[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Studies in Silico-Organic Compounds. XXXI. The Chemistry of Sila Compounds Containing Phosphorus—Preliminary Paper

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Bromomethyltrimethylsilane reacts with di-*n*-butyl sodiophosphonate to form di-*n*-butyl trimethylsilylmethylphosphonate (silicon connected to phosphorus through carbon). This ester is easily hydrolyzed by hydrochloric acid to trimethylsilylmethylphosphonic acid.

Di-*n*-butyl sodiophosphonate also reacts with trimethylchlorosilane to form di-*n*-butyl trimethylsilylphosphonate (silicon connected directly to phosphorus). Water hydrolysis yields hexamethyldisiloxane, trimethylsilanol, and *n*-butyl alcohol, as well as unidentifiable phosphorus acids. Reactions are reported here between this ester and methyl alcohol, phenol, aniline, *n*-butylamine, *n*-butyl mercaptan, and propionic acid.

n-Butylphosphonic acid has been prepared by the hydrolysis of di-*n*-butyl *n*-butylphosphonate, formed by the interaction of *n*-butyl bromide and di-*n*-butyl sodiophosphonate. Trimethylchlorosilane reacts with *n*-butylphosphonic acid to form di-(trimethylsilyl) *n*-butylphosphonate (silicon connected to phosphorus through oxygen). The ester undergoes hydrolysis in hot water.

Infrared spectra are submitted for several of these compounds.

INTRODUCTION

The synthesis and properties of organic compounds containing both phosphorus and silicon have received scant attention. Aylett, Emeleus, and Maddock[1] allowed iodosilane to react with white phosphorus in a vacuum, obtaining trisilylphosphine, trisilylphosphinous iodide, and silylphosphinous diiodide.

p-Trimethylsilylphenyl derivatives of phosphorus have been prepared by Frisch and Lyons:[2]

$$\text{I. } p\text{-}(CH_3)_3SiC_6H_4MgBr + PCl_3 \longrightarrow 3\ MgClBr + P[C_6H_4Si(CH_3)_3\text{-}p]_3.$$

Substitution of phosphorus pentachloride for the trichloride yielded two products:

$$\text{II. } 5\ p\text{-}(CH_3)_3SiC_6H_4MgBr + 2\ PCl_5 \longrightarrow 5\ MgClBr + 2\ Cl_2 + P[C_6H_4Si(CH_3)_3\text{-}p]_3 + [p\text{-}(CH_3)_3SiC_6H_4]_2PCl.$$

Phosphorus oxychloride yielded $[p\text{-}(CH_3)_3SiC_6H_4]_3PO$ and $[p\text{-}(CH_3)_3SiC_6H_4]_2POCl$. The latter compound, on hydrolysis, formed $[p\text{-}(CH_3)_3SiC_6H_4]_2POOH$.

A series of diethyl esters of substituted silylmethylphosphonic acids was prepared by Gilbert and Precopio[3] using the Michaelis-Arbuzov reaction. Pentamethylchloromethyldisiloxane and heptamethylchloromethylcyclotetrasiloxane reacted similarly, as did certain chloromethylsilane polymers. If a siloxane system is bonded to phosphorus, cleavage of silicon to carbon bonds occurs in both acidic and basic media.[3] Gilbert and Precopio[3] also reported an adaptation of the Clayton-Jensen[4] reaction.

Organic compounds with silicon bonded directly to phosphorus have also been prepared. Malatesta[5] heated triethyl phosphite with triethylbromosilane at 150° for three hours, obtaining diethyl triethylsilylphosphonate and ethyl triethylsilyl triethylsilylphosphonate. Identical products were obtained when triethylbromosilane was allowed to react with diethyl ethylphosphonate under the same conditions.

Arbuzov and Pudovik[6] also used the Michaelis-Arbuzov reaction to prepare diethyl triethylsilylphosphonate in 41% yield. A similar reaction with triethoxybromosilane yielded 36% of product.

Yields of 53% were obtained through the sodium derivative. An attempt to extend this reaction to the triphenyl analog yielded only tetraphenylsilane. Cleavage of the silicon-phosphorus bond with chlorine was also reported. Thermal decomposition at 200° formed tetraethoxysilane.

Sauer[7] has synthesized tris-(trimethylsilyl) phosphate by distilling a large excess of hexamethyldisiloxane from phosphorus pentoxide. The phosphorus-oxygen-silicon bond is water hydrolyzable—in fact direct titration against standard sodium hydroxide was possible.

