Aluminium Chloride-catalysed Skeletal Rearrangement of Permethylated Linear Polysilanes

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Summary Permethylated linear polysilanes, $Me(Me_2Si)_nMe$ undergo skeletal rearrangement to branched-chain isomers very easily in the presence of aluminium chloride in boiling benzene.

WE reported recently that certain cyclohexasilanes undergo ring contraction very easily in the presence of aluminium chloride as catalyst to give silylcyclopentasilanes.[1] We now report the first examples of the skeletal rearrangement of three permethylated linear polysilanes (I) to the corresponding branched-chain isomers, (II), (III), and (IV), in the presence of the same catalyst.

$Me(Me_2Si)_nMe$ $(Me_3Si)_3SiMe$ $(Me_3Si)_4Si$
(I) a; $n = 4$ (II) (III)
b; $n = 5$
c; $n = 6$

$(Me_3Si)_3Si\cdot SiMe_2\cdot SiMe_3$
(IV)

Decamethyltetrasilane (Ia)[2,3] was treated with a catalytic amount of aluminium chloride in boiling benzene for 1 hr. G.l.c. showed that the rearrangement was complete at this point. Hydrolysis of the reaction mixture and removal of the solvent were followed by distillation to give tris(trimethylsilyl)methylsilane (II),[4,5] b.p. 106—108°/14 mm, m.p. 53·5—55·0° (lit.[4] b.p. 94—96°/7 mm.) The ^1H n.m.r. spectrum of (II) showed two sharp singlet peaks at τ 9·97 and 9·88 with relative integrated intensities of 1 : 9, attributable to SiMe and $SiMe_3$ protons, respectively.

Under the same conditions, dodecamethylpentasilane (Ib)[3] was converted into tetrakis(trimethylsilyl)silane (III),[5,6] m.p. 263—264° (lit.[6] 261—263°). In all respects, the product was identical with an authentic sample obtained by an independent synthesis.[6]

Tetradecamethylhexasilane (Ic)[3] underwent the skeletal rearrangement under substantially the same conditions as above to give 1-tris(trimethylsilyl)pentamethyltrisilane (IV), m.p. 156—157°. The structure of (IV) was verified by its ^1H n.m.r. spectrum, which exhibited signals at τ 9·90 and 9·79 in the ratio of 3 : 11, attributable, respectively, to the methyl groups attached to silicon in the 3-position, and the overlapping resonance of $(Me_3Si)_3Si$ with the internal Me_2Si group. The latter signal was resolved into two peaks upon measurement with the sweep width of 100 Hz.

In all three cases, yields of the rearrangement products were practically quantitative.

This research was supported by a Grant in Aid for Scientific Research from the Ministry of Education.

(*Received, November 28th*, 1969; *Com.* 1812.)

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