

## Chlorine Abstraction from Chloromethanes by Dimethylsilanediyls

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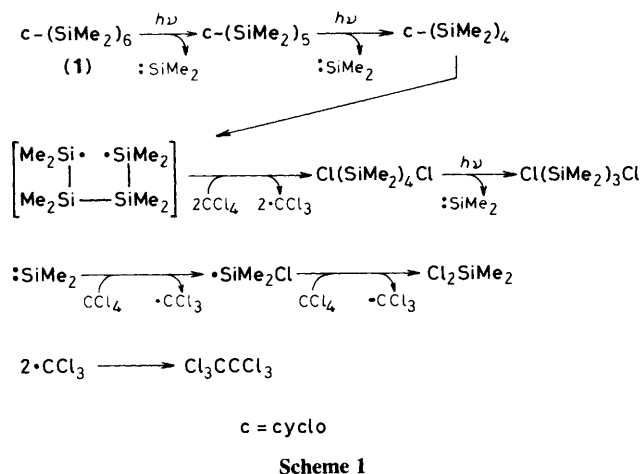
Photolysis of dodecamethylcyclohexasilane in carbon tetrachloride gives hexachloroethane; its formation is a result of chlorine abstraction from carbon tetrachloride by dimethylsilanediyl.

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One of the greatest differences between silanediyl and carbene is their reactivity toward abstraction reactions. Although a great deal is known about silanediyl reactions,<sup>1,2</sup> no abstraction reactions by silanediyls resulting in the formation of silyl radicals have been reported so far, while carbenes can abstract hydrogen from hydrocarbons to give free radicals.

On photolysis of dodecamethylcyclohexasilane (**1**) in the presence of carbon tetrachloride or chloroform, we obtained results which strongly suggest the occurrence of chlorine abstraction from the chloromethanes by dimethylsilanediyl.

A degassed solution of (**1**) (0.04 mmol) in 0.2 ml carbon tetrachloride was irradiated with a 100 W low-pressure



**Table 1.** Competitive reaction of chloroform with hexamethylcyclotrisiloxane.<sup>a</sup>

Reactants, mmol <sup>b</sup>		Products, yield/% <sup>c</sup>	
HCl <sub>3</sub>	(2)	HCl <sub>2</sub> CCl <sub>2</sub> H	(3)
0.20	0	76.3	0
0.41	0	80.6	0
0.34	0.04	75.2	18.0
0.27	0.07	56.6	33.8
0.20	0.11	37.8	43.3
0.14	0.15	29.9	61.1
0.07	0.19	16.8	78.0
0	0.22	0	76.5

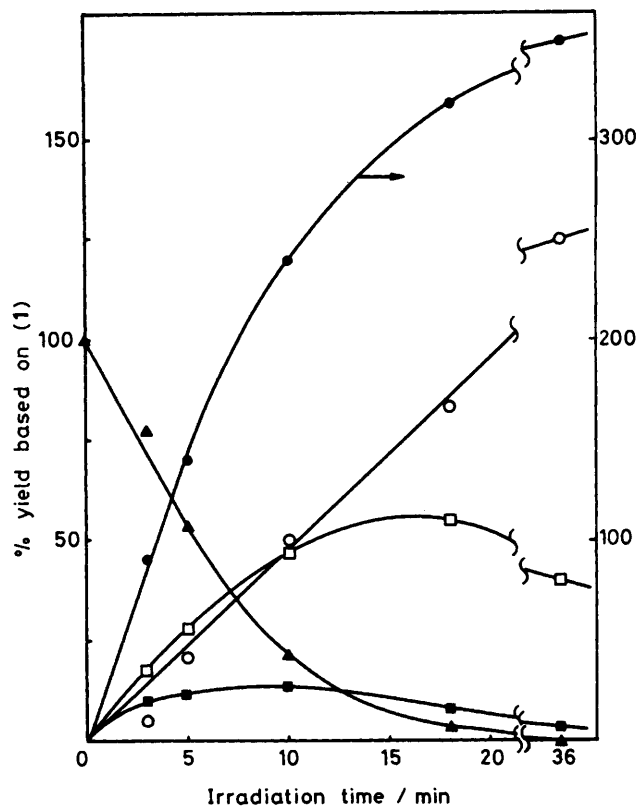
<sup>a</sup> The reactions were carried out in 0.4 ml cyclohexane. <sup>b</sup> Plus 0.04 mmol (1). <sup>c</sup> Based on (1).

mercury lamp (spiral type) without cooling. G.c. and g.c.-mass spectral analyses of the products revealed the presence of four main components: dichlorodimethylsilane, hexachloroethane ( $m/z$  199, 164, 129, 117), 1,3-dichlorohexamethyltrisilane [ $m/z$  244 ( $M^+$ ), 229, 209, 151, 116, 93, 73], and decamethylcyclopentasilane [ $m/z$  290 ( $M^+$ )]. The dependence of the yields on irradiation time is shown in Figure 1. A small amount of hexachloroethane was produced by u.v. irradiation of pure carbon tetrachloride; an allowance was made for this in calculating the yields of hexachloroethane.