DISCUSSION

In this work, di-*n*-butyl phosphonate was first prepared, in accordance with the method of Milo-

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(1) Aylett, Emeleus, and Maddock, *Research* (*London*), **6**, 30S (1953).

(2) Frisch and Lyons, *J. Am. Chem. Soc.*, **75**, 4078 (1953).

(3) Gilbert and Precopio, *Abstracts of Papers Presented at the 125th Meeting, A.C.S.*, 16N (1954).

(4) Clayton and Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948).

(5) Malatesta, *Gazz. chim. ital.*, **80**, 527 (1950).

(6) Arbuzov and Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **59**, 1433 (1948).

(7) Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

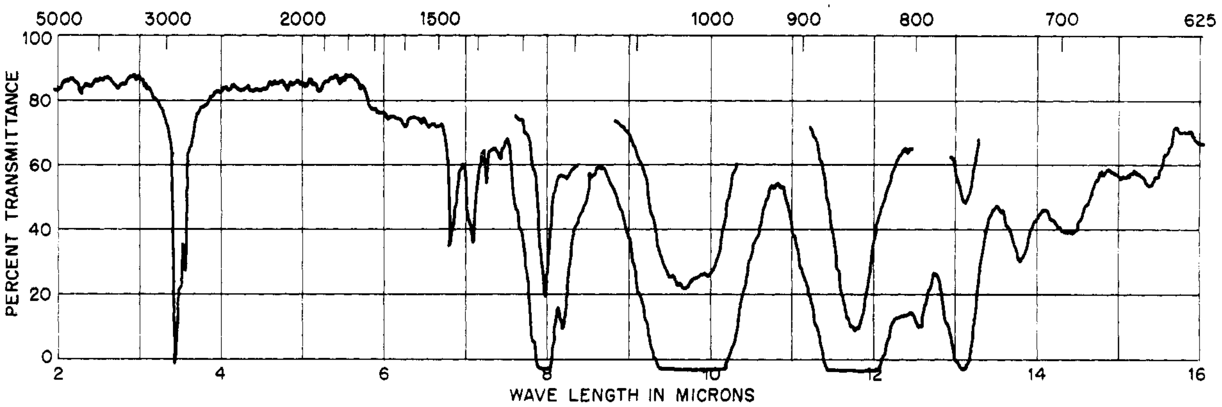

FIG. 1.—INFRARED ABSORPTION SPECTRA OF DI-(TRIMETHYLSILYL) *n*-BUTYLPHOSPHONATE.

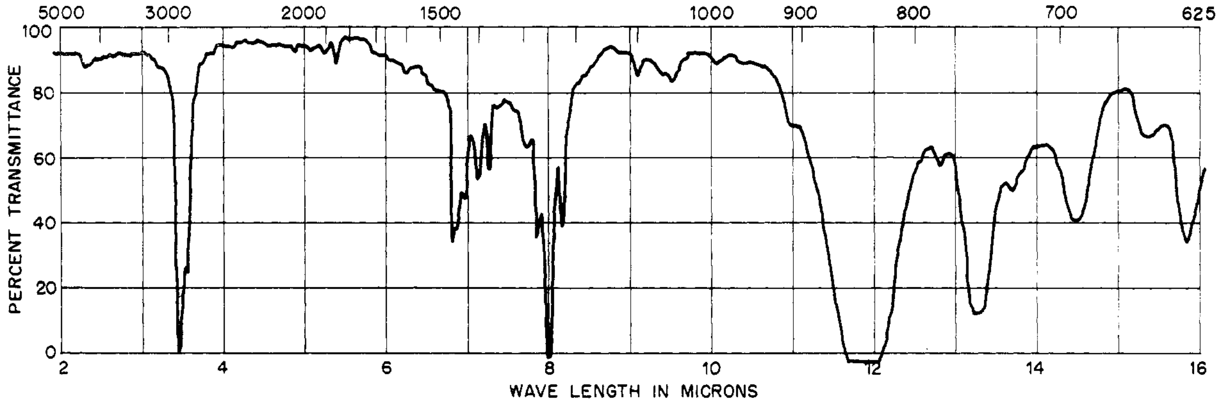

FIG. 2.—INFRARED ABSORPTION SPECTRA OF TRIMETHYL-*n*-BUTYLMERCAPTOSILANE.

