110 pH meter. The 5-phenyl and 5-phenyl-5-ethyl derivatives of 2-thio- and 2-selenobarbituric acid, which were very insoluble in water, were dissolved in an equivalent amount of sodium hydroxide and back-titrated with hydrochloric acid. All determinations were made in duplicate.

Partition Studies.—Solutions containing 1 mg. per 100 cc. of the compounds investigated were prepared in buffer previously saturated with ethyl acetate and their spectra determined. The solutions were then shaken mechanically for 30 minutes with an equal volume of ethyl acetate previously saturated with buffer, the aqueous layer was separated, and the spectra were measured again. From the decrease in the extinction coefficient the solubility in the organic layer was determined. The chloroform studies were carried out in an analogous fashion. Phosphate–citrate buffer was used for the pH 3 and pH 7.4 studies, hydrochloric acid for the pH of 1.2.

No decrease in extinction coefficient was observed when the selenium compounds were shaken for 30 minutes in buffer saturated with ethyl acetate or chloroform; therefore, decomposition must have been negligible.

All determinations were made in duplicate.

NEW HAVEN, CONN.

[CONTRIBUTION NO. 552 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis of Alkylsilylphosphines

BY G. W. PARSHALL AND R. V. LINDSEY, JR.

RECEIVED MAY 14, 1959

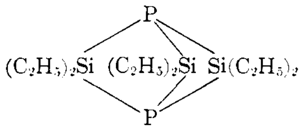
Alkylsilylphosphines have been synthesized by reaction of alkylchlorosilanes with lithium derivatives of phosphine and substituted phosphines. For example, tris-(trimethylsilyl)-phosphine was prepared by reaction of trimethylchlorosilane with trilithium phosphide obtained by absorbing phosphine in butyllithium solution. Cyclic derivatives were obtained from dilithium phosphides and diethyldichlorosilane.

Prior to the inception of the work described herein, only two silylphosphines had been reported, *i.e.*, SiH_3PH_2 and $(SiH_3)_3P$, described by Fritz and Emeleus,[1] respectively. Quite recently, trimethylsilyldiphenylphosphine, the first reported organosilylphosphine, was obtained by Kuchen and Buchwald[2] by reaction of trimethylchlorosilane with the sodium cleavage product of tetraphenylbiphosphine.

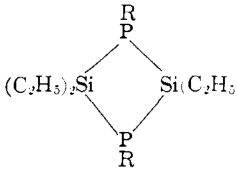
Our own work has led to the discovery of a general synthesis of alkylsilylphosphines that involves the metathesis of alkylchlorosilanes with the lithium phosphides obtained by interaction of alkyllithium compounds and phosphines. For example, reaction of trimethylchlorosilane with monolithium phosphide ($LiPH_2$)[3] has given trimethylsilylphosphine (I) in about 30% yield. When phosphine was rapidly bubbled into a butyllithium solution, a mixture of di- and trilithium phosphides was formed. Reaction of the mixture with trimethylchlorosilane gave as major products, bis-(trimethylsilyl)-phosphine (II) in 35% yield and tris-(trimethylsilyl)-phosphine (III) in 24% yield. Tris-(trimethylsilyl)-phosphine predominated when trimethylchlorosilane was added to a suspension of trilithium phosphide prepared by passing phosphine over the surface of a butyllithium solution. Tris-(trimethylsilyl)-phosphine was also obtained by treating the lithium derivative of II with trimethylchlorosilane.

$(CH_3)_3SiPH_2$ I $[(CH_3)_3Si]_2PH$ II $[(CH_3)_3Si]_3P$ III

The novel cyclic silylphosphines IV and V have been obtained by treating a mixture of di- and trilithium phosphides with diethyldichlorosilane. The cyclic compounds VI and VII which bear substituents on the phosphorus atoms were obtained by reaction of diethyldichlorosilane with the dilithium derivatives of phenylphosphine and trimethylsilylphosphine, respectively.



IV



V, R = H

VI, R = C_6H_5

VII, R = $(CH_3)_3Si$

The alkylsilylphosphines are colorless liquids or low-melting solids which are extremely sensitive to oxygen and water.[4] The compounds containing phosphorus–hydrogen bonds (as determined by proton magnetic resonance) are spontaneously flammable in air. Despite their sensitivity to air and moisture, these compounds are thermally stable. For example, tris-(trimethylsilyl)-phosphine was refluxed in an inert atmosphere at 243° for eight hours without appreciable decomposition.

