# Notes

## Cleavage Reactions of the Silicon–Silicon Bond of Hexaphenyldisilane

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In the course of our current research in the area of organometallic compounds it was necessary to understand the nature of the hydrolytic and oxidative stability of hexaphenyldisilane (I). It is reported that I is cleaved at the silicon–silicon bond by active metals,[2,3] organometallic reagents,[4] and halogens.[5,6] It is apparently stable, however, when subjected to a number of free-radical reactions[4] and to hydrolysis by hot, moist piperidine.[6,7]

It was felt that the studies which have been made are inadequate to explain the hydrolytic and oxidative properties of I and are in fact causes for a degree of uncertainty.[8] Therefore, a short study of the hydrolysis and oxidation reaction of I was undertaken.

It was found that I, like many polysilanes,[9] is hydrolyzed by alcoholic alkali to give hydrogen and triphenylsilanol. This reaction proceeded only when a strong nucleophilic reagent was present. A mixture of tetrahydrofuran (THF), carbon tetrachloride, and 30% hydrogen peroxide was inadequate for the reaction in spite of the fact that I dissolved more readily in the mixed solvent than in alcohol. Triphenylsilanol was obtained as a product when a mixture of I, THF, 30% hydrogen peroxide, and sodium hydroxide was heated at reflux for 24 hr.

Hydrochloric acid in THF and a mixture of iodine and potassium iodide in 95% ethanol failed to react with I.

The oxidative stability of I was investigated by heating the material in the presence of silver and sodium nitrate. When a mixture of I and silver nitrate was slowly heated the first evidence for reaction was noted at 198°. The reaction became violent at 230° and was accompanied by the evolution of a heavy brown gas and suspended solid particles. Attempts to isolate and identify any product were unsuccessful. A much milder reaction occurred when the silver nitrate was replaced with sodium nitrate. Reaction occurred at 360° and hexaphenyldisiloxane was isolated as one of the products.

This same series of reactions was carried out replacing I with tetraphenylsilane. In no instance was there any evidence for reaction.

Infrared spectroscopy was extremely useful in following the course of the reactions studied. The infrared spectrum of I, in addition to the absorption bands common to the tin, germanium, and lead analogs and derived mainly from the attached phenyl groups, exhibits a sharp absorption band at 9.07 $\mu$. The spectrum of hexaphenyldisiloxane exhibits bands at 8.98 and 14.0 $\mu$ in addition to those found for I. It was noted that the published infrared spectra of I, such as that included in the Sadtler Standard Spectra,[10a] are actually those of mixtures of I and its oxide, hexaphenyldisiloxane. The spectrum of triphenylsilanol exhibits a doublet with bands at 11.7 and 12.0 $\mu$. A similar doublet occurs in the spectrum of triphenyltin hydroxide, the bands occurring at 8.3 and 11.0 $\mu$.[10b]

### Experimental Section

Hexaphenyldisilane was purchased from Peninsular Chem-Research, Inc., and was recrystallized from carbon tetrachloride before use, mp 364° (lit.[11] mp 368–370°). All other chemicals were reagent grade and were used without further purification.

All melting points are uncorrected.

Infrared spectra were obtained on a Model 137 Perkin-Elmer Infracord.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Hydrolysis of Hexaphenyldisilane by Various Reagents. A. Alcoholic Potash.**—A mixture of 1.04 g (0.002 mole) of I, 11.2 g (0.2 mole) of potassium hydroxide, and 400 ml of 95% ethyl alcohol contained in a flask fitted with a reflux condenser and attached to an inverted water-filled buret in order to measure gas evolution was heated at reflux for 23 hr. There was collected 45 ml of gas. The reaction mixture was concentrated under vacuum on a rotary evaporator to give a thick liquid. Dilute hydrochloric acid was added and the white solid which precipitated was removed by filtration, 1.10 g. Recrystallization of this material from methyl alcohol gave 0.97 g of triphenylsilanol, mp 148–150° (lit.[12] mp 150.5–151.5°). The infrared spectrum of this material was identical with that of an authentic sample.

**B. Hydrogen Peroxide.**—A mixture of 2.59 g (0.005 mole) of I, 8 ml of 30% hydrogen peroxide, 250 ml of THF, and 100 ml of carbon tetrachloride was heated at reflux for 43 hr. Work-up of the reaction mixture indicated that no reaction had occurred.

