The Production of Organosilicon Radicals in Solution

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SEVERAL important reactions in organosilicon chemistry are believed to involve substituted silyl radicals as intermediates,[1] but lack of an unambiguous source of such radicals has prevented direct study of their reactions. We find that photolysis or pyrolysis of bistrimethylsilylmercury[2] provides such a source.

Thus when degassed solutions of bistrimethylsilylmercury in toluene are heated in the dark at 195° for two weeks, the products (in addition to the expected hexamethyldisilane and mercury[2]), as identified by gas chromatography, include trimethylsilane, bibenzyl, benzyltrimethylsilane, and some unidentified polysilane derivatives. This is consistent with the following reaction scheme:

$$\mathrm{Hg(SiMe_3)_2 \rightarrow Hg + 2Me_3Si\cdot}$$
$$\mathrm{2Me_3Si\cdot \rightarrow Me_3SiSiMe_3}$$
$$\mathrm{Me_3Si\cdot + CH_3{\cdot}Ph \rightarrow Me_3SiH + Ph{\cdot}CH_2\cdot}$$
$$\mathrm{Ph{\cdot}CH_2\cdot + \cdot SiMe_3 \rightarrow Ph{\cdot}CH_2{\cdot}SiMe_3}$$
$$\mathrm{2Ph{\cdot}CH_2\cdot \rightarrow Ph{\cdot}CH_2{\cdot}CH_2{\cdot}Ph}$$

Under similar conditions, benzene gives trimethylsilane and phenyltrimethylsilane, and chlorobenzene gives these products along with chlorotrimethylsilane. In neither case is a detectable amount of biphenyl formed, which suggests that the trimethylsilyl radicals do not directly abstract chlorine or hydrogen from the aromatic compound to give phenyl radicals, but that abstraction follows an initial addition to the ring.

Polymerization occurs when solutions of bistrimethylsilylmercury in styrene or methyl methacrylate are exposed to light.

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[1] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 45—51, 116—117, 122, 199; A. D. Petrov, B. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, "Synthesis of Organosilicon Monomers," Heywood and Co. Ltd., London, 1964, pp. 22—24, 286—293, 387—400; L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2662.

[2] E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbickler, and E. Staude, *Angew. Chem. Internat. Edn.*, 1963, **2**, 507.