The structure of tris-(trimethylsilyl)-phosphine has been established by elemental analysis and by preparation of a crystalline borane complex VIII and by oxidation to the known tris-(trimethylsilyl) phosphate (IX).[5] The oxidation of the phosphine to the phosphate with nitrogen dioxide is unusual, since this reagent is known to convert trialkylphosphines to the corresponding phosphine oxides.[6] The cyclic compounds IV–VII were characterized by elemental analyses, molecular weight and proton magnetic resonance. Molecular models of

$[(CH_3)_3Si]_3P \cdot BH_3$ VIII $[(CH_3)_3SiO]_3PO$ IX

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(1) (a) G. Fritz, *Z. Naturforsch.*, **8b**, 776 (1953); *Z. anorg. allgem. Chem.*, **280**, 332 (1955); (b) B. J. Aylett, H. J. Emeleus and A. Maddock, *Research*, **6**, 30S (1953); *J. Inorg. Nucl. Chem.*, **1**, 187 (1955).

(2) W. Kuchen and H. Buchwald, *Ber.*, **92**, 227 (1959).

(3) N. Kreutzkamp, *ibid.*, **87**, 919 (1954).

(4) The authors wish to acknowledge the efforts of the Physical and Analytical Division of this Department in developing techniques for analyzing these compounds.

(5) F. Feher, G. Kuhlbörsch, A. Blümcke, H. Keller and K. Lippert, *Ber.*, **90**, 134 (1957).

(6) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1705 (1956).

compounds V–VII were readily prepared from Stuart–Briegleb models and it appears that little strain is involved in the formation of four-membered rings of this type. Even the bicyclic compound IV appears to be relatively unstrained and is stable at temperatures up to 280°.

Experimental[7]

Mono-, Bis- and Tris-(trimethylsilyl)-phosphines.—The butyllithium solution prepared from 8.5 g. of lithium, 68.5 g. of 1-bromobutane and 900 ml. of anhydrous ether was filtered into a nitrogen-filled flask fitted with stirrer, condenser, addition funnel and a gas inlet tube which extended below the surface of the liquid. Phosphine was rapidly bubbled through the butyllithium solution until no further phosphine absorption occurred (approximately one hour). The yellow slurry of lithium phosphides thus obtained was stirred and cooled to 0–10° while 50 g. of trimethylchlorosilane was added over a period of 15 minutes. The mixture was allowed to warm to room temperature and was filtered in a nitrogen atmosphere. The filtrate was distilled under a slight (5 mm.) positive pressure of nitrogen. After removal of the ether, a trace (0.4 g.) of a clear, colorless, spontaneously flammable liquid distilled at 69–73°. The proton magnetic resonance of this product was in accord with that to be expected from trimethylsilylphosphine (I). The spectrum consisted of two resonances of relative intensities, 9 and 2. The latter resonance was split into a widely spaced doublet by P^{31}–H^{1} coupling.

Bis-(trimethylsilyl)-phosphine (II), also a clear, colorless, spontaneously flammable liquid, distilled at 170–172°; $n^{25}\text{D}$ 1.4637, yield 12.3 g. (35%).

Anal. Calcd. for $C_6H_{19}PSi_2$: C, 40.4; H, 10.7; P, 17.4; Si, 31.5; mol. wt., 178.3. Found: C, 40.8; H, 10.9; P, 17.2; Si, 31.1; mol. wt., 168.

Tris-(trimethylsilyl)-phosphine (III) distilled at 242–243°, $n^{25}\text{D}$ 1.5027, yield 8.2 g. (24%). This product, also a clear, colorless liquid, was not spontaneously flammable in bulk but ignited readily when dispersed on tissue paper.

Anal. Calcd. for $C_9H_{27}PSi_3$: C, 43.2; H, 10.9; P, 12.4; Si, 33.6; mol. wt., 250.5. Found: C, 43.5; H, 11.0; P, 11.7; Si, 33.6; mol. wt., 246.

When the preparation of the trimethylsilylphosphines was carried out as described above except that the phosphine was passed over the surface of the butyllithium solution, the dominant product was tris-(trimethylsilyl)-phosphine (III) which was formed in 45% yield. Slow absorption of the phosphine into the butyllithium solution probably favored the formation of trilithium phosphide, (Li_3P), from which III is formed.

Trimethylsilylphosphine (I) was formed in 30% yield when monolithium phosphide ($LiPH_2$) was prepared by dropping butyllithium solution into ether saturated with phosphine as described by Kreutzkamp.[3] Pure trimethylsilylphosphine distilled at 77.5°, $n^{25}\text{D}$ 1.4368.

Anal. Calcd. for $C_3H_{11}PSi$: Si, 26.4 Found: Si, 25.9.

