

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)

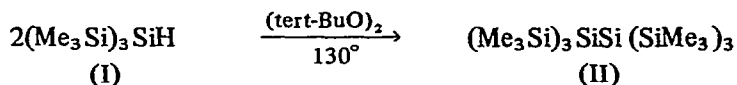
(Received July 16th, 1973)

SUMMARY

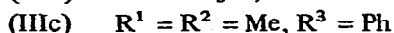
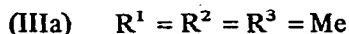
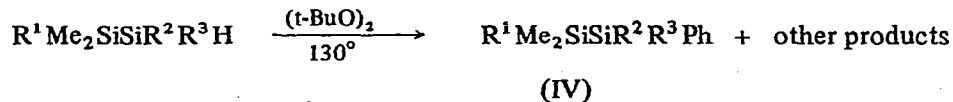
Highly branched-chain methylpolysilanes can be conveniently prepared by coupling of branched-chain polysilyanyl radicals.

Eaborn *et al.* reported that trimethylsilyl radicals generated from bis(trimethylsilyl)mercury by photolysis in aromatic solvents undergo homolytic aromatic substitution to give aryltrimethylsilanes¹. Sakurai and Hosomi have recently shown that trimethylsilyl and pentamethyldisilyl radicals produced by decomposition of di-*tert*-butyl peroxide in the presence of the corresponding hydrosilanes react with aromatic compounds to give substitution products². We report here our results for branched-chain polysilyanyl radicals which show a different behaviour.

When a mixture of tris(trimethylsilyl)silane³ (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)disilane⁴ (II) was obtained in 92% yield.



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



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) polysilylanyl radicals survive until they undergo dimerization processes. Indeed, undecamethylcyclohexasilane⁵ and 2H-heptamethyltrisilane⁶ 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 $(\text{Me}_3\text{Si})_2\text{Si}(\text{Me})\text{SiMe}_2\text{H}$, 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.

REFERENCES

- 1 C. Eaborn, R.A. Jackson and R. Pearce, *Chem. Commun.*, (1967) 920.
- 2 H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, 93 (1971) 1709.
- 3 H. Gilman, J.M. Holmes and C.L. Smith, *Chem. Ind.*, (1965) 848.
- 4 H. Gilman and R.L. Harrell, *J. Organometal. Chem.*, 5 (1966) 199.
- 5 M. Ishikawa and M. Kumada, *Synth. Inorg. Metal-org. Chem.*, 1 (1971) 191.
- 6 M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, 2 (1964) 478.