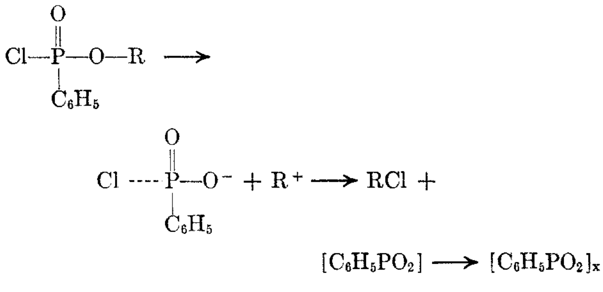
It is also conceivable that such a process might occur through ionization of an alkyl radical with inter- or intramolecular reaction to form the alkyl chloride and an unstable monomer of $C_6H_5PO_2$ which would then undergo stabilization by polymerization.

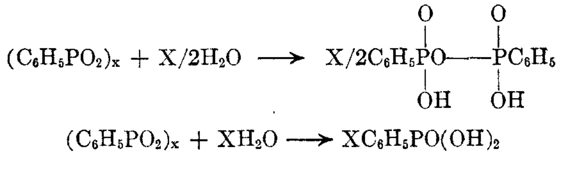


$$\mathrm{Cl{-}}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}\mathrm{{-}O{-}R} \longrightarrow$$

$$\mathrm{Cl\cdots}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}\mathrm{{-}O^-} + \mathrm{R^+} \longrightarrow \mathrm{RCl} +$$

$$[\mathrm{C_6H_5PO_2}] \longrightarrow [\mathrm{C_6H_5PO_2}]_x$$

The identity of the polymetaphosphonate with the product which was first prepared by Michaelis[11] was verified by analysis and by reaction with water (a) at room temperature to yield *P,P'*-diphenyl diphosphonic acid recently described by Anschütz[12] and (b) by complete hydrolysis in boiling water to yield benzene phosphonic acid.



$$(\mathrm{C_6H_5PO_2})_x + \mathrm{X/2H_2O} \longrightarrow \mathrm{X/2C_6H_5}\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}\mathrm{O{-}{-}}\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}\mathrm{C_6H_5}$$

$$(\mathrm{C_6H_5PO_2})_x + \mathrm{XH_2O} \longrightarrow \mathrm{XC_6H_5PO(OH)_2}$$

A solution consisting of equimolar quantities (0.21 mole) of pyridine (16.8 g.) and isoamyl alcohol (18.7 g.) and 60 cc. of ether was added dropwise with mechanical stirring to a solution of 41.4 g. (0.21 mole) of $C_6H_5POCl_2$ diluted with 50 cc. of ether. After an additional 15 min. of stirring the precipitated pyridine hydrochloride was removed by filtration. The ether solvent was removed by warming the solution under vacuum on the steam bath. The residual product was then distilled yielding isoamyl chloride, boiling at 98°.

Anal. Calcd. for $C_5H_{11}Cl$: C, 56.40; H, 10.42. Found: C, 56.38; H, 10.33.

A brown glassy mass remained in the still pot. When an attempt was made to distill the high boiling resin at low pressures, (0.5 mm.), foaming took place and the whole mass solidified. When heated with water this product was converted into phenylphosphonic acid, melting at 161°. Formation of the latter was verified by comparison of the infrared spectrum with that of an authentic sample (melting point, 158°), by the titration curve with sodium hydroxide[13] as well as by analysis.

Anal. Calcd. for $C_6H_5PO(OH)_2$: C, 45.57; H, 4.43. Found: C, 45.74; H, 4.60.

If the polymeric material, obtained as residue after distillation of solutions of any of the alkyl-*P*-phenyl phosphonochloridates, is allowed to stand in contact with water for about 12 hr., there is obtained a fluffy white solid, melting at 78°. Analyses of products so obtained [from solutions originally containing the methyl(I) and ethyl(II) phosphonochloridates] demonstrate that the primary hydrolysis product consists of *P,P'*-diphenyl diphosphonic acid.