TABLE I
NEW COMPOUNDS

Compound	B.p., °C.	Mm.	M.p., °C.	n_D^{25}	d_4^{25}
$(CH_3)_3SiCH_2P(O)(OC_4H_9)_2$	154-158	17		1.4380	0.9465
$(CH_3)_3SiCH_2P(O)(OH)_2$			119-121		
$(CH_3)_3SiP(O)(OC_4H_9)_2$	93-94	4.5		1.4220	0.9194
$HP(O)(OCH_3)OC_4H_9$	89.5-90.5	10		1.4150	1.0531
$HP(O)(OC_4H_9)NHC_6H_5$	56-58	0.07 (impure)			
$HP(O)(OH)ONH_3C_6H_5$			179-182 (+ dec.)		
$C_4H_9P(O)(OH)ONH_3C_6H_5$			150-152		
$C_4H_9P(O)[OSi(CH_3)_3]_2$	107-108	5.5		1.4168	0.9356

bendzki and Sachnowski[8] and was converted to the di-*n*-butyl ester of trimethylsilylmethylphosphonic acid. This compound underwent hydrolysis to the free acid in dilute hydrochloric acid.

III. $NaP(O)(OC_4H_9\text{-}n)_2 + (CH_3)_3SiCH_2Br \longrightarrow NaBr + (CH_3)_3SiCH_2P(O)(OC_4H_9\text{-}n)_2.$

IV. $(CH_3)_3SiCH_2P(O)(OC_4H_9\text{-}n)_2 + 2\ HOH\ (HCl) \longrightarrow 2\ n\text{-}C_4H_9OH + (CH_3)_3SiCH_2P(O)(OH)_2.$

Di-*n*-butyl trimethylsilylphosphonate has been prepared here by the action of trimethylchlorosilane on di-*n*-butyl sodiophosphonate:

V. $(CH_3)_3SiCl + NaP(O)(OC_4H_9\text{-}n)_2 \longrightarrow NaCl + (CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2.$

Hydrolysis of this compound was effected by the action of water alone:

VI. $2(CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + 5\ HOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + 4\ n\text{-}C_4H_9OH + 2\ HP(O)(OH)_2.$

Di-*n*-butyl trimethylsilylphosphonate has been found to react with methyl alcohol and with phenol as follows:

VII. $(CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + CH_3OH \longrightarrow (CH_3)_3SiOCH_3 + HP(O)(OC_4H_9\text{-}n)_2.$

VIII. $HP(O)(OC_4H_9\text{-}n)_2 + CH_3OH \longrightarrow n\text{-}C_4H_9OH + HP(O)(OC_4H_9\text{-}n)OCH_3.$

IX. $(CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + C_6H_5OH \longrightarrow (CH_3)_3SiOC_6H_5 + HP(O)(OC_4H_9\text{-}n)_2.$

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(8) Milobendzki and Sachnowski, *Chemik Polski*, **15**, 34 (1917) [*Chem. Abstr.*, **6**, 2866 (1919)].

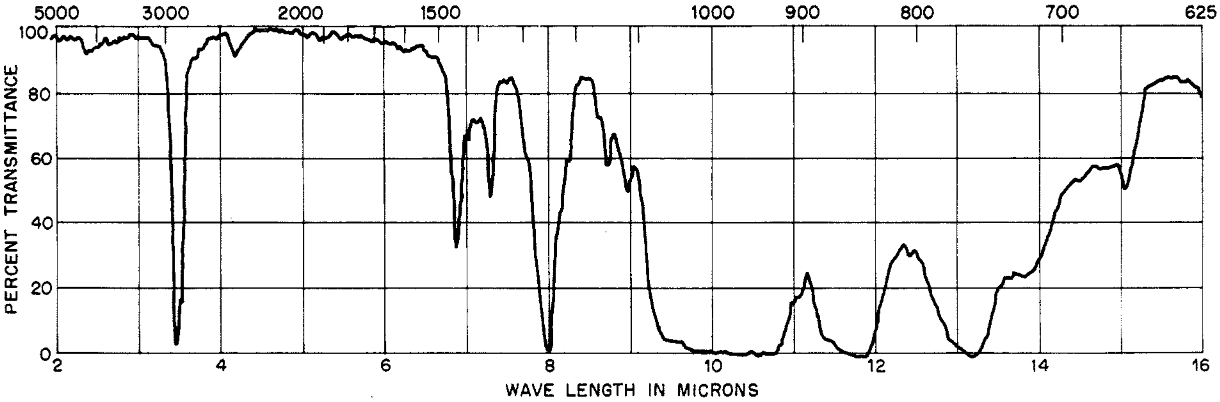

FIG. 3.—INFRARED ABSORPTION SPECTRA OF DI-n-BUTYL TRIMETHYLSILYLPHOSPHONATE.