Tris-(trimethylsilyl)-phosphine (III).—The butyllithium solution prepared from 1.75 g. of lithium, 13.7 g. of 1-bromobutane and 60 ml. of ether was chilled to 0° and stirred vigorously in a nitrogen-filled flask while a solution of 15.0 g. of bis-(trimethylsilyl)-phosphine (II) and 10 ml. of ether was added over a period of 10 minutes. The light green solution thus formed deposited a white precipitate when 9.2 g. of trimethylchlorosilane was added rapidly. The mixture was allowed to warm to room temperature and was filtered in a nitrogen atmosphere. Distillation of the filtrate gave 13.8 g. (66%) of tris-(trimethylsilyl)-phosphine (III) which boiled at 243–244°, $n^{25}\text{D}$ 1.5028.

Tris-(trimethylsilyl)-phosphine–Borane (VIII).—A solution of 0.90 g. of tris-(trimethylsilyl)-phosphine in 9 ml. of tetrahydrofuran was placed in a 150-ml. Carius tube which was then chilled to −190° and evacuated to 0.02 mm. Diborane (150 ml. at 224 mm. and 27°) was added and the tube was sealed. The mixture formed a clear, colorless solution at room temperature. Evaporation of the solvent under reduced pressure left a sticky white residue which was sublimed at 0.01 mm. to give white crystals. The tris-(trimethylsilyl)-phosphine–borane decomposed slowly at room temperature and rapidly at its melting point, 100–107°. The complex formed moderately stable solutions in anhydrous acetone, tetrahydrofuran and benzene, but reacted vigorously with methanol and aqueous acetone.

Anal. Calcd. for $C_9H_{30}BPSi_3$: C, 40.9; H, 11.4; B, 4.1; P, 11.7. Found: C, 40.2; H, 11.7; B, 4.8; P, 12.3.

Tris-(trimethylsilyl) Phosphate (IX).—A solution of 2.9 g. of tris-(trimethylsilyl)-phosphine in 10 ml. of chlorobenzene was cooled to 0° and stirred vigorously as 0.7 g. of nitrogen dioxide in 10 ml. of chlorobenzene was added dropwise. The excess nitrogen dioxide was evaporated under reduced pressure and the liquid residue was distilled. Hexamethyldisiloxane distilled at 101–102°, $n^{25}\text{D}$ 1.3837, yield 0.4 ml. Tris-(trimethylsilyl) phosphate distilled at 48–50° (0.2 mm.), $n^{25}\text{D}$ 1.4087; yield 1.4 ml. Feher, *et al.*,[5] have reported the boiling point of tris-(trimethylsilyl) phosphate as 67–68° (0.5 mm.) and the refractive index as 1.4092. The Raman spectrum of this product contained all the major bands reported by Feher.

Anal. Calcd. for $C_9H_{27}O_4PSi_3$: C, 34.4; H, 8.7; P, 9.9; Si, 26.7. Found: C, 34.9; H, 9.0; P, 9.8; Si, 26.7.

2,2,4,4-Tetraethyl-1,3-diphospha-2,4-disiletane (V) and 2,2,4,4,5,5-Hexaethyl-1,3-diphospha-2,4,5-trisilabicyclo-(1.1.1)pentane (IV).—Phosphine was rapidly bubbled through the butyllithium solution prepared from 8.5 g. of lithium, 68.5 g. of 1-bromobutane and 300 ml. of ether for two hours. The yellow suspension of lithium phosphides was stirred vigorously and maintained at 0° as 60 ml. of diethyldichlorosilane was added dropwise. The mixture was allowed to warm to room temperature and was filtered in a nitrogen atmosphere. Distillation of the filtrate gave 3.5 ml. of a clear, colorless, slightly viscous liquid which boiled at 107–110° (0.06 mm.), $n^{25}\text{D}$ 1.5829. The proton magnetic resonance spectrum showed the presence of phosphorus–hydrogen bonds as well as aliphatic carbon–hydrogen bonds in the proportions expected from compound V. The resonance of the hydrogens bound to phosphorus appeared as a characteristic widely split doublet, whereas the alkyl hydrogen resonance was unresolved.

Anal. Calcd. for $C_8H_{22}P_2Si_2$: C, 40.6; H, 9.4; P, 26.2; Si, 23.7. Found: C, 41.6; H, 9.7; P, 25.0; Si, 23.7.

Compound IV, a colorless, extremely viscous liquid, distilled at 130–134° (0.05 mm.), $n^{25}\text{D}$ 1.6012, yield 3.8 ml. The proton magnetic resonance spectrum did not contain the doublet resonance characteristic of hydrogen bonded to phosphorus.

