Photolysis of Dodecamethylcyclohexasilane

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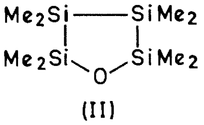
Summary The photolysis of dodecamethylcyclohexasilane produces two of the lower permethylated cyclopolysilanes, $(Me_2Si)_n$, $n = 4$ and 5, and dimethylsilylene Me_2Si:.

THE chemistry of permethylated cyclopolysilanes (I) is a subject of current interest.[1-4] Although the cyclohexasilane (I; $n = 6$)[5,6] has been known for some time and the cyclo-pentasilane (I; $n = 5$)[3,7,8] and -heptasilane (I; $n = 7$)[3] have been prepared recently, the cyclotetrasilane (I; $n = 4$) has not been isolated as yet. We now report that the photolysis of (I; $n = 6$) affords a most convenient and satisfactory approach to the synthesis of both the cyclopentasilane and -tetrasilane and a novel route to the generation of dimethylsilylene Me_2Si:.[9]

$(Me_2Si)_n$

(I)



(II)

$Et_2MeSi(SiMe_2)_nH$

(III)

A solution of (I; $n = 6$) (6·0 g) in 200 ml of dry cyclohexane was irradiated for 20 hr with a low-pressure mercury lamp with Vycor housing (2537 Å) under bubbling nitrogen at *ca.* 45°. Distillation of the reaction mixture gave a product (3·1 g) subliming below 150°/2 mm and a polymer (2·6 g) as residue. G.l.c. analysis of the sublimate revealed that it was composed of 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetrasilacyclopentane (II), cyclotetrasilane (I; $n = 4$), cyclopentasilane (I; $n = 5$) and unchanged cyclohexasilane (I; $n = 6$), in the ratio of 1 : 3 : 14 : 3. Each of these products was isolated by preparative g.l.c. and identified by elemental analyses and i.r., ^1H n.m.r., and mass spectroscopic studies. The cyclotetrasilane (I; $n = 4$) is a snow-white, fairly air-sensitive, crystalline compound, m.p. 105—106°, and its n.m.r. spectrum showed only one singlet peak, at τ 9·77, as expected. The identity of other products was established by comparison of their retention times on g.l.c., and their spectra, with those of authentic samples prepared by independent routes.

The formation of compound (II) may be ascribed to accidental oxidation of the cyclotetrasilane (I; $n = 4$) and that of the polymeric substance to the polymerization of the dimethylsilylene intermediate, Me_2Si:. The generation of this intermediate during the photolysis could be established by isolation of products arising from insertion of it into a silicon–hydrogen bond.[9b,e] Thus the irradiation of (I; $n = 6$) in the presence of diethylmethylsilane gave compounds (III; $n = 1$) and (III; $n = 2$) in the ratio of 2·5 : 1 in high yield, along with small amounts of (I; $n = 4$), (I; $n = 5$), and (II). Polymeric material was produced only in traces.

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