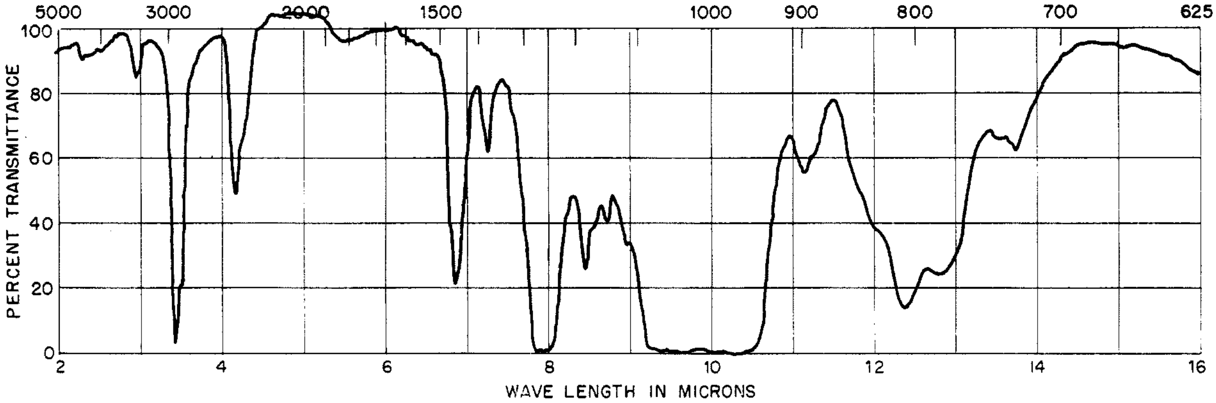

FIG. 4.—INFRARED ABSORPTION SPECTRA OF METHYL n-BUTYLPHOSPHONATE.

Results of the action of di-n-butyl trimethylsilylphosphonate with aniline and with n-butylamine lead to the formulation of the reactions as shown in the equations below.

X. $(CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + C_6H_5NH_2 \longrightarrow$
$n\text{-}C_4H_9OH + (CH_3)_3SiP(O)(OC_4H_9\text{-}n)NHC_6H_5.$
XI. $(CH_3)_3SiP(O)(OC_4H_9\text{-}n)NHC_6H_5 + n\text{-}C_4H_9OH \longrightarrow$
$(CH_3)_3SiOC_4H_9\text{-}n + HP(O)(OC_4H_9\text{-}n)NHC_6H_5.$
XII. $2\ (CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + n\text{-}C_4H_9NH_2 \longrightarrow$
$(CH_3)_3SiP(O)(OC_4H_9\text{-}n)NHC_4H_9\text{-}n +$
$(CH_3)_3SiOC_4H_9\text{-}n + HP(O)(OC_4H_9\text{-}n)_2.$

There was no reaction between di-n-butyl trimethylsilylphosphonate and benzenethiol. With n-butyl mercaptan the following reaction took place:

XIII. $(CH_3)_3SiP(O)(OC_4H_9\text{-}n)_2 + n\text{-}C_4H_9SH \longrightarrow$
$(CH_3)_3SiSC_4H_9\text{-}n + HP(O)(OC_4H_9\text{-}n)_2.$

The reaction with propionic acid yielded n-butyl propionate and trimethylsilylphosphonic acid. n-Butylphosphonic acid and its di-n-butyl ester were also prepared. The free acid was identified as its monoanilinium salt. From n-butylphosphonic acid, di-trimethylsilyl n-butylphosphonate was prepared and was hydrolyzed.

XIV. $n\text{-}C_4H_9P(O)(OH)_2 + 2\ (CH_3)_3SiCl \longrightarrow$
$2\ HCl + n\text{-}C_4H_9P(O)[OSi(CH_3)_3]_2.$
XV. $n\text{-}C_4H_9P(O)[OSi(CH_3)_3]_2 + HOH \longrightarrow$
$(CH_3)_3SiOSi(CH_3)_3 + n\text{-}C_4H_9P(O)(OH)_2.$

EXPERIMENTAL PART

Preparation of di-n-butyl phosphonate. This compound was prepared according to the method of Milobendzki and Sachnowski.[8] The yields were consistently 80–85%. Fractionation yielded 166 g. of di-n-butyl phosphonate, b.p. (found) 110–112° (5 mm.), (literature)[8] b.p. 124–125° (12 mm.); n_D^{25} (found) 1.4222; d_4^{25} (found) 0.9846, d_4^{20} (literature)[8] 0.99503.

