turnings in 43.2 g. (0.6 mole) of tetrahydrofuran and diluted with 85 ml. of tetrahydrofuran, was cooled to 6° with an ice bath and treated with 30.3 g. (0.18 mole) of methylchlorodiethoxysilane. The temperature of the mixture was not allowed to exceed 10° during the addition. After the addition was complete, the product was refluxed 1 hr., diluted with heptane, concentrated by distillation, and filtered. Fractional distillation gave 23.6 g. (58%) of diethoxymethyl-1-naphthylsilane boiling at 114–115° at 0.1 mm., n_D^{25} 1.5393; d_4^{25} 1.039.

Anal. Calcd. for $C_{15}H_{20}O_2Si$: Si, 10.79; MR_D, 78.46. Found: Si, 10.44; MR_D, 78.42.

In a repetition of the experiment with 0.7 mole of 1-bromonaphthalene, the bromide and the silane were added to the reaction mixture concomitantly. The yield of methyl-1-naphthyldiethoxysilane boiling at 100° at 0.05 mm. was 36%.

Diisopropoxymethyl-1-naphthylsilane. When 5.9 g. (0.24 g.-atom) of magnesium was treated with a mixture of 41.4 g. (0.2 mole) of 1-bromonaphthalene, 47.2 g. (0.24 mole) of methylchlorodiisopropoxysilane, and 43.2 g. (0.6 mole) of tetrahydrofuran, diisopropoxymethyl-1-naphthylsilane (37.5%) was obtained boiling 137–143° at 2.7 mm., n_D^{25} 1.5165, d_4^{25} 0.996.

Anal. Calcd. for $C_{17}H_{24}O_2Si$: Si, 9.74; MR_D, 87.72. Found: Si, 9.99; MR_D, 87.46.

Diethoxymethyl-2-naphthylsilane. A mixture of 20.0 g. of 2-bromonaphthalene, 24.9 g. (0.145 mole) of chlorodiethoxymethylsilane, and 20 ml. of ethyl ether was added dropwise to a flask containing 5.0 g. (0.121 mole, total) of 2-bromonaphthalene, 5 ml. of ether, and 5.0 g. (0.206 g.-atom) of magnesium turnings. The contents of the flask were heated under reflux and stirred for 19 hr., and then cooled and filtered. Distillation at 0.5 mm. gave 15.1 g. of unchanged 2-bromonaphthalene between 70° and 99°. Fractional distillation of the remainder of the material gave about 4 g. (13%) of impure diethoxymethyl-2-naphthylsilane boiling 138–138.5° at 2.5 mm., n_D^{25} 1.5518, d_2^{25} 1.066.

Anal. Calcd. for $C_{15}H_{20}O_2Si$: Si, 10.79; MR_D, 78.46. Found: Si, 11.37; MR_D, 78.01.

The product fumed in air and gave a positive Beilstein test. Titration of a hydrolyzed aliquot indicated that the product contained 5.32 weight per cent chlorine, or that about one-third of the material was chloroethoxymethyl-2-naphthylsilane.

A product of about the same purity and in about the same yield was obtained when the reaction was carried out in tetrahydrofuran.

Repetition of the procedure with 25.0 g. of methyltriethoxysilane in place of the methylchlorodiethoxysilane gave 4.6 g. (15%) of diethoxymethyl-2-naphthylsilane boiling 140–144° at 2.2 mm., n_D^{25} 1.5407, d_4^{25} 1.042. About 17 g. of 2-bromonaphthalene was recovered unchanged.

Anal. Found: Si, 10.93; MR_D, 78.53.

2-Biphenylylmethyldiethoxysilane. When 9.6 g. (0.40 g.-atom) of magnesium was treated with a mixture of 76.7 g. (0.33 mole) of 2-bromobiphenyl, 67.5 g. (0.40 mole) of chlorodiethoxymethylsilane, and 71.3 g. (0.99 mole) of tetrahydrofuran and the product was worked up similarly, 42.1 g. (45%) 2-biphenyldiethoxymethylsilane boiling 102° at 0.04 mm. was obtained, n_D^{25} 1.5334, d_4^{25} 1.094.

