83–84°) and n.m.r. spectra obtained both for the pure primary alcohol and the residue of the mother liquor. There were no extraneous resonance signals indicating the presence of the secondary alcohol. The n.m.r. spectrum displayed the two triplets (in δ values) at 1.63 and 3.72.

H. Epoxyethyltris(*p*-trifluoromethylphenyl)silane.—The crude reduction product could not be analyzed quantitatively by gas chromatography due to the negative polarity ionization characteristics of the fluoro derivative. However, qualitatively the absence of olefin or starting epoxide could be confirmed, and the presence of a major and a very minor component could be detected. The crude product (3.42 g.) was introduced onto a Florisil column in a minimum amount of ethyl ether. The following eluents and fractions were employed: (1) petroleum ether (b.p. 30–60°), 0.07 g. of oil; (2) 10% ethyl ether in petroleum ether, 0.71 g. of solid; (3) fraction 2 eluent, 1.33 g. of solid; (4) fraction 2 eluent, 0.76 g. of solid; and (5) fraction 2 eluent, 0.08 g. of oil. Fraction 2 and 4 were recrystallized from cyclohexane individually (m.p. 120–121 and 102–103°, respectively) and submitted for elemental analysis. Fraction 2 gave satisfactory carbon and hydrogen values for a substituted ethanol, but the values for fraction 4 were 0.76% high on carbon and 0.52% high on hydrogen. The infrared spectra of fractions 2 and 4 were identical, except for a weak absorption at 1225 cm.$^{-1}$ in fraction 4. The n.m.r. spectra of both samples were consistent with the major constituent in both fractions being 2-tris(*p*-trifluoromethylphenyl)silane. Only two unexplained singlets of modest intensity in the n.m.r. spectrum of fraction 4 distinguished the spectra. It is, therefore, concluded that fraction 2 and 4 represent different crystal forms of the primary alcohol, the latter being somewhat impure, and that no secondary alcohol could be detected. The total yield of primary alcohol was estimated to be >90%.

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Notes

Chemistry of Alkali Metal–Unsaturated Hydrocarbon Adducts. V. Reductive Coupling of Vinylsilanes and the d_π–p_π Effect[1]

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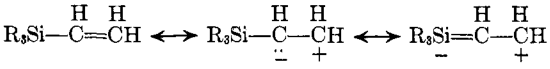
The ability of organic compounds containing carbon–carbon double bonds to form alkali metal adducts in ether solution has been associated with the presence of conjugated unsaturation. Arylethylenes and 1,3-butadienes readily form alkali metal addition compounds which can undergo subsequent dimerization or polymerization.[3] Typical of this behavior is the reaction of 1,1-diphenylethylene with metallic sodium in ether; hydrolysis of the resulting metal adduct yields 1,1,4,4-tetraphenylbutane.[4]

Accumulated physical and chemical evidence derived from vinylsilanes strongly supports the view that the available d-orbitals of silicon can interact with the π-electron cloud of the vinyl group (d_π–p_π effect), as shown in structures I–III.[5] Most recently, an infrared study of a series of vinylsilanes uncovered a correlation between the CH_2 out-of-plane deformation frequency of the vinyl group and electronic parameters of the group R.[6] This relation accords with a variation in the d_π–d_π interaction (III) as the electron-attracting character of the silicon is modified by its substituent R.



$$R_3Si{-}\overset{H}{C}{=}\overset{H}{C}H \longleftrightarrow R_3Si{-}\underset{\ddot{-}}{\overset{H}{C}}{-}\underset{+}{\overset{H}{C}H} \longleftrightarrow R_3\underset{-}{Si}{=}\overset{H}{C}{-}\underset{+}{\overset{H}{C}H}$$

I II III

The resemblance of such electronic effects to the conjugative delocalizations attainable in arylethylenes prompted an investigation of the ability of vinylsilanes to form alkali metal adducts. Although two recent investigations of alkali metal–arylsilane interactions by means of electron spin resonance spectroscopy have demonstrated the formation of radical-anion intermediates,[7] no such evidence has been obtained for the unconjugated olefinic linkage of vinylsilanes. The present study reports the facile reductive coupling of vinylsilanes by lithium metal and thereby presents strong chemical evidence in favor of the capacity of vinyl groups adjacent to silicon to yield reactive alkali metal adducts because of d_π–p_π delocalization. Thus, when triphenylvinylsilane in tetrahydrofuran solution was treated with one equivalent of lithium metal at −75°, a pale yellow precipitate was slowly deposited. Subsequent hydrolysis under mildly acidic conditions gave no discernible products of silicon–carbon bond cleavage,[8] but only starting material and a good yield of the reduction product V. The identity of V as 1,4-bis(triphenylsilyl)butane was established by its un-

