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Preliminary communication

Thermal Si–Si/Si–Si redistribution of hexaorganodisilane. A new thermally 'forbidden' molecular reaction

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Two types of thermal reaction of hexamethyldisilane have been reported: homolysis of the Si–Si bond followed by a structural rearrangement by chain reactions involving silyl radicals[1-4] and homolysis of the Si–Si bond followed by non-chain reactions[5]. We report here a third type of thermal reaction of hexaorganodisilanes.

When n-propylpentamethyldisilane (Ia, 10.88g, 5.02 mmoles) was thermolyzed at 200° for 73 days in a sealed tube[★], symmetrized products, hexamethyldisilane (II, 0.67 mmole, 13.3%) and 1,2-di-n-propyltetramethyldisilane (IIIa, 0.68 mmole, 13.5%), were obtained in almost equal amounts along with unchanged I and a trace amount of low boiling products, presumably trimethylsilane and n-propyldimethylsilane (by VPC).

The reaction was reversible. Thus, an equimolar mixture of II and IIIa was synproportionated to Ia under similar reaction conditions.

$$\begin{array}{cccc} 2\text{n-PrMe}_2\text{SiSiMe}_3 & \xrightleftharpoons{\Delta} & (\text{Me}_3\text{Si})_2 & + (\text{n-PrMe}_2\text{Si})_2 \\ (\text{Ia}) & & (\text{II}) & (\text{IIIa}) \end{array}$$

Some other disilanes of a general formula of $RMe_2SiSiMe_3$ were also disproportionated to II and symmetrically substituted disilanes. These reactions were always very clean, no by-product being formed except a trace amount of low boiling materials.

$$\begin{array}{cccc} 2\text{RMe}_2\text{SiSiMe}_3 & \xrightleftharpoons{\Delta} & (\text{Me}_3\text{Si})_2 & + (\text{RMe}_2\text{Si})_2 \\ (\text{Ia-d}) & & (\text{II}) & (\text{IIIa-d}) \end{array}$$

(a, R = n-Pr; b, R = cyclo-Pr; c, R = Ph; d, R = $PhCH_2$)

[★] This lengthy but important method of thermolysis was used first by Eaborn and Simmie[4].

It is tempting to interpret these results in terms of the intermediacy of silyl radicals by either a dissociation–coupling mechanism, (*i*), or a substitution mechanism (*ii*).

(*i*) Dissociation–coupling mechanism:

$$2\mathrm{RMe_2SiSiMe_3} \rightleftharpoons 2\mathrm{RMe_2Si\cdot} + 2\mathrm{Me_3Si\cdot} \rightleftharpoons (\mathrm{Me_3Si})_2 + (\mathrm{RMe_2Si})_2$$

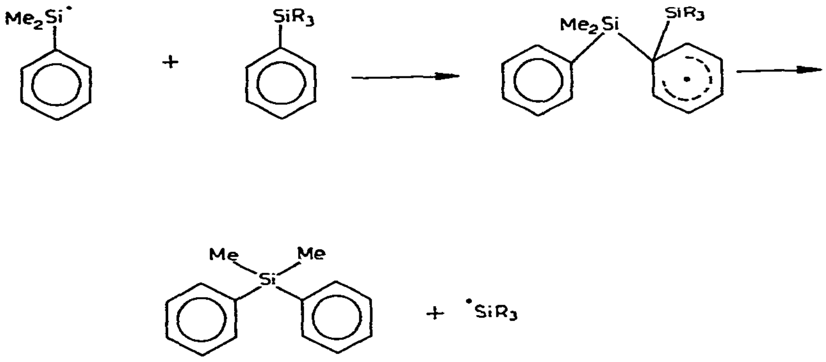
(*ii*) Homolytic substitution mechanism:

$$\mathrm{RMe_2SiSiMe_3} \longrightarrow \mathrm{RMe_2Si\cdot} + \mathrm{Me_3Si\cdot}$$

$$\mathrm{Me_3Si\cdot} + \mathrm{RMe_2SiSiMe_3} \longrightarrow (\mathrm{Me_3Si})_2 + \mathrm{RMe_2Si\cdot}$$

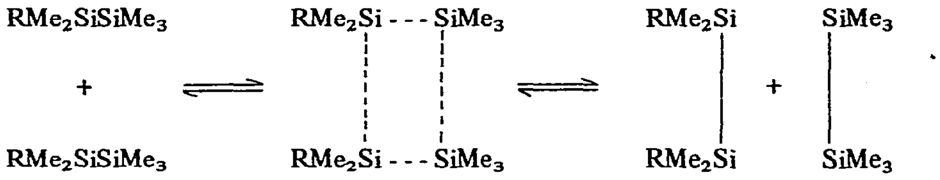
etc.

However, no redistribution of phenyl groups on silicon was observed in the reaction of Ic. If $\mathrm{PhMe_2Si\cdot}$ was actually produced under the condition from Ic, extensive phenyl–silyl exchange should occur to give $\mathrm{Ph_2SiMe_2}$ or other polyphenylated products[6,7].



Furthermore, when the reaction was carried out in chlorobenzene, redistribution took place invariably as above and no chlorosilane was detected in the products, although under these conditions silyl radicals are expected to abstract a chlorine atom from chlorobenzene[8,9].

The facts exclude silyl radicals as possible intermediates in this reaction, and we suggest instead a molecular mechanism, as follows:



This type of four-center molecular reaction should be thermally forbidden on the basis of orbital symmetry conservation[10, 11], and will have a substantial activation energy. The activation energies of such thermally 'forbidden' reactions may be estimated on the basis of dissociation energies of bonds both broken and formed[12]. In the present case, the strengths of bonds both broken and formed are almost identical and the maximum value of the activation energy may be calculated to be 67 kcal· mole^{-1} from a recent value of $D(\mathrm{Me_3Si{-}SiMe_3})$[13]. This value, though probably an overestimate, is not unlikely for the activation energy of a reaction as slow as that reported here.

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