Anal. Calcd. for $C_{15}H_{22}O_2Si$: Si, 9.81; MR_D, 85.27. Found: Si, 9.84; MR_D, 84.64.

Titration of a hydrolyzed aliquot indicated that the product contained 0.36 weight per cent hydrolyzable chlorine.

Hydrolysis procedure. A mixture of 5 ml. of 95% ethyl alcohol, 5 ml. of concd. hydrochloric acid, and 10 ml. of the silane monomer was refluxed 2 hr., diluted with 15 ml. of benzene, and refluxed for an additional 4 hr. The product, washed with water until it was neutral, was heated to 100° *in vacuo* to remove the solvents.

Rearrangement of the siloxanes with sodium hydroxide. Five grams of the polymer and 0.2 g. of 50% sodium hydroxide was heated at 145° for 5 hr. The cooled product, diluted with 20 ml. of benzene, was washed with portions of water until the washings were neutral, and then heated at 100° overnight *in vacuo*. In each case a cleavage product, either naphthalene or biphenyl, was collected as a sublimate during the initial heating period. Although no attempt was made to recover the decomposition products quantitatively, the solid material recovered usually represented about 5% of the organic groups present in the polymer.

Polymer molecular weights given in Table I were determined cryoscopically in benzene, K_f = 5.32. Softening points of the four polymers were determined as follows: A few milligrams of the sample was placed between two-micro cover glasses on a Fisher-Johns melting point apparatus heated at the rate of 5°/min. A slight pressure was applied on the top cover glass, and the temperature at which the material flowed freely between the plates was recorded. These results are also recorded in Table I.

DIVISION OF CHEMISTRY AND
CHEMICAL ENGINEERING
MIDWEST RESEARCH INSTITUTE
KANSAS CITY 10, MO.

Reactions of Triphenylsilyllithium with Triaryl Phosphates

HENRY GILMAN AND BERNARD J. GAJ

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Recent publications[1,2] from this laboratory described the reactions of triphenylsilyllithium with trialkyl phosphates. High yields of alkyltriphenylsilanes were realized when the reactions were carried out in a 1:1 mole ratio. The use of three equivalents of triphenylsilyllithium in attempts to utilize all three alkyl groups of tri-*n*-butyl phosphate in this reaction, however, resulted in the isolation of considerable amounts of hexaphenylisildane together with other products.[2] A mechanism involving the displacement of a butoxyl group, and the subsequent cleavage of the intermediate silylphosphorus compound by triphenylsilyllithium, was proposed to account for the formation of the disilane.

The reactions of triphenylsilyllithium in various ratios with triaryl phosphates, likewise gave sizeable amounts of hexaphenyldisilane. After hydrolysis, the reaction mixtures had pronounced phosphine-like odors, as did the 3:1 reactions of triphenylsilyllithium with tri-*n*-butyl phosphate.[2] Thus, it appears as though a similar mechanism is involved in these reactions.

This reaction path is not surprising since carbon-metallic compounds react with substances having the P—O—R linkage *via* displacements of —O—R groups from phosphorus.[3] Furthermore, resonance

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(1) M. V. George, B. J. Gaj, and H. Gilman, *J. Org. Chem.*, 24, 624 (1959).

(2) H. Gilman and B. J. Gaj, *J. Org. Chem.* (in press).

(3) For references to reactions of this type, see the publication cited in ref. (2) of this paper.

interaction between oxygen and the aryl group should also favor the displacement mechanism in spite of the steric factors involved.