Preparation of di-n-butyl trimethylsilylmethylphosphonate. Di-n-butyl phosphonate (0.25 mole, 48.6 g.) was added dropwise to a suspension of 0.25 gram-atom of sodium shot in 250 cc. of dry ligroin (b.p. 60–90°) in a 500-cc. three-neck flask. The mixture was stirred and gently refluxed until the sodium had dissolved. Bromomethyltrimethylsilane (0.28 mole, 46.7 g.) then was slowly added. Precipitation of sodium bromide began after 10 minutes, and gentle reflux with agitation was maintained for 10 hours. The mixture then was cooled and the sodium bromide was separated by centrifugation. The solvent was removed by distillation and the resultant mixture was fractionated yielding di-n-butyl trimethylsilylmethylphosphonate, 25.5 g., b.p. 154–158° (17 mm.), n_D^{25} 1.4380, d_4^{25} 0.9465, 28% yield.

Anal. Calc'd for $C_{12}H_{29}O_3PSi$: P, 11.05; Si, 10.02; Mol. Wt. 280.4; M.R., 77.81. Found: P, 11.08, 11.06, 10.93; Si, 9.82, 9.83; Mol. Wt. (cryoscopic from benzene) 277; M.R. 76.8.

Hydrolysis of di-n-butyl trimethylsilylmethylphosphonate. Di-n-butyl trimethylsilylmethylphosphonate (11.5 g., 0.04 mole) was refluxed with 100 cc. of concentrated hydrochloric acid until the original two-phase system had condensed into one (24 hours). After the system had been evaporated to 10 cc. crystals of trimethylsilylmethylphosphonic acid separated out, and were recrystallized from

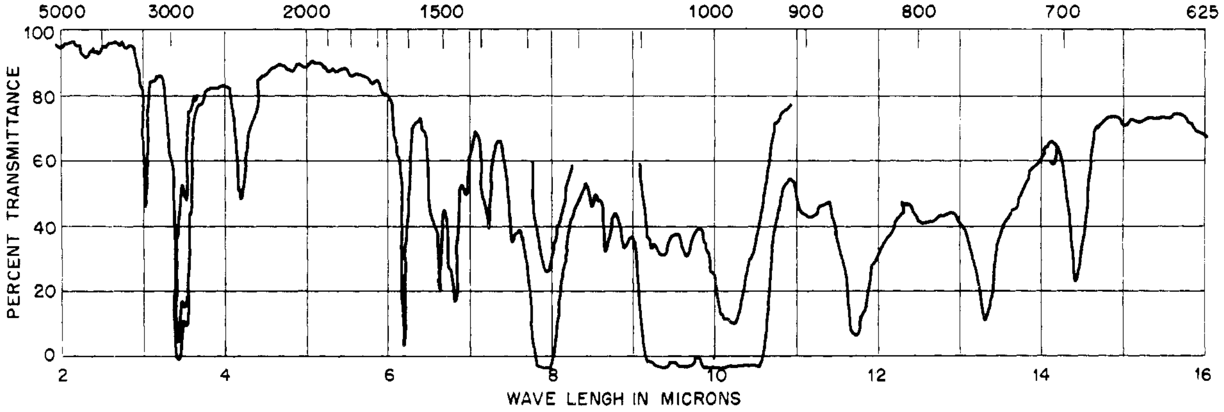

Fig. 5.—Infrared Absorption Spectra of *n*-Butyl N-Phenylphosphonamide.

ligroin (b.p. 60–90°), 6 g., m.p. 118–119°, 85% yield. The analytical sample was further recrystallized from ligroin to a constant melting point (120–121°).

Anal. Calc'd for $C_3H_{11}O_3PSi$: Si, 16.70; P, 18.40; Mol. Wt. 168.2. Found: Si, 16.55, 16.65; P, 18.55, 18.46; Mol. Wt. 168; K_{a1}, 6 × 10^{-4}; K_{a2}, 2 × 10^{-9}.