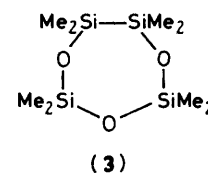
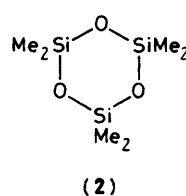
The formation of hexachloroethane cannot be explained as arising from dimethylsilanediyl insertion into the C-Cl bond of carbon tetrachloride, since the possible product ( $\text{Cl}_3\text{CSiMe}_2\text{Cl}$ ) has not been detected even though the authentic compound was shown not to decompose under these reaction conditions. If we assume that dimethylsilanediyl produced by photolysis of (1) abstracts chlorine from carbon tetrachloride, the formation of all products may reasonably be interpreted as in Scheme 1,<sup>†</sup> by analogy with Ishikawa's mechanism for the photolysis of (1) in cyclohexane.<sup>3,4</sup>

Taking a run at 5 min in Figure 1 as an example, the balance of (1) consumed, hexachloroethane, 1,3-dichlorohexa-

<sup>†</sup> Photo-induced degradation of (1) in cyclohexane<sup>3,4</sup> has been reported to occur as follows: (1)  $\rightarrow$  c-(Me<sub>2</sub>Si)<sub>5</sub>  $\rightarrow$  c-(Me<sub>2</sub>Si)<sub>4</sub>  $\rightarrow$  [·(Me<sub>2</sub>Si)<sub>4</sub>·]  $\rightarrow$  H(Me<sub>2</sub>Si)<sub>4</sub>H  $\rightarrow$  H(Me<sub>2</sub>Si)<sub>3</sub>H. In carbon tetrachloride, it seems reasonable to assume that Cl(Me<sub>2</sub>Si)<sub>4</sub>Cl is produced instead of H(Me<sub>2</sub>Si)<sub>4</sub>H. Indeed, Cl(Me<sub>2</sub>Si)<sub>4</sub>Cl has been detected by g.c.-mass spectral analysis in the irradiated mixture. It has not been shown that Cl(Me<sub>2</sub>Si)<sub>4</sub>Cl gives Me<sub>2</sub>Si· and Cl(Me<sub>2</sub>Si)<sub>3</sub>Cl, but we presume that it degrades in a similar manner to H(Me<sub>2</sub>Si)<sub>4</sub>H.



**Figure 1.** Photo-induced reaction of (1) with carbon tetrachloride. ○, Dichlorodimethylsilane; ●, hexachloroethane; □, 1,3-dichlorohexamethyltrisilane; ■, decamethylcyclopentasilane; ▲, (1).



methyltrisilane, and decamethylcyclopentasilane produced was consistent with Scheme 1, but the yield of dichlorodimethylsilane was considerably smaller than that expected. This deficiency is probably due to its further reaction<sup>‡</sup> and/or to vaporization when the irradiated tube was opened prior to g.c. analysis. To check these possibilities an experiment in a sealed quartz n.m.r. tube was attempted using chloroform to quantify the recombination product by means of <sup>1</sup>H n.m.r. spectroscopy. A solution of (1) (0.14 mmol) in chloroform (0.4 ml) was irradiated for 18 min. Dichlorodimethylsilane and 1,1,2,2-tetrachloroethane were obtained in the molar ratio of 0.69 : 1. The ratio expected from Scheme 1 is 0.75 : 1. Allowing for the subsequent reaction of dichlorodimethylsilane mentioned above, this ratio seems reasonable.

<sup>‡</sup> Photolysis of (1) in dichlorodimethylsilane was reported to give 1,2-dichlorotetramethylsilane and 1,3-dichlorohexamethyltrisilane.<sup>4</sup>

To confirm that (1) undergoes primary photolysis rather than reacts with the products of carbon tetrachloride decomposition, irradiation was carried out through a 2 cm chloroform filter. A mixture of (1) (0.04 mmol) and chloroform§ (0.41 mmol) in cyclohexane was irradiated for 30 min through the filter. The irradiated mixture gave 0.032 mmol of 1,1,2,2-tetrachloroethane and 0.013 mmol of decamethylcyclopentasilane. The irradiating light,  $\lambda < 245$  nm (absorption band of chloroform), is almost perfectly cut off by the filter. The molar extinction coefficient,  $\epsilon$ , of (1) is  $1.6 \times 10^5$  times larger than that of chloroform at 255 nm, which is the absorption maximum of (1). Primary photo-decomposition of chloroform is therefore excluded.

Furthermore, one may suspect that hexachloroethane and the tetrachloroethane are also formed *via* non-silane-diyl participating reactions of chloromethanes: *e.g.*, with photo-excited (1) directly,¶ or with silyl radicals which can be produced by photolysis of (1) and are known to abstract chlorine atoms. To eliminate this possibility, we carried out

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§ Since absorption bands of (1) and carbon tetrachloride overlap, chloroform was used.

¶ Although direct reaction of photochemically-excited (1) with chlorosilane has been proposed,<sup>4</sup> the reaction with chloroform has not been reported.

the photolysis experiment in the presence of hexamethylcyclotrisiloxane (2) which is known to give octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane (3) by a rapid reaction with dimethylsilane-diyl. Cyclohexane solutions of (1) were irradiated in the presence of chloroform and/or (2) for 30 min through a 2 cm chloroform filter. The results are summarized in Table 1. That chloroform and (2) inhibit the production of (3) and 1,1,2,2-tetrachloroethane, respectively, demonstrate that the same reactive species is participating in both reactions; namely, that dimethylsilane-diyl plays an important role in the formation of the tetrachloroethane.

We have no explanation for these conclusions yet. However, the results obtained suggest that chlorine abstraction from chloromethanes by dimethylsilane-diyl occurs.

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## References

- 1 P. P. Gaspar, in 'Reactive Intermediates,' vol. 1, eds. M. Jones, Jr., and R. A. Moss, Wiley-Interscience, New York, 1978, pp. 229–277.
- 2 Ref. 1, vol. 2, pp. 335–385.
- 3 M. Ishikawa and M. Kumada, *Chem. Commun.*, 1970, 612.
- 4 M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, 1972, **42**, 325.
- 5 H. S. D. Soysa, H. Okinoshima, and W. P. Weber, *J. Organomet. Chem.*, 1977, **133**, C17.