Formation and Selectivity of Tetrasila-adamantyl Silicon-centred Radical

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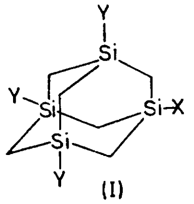
Summary The sila-adamantyl silicon-centred radical is readily formed from trimethyltetrasila-adamantane in the reaction with CCl_4 initiated by dibenzoyl peroxide and was found to have a selectivity toward halogen abstraction similar to that of simple triorganosilyl radicals when the reaction was carried out with $CBrCl_3$.

The tetrasila-adamantane system is relatively rigid and strain free.[1] This unique geometry is undoubtedly responsible for the unusually low reactivity observed for the tetrasila-adamantyl chlorides (Ib) and (Ic) toward a variety of common nucleophilic reagents.[2] Since it has been shown that acyclic non-rigid silyl radicals from optically active precursors can generally maintain their chirality,[3] it was of considerable interest to determine whether the formation and reactions of the sila-adamantyl silicon-centred radical have any unusual features in view of the relatively rigid cage-like structure of this radical. We now report our preliminary results with (Ia) which clearly show that the sila-adamantyl radical is readily formed and shows a selectivity in halogen abstraction comparable with that of triorgansilyl radicals.[4]



(I)

(I)

a; Y = Me, X = H
b; Y = Me, X = Cl
c; Y = X = Cl
d; Y = Me, X = Br

The tetrasila-adamantane (Ia) was treated with CCl_4 at 77 °C with dibenzoyl peroxide initiator (In) to give the chloride (Ib) in high yield. This reaction is known to proceed by a free-radical chain reaction involving the formation of silicon radicals which abstract halogen from the solvent CCl_4 to give the chlorosilane.[5] The general reaction is shown in equations (1—3). The formation of

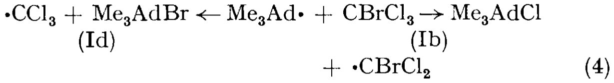
$$R_3SiH + In \rightarrow R_3Si\cdot + InH \qquad (1)$$

$$R_3Si\cdot + CCl_4 \rightarrow R_3SiCl + \cdot CCl_3 \qquad (2)$$

$$R_3SiH + \cdot CCl_3 \rightarrow R_3Si\cdot + CHCl_3 \qquad (3)$$

(Ib) from (Ia) was complete in *ca.* 1 h as determined by g.l.c analysis. The acyclic analogue of (Ia), $(Me_3SiCH_2)_3SiH$, reacted more slowly with CCl_4 under the same conditions, and this reaction was only 50% complete after 8 h. Thus the sila-adamantyl radical not only forms readily, but does so even faster than its acyclic analogue. The isolated products and the starting materials for both systems were characterized by i.r., n.m.r., and mass spectroscopy, and elemental analysis.

The selectivity of the sila-adamantyl radical toward halogen abstraction was determined by measuring the ratio of (Id) to (Ib) in the reaction of (Ia) with $CBrCl_3$ at 77 °C, by g.l.c. analysis of the reaction mixture using a detector response factor calculated from standard solution mixtures of authentic (Ib) and (Id) in $CBrCl_3$. The (Id)/(Ib) ratio was 2·55 ± 0·10. This product ratio is essentially the same as the ratios observed for a variety of silyl radicals of the general structure $R_3Si\cdot$, where R is alkyl and/or aryl.[4] Thus the sila-adamantyl radical appears to show no unusual properties either in its formation or selectivity in spite of its relatively rigid geometry.



$$\cdot CCl_3 + \underset{(Id)}{Me_3AdBr} \leftarrow Me_3Ad\cdot + CBrCl_3 \rightarrow \underset{(Ib)}{Me_3AdCl} + \cdot CBrCl_2 \qquad (4)$$

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[1] L. H. Sommer, 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965, ch. 9; C. L. Frye, J. M. Klosowski, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1970, **92**, 6379.

[2] A. L. Smith and H. A. Clark, *J. Amer. Chem. Soc.*, 1961, **83**, 3345; C. L. Frye and J. M. Klosowski, *ibid.*, 1972, **94**, 7186; G. D. Homer and L. H. Sommer, *J. Organometallic Chem.*, submitted for publication.

[3] H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, 1969, **91**, 519; A. G. Brook and J. M. Duff, *ibid.*, p. 2118; L. H. Sommer and L. A. Ulland, *J. Org. Chem.*, in the press.

[4] L. H. Sommer and L. A. Ulland, *J. Amer. Chem. Soc.*, in the press.

[5] Y. Nagai, K. Yamayaki, I. Shiojima, N. Kobori, and M. Hayashi, *J. Organometallic Chem.*, 1967, **9**, P21.