silver chloride in 150 ml. of water was added dropwise with vigorous stirring a solution of 29 g. (0.1 mole) of I in 60 ml. of water. The addition required about 30 min. The mixture was stirred for an additional 2 hr. until no iodide ion was detected by a spot test.[14] The resulting mixture was filtered, and the filtrate was concentrated under diminished pressure to about 45 ml. The residue was treated as above to yield 17.6 g. (88%) of IV, which melted at 137–138° dec.

Methioninemethylsulfonium fluosilicate (XVII). To a solution of 29.1 g. (0.1 mole) of I in 50 ml. of water was added 37 g. of freshly prepared 48% aqueous silver fluosilicate solution, and the mixture was treated as above to yield 21.4 g. (91%) of XVII as hygroscopic colorless needles, m.p. 109–110° dec. XVII was found to decompose slowly *in vacuo* at room temperature. XVII could be converted in good yield into IV by a procedure similar to that for XI.

KYOTO, JAPAN

[CONTRIBUTION FROM THE MATERIALS & PROCESSES STAFF, AERO-SPACE DIVISION, BOEING AIRPLANE COMPANY]

Synthesis of Monomeric Silanes

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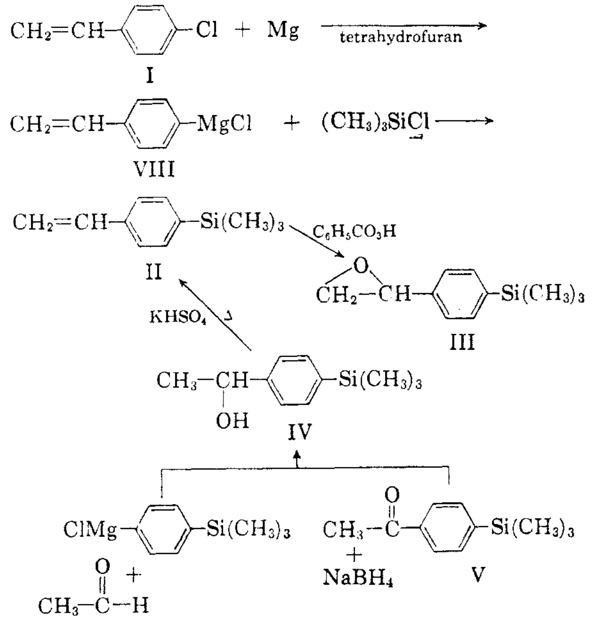
The preparations of 4-trimethylsilylstyrene and of 4-epoxyethylphenyltrimethylsilane are described, as well as attempts to extend these reactions to the preparation of the analogous difunctional monomers.

Two methods for the preparation of 4-trimethylsilylstyrene (II) have recently been described. Winslow[2] prepared it by the vapor phase dehydration of 1′-(4-trimethylsilylphenyl)ethanol (IV). Later Lewis[3] described the reaction of 4-styryltrichlorosilane with methylmagnesium bromide. In the present report, the synthesis of II from 4-styrylmagnesium chloride (VIII)[4] and trimethylchlorosilane is described. The conversion of the styrylsilane (II) to the corresponding epoxide (III) is also included. In addition, details are given for the preparation of Winslow's alcohol (IV) in crystalline form by the reduction of 4-trimethylsilylacetophenone[5,6] as well as from *p*-dichlorobenzene instead of the more expensive *p*-dibromo compound.



A number of attempts were made to prepare the analogous difunctional compounds, di(4-styryl)dimethylsilane and di(4-epoxyethyl)dimethylsilane. Reaction of 4-styrylmagnesium chloride (VIII) with dimethyldichlorosilane appears to proceed normally, but attempts to isolate the product invariably led to polymer formation.

Reduction of di(4-acetylphenyl)dimethylsilane to the dialcohol, followed by dehydration, was next attempted. Although the reduction proceeded smoothly, attempts to dehydrate the dialcohol led to splitting of the silicon-phenyl bond.

In a previous paper from this laboratory, the use of 2-(4′-bromophenyl)-2-methyl-1,3-dioxolane as a reagent for the introduction of the 4-acetylphenyl group into silanes was described.[6] During the present work, we have discovered that the 1,3-dioxolane (ketal) structure is more stable than anticipated. Depending on the method of working up the Grignard product, it is possible to isolate pure ketals, pure ketones, or mixtures of these compounds. When water is used to decompose the Grignard product from trimethylchlorosilane, a ketal can be isolated. Treatment of this Grignard product with dilute hydrochloric acid in the cold yields a mixture of ketal and ketone. Use of hydrochloric acid plus gentle heat yields the ketone. Treatment of the difunctional Grignard product derived from dimethyldichlorosilane with water to yield the diketal proceeds smoothly. Acid treatment of this Grignard product, designed to split the ketal groups, yields a mixture of ketal, ketone, and decomposition products which is difficult to purify. After purifica-

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[1] Present address: Propulsion Dept., Missile and Space Division, Lockheed Aircraft Corp., Palo Alto, Calif.