At room temperature, the reaction of three equivalents of triphenylsilyllithium with triphenyl phosphate afforded 27% of hexaphenyldisilane and 52% of triphenylsilanol subsequent to hydrolysis. All of the organosilyllithium compound was consumed as evidenced by a negative Color Test I.[4] When six equivalents of this reagent were employed, these products were isolated in 33 and 41% yields, respectively, together with hexaphenyldisiloxane (3%) and triphenylsilane (14%). The hydrolysis of unchanged triphenylsilyllithium probably accounts for the formation of the last-mentioned product. These results can best be explained *via* the following reaction scheme:

$$(C_6H_5)_3SiLi + (C_6H_5O)_3PO \longrightarrow C_6H_5Li + \underset{\text{I.}}{(C_6H_5)_3SiP(O)(OC_6H_5)_2}$$

$$\begin{tikzcd}[column sep=small] & \underset{\text{II.}}{(C_6H_5)_6Si_2 + LiP(O)(OC_6H_5)_2} \\ (C_6H_5)_3SiLi + (C_6H_5)_3SiP(O)(OC_6H_5)_2 \arrow[ur] \arrow[dr] & \\ & \underset{\text{III.}}{C_6H_5OLi + ((C_6H_5)_3Si)_2P(O)OC_6H_5} \end{tikzcd}$$

$$\begin{tikzcd}[column sep=small] & \underset{\text{IV.}}{(C_6H_5)_6Si_2 + (C_6H_5)_3SiP(O)(Li)(OC_6H_5)} \\ (C_6H_5)_3SiLi + \underset{\text{III}}{((C_6H_5)_3Si)_2P(O)OC_6H_5} \arrow[ur] \arrow[dr] & \\ & \underset{\text{V.}}{C_6H_5OLi + ((C_6H_5)_3Si)_3PO} \end{tikzcd}$$

$$(C_6H_5)_3SiLi + \underset{\text{V.}}{((C_6H_5)_3Si)_3PO} \longrightarrow (C_6H_5)_6Si_2 + \underset{\text{VI.}}{((C_6H_5)_3Si)_2P(O)Li}$$

Since Color Test I was negative in the 3:1 reaction, and hexaphenyldisilane was isolated in only 27% yield, it is evident that at least some of the ester molecules are undergoing displacement of all three phenoxide groups. If this were not so, the yield of the disilane should have been nearer to 67% than to 33%, and the yield of triphenylsilanol would have been somewhere around 33% or less. The fact that less than one-third of the silicon appeared as hexaphenyldisilane in this reaction, indicates that a considerable amount of III and V, as well as their cleavage products (IV and VI) were formed. There is nothing to prevent two or three displacements from occurring, except possibly steric factors.

The cleavage of a triphenylsilyl group from I, III or V would be expected to occur with relative ease, based on considerations presented earlier.[3] However, the removal of a triphenylsilyl group from anions such as IV and VI, or the displacement of a phenoxide group from II, IV or VI would not be expected to occur readily. Such reactions would involve anionic attack at positions of high electron density. This may account for the failure to realize more than 33% of the disilane from the reaction employing six equivalents of triphenylsilyllithium at room temperature.

Hydrolysis of the silylphosphorus intermediates (I, III, IV, V, VI), accounts for the isolation of triphenylsilanol from these reactions, as well as for the phosphine-like odors noticed after hydrolysis. Using IV as an example, this hydrolysis may be formulated as follows:

$$\underset{\text{IV.}}{(C_6H_5)_3SiP(O)(Li)(OC_6H_5)} \xrightarrow{H_2O} (C_6H_5)_3SiOH + \underset{\text{VII.}}{H_2P(O)(OC_6H_5)} + LiOH$$

Hydrolytic reactions of this type are well-known.[5]

Although products of type VII were not isolated from these reactions, the fact that the phosphine-like odors were carried into the organic layer after hydrolysis indicates strongly that they exist in the reaction mixtures.

In order to determine whether or not forced conditions might cause cleavage of a second triphenylsilyl group from intermediates of type IV and VI, the reaction using six equivalents of triphenylsilyllithium was repeated under reflux conditions for 21 hours. Color Test I was negative after this time. The products isolated were: hexaphenyldisilane, hexaphenyldisiloxane, 4-triphenylsilylbutanol, triphenysilanol, and phenol (isolated as the tribromoderivative), in yields of 39.6, 11.8, 3.75, 30, and 81%, respectively. The slight increase in yield of hexaphenyldisilane together with the high yield of phenol suggests that placing a second negative charge on phosphorus *via* this reaction is possible, but not readily accomplished, and that all three phenoxide groups are capable of displacement in this reaction.