Anal. Calcd. for $C_{12}H_{30}P_2Si_3$: C, 45.0; H, 9.4; P, 19.3; mol. wt., 321. Found: C, 45.3; H, 9.4; P, 20.1; mol. wt., 379.

1,3-Diphenyl-2,2,4,4-tetraethyl-1,3-diphospha-2,4-disiletane (VI).—Phenyllithium solution prepared from 3.0 g. of lithium, 31.4 g. of bromobenzene and 150 ml. of ether was stirred in a nitrogen-filled flask as 9.1 g. of phenylphosphine[8] was added over a period of ten minutes. The slurry of dilithium phenylphosphide thus formed was stirred at room temperature for one hour. Diethyldichlorosilane (11.8 ml.) was added dropwise over a period of 10 minutes and the mixture was stirred for 2 hours. The mixture was filtered and the filtrate was distilled. A yellow liquid which distilled at 135–160° (0.05 mm.) was redistilled to give 3.5 g. of light-yellow solid, b.p. 151–153° (0.02 mm.). Two recrystallizations from petroleum ether gave white needles of VI, m.p. 43–47°. The product was very sensitive to water and oxygen and rapidly developed the odor of phenylphosphine on exposure to air.

Anal. Calcd. for $C_{20}H_{30}P_2Si_2$: P, 15.9; Si, 14.4; mol. wt., 388.5. Found: P, 15.4; Si, 15.4; mol. wt., 389.

1,3-Bis-(trimethylsilyl)-2,2,4,4-tetraethyl-1,3-diphospha-2,4-disiletane (VII).—The butyllithium solution prepared from 2.1 g. of lithium, 16.0 g. of 1-bromobutane and 75 ml. of ether was stirred and cooled to 0–10° while a solution of 6.1 g. of trimethylsilylphosphine in 25 ml. of ether was added over a period of 10 minutes. The white slurry of dilithium trimethylsilylphosphide was stirred and maintained at 0–10° while 8.2 ml. of diethyldichlorosilane was added over a period of 10 minutes. The mixture was allowed to warm to room temperature and was filtered in a nitrogen atmosphere.

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[7] Melting points and boiling points are uncorrected.

[8] R. J. Horvat and A. Furst, THIS JOURNAL, **74**, 562 (1952).

Distillation of the filtrate gave 1.6 ml. of VII, a clear, colorless, viscous liquid which boiled at 96–98° (0.2 mm.), n^{25}_D 1.5522. The product crystallized to white needles when cooled slightly below room temperature.

Anal. Calcd. for $C_{14}H_{38}P_2Si_4$: P, 16.3; Si, 29.5; mol. wt., 380.6. Found: P, 16.4; Si, 28.5; mol. wt., 377.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE FATTY ACID PRODUCERS' COUNCIL OF THE ASSOCIATION OF AMERICAN SOAP AND GLYCERINE PRODUCERS, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Phosphorus Derivatives of Fatty Acids. VII.[2] Addition of Dialkyl Phosphonates to Unsaturated Compounds

BY RICHARD SASIN,[3] WILLIAM F. OLSZEWSKI, JOHN R. RUSSELL AND DANIEL SWERN

RECEIVED MAY 7, 1959

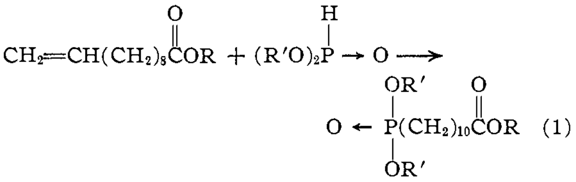
The addition of dialkyl phosphonates to unsaturated compounds under free radical conditions has been shown to be a general reaction of wide applicability. Addition proceeds smoothly with unsaturated compounds containing a terminal or an isolated double bond and also with a series of vinyl esters. Trialkyl ω-phosphonoundecanoates were prepared in 53–66% yield by the addition of dialkyl phosphonates to alkyl undecenoates (eq. 1), R = R′ = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl; R = 2-ethylhexyl, R′ = C_2H_5; R = C_2H_5, R′ = 2-ethylhexyl. These reactions were catalyzed by decomposing peroxides and also by ultraviolet radiation. Addition of dialkyl phosphonates to alkyl oleates in the presence of peroxides yielded trialkyl 9(10)phosphonostearates in 66–77% yield (eq. 2), R = R′ = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl; R = C_2H_5, R′ = n-C_4H_9; R = n-C_4H_9, R′ = C_2H_5; R = 2-ethylhexyl, R′ = C_2H_5. Similarly, addition of dialkyl phosphonates to vinyl esters gave dialkyl 2-acyloxyethylphosphonates in 45–61% yield (eq. 3), R = C_2H_5, $CH_3(CH_2)_2$, $CH_3(CH_2)_7$, $CH_3(CH_2)_{10}$, $CH_3(CH_2)_{16}$; R′ = CH_3, C_2H_5, n-C_4H_9, 2-ethylhexyl. All the phosphonates are colorless, thermally stable, high-boiling liquids, except dimethyl and diethyl 2-stearoxyethylphosphonates, which are white solids melting at 45 and 47°, respectively.

