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.

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

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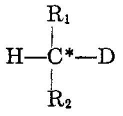
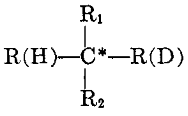
Received April 13, 1966

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.



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

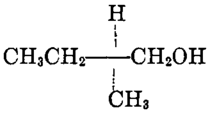
I



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

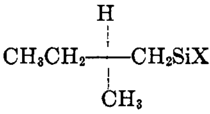
II

(+)-(*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]



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

III



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

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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[1] Visiting Research Associate (under Ohio State University Research Foundation contract) on summer leave from Department of Chemistry, University of Dayton, Ohio.

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

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

[4] A. Streitwieser, *ibid.*, **75**, 5014 (1953).

[5] G. K. Helmkamp, C. D. Joel, and H. Sharman, *J. Org. Chem.*, **21**, 844 (1956).

[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).

Compounds IV and V appear to be the first reported compounds possessing an asymmetric alkyl group attached directly to silicon.

Experimental Section

(+)-(*S*)-2-Methyl-1-chlorobutane (VI).—(−)-(*S*)-2-Methylbutanol (III), commonly known as primary active amyl alcohol, (obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, and further fractionally distilled to 98+% optical purity)[14] was converted to the chloride, (+)-(*S*)-2-methyl-1-chlorobutane, in 73% yield, by reaction with thionyl chloride and pyridine, according to the method of Brown and Groot.[9] The product, bp 98.5–99.0° at 755 mm, had $\alpha^{20}\text{D}$ 1.45° (neat, 1 dm), corresponding to 95+% optical purity.[15]

(+)-(*S*)-2-Methylbutyltrichlorosilane (IV).—Into a 1-l. three-necked, round-bottom flask equipped with a drying tube, condenser, and magnetic stirrer were placed 10.10 g (0.415 mole) of magnesium turnings, 1 ml of (+)-(*S*)-2-methyl-1-chlorobutane, (active amyl chloride, VI), and 10 ml of anhydrous ethyl ether. With the addition of a small crystal of iodine, the reaction to give the Grignard reagent was initiated. The mixture was diluted with 350 ml of ethyl ether and a total of 42.90 g (0.403 mole) of active amyl chloride (VI) was added over a period of 1 hr, with stirring. After the addition, the system was kept at reflux temperature by external heating for another hour. The solution was filtered through a glass wool plug into a 500-ml dropping funnel and slowly added to a solution of 98.10 g (0.577 mole) of freshly distilled silicon tetrachloride in 350 ml of ethyl ether over a period of 1.5 hr. After another hour of heating, the solution was filtered from the heavy precipitate of magnesium halide. The filtrate and ether washings of this latter salt were combined and fractionally distilled. There was obtained 61.6 g (74.5% yield) of (+)-(*S*)-2-methylbutyltrichlorosilane (IV), bp 165–167° at 755 mm, $\alpha^{20}\text{D}$ +12.470° (neat, 1 dm), d^{20}_4 1.1270, $[\alpha]^{20}\text{D}$ +11.065°.

Anal. Calcd for $C_5H_{11}SiCl_3$: C, 29.21; H, 5.39; Si, 13.66; Cl, 51.73. Found: C, 29.44; H, 5.50; Si, 13.45; Cl, 51.65.

(+)-(*S*)-2-Methylbutylsilane (V).—To a solution of 6.60 g of lithium aluminum hydride in 350 ml of previously dried and distilled di-*n*-butyl ether was slowly added, over a period of 90 min, 28.24 g (0.138 mole) of (+)-(*S*)-2-methylbutyltrichlorosilane. After standing overnight at room temperature, the reaction mixture was distilled until the fractions condensing showed, by vapor phase chromatography on a Barber–Colman Model 61C capillary chromatograph, no component peaks earlier than the solvent dibutyl ether. The collected forerun was redistilled through a glass helices packed column to give 9.7 g (69% yield) of (+)-(*S*)-2-methylbutylsilane, bp 77–79° at 755 mm, $\alpha^{20}\text{D}$ +13.289° (neat, 1 dm), d^{20}_4 1.4056, $[\alpha]^{20}\text{D}$ +9.454°.

Anal. Calcd for $C_5H_{14}Si$: C, 58.74; H, 13.79; Si, 24.47. Found: 58.47; H, 13.76; Si, 24.67.