Anal. Calcd. for $[C_6H_5PO(OH)]_2O$: C, 48.32; H, 4.02. (I) Found: C, 47.65; H, 4.20. (II) Found: C, 47.92; H, 4.32.

The uncorrected melting point given by Anschütz[12] for this compound is 79.5–80°. Further heating in all cases with water caused hydrolysis to benzene phosphonic acid.

The original glassy residue becomes more and more brittle when allowed to stand under anhydrous ether. If ground, and stored under high vacuum, it was found to melt between 105–107°. The melting point given for phenyl metaphosphonate by Michaelis[11] is 100°. Analytical results obtained by Michaelis are compared with those obtained in the present study.

Anal. Calcd. for C_6H_5PO: C, 51.43; H, 3.57. Found: C. 51.68; H, 5.80. Michaelis:[11] C, 51.42; H, 4.0.

The product is very hygroscopic and is moderately soluble in benzene, but insoluble in ether.

URBANA, ILL.

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[11] A. Michaelis and F. Rothe, *Ber.*, **25**, 1747 (1892).

[12] L. Anschütz and H. Wirth, *Chem. Ber.*, **89**, 688 (1956).

[13] Product furnished by Victor Chemical Works Research Laboratory, Chicago Heights, Ill.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, WESTINGHOUSE ELECTRIC CORP.]

Preparation and Properties of Styrenyl-Substituted Organosilicon Compounds

DANIEL W. LEWIS

Received May 21, 1958

The preparation and physical properties of five *p*-styrenyl-substituted silane monomers and one disiloxane are described.

There are two references in the literature to the preparation of styrenyl-substituted silanes; Bunnell and Hatcher[1] described the preparation of trichloro(*p*-styrenyl)silane and Winslow[2] describes the preparation of trialkyl(*p*-styrenyl)silanes. However, few data are given on the physical properties of these compounds.

In the preparation of reactive silicone casting resins, five *p*-styrenyl-substituted silane monomers and one disiloxane were prepared. The silanes range in functionality from zero to three, with respect to siloxane condensation, *i.e.*, the number of hydrolyzable groups attached to silicon ranges from zero to three. The monomers were, trimethyl(*p*-styrenyl)silane, methoxydimethyl(*p*-styrenyl)silane, dimethoxymethyl(*p*-styrenyl)silane, trimethoxy(*p*-styrenyl)silane and trichloro(*p*-styrenyl)silane. The latter was prepared according to the method of Bunnell and Hatcher.[1] Also prepared was tetramethyl-1,3-bis(*p*-styrenyl)disiloxane.

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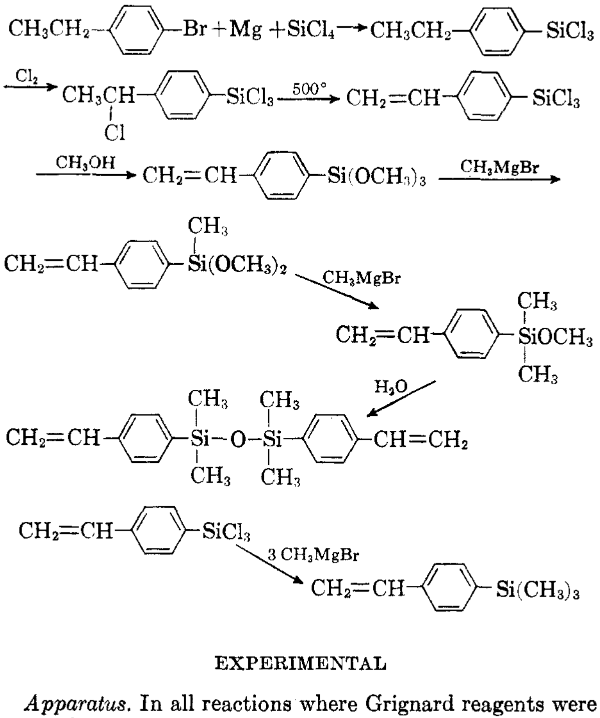
[1] D. B. Bunnell and R. H. Hatcher, U. S. Patent **2,469,154**.

[2] F. H. Winstow, U. S. Patent **2,642,415**.