Study of the radical-catalyzed addition of dialkyl phosphonates to unsaturated compounds has been confined largely to compounds containing relatively reactive double bonds. The patent literature, for example, describes the radical-catalyzed addition of dialkyl phosphonates to 1-octene, 1-dodecene, allyl dodecyl ether, allyl acetate and methyl undecenoate.[4] The peroxide-catalyzed addition of diethyl phosphonate to vinyl acetate also was reported recently.[5] These authors unequivocally proved that the reaction product is diethyl 2-acetoxyethylphosphonate.

Little has been published on the radical-catalyzed addition of dialkyl phosphonates to non-terminal or relatively unreactive double bonds. While the present work was in progress, Stiles, Vaughan and Rust[6] reported the preparation of dialkyl alkylphosphonates by the addition of dialkyl phosphonates to some non-terminal olefins, as well as to terminal ones, in the presence of decomposing peroxides or ultraviolet radiation. The non-terminal olefins used were 2-butene, cyclohexene and diisobutylene; yields of addition products were generally low.

In this paper we show that the radical-catalyzed addition of dialkyl phosphonates to unsaturated compounds is a general reaction and that fair to good yields (45–77%) of products readily are obtained. The phosphonates employed are dimethyl, diethyl, di-n-butyl and di-2-ethylhexyl phosphonates, and the unsaturated compounds are a series of alkyl undecenoates (terminal double bond), alkyl oleates (non-terminal, isolated double bond) and vinyl esters (terminal, activated double bond). The physical properties of the phosphonates obtained also are described.

ω-Dialkyl phosphonoundecanoates were prepared in 53–66% yield by adding dialkyl phosphonates to alkyl undecenoates in the presence of decomposing t-butyl perbenzoate or ultraviolet radiation. Yields were essentially the same with decomposing peroxide or ultraviolet catalysis.



$$CH_2{=}CH(CH_2)_8\overset{\overset{\displaystyle O}{\|}}{C}OR + (R'O)_2\overset{\overset{\displaystyle H}{|}}{P} \rightarrow O \longrightarrow O \leftarrow \underset{\underset{\displaystyle OR'}{|}}{\overset{\overset{\displaystyle OR'}{|}}{P}}(CH_2)_{10}\overset{\overset{\displaystyle O}{\|}}{C}OR \qquad (1)$$

Symmetrical trialkyl ω-phosphonoundecanoates prepared include: trimethyl, triethyl, tri-n-butyl and tri-2-ethylhexyl. The indices of refraction and infrared spectra of these compounds were identical to those prepared from the ω-bromoundecanoate and trialkyl phosphite in a Michaelis–Arbuzov reaction,[2] thus proving that the phosphorus was attached to the terminal carbon. The mixed ω-phosphonoundecanoates synthesized include: 2-ethylhexyl-ω-diethyl and ethyl-ω-di-2-ethylhexyl. All of these compounds are thermally stable, colorless liquids at room temperature, insoluble in water and soluble in organic solvents. The physical properties, yields obtained and analyses of the ω-dialkyl phosphonoundecanoates are summarized in Table I.

Trialkyl 9(10)-phosphonostearates were prepared in 66–77% yield by adding dialkyl phosphonates to alkyl oleates in the presence of t-butyl perbenzoate.

The symmetrical trialkyl 9,(10)-phosphonostearates prepared include: trimethyl, triethyl, tri-n-butyl and tri-2-ethylhexyl. The mixed 9(10)-phosphonostearates synthesized include: ethyl 9(10)-di-n-butylphosphono, n-butyl 9(10)-diethylphosphono

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(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented at the Fall Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959. Paper VI in this series is THIS JOURNAL, **81**, 4335 (1959).

(3) Formerly Fellow of the Fatty Acid Producers' Council of the Association of American Soap and Glycerine Producers, Inc.

(4) United States Rubber Co., British Patent 694,772 (1953).

(5) R. L. McConnell and H. W. Coover, Jr., THIS JOURNAL, **79**, 1961 (1957).

(6) A. R. Stiles, W. E. Vaughan and F. F. Rust, *ibid.*, **80**, 714 (1958).