Preparation of di-n-butyl trimethylsilylphosphonate. Di-*n*-butyl sodiophosphonate (0.25 mole) was treated with 0.25 mole (27.1 g.) of freshly distilled trimethylchlorosilane over a period of one hour. Fifteen minutes after the addition was begun sodium chloride began to form. The system was refluxed gently and agitated for eight hours. Sodium chloride was separated by centrifugation. The salt cake was slurried with 100 cc. of anhydrous ligroin, centrifuged, and the supernatant liquids were combined. Distillation yielded di-*n*-butyl trimethylsilylphosphonate, 48 g., b.p. 93–94° (4.5 mm.), n_D^{25} 1.4220, d_4^{25} 0.9194, yield 73%.

Anal. Calc'd for $C_{12}H_{27}O_3PSi$: Si, 10.53; P, 11.63; Mol. Wt. 266.4. Found: Si, 10.21, 10.30; P, 11.61, 11.54; Mol. Wt. 259.

Hydrolysis of di-n-butyl trimethylsilylphosphonate. Di-*n*-butyl trimethylsilylphosphonate (30 g., 0.11 mole) was refluxed with 250 cc. of water for four hours. The water-insoluble layer was separated, dried, and fractionated. Since hexamethyldisiloxane (b.p. 100.4°)[9] and trimethylsilanol (b.p. 99.5°)[7] form an azeotrope, b.p. 90°,[7] a fraction boiling between 90° and 102° (6.2 g.) was taken and dehydrated over phosphorus pentoxide for complete conversion to hexamethyldisiloxane. A two-gram center fraction from this, b.p. 100–101°, n_D^{25} 1.3745 was taken for identification (literature)[9] b.p. 100.4°, n_D^{25} 1.3748.[9] The homogeneous hydrolyzate, smelling strongly of *n*-butyl alcohol, was steam-distilled. The organic layer was separated from the first 30 cc. of distillate and was dried over potassium carbonate. It was identified as *n*-butyl alcohol, 3,5-di-nitrobenzoate m.p. 65–66° (literature)[10] 64°. The remaining hydrolyzate was acidified with nitric acid. A yellow precipitate with ammonium molybdate solution indicated the presence of phosphate ion.

The reaction of di-n-butyl trimethylsilylphosphonate with methyl alcohol. Absolute methyl alcohol (60 g., 1.9 moles) was refluxed with di-*n*-butyl trimethylsilylphosphonate (0.25 mole, 66.3 g.) for 16 hours. The reaction mixture was fractionated. Methyl alcohol and trimethylmethoxysilane form an azeotrope, b.p. 49.5° containing 14–16% of the alcohol by weight.[7] To establish the presence of trimethylmethoxysilane, the distillate, b.p. 49.5–64°, was extracted twice with water and the organic layer was dried over calcium sulfate and refractionated, yielding trimethylmethoxysilane, 10 g., b.p. (found) 56–57°, (literature)[7] 57°; n_D^{20} (found) 1.3682, (literature)[7] 1.3678; n_D^{24} (found) 1.3669; d_4^{24} (found) 0.7579, yield 39%. *n*-Butyl alcohol was isolated. Methyl *n*-butyl phosphonate was found, 9.5 g., b.p. 89.5–90.5° (10 mm.), n_D^{24} 1.4150, d_4^{24} 1.0521, 40% yield.

Anal. Calc'd for $C_5H_{13}O_3P$: P, 20.36; Mol. Wt., 152.1, M.R. 36.30. Found: P, 20.18, 20.10; Mol. Wt., 148, M.R. 35.2.

The reaction of di-n-butyl trimethylsilylphosphonate with phenol. Freshly distilled phenol (174 g., 1.85 moles) was mixed with 0.225 mole of di-*n*-butyl trimethylsilylphosphonate (59.5 g.) and the system was maintained at 100° for 24 hours. Distillation yielded a fraction b.p. 99–110° (40 mm.) which was dissolved in ether and extracted with four one-liter portions of ice-cold *N* sodium hydroxide. The ether layer was dried over calcium chloride and was fractionated at atmospheric pressure giving 18 g. of trimethylphenoxysilane b.p. (found) 178–179° (literature) 178–181°,[11] 182.5°[12]; n_D^{25} (found and literature)[11] 1.4752, (literature)[12] 1.4753; d_4^{25} (found) 0.9218, (literature)[11] 0.9242, (literature)[12] 0.920, yield 44%. Di-*n*-butyl phosphonate was also identified by boiling point and refractive index.