It might be mentioned that styrenyl silanes which have methyl and chlorine groups attached to silicon seem to be much less stable than those described here, which have methoxyl as the hydrolyzable group. For example, chlorodimethylstyrenylsilane was prepared but purification was difficult because of exothermic polymerization during distillation. (Chloroethyl)phenyldimethylchlorosilane dehydrochlorinated and polymerized exothermally, when an attempt was made to distil it from the ether-soluble products of the reaction of trichloro-*p*(chloroethyl)phenylsilane with two moles of methylmagnesium bromide.

Molar refractions of the styrenyl silanes were calculated using the bond refractions of Warrick.[3] These values are from 1.46 to 1.70 ml lower than the observed values. This discrepancy, observed in other conjugated systems,[4] is probably due to the conjugation of the vinyl group with the benzene ring. The observed and calculated values of trichloro-*p*(ethyl)phenylsilane, on the other hand, agree within 0.24 ml.

The following is a reaction scheme for the preparation of the compounds described.



EXPERIMENTAL

Apparatus. In all reactions where Grignard reagents were used, the apparatus consisted of a three-necked flask fitted with an air-tight stirrer, a dropping funnel, and a reflux condenser. Before use, the system was swept out with dry nitrogen. The dropping funnel and condenser were capped with $CaCl_2$ tubes.

p-Ethylbromobenzene. *p*-Ethylbromobenzene was isolated from a mixture of isomeric ethylbromobenzenes by fractionation through a 4-ft. Podbielniak Hyper-Cal column. The isomeric mixture, known as Alkazene 40, was obtained from the Dow Chemical Co. The physical constants of the material isolated are: b.p. 204°, n_D^{25} 1.5422. Dreisbach and Martin[5] report a boiling point of 205° and a refractive index of n_D^{25} 1.54228 for *p*-ethylbromobenzene.

Trichloro-p(ethyl)phenylsilane. An ether solution of 8 moles of *p*-ethylphenylmagnesium bromide was added with stirring and cooling to 2 kg. (11.75 moles) of $SiCl_4$, dissolved in an equal volume of dry benzene. After standing overnight, the reaction mixture was freed of magnesium salts by filtration. More salts precipitated as solvent and excess $SiCl_4$ were distilled from the filtrate. After these were filtered off, the product was isolated by distillation through a 4-ft. column packed with glass-helices. There was obtained 1113 g. (59%) of product having a boiling point of 75–76°/0.8 mm.; n_D^{25} 1.5200; and d^{25} 1.245.

Anal. Calcd. for $C_8H_9Cl_3Si$: Si, 11.72. Found: Si, 11.97, 12.02.

Trichloro-p(chloroethyl)phenylsilane. Four and eight-tenths moles of *p*-ethylphenyltrichlorosilane was chlorinated in two batches by passing in dry chlorine while the silane was exposed to two 15 watt blue fluorescent lamps. The chlorination vessel was a large "test tube," 1 3/4 inches in diameter and 22 inches long. Through the stopper were inserted a sintered glass gas dispersion tube and a U-tube through which cooling water was passed to moderate the temperature of the reaction mixture. A reflux condenser was also attached through the stopper.

The two batches gained a total of 143 g. (4.1 gram atoms) of chlorine during 6.5 hr. reaction time. The temperature was kept at 25–30°.

The chlorinated material was distilled through a 4-ft. glass helix-packed column for separation. Forty-three g. of starting material was obtained. An attempt was made to distill the chlorinated product through this column at reduced pressures, but dehydrochlorination began to take place. It was then transferred to an 18″ Vigreux column where it was distilled at 0.4 mm. Three and six-tenths moles (75%) of trichloro-*p*(chloroethyl)phenylsilane was obtained, b.p. 87–88°/0.4 mm.; n_D^{25} 1.5370; d^{25} 1.348. This, no doubt, is a mixture of the α and β chloroethyl isomers.

Anal. Calcd. for $C_8H_8Cl_4Si$: Si, 10.25. Found: Si, 10.37, 10.52.