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[1] Previous papers in this series: (a) J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963); (b) J. J. Eisch, *ibid.*, **28**, 707 (1963); (c) J. J. Eisch and R. M. Thompson, *ibid.*, **27**, 4171 (1962); and (d) J. J. Eisch and W. C. Kaska, *ibid.*, **27**, 3745 (1962).

[2] (a) To whom inquires should be addressed at the Department of Chemistry, Catholic University of America, Washington 17, D. C.; (b) Undergraduate Research Participant, National Science Foundation, 1962–1963.

[3] G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 27–42.

[4] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 477 (1914).

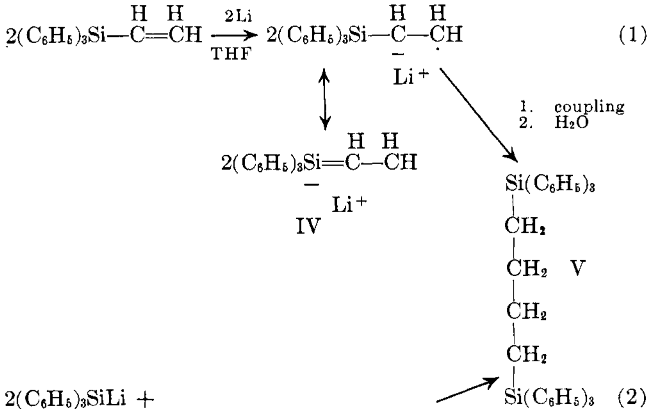
[5] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 91–113.

[6] J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963).

[7] (a) M. G. Townsend, *J. Chem. Soc.*, 51 (1963); (b) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963).

[8] If silicon–carbon bond cleavage had occurred, the resulting silyllithium compound, R_3SiLi, would be expected to produce either R_3SiH or its hydrolysis products, R_3SiOH and $R_3Si{-}O{-}SiR_3$, upon treatment with water [*cf.* D. Wittenberg and H. Gilman, *Quart. Rev.*, **13**, 116 (1959)].

ambiguous synthesis from the known reaction[10] of 1,4-dichlorobutane with triphenylsilyllithium (equation 2). Consequently, the formation of V from triphenylvinylsilane and lithium metal can be formulated most reasonably as a reductive coupling proceeding by way of transitory 1:1 lithium–vinylsilane adducts (radical-anion IV, equation 1). The similarity to the behavior of 1,1-diphenylethylene is most striking.



Added assurance that V was not known compound 1,2-bis(triphenylsilyl)ethane (VI) (possibly arising by the cleavage of triphenylvinylsilane to produce triphenylsilyllithium and the addition of the latter to unchanged triphenylvinylsilane) was obtained by comparing V with an authentic sample of VI. Infrared spectral and mixture melting point comparison showed V and VI to be different.

The generality of this reductive coupling reaction is reflected in the ability of alkylvinylsilanes, such as triethylvinylsilane and dimethyldivinylsilane, also to react readily with alkali metals in tetrahydrofuran.[9] In these cases a styrene-like polymerization under agency of the alkali metal also appears to occur. The large number of vinyl derivatives available of both metals and metalloids offers the opportunity of extending the foregoing observations to the dimerization and polymerization of many related systems. This aspect is being actively considered in this laboratory.

Experimental

Starting Materials and General Procedures.—Reactions involving metals or organometallic reagents were conducted under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran employed in such reactions was purified by successive treatments with sodium hydroxide pellets, sodium metal slices, and lithium aluminum hydride. The purified tetrahydrofuran was distilled finally from the lithium aluminum hydride directly into the reaction vessel.

The lithium metal ribbon (carefully scraped free of oxide and nitride while under dry benzene) contained 0.6% of sodium metal. The triphenylvinylsilane was prepared from trichlorovinylsilane and phenylmagnesium bromide in tetrahydrofuran by following a recent procedure.[6] The authentic 1,4-bis(triphenylsilyl)butane was prepared from 1,4-dichlorobutane and triphenylsilyllithium, m.p. 214–215° (lit.[10] m.p. 215–216°).