The reaction of aniline with di-n-butyl trimethylsilylphosphonate. Redistilled aniline (1.65 moles, 153 g.) was heated with di-*n*-butyl trimethylsilylphosphonate (0.204 mole, 54.2 g.) for 14 hours at 120–130°. The only product which could be isolated in a pure state was trimethyl-*n*-butoxysilane, 2.0 g., b.p. (found) 121–122°, (literature)[7] 124°; n_D^{20} (found) 1.3926, (literature)[7] 1.3925; n_D^{25} (found) 1.3900; d_4^{25} (found) 0.7721.

A nitrogen- and phosphorus-containing compound, b.p. 56–58° (0.07 mm.) which underwent slight decomposition on distillation, was isolated. An infrared spectrum (Spectrum III) showed the following characteristic absorptions: 3.02 μ, N—H; 4.20 μ, P—H; 6.20 μ, C=C (aromatic); 7.97 μ, P → O. Hydrolysis with hydrochloric acid and steam-distillation yielded *n*-butyl alcohol, (3,5-dinitrobenzoate m.p. (found) 65–66°, (literature)[10] 64°.) Addition of sodium hydroxide to the hydrolyzate and again steam-distilling yielded aniline (hydrochloride m.p. (found) 195–197°. (literature)[13] 198°). The compound is tentatively identified as *n*-butyl N-phenylphosphonamidate.

The reaction of n-butylamine with di-n-butyl trimethylsilylphosphonate. *n*-Butylamine (94.9 g., 1.23 moles) was refluxed with di-*n*-butyl trimethylsilylphosphonate (0.25 mole, 66 g.) for 12 hours. The reaction mixture was distilled

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(9) Krieble and Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945).

(10) Shriner and Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, New York (1948).

(11) Kumada and Hattori, *J. Inst. Polytech. Osaka City University*, **2**, (Ser. C) (No. 2) 131 (1952).

(12) Speier, *J. Am. Chem. Soc.*, **74**, 1005 (1952).

(13) McElvain, *The Characterization of Organic Compounds*, The Macmillan Co., New York (1947).

with isolation of 6.7 g. of trimethyl-*n*-butoxysilane, b.p. 121–123°, 44–46° (46 mm.), n_D^{25} 1.3902, 22% yield. Di-*n*-butyl phosphonate was also isolated.

The reaction of n-butyl mercaptan with di-n-butyl trimethylsilylphosphonate. One mole of *n*-butyl mercaptan, b.p. 96–97°, was refluxed for 12 hours with 0.20 mole of di-*n*-butyl trimethylsilylphosphonate (53 g.). Fractionation yielded 4 g. of trimethyl-*n*-butylmercaptosilane, b.p. (found) 75.5–78.0° (40 mm.), (literature) 169–171° (760 mm.), 76–77° (40 mm.)[14]; n_D^{27} 1.4510, d_4^{27} (found) 0.8390, d_4^{25} (literature) 0.835,[14] yield 16%.

The reaction of propionic acid with di-n-butyl trimethylsilylphosphonate. Propionic acid (112 g., 1.5 moles) was refluxed with di-*n*-butyl trimethylsilylphosphonate (63 g., 0.24 mole) for 12 hours. The system was fractionated, yielding 50.2 g. of *n*-butyl propionate, b.p. (found) 143–144°, (literature) 144°,[10] yield 82%. The silicon-phosphorus fractions of the distillate produced no compound capable of isolation. However, the residue was suspended in absolute ether and treated with an ether solution of aniline. An immediate white precipitate formed which contained phosphorus but no silicon. After filtration the solid was recrystallized twice from ethyl alcohol yielding 4.2 g. of the monoanilinium salt of phosphorus acid, m.p. 179–182° with decomposition.

Anal. Calc'd for $C_6H_9NO_3P$: N, 8.16; Eq. Wt., 87.1. Found: N, 7.8, 7.9; Eq. Wt., 87.4, 87.6.

When a sample of this salt was dissolved in sulfuric acid and treated with metallic zinc, phosphine was evolved.

Preparation of n-butylphosphonic acid. To 65 g. (0.33 mole) of di-*n*-butyl phosphonate in 250 cc. of anhydrous ligroin (b.p. 60–90°), 7.0 g. (0.33 g.-atom) of sodium was added. After the sodium had dissolved 1-bromobutane (45.6 g., 0.33 mole) was added slowly to the refluxing solution. In approximately ten minutes precipitation of sodium bromide began. After refluxing and agitation overnight, the mixture was cooled and the sodium bromide was centrifuged off. Distillation yielded 56.9 g. (0.23 mole) of di-*n*-butyl *n*-butylphosphonate, b.p. 131–133° (5 mm.), n_D^{25} (found) 1.4300, (literature)[15] 1.4302, 69% yield.