[2] F. H. Winslow. U. S. Patent 2,642,415, June 16, 1953.

[3] D. W. Lewis, *J. Org. Chem.*, **23**, 1893 (1958).

[4] J. R. Leebrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1958).

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[6] R. G. Neville, *J. Org. Chem.*, **24**, 111 (1959).

tion, however, the diketal can be hydrolyzed to the diketone readily. Compounds previously identified as ketones[6] have been shown to be largely ketals, containing enough ketonic impurities to account for the formation of the derivatives described. In the Experimental section, the physical properties of both ketals and ketones are given.

EXPERIMENTAL[7]

2-(4′-Trimethylsilylphenyl)-2-methyl-1,3-dioxolane. The reaction between the Grignard reagent of 2-(4′-bromophenyl)-2-methyl-1,3-dioxolane and trimethylchlorosilane has been previously described.[6] The reaction mixture was poured over cracked ice, the organic layer separated,[8] washed with water, dried over sodium sulfate, and distilled to give a liquid, b.p. 150–190°/2.5 mm. in 59% yield. It crystallized in the receiver and after recrystallization from isopropanol melted at 59–60°. The material previously described,[6] m.p. 41°, was apparently this compound with some ketone as an impurity.

Anal. Calcd. for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53; Si, 11.88. Found: C, 66.00; H, 8.25; Si, 11.68.

The infrared spectrum showed a ketal doublet[9] at 1075 and 1030 cm.$^{-1}$, no absorption in the carbonyl region at 1680 cm.$^{-1}$, *p*-substitution band at 820 cm.$^{-1}$, and trimethylsilyl bands at 756, 836, and 1250 cm.$^{-1}$

4-Trimethylsilylacetophenone, (V).[5,6] Twenty-seven g. of the ketal was dissolved in 150 ml. of methanol and 30 ml. of concentrated hydrochloric acid. After 0.5 hr. 400 ml. of water was added and the product taken up in benzene. After washing and drying over sodium sulfate, distillation yielded 11.6 g. (53%) of liquid, b.p. 93–95°/1.5 mm., $n_{\mathrm{D}}^{25^\circ}$ = 1.5178, which solidified at 11°, showing a strong carbonyl band at 1680 cm.$^{-1}$; *p*-substitution at 818 cm.$^{-1}$; trimethylsilyl bands at 760, 842, and 1248 cm.$^{-1}$; Si-C_6H_5 at 1112 and 1382 cm.$^{-1}$

1′-(4-Trimethylsilylphenyl)ethanol, (IV). (*a*). *By reduction:* To 10 g. (0.052 mole) of 4-trimethylsilylacetophenone in 40 ml. of methanol was added a solution of 2.3 g. (0.060 mole) of sodium borohydride in 20 ml. of methanol, maintaining the temperature at 25–30°. After 20 hr. 300 ml. of 2% hydrochloric acid was added. The product was taken up in ether, washed with water, dried, and distilled to yield 7.2 g. (72%) of carbinol, b.p. 110–111°/4.5 mm. The product crystallized on cooling to give a solid. A sample redistilled for analysis melted at 46–47°.

Anal. Calcd. for $C_{11}H_{18}O$ Si: C, 67.98; H, 9.34; Si, 14.45. Found: C, 68.09; H, 9.32; Si, 14.59.

The infrared spectrum showed an associated O—H stretch, strong at 3333 cm.$^{-1}$; *p*-substitution at 823 cm.$^{-1}$; trimethylsilyl bands at 760, 846, 1250 cm.$^{-1}$; Si-C_6H_5 at 1111 and 1390 cm.$^{-1}$

(*b*) *By the Grignard synthesis:* 4-Chlorophenyltrimethylsilane,[10] synthesized from *p*-dichlorobenzene and trimethylchlorosilane by a Grignard reaction in tetrahydrofuran, was converted to the Grignard reagent in tetrahydrofuran, a 20% excess of acetaldehyde vapor was swept into the solution, and after refluxing 1 hr. and working up as usual, a liquid, b.p. 156–61°/25 mm. was isolated in 50% yield. The infrared spectrum of the liquid product was identical with that of the solid described above. Unless the 4-chlorophenyltrimethylsilane used was carefully fractionated, a solid, m.p. 92–93°, distilled as a forerun. This was shown to be *p*-di(trimethylsilyl)benzene by its infrared spectrum and melting point,[11] and was presumed to have arisen as a by-product in the preparation of 4-chlorophenyltrimethylsilane from *p*-dichlorobenzene.