All melting points are uncorrected. The infrared spectral data were obtained from samples recorded in mineral oil mulls on a Perkin-Elmer infrared spectrophotometer, Model 21.

Reaction of Triphenylvinylsilane with Lithium Metal in Tetrahydrofuran.—A 500-ml., three-necked, round-bottomed flask, equipped with a low-temperature thermometer and a sealed polytetrafluoroethylene paddle stirrer was charged with 250 ml. of pure, dry tetrahydrofuran and 14.3 g. (0.050 mole) of triphenylvinylsilane. The reaction system was purged with dry nitrogen gas. Through the third neck of the flask, 0.12 g. of finely cut lithium metal ribbon pieces was introduced. The flask was restoppered and the stirrer was started. A yellow coating soon formed on the surface of the lithium pieces and eventually the whole solution developed a light orange color. The triphenylvinylsilane solution was thereupon cooled to −70° to −75° with a Dry Ice–acetone bath. After 80 min. of vigorous stirring at this temperature the second 0.12-g. portion of lithium pieces was introduced into the reaction mixture. The system gradually became a light yellow fluid paste. (Some of the material which had splashed up into the warmer parts of the flask turned brown.) After an additional 100 min. of reaction the third and last 0.12-g. portion of lithium pieces was added [total, 0.36 g. (0.052 g.-atom) of lithium]. The reaction system was stirred for another hour (total reaction time, 4 hr.) and then diluted with 175 ml. of pure tetrahydrofuran. The suspension was allowed to stir for three more hours and then it was cautiously treated with 200 ml. of *N* sulfuric acid at −75°. After the mixture was allowed to come to room temperature, 200 ml. of ether was added. The separated organic layer was washed successively with water, aqueous sodium bicarbonate solution and, finally, again with water. After drying over anhydrous magnesium sulfate the organic extract was freed of solvent to give 13.8 g. of crude organic product, whose infrared spectrum showed no absorption bands characteristic of triphenylsilane (Si-H, 2270), triphenylsilanol (Si-OH, 3300), hexaphenyldisiloxane (Si-O-Si, 1095), or 1,2-bis(triphenylsilyl)ethane (1140 cm.$^{-1}$).

The crude product was digested with 200 ml. of hot benzene and the resulting suspension allowed to cool to room temperature. The colorless precipitate, upon collection and drying at 100°, weighed 8.92 g. (62%) and melted at 209–212°. Recrystallization from cyclohexane yielded fine needles melting consistently at 214–215°. Comparison of this product with an authentic sample of 1,4-bis(triphenylsilyl)butane by means of mixture melting point and infrared spectra established the identity of the two samples. Moreover, admixture of the product from triphenylvinylsilane and lithium metal with authentic 1,2-bis(triphenylsilyl)ethane[11] (m.p. 210–212°) caused a definite melting point depression.

The evaporation of the mother liquor from the benzene extraction of the crude product yielded a viscous, straw-colored oil, whose infrared spectrum showed no indication of Si-H, Si-O-H, or Si-O-Si linkages. The spectral absorptions suggested the presence only of triphenylvinylsilane and 1,4-bis(triphenylsilyl)butane.

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[9] J. J. Eisch and L. L. Libit, unpublished studies.

[10] W. K. Johnson and K. A. Pollart, *J. Org. Chem.*, **26**, 4092 (1961).

[11] The authors are indebted to Professor Henry Gilman, Department of Chemistry, Iowa State University, Ames, Iowa, for providing them with an authentic sample of this compound.

Substituted Quinodimethans. VI. 7,7,8,8-Tetrafluoroquinodimethan Polymer

W. R. Hertler

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Recent work in these laboratories has led to the synthesis of several stable quinodimethans, including 7,7,8,8-tetracyanoquinodimethan,[1a] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethan,[1a] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethan,[1b] and 11,11,12,12-tetracyanonaphtho-2,6-quinodimethan.[1c] The stability of these quinodimethans may be attributed to the presence of electron-withdrawing substituents which permit

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[1] (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) W. R. Hertler and R. E. Benson, *ibid.*, **84**, 3474 (1962); (c) J. Diekmann, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963).