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 $\alpha^{20}{}_{\mathrm{D}}$ 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, $\alpha^{20}{}_{\mathrm{D}}$ +12.470° (neat, 1 dm), $d^{20}{}_4$ 1.1270, $[\alpha]^{20}{}_{\mathrm{D}}$ +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, $\alpha^{20}{}_{\mathrm{D}}$ +13.289° (neat, 1 dm), $d^{20}{}_4$ 1.4056, $[\alpha]^{20}{}_{\mathrm{D}}$ +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 $\alpha^{18}{}_{\mathrm{D}}$ (neat, 2 dm) −9.63°, $[\alpha]^{18}{}_{\mathrm{D}}$ −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 $\alpha^{18}{}_{\mathrm{D}}$ (neat, 2 dm) +2.93°, $[\alpha]^{14}{}_{\mathrm{D}}$ 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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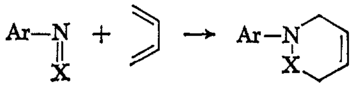
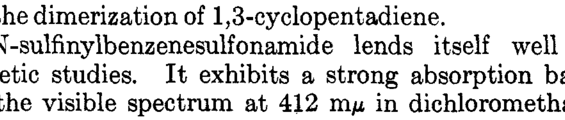
The N-sulfinyl group resembles the nitroso group in its behavior as a dienophile toward conjugated dienes.[2,3] The reactivity of N-sulfinylaniline[2,3] in a 1,4-cycloaddition reaction is much less than the reactivity of the corresponding nitroso compound, nitrosobenzene. This is somewhat surprising, 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

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[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.

law. This absorption band is absent in the 1,4 cycloadduct and in 1,3-cyclopentadiene.

The equilibrium constant for the reaction between N-sulfinylbenzenesulfonamide and 1,3-cyclopentadiene was determined by preparing solutions of diene and dienophile of known initial concentrations, measuring the concentration of the N-sulfinyl derivative at equilibrium, and calculating the concentrations of diene and cycloadduct at equilibrium. This was done for three different sets of initial concentrations at four different temperatures, as summarized in Table I.

TABLE I

DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE REACTION BETWEEN N-SULFINYLBENZENESULFONAMIDE AND 1,3-CYCLOPENTADIENE IN DICHLOROMETHANE

Temp, ±0.1°C	Initial concn of N-sulfinylbenzenesulfonamide, moles/l. × 10^2	Initial concn of 1,3-cyclopentadiene, moles/l. × 10^2	Equil concn of 1,4-cycloadduct, moles/l. × 10^3	Equil const	Equil const, av
10	2.252	2.383	8.03	35.1	
10	2.163	2.217	7.31	35.2	35.9
10	1.820	2.000	6.19	37.3	
15	2.252	2.383	6.52	23.6	
15	2.163	2.217	5.87	23.0	23.8
15	1.820	2.000	4.95	24.8	
20	2.252	2.383	5.73	18.9	
20	2.163	2.217	5.14	18.3	18.8
20	1.820	2.000	4.24	19.3	
25	2.252	2.383	4.13	11.4	
25	2.163	2.217	3.63	10.9	11.2
25	1.820	2.000	2.95	11.3	

A plot of the logarithm of the average equilibrium constant *vs.* the inverse absolute temperature yielded a straight line. The standard heat of reaction was obtained from the slope of the straight line, using the Gibbs–Helmholtz equation, and was found to be −13.9 kcal. The standard free-energy change was found to be −1.4 kcal at 25°, and the standard entropy change was −41.9 eu, also at 25°.

These results are quite comparable to the thermodynamic parameters recently reported[6] for the corresponding 1,4-cycloaddition reaction between nitrosobenzene and 1,3-cyclopentadiene. For this reaction, $\Delta H° = -14.8$ kcal and $\Delta S° = -44.6$ eu at 25°. For both equilibria, the standard heats of reaction are somewhat lower than for "conventional" Diels–Alder reactions, such as the dimerization of 1,3-cyclopentadiene in either the gaseous or the condensed state.[7] On the other hand, the standard entropy change is somewhat higher.[7] Both parameters however seem to fall well within the general pattern of a 1,4-cycloaddition pattern.

Experimental Section

Materials.—1,3-Cyclopentadiene (bp 39–40°, n_D 1.4446) was prepared by pyrolytic depolymerization and distillation of the commercially available dicyclopentadiene at atmospheric pressure.[8] The purity of the monomer was ascertained by gas–liquid partition chromatography. The Perkin-Elmer Model 154 gas chromatograph was also used for this analysis with 20% QF-1 on Chromosorb P 30–60 mesh, column packing. The gas–liquid partition chromatographic analysis of the cyclopentadiene was carried out at two different column temperatures (~100 and ~180°) to ascertain the absence of impurities such as cyclopentane or polymerized cyclopentadiene. In each case a single peak was obtained.

N-Sulfinylbenzenesulfonamide was prepared by the reaction of benzenesulfonamide and thionylchloride in 20% yield, mp 70–71° (lit.[9] mp 70–71°).

Spectrograde quality dichloromethane was obtained from Eastmen Organic Chemicals.

Equilibrium Constant Measurements. Mechanics of Measurements.—A Beckman Model DB spectrophotometer was used for these studies. Volumes of the solutions were measured in a 1.0-cm silica cell (3-ml capacity) fitted with a ground-glass stopper. The spectrophotometer cell compartment was thermostated by means of circulating water jacket. Within the cell compartment temperature measurements were made with a calibrated thermometer. Observations of the temperature of the closed compartment over prolonged periods showed that temperature variation was less than ±0.1° at the temperatures employed (10, 15, 20, and 25°). A Mettler analytical balance was used for weighings and hypodermic syringes were employed to measure the small volumes of liquids.

Determination of the Equilibrium Constant.—Samples of conjugated diene, 1,3-cyclopentadiene, and N-sulfinylbenzenesulfonamide were accurately weighed into volumetric flasks and solutions were made up with the Spectrograde quality solvent dichloromethane. Plots of absorbances *vs.* concentrations were constructed for N-sulfinylbenzenesulfonamide at 412 mμ in dichloromethane at various temperatures. The concentrations of N-sulfinylbenzenesulfonamide employed were such that they obeyed the Beer–Lambert law. One-half hour before each run, the reactant solutions were placed in a water bath thermostated at the reaction temperature. At time zero, a 5.0-ml portion of the N-sulfinylbenzenesulfonamide solution was transferred by means of a syringe into 5.0 ml of 1,3-cyclopentadiene solution. Mixing was carried out in a flask (25-ml capacity) maintained at the reaction temperature. A portion (3 ml) of the reaction mixture was transferred by means of a hypodermic syringe into the cell and placed in the thermostated cell compartment, and the absorbance was measured after each 30 min till the absorbance was constant at equilibrium. Data have been summarized in Table I.

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N-Haloalkylamines. Analyses and Amination of Toluene[1]

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Although a number of different analytical procedures, *e.g.*, iodometry[6] and ultraviolet[7] and nmr spectroscopy,[6] have been used for analysis of N-halamines, this area has need for more thorough and systematic study. As examples of difficulties that have been encountered, one can cite the inability to obtain many of the members

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(1) Chemistry of N-Halamines. V.

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(6) P. Kovacic, C. T. Gorlaski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965).

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