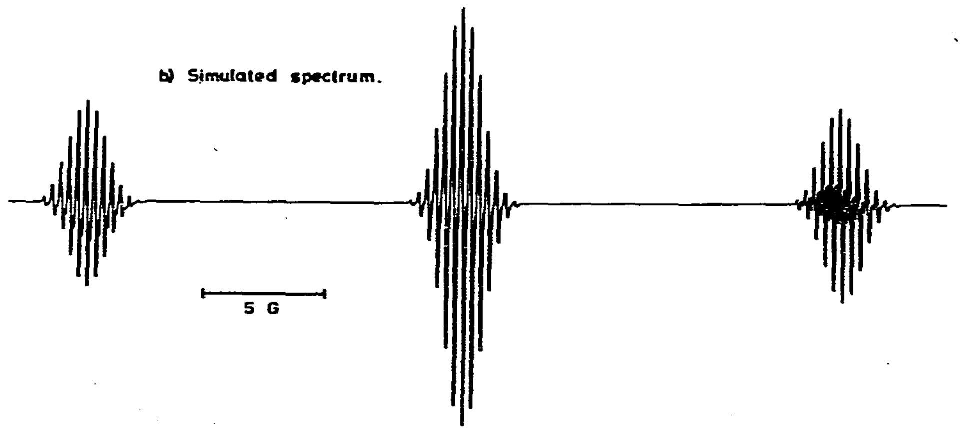
*For an alternative explanation, see ref. 8.

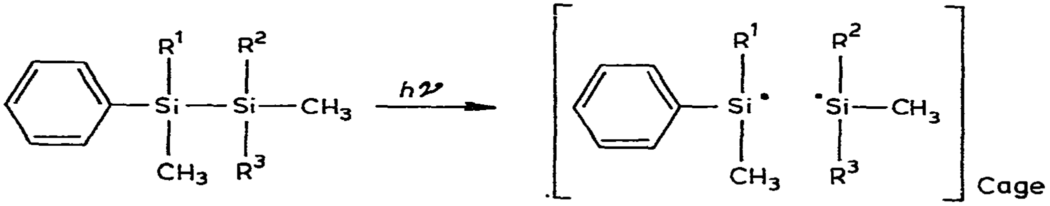


a) Observed spectrum.



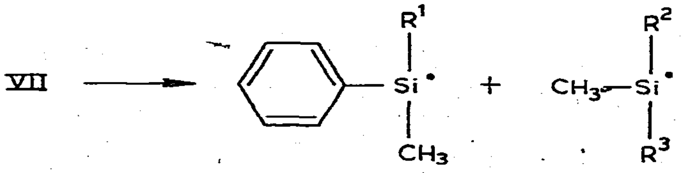
b) Simulated spectrum.

Fig. 2. ESR spectra of adduct radicals derived from 1-phenyl-2-t-butoxy-1,1,2,2-tetramethyldisilane and 1,1-di-t-butylethylene: (a) experimental, (b) simulated as a composite of V (R^1 = H) and VI (R^2 = t-BuO) (without ^{29}Si; and ^{13}C (γ)).



(VII)

(7)



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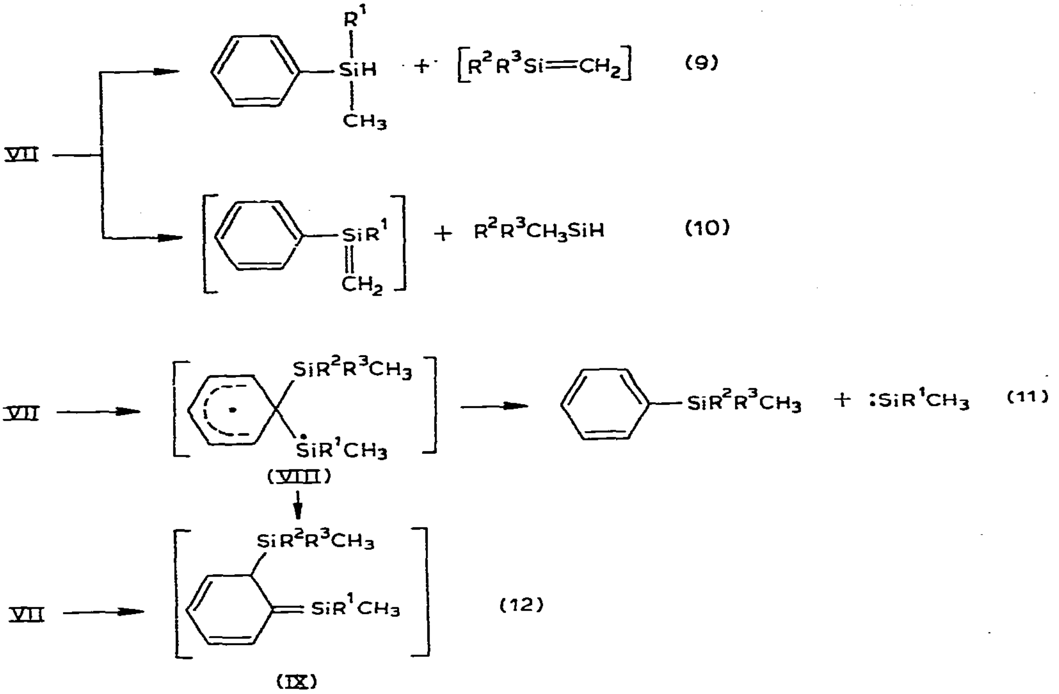

Photolysis of aryldisilanes results in the formation of a geminate pair of two silyl radicals, some of which may escape from the solvent cage and be trapped by II. An observed temperature effect on the intensity of the spectra is consistent with the idea of a cage process. The initial radical pair VII may undergo disproportionation in the solvent cage to result in the type 1 reaction (eq. 9 and 10) and *ipso*-substitution to form VIII. The latter may undergo further rearrangement and/or reactions with stable molecules to give type 2 products. The pair of radicals also can form IX. The intermediate VIII also can be a precursor of the silylenes (eq. 12). The facile *ipso*-substitution of silyl radicals has been reported recently [9]. Related work is in progress.

Acknowledgment

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