**C. Alkaline Hydrogen Peroxide.**—A mixture of 2.59 g (0.005 mole) of I, 10 ml (0.088 mole) of 30% hydrogen peroxide, 10 ml (0.088 mole) of 35.5% sodium hydroxide, and 500 ml of THF was heated at reflux for 24 hr. The reaction mixture was concentrated under reduced pressure, the concentrate was treated with methyl alcohol, and the white solid was removed by filtration. The solid material was dissolved in carbon tetrachloride and after further work-up there was obtained 0.1 g of hexaphenyldisiloxane, mp 225–228° (lit.[8] mp 226°). The infrared spectrum of this material was identical with that of an authentic sample.

The white precipitate which formed when the methyl alcohol filtrate was diluted with water was removed by filtration, and taken up in and recrystallized from carbon tetrachloride. There

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(2) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(3) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(4) H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *ibid.*, **81**, 5320 (1959).

(5) T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 913 (1958).

(6) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 647 (1921).

(7) F. S. Kipping and J. E. Sands, *ibid.*, **119**, 848 (1921).

(8) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p 354.

(9) F. G. A. Stone and R. West, *Advan. Organometal. Chem.*, **7**, 106 (1964).

(10) (a) "Sadtler Standard Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1959, Spectrum No. 1613. (b) B.Kushlefsky, I. Simmons, and A. Ross, *Inorg. Chem.*, **2**, 187 (1963).

(11) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 3762 (1953).

(12) H. Marsden and F. S. Kipping, *J. Chem. Soc.*, **93**, 198 (1908).

was obtained 1.83 g of triphenylsilanol, mp 148–150° (lit.[11] mp 150.5–151.5°). The over-all yield of hydrolysis products was 74.5%

*Anal.* Calcd for $C_{18}H_{16}OSi$: C, 78.26; H, 5.79; Si, 10.14. Found: C, 78.76, 78.87; H, 6.05, 6.15; Si, 10.06, 10.10.

**D. Hydrochloric Acid.**—A mixture of 5.18 g (0.01 mole) of I, 20 ml of 37% hydrochloric acid, and 20 ml of THF was stirred at room temperature for 28 hr. All of the starting I was recovered unchanged.

**E. Iodine and Potassium Iodide.**—A small amount of iodine and potassium iodide was added to a suspension of 1 g of I in 200 ml of 95% ethanol. The mixture was heated at reflux overnight. The iodine color persisted indicating the lack of any reaction.

**Oxidation of I by Nitrate Salts. A. Silver Nitrate.**—A mixture of 2.07 g (0.004 mole) of I and 1.02 g (0.006 mole) of silver nitrate was heated in a test tube. At 198° the mixture began to turn brown and at 230° a vigorous reaction occurred with the evolution of a heavy brown gas and suspended particles. Attempts to isolate and identify products were unsuccessful.

**B. Sodium Nitrate.**—A mixture of 3.0 g of hexaphenyldisilane and an excess of sodium nitrate was heated in a test tube. The solid material started to melt and turn brown at 360° and the temperature was held at this point for 1 hr. After cooling to room temperature, the reaction mixture was extracted with carbon tetrachloride. The extract was concentrated and the unreacted disilane which precipitated was removed by filtration. Concentration of the filtrate gave a solid which had an infrared spectrum identical with that of hexaphenyldisiloxane.

**Reactions of Tetraphenylsilane.**—All of the above reactions were repeated using tetraphenylsilane in place of I. In no case was any reaction observed.

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## (+)-(*S*)-2-Methylbutylsilane. Optical Asymmetry Due to Silicon *vs.* Carbon

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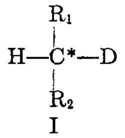
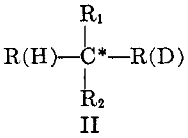
The physical observability of asymmetry in molecular structures of type I has been theoretically explained[2] and is well established by experimental studies on compounds such as α-deuterioethylbenzene,[3] 1-butanol-1-*d*,[4] butane-2-*d*,[5] and ethanol-1-*d*.[6] In these compounds the unequivalent rotatory contributions of hydrogen and deuterium atoms, compared at the optical center, give rise to a net rotation of transmitted plane-polarized light. Compounds of structure type II, wherein R(H) and R(D) are the same organic groups differing only in hydrogen isotope content, have also been described as displaying optical activity.[7] An analogous comparison has not previously been made for an asymmetric center resulting from replacement of a carbon atom by silicon. We wish to report an example of such a case.