Similar results were obtained from reactions employing either two or three equivalents of triphenylsilyllithium with tri-*p*-tolyl phosphate. The former reaction gave 35.8% of hexaphenyldisilane together with triphenylsilanol, (47.8%) and recovered ester (14.9%). The 3:1 reaction afforded the disilane, triphenylsilanol, triphenylsilane, and *p*-cresol in yields of 33, 45.2, 3.8, and

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[4] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[5] See, for example: G. Fritz, *Z. Naturforsch*, **8b**, 776 (1953); G. Fritz, *Z. anorg. u. allegem. Chem.*, **280**, 332 (1955); W. Keeber and H. W. Post, *J. Org. Chem.*, **21**, 509 (1956); G. Fritz and H. O. Berkénhoff, *Z. anorg. u. allegem. Chem.*, **289**, 250 (1957); F. Fehér, G. Kulbörsch, A. Blüneke, H. Keller, and K. Lippert, *Chem. Ber.*, **90**, 134 (1957); G. W. Parshall and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 6273 (1959).

57.2%, respectively. These yields are also consistent with the proposed mechanism.

EXPERIMENTAL[6]

Reaction of triphenylsilyllithium with triphenyl phosphate (3:1). A solution of 4.20 g. (0.0133 mole) of triphenyl phosphate in 10 ml. of tetrahydrofuran was added to a stirred solution of 0.04 mole of triphenylsilyllithium[7] in 90 ml. of the same solvent. The reaction was mildly exothermic and a suspension developed after the first few ml. of solution had been added. Upon complete addition, Color Test I[4] was negative, hence the mixture was hydrolyzed with water in a hood (strong phosphine-like odor). Filtration and thorough washing with water and diethyl ether left 2.8 g. (27%) of hexaphenyldisilane, melting point and mixed m.p. 362–364°. The phenol was extracted from the organic layer with 10% sodium hydroxide solution and discarded.

The solvents were removed from the dried organic layer, which still smelled strongly of phosphine, to leave an oily solid. Crystallization from cyclohexane gave in several crops, 5.73 g. (52%) of triphenylsilanol, identified by mixed melting point and infrared spectra.

Reaction of triphenylsilyllithium with triphenyl phosphate (6:1). A mixture of 0.12 mole of triphenylsilyllithium and 6.32 g. (0.02 mole) of triphenyl phosphate in 250 ml. of tetrahydrofuran was stirred at room temperature for 2 days to give a brown suspension. Color Test I was pale green. The mixture was hydrolyzed with 100 ml. of dilute hydrochloric acid, filtered, and the insoluble material was washed thoroughly with water and diethyl ether to leave 10.2 g. (33%) of hexaphenyldisilane, melting point and mixed m.p. 363-365°.

The layers of the filtrate, which had a pronounced phosphine-like odor, were separated and the organic layer was washed with 10% sodium hydroxide to remove phenol, then dried over sodium sulfate. Removal of the solvents by distillation and treatment of the residue with cyclohexane afforded 11.25 g. (34%) of triphenylsilanol, m.p. 149–152° (mixed melting point and infrared spectra). The material in the cyclohexane filtrate oiled upon further concentration, hence the solvent was removed and the residue passed through a column of alumina. Elution with 600 ml. of petroleum ether (b.p. 60–70°) gave 4.5 g. (14%) of triphenylsilane, m.p. 42–44° (identified by mixed melting point and infrared spectra). The next 600 ml. of the same solvent gave 0.8 g. (3%) of hexaphenyldisiloxane, m.p. 224–226° after two crystallizations from cyclohexane. Ethyl acetate then eluted 2.5 g. of triphenylsilanol, m.p. 152–154°, (total yield, 13.25 g., 41%).

Reaction of triphenylsilyllithium with triphenyl phosphate (6:1) at reflux. The preceding reaction was repeated using the same quantities of material; however, the mixture was refluxed gently for 21 hr., at the end of which time, Color Test I was negative. The mixture was worked up as in the previous reaction to give 12.3 g. (39.6%) of hexaphenyldisilane, melting point and mixed m.p. 366–368°.