The infrared absorption spectrum of a film of the neat product, obtained with a Perkin-Elmer Model 21 instrument, showed a strong sharp peak at 4.65 μ, characteristic of Si–H bond stretching, and absent in the starting material. The ultraviolet absorption spectrum, taken on a Cary Model 14 spectrophotometer, for a 5% solution of the silane in spectroquality *n*-hexane in a 1-cm cell showed no significant bands or absorption down to 2200 A (45,500 cm^{-1}).

Optical Rotatory Dispersion.—The ORD curves were obtained on the Bendix Model 460-C Polarmatic recording spectropolarimeter. No Cotton effect or other unusual features were noted in the data. (−)-(*S*)-2-methylbutanol exhibited a negative plain rotatory dispersion curve [$[\alpha]^{20}$ −8.3° (5000 A), −18.5° (4000°), −60.5° (3000 A)]; while (+)-(*S*)-2-methylbutylsilane showed a positive plain curve [$[\alpha]^{20}$ +13.6° (5000 A), +23.5° (4000 A), +56.5° (3000 A)].

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[14] Optical purity calculation is based on pure reference values of $\alpha^{18}\text{D}$ (neat, 2 dm) −9.63°, $[\alpha]^{18}\text{D}$ −5.88°, d^{18}_4 0.8187, of P. LeCouteur, J. Kenyon, and T. A. Rohan, *J. Appl. Chem.*, **1**, 341 (1951).

[15] Calculation based on pure reference values of $\alpha^{18}\text{D}$ (neat, 2 dm) +2.93°, $[\alpha]^{14}\text{D}$ 1.71°, d^{18} 0.8862, estimated from the data of A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 687 (1913); P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, **24**, 1399 (1959).

The 1,4-Cycloaddition Reaction between N-Sulfinylbenzenesulfonamide and 1,3-Cyclopentadiene. An Equilibrium Study

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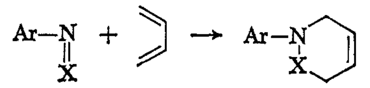
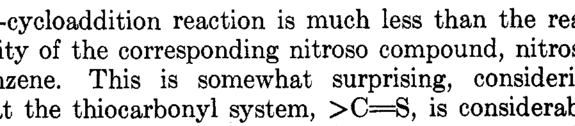
The N-sulfinyl group resembles the nitroso group in its behavior as a dienophile toward conjugated dienes.[2,3] The reactivity of N-sulfinylaniline[2,3] in a 1,4-cycloaddition reaction is much less than the reactivity of the corresponding nitroso compound, nitrosobenzene. This is somewhat surprising, considering that the thiocarbonyl system, >C═S, is considerably more reactive than the carbonyl system in a 1,4-cycloaddition reaction.[4,5]



X = O or S→O

Electron-withdrawing substituents generally tend to increase the reactivity of the N-sulfinyl group. Thus, N-sulfinylbenzenesulfonamide appears to have about the same reactivity as nitrosobenzene. Either compound may react explosively with undiluted 2,3-dimethyl-1,3-butadiene at room temperature. Essentially quantitative yields of 1,4 cycloadducts have been obtained from this N-sulfinyl derivative and a variety of 1,3-conjugated dienes[3] including 1,3-cyclohexadiene.

A 1,4 cycloadduct[2] of N-sulfinylbenzenesulfonamide and 1,3-cyclopentadiene may be isolated at low temperatures (<−5°). This adduct dissociates into its components at room temperatures. Although nitrosobenzene and 1,3-cyclopentadiene behave similarly, N-sulfinylaniline has been reported not to form a 1,4 cycloadduct under these reaction conditions.[2,3]



Determination of the equilibrium constant at various temperatures of the reversible reaction between N-sulfinylbenzenesulfonamide and 1,3-cyclopentadiene provides not only a comparison with the reaction between nitrosobenzene and 1,3-cyclopentadiene but also with "conventional" Diels–Alder reactions such as the dimerization of 1,3-cyclopentadiene.

N-sulfinylbenzenesulfonamide lends itself well to kinetic studies. It exhibits a strong absorption band in the visible spectrum at 412 mμ in dichloromethane solution, and dilute solutions follow the Beer–Lambert

[1] Abstracted from the Ph.D. dissertation of A. Macaluso presented to Tulane University, Aug 1965.

[2] G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem. Intern. Ed. Engl.*, **1**, 89 (1962).

[3] G. Kresze, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 13.

[4] W. J. Linn, *J. Org. Chem.*, **29**, 3111 (1964).

[5] J. Hamer and J. A. Turner, ref 3, Chapter 8.