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Preliminary communication

CYCLIC POLYSILANES

VII *. NEW, STABLE CYCLOTETRASILANES BY DIRECT SYNTHESIS

MICHAEL BIERNBAUM and ROBERT WEST

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

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Permethylcyclopolysilanes, $(Me_2Si)_n$ with $n = 5$ to 8, can be obtained by condensation of dimethyldichlorosilane with alkali metals [2] but the very reactive $(Me_2Si)_4$ has been made only by photolysis of $(Me_2Si)_6$ [3]. We now find that t-butylmethyldichlorosilane undergoes condensation to give highly unreactive four-membered ring compounds, $(t\text{-}BuMeSi)_4$, as the only isolated cyclopolysilane products. These new cyclotetrasilanes show unusual electronic properties and interesting isomeric structures.

Reductive coupling t-butylmethyldichlorosilane with sodium—potassium alloy in tetrahydrofuran under the conditions described earlier for Me_2SiCl_2 [2] gave 1,2,3,4-tetra-t-butyl-1,2,3,4-tetramethylcyclotetrasilane (I) in crude yields of about 25%. After 4 h of refluxing the reaction product was filtered and solvent was stripped off leaving a white residue which was recrystallized from acetone to give colorless needles of I, m.p. 228.5—230°. (Anal. Found: C, 59.65; H, 11.79; Si, 27.92. $C_{20}H_{48}Si_4$ calcd.: C, 59.91; H, 12.07; Si, 28.02%.)

Compound I is obtained as an approximately 2/1 mixture of two isomers, Ia and Ib possibly accompanied by traces of a third isomer. A small quantity of isomer Ia was obtained pure as white prisms, m.p. 232—232.5°, by slow evaporation of an ether solution of I. The NMR spectrum (CCl_4) of Ia only showed absorptions at δ 1.03 (s, $Si(CH_3)_3$, 3) and δ 0.43 (s, $Si\text{-}CH_3$, 1), consistent with an all *trans* structure. X-ray crystallography confirms the all *trans* structure of Ia [4]; the four-membered ring is folded so as to bring all of the t-butyl groups into quasi-equatorial positions.

The crude crystalline product I shows, in addition to peaks for Ia, NMR absorptions at δ 1.15, 1.08, 0.35 and 0.25, with relative intensities 3/9/3/1 respectively, attributed to Ib. The spectrum suggests a structure with three nearly equivalent and one nonequivalent t-BuSiMe groups. A possible structure is that shown for Ib, which has one quasi-axial t-butyl group and one quasi-equatorial methyl.

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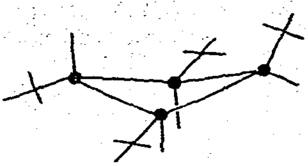
[*] For part VI see ref. 1.

(Ia)



(Ib)

Two properties of Ia are especially noteworthy: an ultraviolet absorption at 300 nm ($\epsilon = 290$) and a first ionization potential at 7.2 eV (photoelectron spectroscopy). Both values are much lower in energy than for other cyclopolysilanes and in fact are the lowest yet recorded for any polysilanes.

Unlike the permethyl analog which undergoes very rapid oxidation in air, I is entirely inert to oxygen at ordinary temperatures. Moreover, I is not even attacked by warm H_2SO_4 or $HCl{-}AlCl_3$, standard demethylation reagents for permethylpolysilanes. Like other peralkylcyclosilanes, I undergoes reduction to form an anion radical observable by electron spin resonance spectroscopy. Further studies of the electronic properties, structures and reactions of these four-membered ring silanes are in progress.

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