4-Trimethylsilylstyrene, (II). (*a*) *By dehydration.* 1′-(4-Trimethylsilylphenyl)ethanol, (IV), was dehydrated by the potassium bisulfate method,[12] utilizing a pressure of 25 mm. and a bath temperature of 240°. Upon redistillation, after a forerun, b.p. 60–85°/25 mm., the product was obtained in 43% yield as a colorless liquid, b.p. 117–126°/25 mm., $n_{\mathrm{D}}^{25^\circ}$ = 1.5253.

Anal. Calcd. for $C_{11}H_{16}Si$: C, 74.92; H, 9.15. Found: C, 75.07; H, 9.18.

The infrared spectrum showed conjugated vinyl at 1636 cm.$^{-1}$$=CH_2$; deformation at 908 cm.$^{-1}$; *p*-substitution at 826 cm.$^{-1}$, trimethylsilyl bands at 756–763 (doublet), 846, and 1250 cm.$^{-1}$; Si-C_6H_5 at 1107 and 1392 cm.$^{-1}$

(*b*). *By the Grignard synthesis. p*-Chlorophenylmethylcarbinol[4] was dehydrated to *p*-chlorostyrene in 68% yield by dripping slowly through a 15-in. column packed with 8–14 mesh alumina at 300° and 60-mm. pressure. To the Grignard reagent[4] from 84.0 g. (0.60 mole) of the *p*-chlorostyrene was added a solution of 58.8 g. (0.54 mole) of trimethylchlorosilane in 225 ml. of tetrahydrofuran so that the solution refluxed. After 15 min. of additional reflux 1 g. of hydroquinone was added and the mixture stirred 1 hr. The mixture was poured over cracked ice, and the organic layer separated, washed with water, dried with sodium sulfate, and distilled to yield 58.5 g. (62%) of liquid, b.p. 120–136°/25 mm., $n_{\mathrm{D}}^{25^\circ}$ = 1.5218,[2] with an infrared spectrum identical with that of the above dehydration product.

4-Epoxyethylphenyltrimethylsilane, (III). At 0° 600 ml. (0.30 mole) of a 0.5*M* benzene solution of perbenzoic acid[13] was added to 49.2 g. (0.28 mole) of 4-trimethylsilylstyrene in 300 ml. of benzene. After the peroxide titer had fallen to a constant value (20 hr.), the solution was washed acid free with cold sodium carbonate solution, washed with water, dried with sodium sulfate, and distilled to yield 25.5 g. (50%) of a liquid, b.p. 105–108°/8 mm., $n_{\mathrm{D}}^{25^\circ}$ = 1.5150.

Anal. Calcd. for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39; epoxide equivalent 192. Found: C, 68.85; H, 8.44; epoxide equivalent 215.[14]

Di-[4-(2′-methyl-1′,3′-dioxolyl-2′)-phenyl]dimethylsilane. This is the compound previously reported[6] to be the ketone. An analytical sample recrystallized from isopropanol melted at 132–133°.

Anal. Calcd. for $C_{22}H_{28}O_4Si$: C, 68.71; H, 7.34; Si 7.31. Found: C, 68.50; H, 7.09; Si, 7.44.

The infrared spectrum showed a ketal doublet at 1032 and 1075 cm.$^{-1}$; no absorption in the carbonyl region at 1680 cm.$^{-1}$; *p*-substitution at 826 cm.$^{-1}$; $=Si(CH_3)_2$ bands at 815 and 1252 cm.$^{-1}$; Si-C_6H_5 at 1116 and 1382 cm.$^{-1}$

Di(4-acetylphenyl)dimethylsilane. To 157 g. (0.361 mole) of recrystallized ketal dissolved in 4.8 l. of methanol was added 800 ml. of concentrated hydrochloric acid. After

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(7) Melting points are uncorrected. Potassium bromide pellets were used in the determination of spectra of solids, and thin films in the case of liquids. Distillations were carried out in standard taper glassware without distilling columns.

(8) Following the suggestion of Dr. Thomas Waugh, Arapahoe Chemicals, Inc., we have found the addition of the disodium salt of ethylenediaminetetraacetic acid to be very helpful in breaking the persistent emulsions that frequently result from the use of tetrahydrofuran as a Grignard solvent.

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(11) H. A. Cook, British Patent **671,553**, May 7, 1952.

(12) E. C. Hornung, *Org. Syntheses*, **Coll. Vol. III**, 204 (1955).

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(14) By the pyridine hydrochloride method, method 7, page 136, from J. L. Jungnickel, *et al.* in *Organic Analysis*, **Vol. I**, Interscience, New York, 1953. This method gives slightly high results with styrene oxides due to acid-catalyzed rearrangement to acetyl compounds.

stirring 0.5 hr., the solution was poured into 15 l. of water, and the product extracted with three portions of benzene. Removal of the solvent left an oil which readily crystallized, yield 105 g. (87%). An analytical sample, recrystallized from isopropanol and methanol melted at 77.5–78.0°.

