Ring Contraction of Cyclohexasilanes to Silylcyclopentasilanes and the Preparation of Monofunctional Nonamethylcyclopentasilanes

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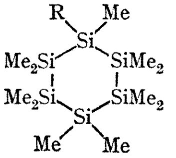
Summary Dodecamethylcyclohexasilane undergoes ring contraction with aluminium chloride as catalyst in the presence or absence of trimethylchlorosilane to give, respectively, chlorodimethylsilyl- or trimethylsilyl-cyclopentasilane, the former being convertible into monofunctional nonamethylcyclopentasilanes.

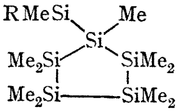
THE cyclohexane–methylcyclopentane isomerization catalysed by aluminium halides has been known for a long time.[1] We have now found that dodecamethylcyclohexasilane (Ia)[2,3] undergoes an analogous skeletal rearrangement to a silyl-substituted cyclopentasilane system very easily. Thus, treatment of (Ia) with a catalytic amount of aluminium chloride in benzene at room temperature or in refluxing cyclohexane produced trimethylsilylnonamethylcyclopentasilane (IIa) in almost quantitative yield, whilst chlorodimethylsilylnonamethylcyclopentasilane (IIb) was obtained along with (IIa) and other unidentified compounds as by-products when (Ia) was stirred at room temperature with a large excess of trimethylchlorosilane in the presence of the same catalyst. The structure of (II) was verified by mass and ^1H n.m.r. spectra and elemental analyses. Further evidence comes from chemical transformation of (IIb) (see below).

Chloroundecamethylcyclohexasilane (Ib) was obtained in 65% yield when dry HCl was passed at room temperature into a solution of (Ia) in cyclohexane containing aluminium chloride as catalyst, with the extent of reaction being monitored by g.l.c., and the reaction was quenched by the addition of a small quantity of acetone after a suitable time. Compound (Ib) was identified by conversion into (Ia) by the action of methylmagnesium bromide.

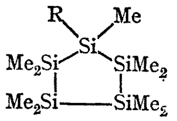
Compound (Ib) readily underwent almost complete rearrangement to (IIb) with aluminium chloride as catalyst in cyclohexane at room temperature, under which conditions (Ia) remained unchanged. Therefore, a possible mechanism for the rearrangement of (Ia) to (IIa) may involve initial formation of (Ib) as an intermediate, which arises from the aluminium chloride-catalysed chlorodemethylation[4,5] of (Ia) by HCl possibly present in traces in the reaction system. The ring contraction of this intermediate then proceeds, and finally, the aluminium chloride-catalysed Me–Si/Cl–Si exchange[6] between (IIb) and the starting material (Ia) completes the reaction cycle to afford the final product (IIa) and the intermediate (Ib).



(I) a; R=Me
b; R=Cl



(II) a; R=Me
b; R=Cl
c; R=Ph



(III) a; R=EtO
b; R=Cl
c; R=Me

Compound (IIb) proved to be a convenient starting material for the synthesis of hitherto unknown monofunctional nonamethylcyclopentasilanes. The method involves phenylation of (IIb) to (IIc) in the usual way, and subsequent treatment of the latter with 0·1N-sodium ethoxide in ethanol at room temperature to give ethoxynonamethylcyclopentasilane (IIIa) (65% yield), which could be converted into the corresponding chloro-compound (IIIb) in 88% yield by heating under reflux with a large excess of acetyl chloride, and into the known decamethylcyclopentasilane (IIIc)[7] by treatment with methyllithium.

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