Trichloro(p-styrenyl)silane. Seven hundred and twenty-nine g. (2.63 moles) of trichloro-*p*(chloroethyl)phenylsilane was added drop-wise into a flash-distillation apparatus, the flask of which was surrounded by a sand bath held at 500–525°. A very slow stream of dry nitrogen was passed through the system during the dehydrochlorination. The receiver was cooled by an ice bath to prevent loss of product. Both the dropping funnel and the outlet of the receiver adapter were opened to the atmosphere through $CaCl_2$ tubes. Six hundred and thirty g. of crude product was obtained. One g. of charred residue remained in the pyrolysis flask. The product was distilled using an 18″ Vigreux column. There was obtained 490 g. (78%) of trichloro(*p*-styrenyl)silane boiling at 59–60°/0.6 mm.; n_D^{25} 1.5534; d^{25} 1.282. One hundred and twenty-one g. of polymerized residue remained in the still pot.

Anal. Calcd. for $C_8H_7Cl_3Si$: Si, 11.82. Found: Si, 11.99, 12.04.

Trimethyl(p-styrenyl)silane. An ether solution of 0.4 mole of trichloro(*p*-styrenyl)silane was treated with 1.3 moles of methylmagnesium bromide, using efficient stirring and cooling. After addition was complete, crushed ice was cautiously added. This was followed by enough 5% HCl to give two clear liquid layers. The organic layer was washed free of acid and dried over anhydrous Na_2SO_4. It was distilled through an 18″ Vigreux column. Thirty-eight g. (54%) of trimethyl(*p*-styrenyl)silane was obtained, b.p. 53–54°/1.2 mm., n_D^{25} 1.5212, d^{25} 0.886.

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[3] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

[4] N. Bauer and K. Fajans, *Technique of Organic Chemistry*, A. Weissberger, Ed., Vol. I, Part II, Interscience Publishers, New York, 1949, p. 1167.

[5] R. R. Dreisbach, and R. A. Martin, *Ind. & Eng. Chem.*, 41, 2875, (1949).

TABLE I

PROPERTIES AND ANALYSES

Compound	B.p., °C./mm.	n_D^{25}	d^{25}	Silicon, % Calcd.	Silicon, % Found
$C_2H_5C_6H_4SiCl_3$	75–76/0.8	1.5200	1.245	11.72	11.97, 12.02
$C_2H_4ClC_6H_4SiCl_3$	87–88/0.4	1.5370	1.348	10.25	10.37, 10.52
$H_2C{=}\overset{H}{C}C_6H_4SiCl_3$	59–60/0.6	1.5534	1.282	11.82	11.99, 12.04
$H_2C{=}\overset{H}{C}C_6H_4Si(OCH_3)_3$	66.5/0.1	1.5038	1.057	12.52	12.52, 12.61
$H_2C{=}\overset{H}{C}C_6H_4Si(OCH_3)_2CH_3$	60/0.5	1.5111	1.005	13.48	13.33, 13.26
$H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_2OCH_3$	42–43/0.1	1.5179	0.953	14.60	14.50, 14.51
$H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_3$	53–54/1.2	1.5212	0.886	15.93	15.71, 16.09
$\left[H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_2\right]_2O$	115–116/0.05	1.5427	—	16.59	16.61, 16.75

Anal. Calcd. for $C_{11}H_{16}Si$: Si, 15.93. Found: Si, 15.71, 16.09.

Trimethoxy(p-styrenyl)silane. Four hundred and ninety g. (2.06 moles) of trichloro(*p*-styrenyl)silane, dissolved in an equal volume of dry benzene was added with stirring and cooling to 1.5 l. of anhydrous methanol which had been saturated with anhydrous ammonia. Ammonium chloride, which precipitated, was filtered from the mixture. As benzene and methanol were distilled from the filtrate, more NH_4Cl precipitated. This was filtered and the filtrate was distilled under vacuum. There was obtained 377 g. (1.68 moles) (82%) of trimethoxy(*p*-styrenyl)silane boiling at 66.5°/0.1 mm., n_D^{25} 1.5038; d^{25} 1.057.

Anal. Calcd. for $C_{11}H_{16}O_3Si$: Si, 12.52. Found: Si, 12.52, 12.61.