Anal. Calcd. for $C_{18}H_{20}O_2Si$: C, 72.93; H, 6.80; Si, 9.48. Found: C, 72.63; H, 6.67; Si, 9.28.

The infrared spectrum showed a strong carbonyl band at 1680 cm.$^{-1}$; *p*-substitution at 842 cm.$^{-1}$; $=Si(CH_3)_2$ bands at 818 and 1248 cm.$^{-1}$; Si-C_6H_5 at 1112 and 1382 cm.$^{-1}$

Di[4-(1′-hydroxyethyl)phenyl]dimethylsilane. The sodium borohydride reduction of the diketone to the dialcohol proceeded as described above. Removal of the solvent yielded 91% of an oil which readily crystallized. An analytical sample, recrystallized from isopropanol, melted at 97–98°.

Anal. Calcd. for $C_{18}H_{24}O_2Si$: C, 71.95; H, 8.05; Si, 9.35. Found: C, 71.47; H, 8.19; Si, 9.78.

The infrared spectrum showed an associated O—H stretch strong at 3280 cm.$^{-1}$; *p*-substitution at 843 cm.$^{-1}$; $=Si(CH_3)_2$ at 816 and 1252 cm.$^{-1}$; Si-C_6H_5 at 1112 and 1390 cm.$^{-1}$

Attempted preparation of di(4-styryl)dimethylsilane. (*a*). *By dehydration.* Attempts to use the phosphorus pentoxide dehydration of Gilman *et al.*,[15] led to polymer formation. After passing the dialcohol over alumina at either 300° or 400° and 1 mm. pressure, only styrene, in the form of styrene dibromide, could be isolated from the products.

(*b*) *By Grignard synthesis.* A vigorous reaction took place on the addition of dimethyldichlorosilane to 4-styrylmagnesium chloride. Occasionally the reaction mixture polymerized to a rubbery mass at this stage. With carefully purified reagents, and addition of an antioxidant, the reaction mixture could be worked up as usual, so that solvent removal yielded a fluid liquid. Attempts to distill this material alone or with polymerization inhibitors led to immediate polymerization. The crude product consumed approximately 50% of the calculated amount of perbenzoic acid but no diepoxide could be isolated from the reaction. Addition of bromine produced a crystalline material, m.p. 134–135°, which had the following analysis: C, 41.12; H, 3.69; Br, 55.28%. In view of the apparent absence of silicon in this product, and the known case of cleavage of the phenyl-silicon bond by bromine,[16] this was not investigated further.

Acknowledgment. We wish to thank Mr. Murray Taylor of this laboratory for the microanalyses reported, and Mr. Harry Goldberg and Mrs. Katharine Haldorsen for measurements of infrared spectra.

SEATTLE, WASH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Trimethyl(iso)cyanogermane and Trimethyltin (Iso)cyanide[1]

DIETMAR SEYFERTH AND NORBERT KAHLEN

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Trimethyl(iso)cyanogermane, on the basis of its infrared spectrum and its physical and chemical properties consists of an equilibrium mixture of the normal and the isocyano isomers. It reacts with sulfur, forming trimethylisothiocyanatogermane, and with boron trifluoride to give $(CH_3)_3GeCN\cdot BF_3$. Trimethyltin (iso)cyanide has properties consistent with its formulation as a highly polar cyanide. It reacts with sulfur, giving trimethyltin thiocyanate, and does not form an adduct with boron trifluoride. The preparation of trimethyl(iso)cyanogermane and trimethyltin (iso)cyanide is described.

Trimethyl(iso)cyanosilane could have the normal cyanide structure, I, or the isocyanide structure II.

$$(CH_3)_3Si-C\equiv N\,(I) \qquad (CH_3)_3Si-N=C\,(II)$$

The question of the correct structure has been the subject of much discussion in recent years[2-7] and it is now assumed, on the basis of infrared[6] and chemical[3,6] studies, that "trimethyl(iso)cyanosilane" consists of an equilibrium mixture of trimethylcyanosilane and trimethylisocyanosilane, the former isomer predominating at room temperature. We report here the results of an investigation concerning the preparation and properties of the germanium and tin analogs of trimethyl(iso)cyanosilane: trimethyl(iso)cyanogermane and trimethyltin (iso)cyanide.

Trimethyl(iso)cyanogermane. Tetra(iso)cyanogermane has been described,[6,8] as has (iso)cyanogermane.[9] No convincing proof was given for the postulated isocyanide structure of the latter. Two organogermanium (iso)cyanides, triethyl- and tri-*n*-

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[1] The "(iso)cyano" and "(iso)cyanide" nomenclature used in this paper has no structural implications when the iso prefix is in parentheses and merely indicates the presence of the CN and/or the NC grouping.

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