PRELIMINARY NOTES

The interaction of aryl-silicon compounds and substituted silyl radicals

Nelson, Angelotti, and Weyenberg recently described the disproportionation of liquid phenylsilanes under the influence of ultraviolet radiation at 70–130° or in presence of peroxides or similar catalysts at 130–180°, and attributed it to the novel radical displacement reactions of type (1)[1]. The compound $PhMe_2SiH$ underwent such disproportionation,

$$\equiv Si^{*}\cdot + Ph{-}Si\equiv \rightleftharpoons Ph{-}Si^{*}\equiv + \equiv Si\cdot \qquad (1)$$

but no exchange of groups occurred between the compounds *o*-$MeC_6H_4SiMe_2Pr$ and Et_2MeSiH.

We now find that in the gas-phase at 500°, phenyltrimethylsilane and trichlorosilane react to give phenyltrichlorosilane and trimethylsilane; thus in a run involving initially 60 mm of trichlorosilane and 20 mm of phenyltrimethylsilane, 8.8 mm of the latter had disappeared after about 20 min. and 7.3 mm of phenyltrichlorosilane had been formed. (There were some side products, but formation of phenyltrichlorosilane accounted for 83 ± 8 % of the reaction.) The reverse reaction was found to occur about one-third as fast, indicating that an equilibrium, (2), is established.

$$Cl_3SiH + PhSiMe_3 \rightleftharpoons Me_3SiH + PhSiCl_3 \qquad (2)$$

The reaction between *p*-tolyltrimethylsilane and trichlorosilane is slower, and was studied at 543°; the main product was *p*-tolyltrichlorosilane, and no detectable amount of the *o*- or *m*-isomer was formed.

Under the conditions used, silicon hydrides are known to give radicals[2], and it can reasonably be assumed that the observed reactions involve radical displacements of type (1) [it being remembered that eqn. (1) indicates only the overall course of the displacement, and not the detailed mechanism, which may involve more than one step]. The high temperatures used are necessary to produce radicals from silicon hydrides in absence of catalysts, but the subsequent radical displacements would be expected to occur at much lower temperatures, and, in agreement, decomposition of bis(trimethylsilyl)mercury in phenyltrichlorosilane at 190° yields phenyltrimethylsilane[3].

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1 L. E. Nelson, N. C. Angelotti and D. R. Weyenberg, *J. Am. Chem. Soc.*, 85 (1963) 2662.
2 A. D. Petrov, V. F. Mironov, V. A. Ponomarenko and E. A. Chernyshev, *Synthesis of Organosilicon Monomers*, Heywood, London, 1964, p. 292; C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 47–50, 116.
3 C. Eaborn, R. A. Jackson and R. W. Walsingham, unpublished work.

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