The solvents were removed from the dried organic layer and the residue was chromatographed on alumina to give 3.9 g. (11.8%) of hexaphenyldisiloxane, melting point and mixed m.p. 226–228°, after crystallization of the material eluted with petroleum ether (b.p. 60–70°) and benzene from cyclohexane. The first 30 ml. of ethyl acetate eluates gave an oil, which when recrystallized from petroleum ether (b.p. 60–70°), afforded 1.5 g. (3.75%) of 4-triphenylsilylbutanol, m.p. 107–109° (mixed melting point and infrared spectra). Further elution with the same solvent gave, after recrystallization from cyclohexane, 9.95 g. (30%) of triphenylsilanol and *ca.* 2 g. of an oil whose infrared spectrum indicated it to be a mixture of triphenylsilanol and 4-triphenylsilylbutanol. This material was not worked up any further.

The basic extract of the organic layer was acidified and extracted with diethyl ether. Drying and removing the ether gave, upon bromination, 16 g. (81%) of tribromophenol, m.p. 92–94° (mixed melting point).

Reaction of triphenylsilyllithium with tri-p-tolyl phosphate (2:1). A mixture of 0.04 mole of triphenylsilyllithium and 7.37 g. (0.02 mole) of tri-*p*-tolyl phosphate in 110 ml. of tetrahydrofuran was stirred overnight at room temperature (12 hr.) then hydrolyzed with 10% hydrochloric acid. Filtration and washing gave 3.7 g. (35.8%) of hexaphenyldisilane, melting point and mixed m.p. 365–367°.

The organic layer was separated and washed with 10% sodium hydroxide to remove the *p*-cresol, then dried. The dried organic layer was distilled to remove solvent and the residue was dissolved in cyclohexane. Concentration afforded 4.78 g. (43.3%) of triphenylsilanol, m.p. 152–154° (mixed melting point). Further concentration gave an oil which had a pronounced phosphine-like odor. Passage through a short column of alumina gave a trace of hexaphenyldisiloxane, m.p. 222–224° (mixed melting point); 1.1 g. (14.9%) of recovered tri-*p*-tolyl phosphate, m.p. 74–76° (mixed melting point); and 0.5 g. (4.5%) of triphenylsilanol, m.p. 152–154° (after crystallization from cyclohexane).

Reaction of triphenylsilyllithium with tri-p-tolyl phosphate (3:1). A mixture of 0.06 mole of triphenylsilyllithium in 100 ml. of tetrahydrofuran was allowed to react for 3 hr. with a solution of 7.37 g. (0.02 mole) of tri-*p*-tolyl phosphate in 50 ml. of the same solvent. Hydrolysis with 100 ml. of water followed by acidification and filtration gave 5.15 g. (33%) of hexaphenyldisilane, melting point and mixed m.p. 360–364°.

The separated organic layer was extracted with 10% sodium hydroxide, then dried. The basic extract was acidified and extracted with diethyl ether and the ether extracts were dried. Solvent removal from the ether extract left an oil which was distilled to give 3.7 g. (57.2%) of *p*-cresol, b.p. 95–97° (20 mm.), identified by infrared spectra. A considerable amount of distillation residue remained and attempts to distill it at a lower pressure led to decomposition by charring and fuming.

The neutral organic layer was chromatographed on alumina to give 0.6 g. (3.8%) of triphenylsilane, identified by infrared spectra, and 7.5 g. (45.2%) of triphenylsilanol, m.p. 152–154° (mixed melting point).

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CHEMICAL LABORATORY
IOWA STATE UNIVERSITY
AMES, IOWA

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(6) Melting points and boiling points are uncorrected. All reactions were carried out in oven-dried glassware under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was dried by refluxing over sodium wire for at least 24 hr., followed by distillation into a refluxing suspension of lithium aluminum hydride under dry nitrogen. It was then distilled immediately before use from this suspension.

(7) Prepared by the lithium cleavage of hexaphenyldisilane according to the reported procedure of H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).