This ester was hydrolyzed to *n*-butylphosphonic acid by refluxing with 100 cc. of concentrated hydrochloric acid for six hours. After distillation of the liquid portion of the system, the remaining solid was crystallized twice from ligroin (b.p. 60–90°) yielding 27.2 g. (0.197 mole) of *n*-butylphosphonic acid, m.p. (found) 101.5–103.5° (literature)[15] 103.5–104.0°. The monoanilinium salt was prepared by slowly adding a solution of aniline in benzene to a benzene solution of *n*-butylphosphonic acid until no further precipitation was evident. The crude salt was recrystallized from benzene to constant m.p. 150–152°.

Anal. Calc'd for $C_{10}H_{18}NO_3P$: N, 6.06; Mol. Wt. 231. Found: N, 5.95, 5.86; Mol. Wt., 232.

The molecular weight was determined by titrating a 0.07273-g. sample with 0.0658 *N* sodium hydroxide to a Bromocresol Purple end point.

Preparation of di-trimethylsilyl n-butylphosphonate. n-Butylphosphonic acid (27.2 g., 0.197 mole) was heated and agitated with 300 cc. of dry ligroin (b.p. 60–90°). Trimethylchlorosilane (55 g., 0.5 mole) was slowly added to the refluxing mixture. During the addition, large quantities of hydrogen chloride were evolved and the original two-phase system condensed to a single phase. After refluxing for 12 hours, distillation yielded 8.0 g. of di-(trimethylsilyl) *n*-butylphosphonate, b.p. 107–108° (5.5 mm.), n_D^{25} 1.4168, d_4^{25} 0.9356, 15% yield.

Anal. Calc'd for $C_{10}H_{27}O_3PSi_2$: Si, 19.89; P, 10.96; Mol. Wt. 282.5. Found: Si, 20.4, 20.3; P, 10.45, 10.62; Mol. Wt., 284.

The molecular weight was determined by dissolving 0.1718 g. in 3 cc. of ethyl alcohol and 20 cc. of water. Hydrolysis was immediate. Titration to a Methyl Red end point required 3.20 cc. of 0.1864 *N* sodium hydroxide. The residue (40 g.) from the synthesis was identified as containing *n*-butylphosphonic acid, by the formation of the monoanilinium salt, m.p. 150–152°.

Hydrolysis of di-(trimethylsilyl) n-butylphosphonate. Di-(trimethylsilyl) *n*-butylphosphonate (2.2 g.) was added to 10 cc. of water and the mixture was steam-distilled. The organic layer was separated from the first 25 cc. of distillate and dried over calcium sulfate. By comparison of its infrared spectrum with that of an authentic sample, it was identified as hexamethyldisiloxane. The hydrolyzate was evaporated to dryness. The residue, *n*-butylphosphonic acid, was dissolved in hot benzene and precipitated as the anilinium salt by slow addition of a benzene solution of aniline. After four recrystallizations from benzene, the melting point was 150–152°. A mixture melting with an authentic sample showed no depression.

ANALYTICAL

Bond refractions were calculated from the data available in the literature for the P—H, P—O, P → O and P—C bonds. The refraction of the P—O bond was obtained from the molar refractions of a series of 9 trialkyl phosphites using the values of Warrick[16] for C—C and C—H Using the value for the P—O refraction, that of the P → O bond was obtained from the molar refractions of 8 trialkyl phosphates. The refractions of the P—C and the P—H bonds were obtained from a series of 12 di-*n*-butyl alkylphonates and 7 dialkyl phosphonates respectively. Table II lists these values.

TABLE II

BOND REFRACTIONS OF VARIOUS PHOSPHORUS BONDS

Bond	Bond Refraction (cc.$^{-1}$)
P—O	3.04
P → O	0.91
P—C	1.29
P—H	2.26

Both silicon and phosphorus were determined gravimetrically, after organic matter had been destroyed by sodium peroxide fusion in a "Parr Peroxide Bomb."

Nitrogen was determined by the semi-micro Kjeldahl method. Infrared spectra were prepared on a Baird Associates double-beam recording spectrometer in a sodium chloride cell. No solvent was used for liquid samples. A sodium chloride plate was used as reference.

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(14) Plumb, Unpublished.

(15) Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

(16) Warrick, *J. Am. Chem. Soc.*, **68**, 2456 (1946).