Dimethoxymethyl(p-styrenyl)silane. An ether solution of 1.66 moles of methylmagnesium bromide was added with stirring and cooling to 373 g. (1.66 moles) of trimethoxy(*p*-styrenyl)silane, dissolved in 500 ml. dry benzene. After addition was complete, the mixture was stirred at room temperature for 0.5 hour. Salts were filtered off and the filtrate was distilled, giving 171.5 g. (0.83 moles) (50%) of dimethoxymethyl(*p*-styrenyl)silane, b.p. 60°/0.5 mm. n_D^{25} 1.5111, d^{25} 1.005.

Anal. Calcd. for $C_{11}H_{16}O_2Si$: Si, 13.48. Found: Si, 13.33, 13.26.

Methoxydimethyl(p-styrenyl)silane. An ether solution of 0.5 mole of methylmagnesium bromide was added with stirring and cooling to 104 g. (0.5 mole) of dimethoxymethyl(*p*-styrenyl)silane, dissolved in 600 ml. dry benzene. Salts were filtered off. The filtrate was distilled giving 57 g. (60%) of the desired silane, b.p. 42–43°/0.1 mm., n_D^{25} 1.5179, d^{25} 0.953.

Anal. Calcd. for $C_{11}H_{16}OSi$: Si, 14.60. Found: Si, 14.50, 14.51.

Tetramethyl-1,3-bis(p-styrenyl)disiloxane. Seventy-eight g. of methoxydimethyl(*p*-styrenyl)silane, dissolved in 125 ml. ether was stirred for 3 hr. with 125 ml. of 5% H_2SO_4. The ether layer was separated, washed free of acid, and dried over anhydrous Na_2SO_4. Distillation of this reaction mixture gave 5 g. of unhydrolyzed silane, 20 g. of crude disiloxane and 40 g. of polymerized residue. On redistilling the crude material, a middle fraction (5.5 g.) of the disiloxane boiled at 115–116°/0.05 mm., n_D^{25} 1.5427.

Anal. Calcd. for $C_{20}H_{26}OSi_2$: Si, 16.59. Found: Si, 16.61, 16.75.

PITTSBURGH 35, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

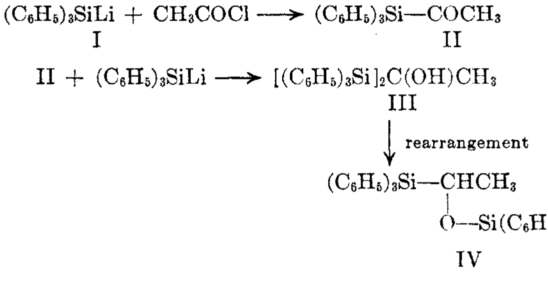
Reactions of Silyllithium Compounds with Derivatives of Carboxylic Acids. II

HENRY GILMAN AND DONALD J. PETERSON

Received May 29, 1958

The reactions of triphenylsilyllithium with acetic anhydride, ethyl acetate, propionyl chloride, phenylacetyl chloride, acetonitrile, and benzonitrile were investigated. The formation of the reaction products is discussed and evidence for their structures is presented.

It has been reported recently[1] that triphenylsilyllithium (I) reacts with acetyl chloride to give low yields of acetyltriphenylsilane (II), whereas the chief products were triphenylsilane, 1,1-bis(triphenylsilyl)ethanol (III), and triphenyl(1-triphenylsiloxyethyl)silane (IV).



$$\underset{\text{I}}{(C_6H_5)_3SiLi} + CH_3COCl \longrightarrow \underset{\text{II}}{(C_6H_5)_3Si{-}COCH_3}$$

$$\text{II} + (C_6H_5)_3SiLi \longrightarrow \underset{\text{III}}{[(C_6H_5)_3Si]_2C(OH)CH_3} \xrightarrow{\text{rearrangement}} \underset{\text{IV}}{(C_6H_5)_3Si{-}\underset{O-Si(C_6H_5)_3}{\underset{|}{C}}HCH_3}$$

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[1] For paper No. I of this series, see D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 4529 (1958).