Silyl Radicals. Formation and Reactions of Cyclopropyldimethylsilyl Radicals[1]

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Although silyl radicals have been cited as possible intermediates in some reactions,[2-4] no detailed investigation on the nature of these radicals has been done until quite recently.[5-7] Especially, there has been little evidence to show the formation of triorganosilyl radicals from triorganohydrosilanes by hydrogen abstraction.

As a part of program, concerning the reactivities of silyl radicals, we have examined the reaction of cyclopropyldimethylsilane (I), with di-*t*-butyl peroxide (II). In a typical run, 3.45 mmol of II was decomposed in 7.40 mmol of I in a sealed tube at 140°C in a period of 17 hr. The products were isolated by preparative g. l. c. and identified by comparing the physical properties with those of samples prepared by alternative and unequivocal route.[8] The amounts of these products were determined by g.l.c., the results being listed in Table 1.

The formation of 1,2-dicyclopropyltetramethyldisilane (III) is a good evidence of the silyl radical as an intermediate in the present reaction.

$$\underset{\text{(I)}}{(CH_3)_3COOC(CH_3)_3} \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot + \triangleright\text{-}Si(CH_3)_2H \longrightarrow (CH_3)_3COH + \triangleright\text{-}\dot{S}i(CH_3)_2 \qquad (2)$$

$$2\,\triangleright\text{-}\dot{S}i(CH_3)_2 \longrightarrow \underset{\text{(III)}}{\triangleright\text{-}Si(CH_3)_2Si(CH_3)_2\text{-}\triangleleft} \qquad (3)$$

TABLE 1. PRODUCTS OF DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN CYCLOPROPYLDIMETHYLSILANE AT 140°C

Compound	mmol
Original cyclopropyldimethylsilane	7.40
Original di-*t*-butyl peroxide	3.45
Recovered cyclopropyldimethylsilane	2.74
t-Butyl alcohol	4.07
t-Butoxy(cyclopropyl)dimethylsilane	1.99
Isopropoxy(cyclopropyl)dimethylsilane	0.44
1,2-Dicyclopropyltetramethyldisilane	1.04
% Cyclopropyldimethylsilyl group accounted for	98
% *t*-Butyl group accounted for	95

The reaction products include virtually no acetone that would be expected as an product of the fragmentation reaction of *t*-butoxy radicals. Presumably acetone gave isopropoxy(cyclopropyl)dimethylsilane (IV) by the reaction with the intermediate silyl radical.

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (4)$$

$$(CH_3)_2CO + \triangleright\text{-}\dot{S}i(CH_3)_2 \longrightarrow \triangleright\text{-}Si(CH_3)_2O\dot{C}(CH_3)_2 \qquad (5)$$

$$\triangleright\text{-}Si(CH_3)_2O\dot{C}(CH_3)_2 + I \longrightarrow IV + \triangleright\text{-}\dot{S}i(CH_3)_2 \qquad (6)$$

The driving force of reaction 5 must be the formation of a new Si-O bond.

It should be noteworthy that *t*-butoxy(cyclopropyl)dimethylsilane (V) was formed in a considerable amount. Two possibilities can be considered for the formation of V; ionic reduction involving four-centered or other molecular mechanisms, as well as an induced decomposition of II by the cyclopropyldimethylsilyl radical.

Cyclopropyl group has been intact throughout the reaction. This would be an interesting contrast with behaviors of the analogous carbon radicals.[9]

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[1] Presented in part at the 20 th Annual Meeting of the Chemical Society of Japan, April, 1967, Tokyo.

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[3] J. Curtice, H. Gilman and G. S. Hammond, *J. Am. Chem. Soc.*, **79**, 4754 (1957).

[4] L. E. Nelson, N. C. Angelotti and D. R. Weyenberg, *ibid.*, **85**, 2662 (1963).

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[6] J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson and J. C. Young, *Chem. Commun.*, **1966**, 157.

[7] Y. Nagai, K. Yamazaki, N. Kobori and M. Kosugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 793 (1967).

[8] All the new compounds, I, III, IV and V, gave satisfactory analyses and IR and NMR spectra.

[9] R. Breslow, "Molecular Rearrangement," Part 1, P. de Mayo ed., Interscience, New York and London (1963), p. 233.