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Preliminary communication

Stable silyl radicals; a novel route to branched-chain methylpolysilanes

MITSUO ISHIKAWA, AKIRA NAKAMURA and MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)
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SUMMARY

Highly branched-chain methylpolysilanes can be conveniently prepared by coupling of branched-chain polysilanyl radicals.

Eaborn *et al.* reported that trimethylsilyl radicals generated from bis(trimethylsilyl)mercury by photolysis in aromatic solvents undergo homolytic aromatic substitution to give aryltrimethylsilanes[1]. Sakurai and Hosomi have recently shown that trimethylsilyl and pentamethyldisilanyl radicals produced by decomposition of di-tert-butyl peroxide in the presence of the corresponding hydrosilanes react with aromatic compounds to give substitution products[2]. We report here our results for branched-chain polysilanyl radicals which show a different behaviour.

When a mixture of tris(trimethylsilyl)silane[3] (I) and a small excess of di-tert-butyl peroxide was heated at 130° in benzene for 24 h in a sealed glass tube, hexakis(trimethylsilyl)disilane[4] (II) was obtained in 92% yield.

$$\underset{\text{(I)}}{2(Me_3Si)_3SiH} \xrightarrow[130^\circ]{(\text{tert-BuO})_2} \underset{\text{(II)}}{(Me_3Si)_3SiSi(SiMe_3)_3}$$

Under the same conditions, the reaction of compounds (IIIa) – (IIId) with di-tert-butyl peroxide gave only less than 1% yields of the coupling products, along with

$$R^1Me_2SiSiR^2R^3H \xrightarrow[130^\circ]{(\text{t-BuO})_2} \underset{\text{(IV)}}{R^1Me_2SiSiR^2R^3Ph} + \text{other products}$$

(IIIa) $R^1 = R^2 = R^3 = Me$
(IIIb)[2] $R^1 = Me_3Si, R^2 = R^3 = Me$
(IIIc) $R^1 = R^2 = Me, R^3 = Ph$
(IIId) $R^1 = Me, R^2 = R^3 = Ph$

14–19% yield of homolytic aromatic substitution products (IV), other volatile products, and 40–55% yield of polymeric substances.

The present data suggest that only branched-chain (secondary or tertiary) polysilanyl radicals survive until they undergo dimerization processes. Indeed, undecamethylcyclohexasilane[5] and 2H-heptamethyltrisilane[6] were converted into bi-(undecamethylcyclohexasilanyl) (V) (66% yield) and 1,1,2,2-tetrakis(trimethylsilyl)-dimethyldisilane (VI) (52% yield), respectively, by similar treatment with di-tert-butyl peroxide in benzene, whereas the reaction of $(Me_3Si)_2Si(Me)SiMe_2H$, an isomer of (I), gave only 11% yield of the coupling product (VII); in this case, phenylated products (16% yield) and polymeric substances (42% yield) constituted the major products. The coupling products (II), (V), (VI) and (VII) were isolated by distillation or crystallization and characterized by IR, NMR and mass spectroscopy.

In general, the Wurtz-type reaction of highly branched-chain chloropolysilanes with alkali metal or silyllithium reagent gives very low yields of coupling products; for instance, the reaction of tris(trimethylsilyl)chlorosilane and tris(trimethylsilyl)silyllithium has been reported to produce only 7% yield of compound (II). In the light of this, the method described here affords a novel, convenient route to certain highly branched-chain methylpolysilanes from appropriate hydropolysilanes.

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