$$H-\overset{R_1}{\underset{R_2}{C^*}}-D$$

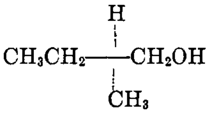
I



$$R(H)-\overset{R_1}{\underset{R_2}{C^*}}-R(D)$$

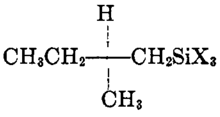
II

(+)-(*S*)-2-Methylbutylsilane[8] was synthesized by a sequence involving conversion of (−)-(*S*)-2-methylbutanol (III), by thionyl chloride and pyridine to (+)-(*S*)-2-methyl-1-chlorobutane,[9] transformation to the corresponding Grignard reagent,[10] and condensation with silicon tetrachloride to give a 74.5% yield of (+)-(*S*)-2-methylbutyltrichlorosilane, (IV), bp 166–167°, $d^{20}_4$ 1.1277, $[\alpha]^{20}{}_D$ 11.065°.[11] Treatment of the chlorosilane with lithium aluminum hydride in butyl ether yielded (69%) of (+)-(*S*)-2-methylbutylsilane, (V), bp 78–79°, $d^{20}_4$ 0.7085, $n^{20}{}_D$ 1.4056, $[\alpha]^{20}{}_D$ 9.454°. The ultraviolet absorption spectra for compounds III and V showed no bands from 7000 to 2200 A. Their optical rotatory dispersion curves from 6600 to 2300 A were negative plain and positive plain, respectively, as is typical of compounds devoid of optically active absorptions bands in the spectral range covered.[12]



$$CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-CH_2OH$$

III



$$CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-CH_2SiX_3$$

IV, X = Cl
V, X = H

From the observed rotation value it appears that the asymmetric contribution of the $-CH_2SiH_3$ group is very similar in magnitude and sign to that of the propyl group, based on the semiempirical correlating concepts of Brewster,[13] in optical activity. The analogous molar rotation values for (+)-(*S*)-3-methylhexane are +10.0° (calcd) and +9.9° (obsd).

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[2] W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

[3] E. L. Eliel, *ibid.*, **71**, 3972 (1949).

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[6] H. R. Levy, F. A. Loewus, and B. Vennesland, *J. Am. Chem. Soc.*, **79**, 2949 (1957); F. A. Loewus, F. H. Westheimer, and B. Vennesland, *ibid.*, **75**, 5018 (1953).

[7] K. Mislow, R. E. O'Brien, and H. Schaefer, *ibid.*, **82**, 5512 (1960); C. Martius and G. Schorre, *Ann.*, **570**, 140 (1950).

[8] For the R–S configurational nomenclature and conventions, see R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

[9] H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2563 (1942).

[10] L. Lardicci and L. Conti [*Ann. Chim.* (Rome), **51**, 823 (1961)] claim that less than 3% racemization occurs in this step.

[11] NOTE ADDED IN PROOF.—After the submission of this paper, E. I. Klabunovskii, L. F. Godunova, and A. A. Balandin [*Vysokomolekul. Soedin.*, **8**, 441 (1966)] published a report on an optically active organosilicon polymer obtained by hydrolysis of (+)-2-methylbutyltrichlorosilane. However, their rotation value for this trihalide, $[\alpha_D]$ +6.18°, is significantly lower than ours, as is also their density determination, $d^{20}_4$ 1.0552. Moreover, this latter is also at substantial variance with others reported for the various other isomeric pentyltrichlorosilanes: *n*-pentyl, $d^{20}_4$ 1.1330 [M. G. Voronkov and B. N. Dolgov, *Zh. Obshch. Khim.*, **24**, 1082 (1954)]; 3-methylbutyl, an old doubtful density value of 1.066 at an unspecified temperature [(W. Melzer, *Ber.* **41**, 3390 (1908)]; 1-methylbutyl, $d^{20}_4$ 1.150 [M. G. Voronkov, N. G. Romanova, and L. G. Smirnova, *Chem. Listy*, **52**, 640 (1958)]; 1,2-dimethylpropyl, $d^{20}_4$ 1.155 [V. A. Kolesova and M. G. Voronkov, *Chem. Listy*, **51**, 686 (1957); *Collection Czech. Chem. Commun.*, **22**, 851 (1957)]. Analogous discrepancies are also apparent in the refractive index value. Unfortunately, Klabunovskii, *et al.*, give no preparative details for the alkyltrichlorosilane. They state (translated): "synthesis and properties... are described earlier," but no reference is cited and we have been unable to locate any. We had also, prior to the Russian publication, prepared the hydrolytic product, the polysiloxane polymer (to be described elsewhere), but found it to be a very viscous liquid and not, as reported, a solid softening at 99–102°. We are at a loss to understand the cause of the disagreement but feel, as a result of successful multiple repetitions of our work, that we will maintain the claims of our paper.

[12] P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, p 14.

[13] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).