1 simplifies in this case to

$$\delta' = x_1'\delta_1' + x_2'\delta_2' + x_3'\delta_3' \qquad (1')$$

where δ' is the measured chemical shift, δ_1', δ_2' and δ_3' the chemical shifts of the non-, mono- and diionized species, and x_1', x_2', x_3' their corresponding mole fractions. The pK_A values which were used to calculate x_1, x_2 and x_3 are[14]: $pK_A{}^{I} = 4.19$ and $pK_A{}^{II} = 5.48$. The results are: $\delta_1' = 30.9 \pm 0.3$ c./s., $\delta_2' = 42.3 \pm 0.2$ c./s.[11] and $\delta_3' = 47.8 \pm 0.3$ c./s. Hence, the chemical shifts associated with the ionization are

single ionization: $42.3 - 30.9 = 11.4 \pm 0.4$ c./s.
double ionization: $47.8 - 30.9 = 16.9 \pm 0.4$ c./s.

In the monomethyl succinate ion the chemical shift of the α-methylene group was measured and found to be 11.3 ± 1.7 c./s. This value is in good agreement with the value of 11.4 c./s. obtained from the analysis of the titration curve. That these two values should be the same is obvious since in the monoionized succinic acid both carboxyl groups have equal ionization probabilities. It is also rather close to the value of b/2 as given above. The β-methylene group in the methyl succinate ion is shifted only 4.4 c./s., which indicates the small effect of the negative charge at the far end of the ion.

In the non-ionized methyl succinate, there is no chemical shift between the α- and β-methylene groups (same as in the non-ionized methyl citrates). This indicates again that the methyl ester group behaves like a non-ionized carboxyl group with respect to the chemical shift of the adjacent methylene group.

PASADENA, CALIF.

(14) H. C. Brown, D. H. McDaniel and O. Häfliger in E. A. Braude and F. C. Nachod, "Determination of Organic Structure by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 624.

[CONTRIBUTION FROM THE RICHMOND LABORATORY OF THE STAUFFER CHEMICAL CO., RICHMOND 4, CALIF.]

Preparation and Some Reactions of Tris-trimethylsilylphosphine[1]

BY AMOS J. LEFFLER AND EUGENE G. TEACH

RECEIVED NOVEMBER 20, 1959

Tris-trimethylsilylphosphine was prepared by the reaction of sodium dihydrogen phosphide and trimethylchlorosilane in a non-ammoniacal medium. A number of reactions were investigated to determine the characteristics of this compound. It was found slowly to decompose thermally above 100° in a sealed vessel.

The preparation and some of the reactions of tris-trimethylsilylphosphine recently have been described in the literature.[2] This work was carried out independently and differences in the method of synthesis and unreported reactions have prompted us to publish the new information.

In this work sodium dihydrogen phosphide was prepared directly from the alkali metal and phosphine without any intermediate metal alkyl step. This was accomplished by dispersing sodium in an aromatic hydrocarbon, and adding on cooling an equal amount of a glycol ether such as Ansul 121 or 141, and then passing in PH_3 until the reaction was complete. In this system there was no isolation of the intermediate mono- and bis-trimethylsilylphosphines. It is assumed that the reaction is a stepwise one in which the intermediates react with $NaPH_2$ or disproportionate to form the tertiary compound as

$$(CH_3)_3SiPH_2 + NaPH_2 \longrightarrow (CH_3)_3SiPHNa + PH_3$$

$$+ (CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_2PH + NaCl, \text{ etc.} \qquad (1)$$

or

$$2(CH_3)_3SiPH_2 \longrightarrow [(CH_3)_3Si]_2PH + PH_3, \text{ etc.} \qquad (2)$$

It seems unlikely that reaction occurs between the intermediate and the silyl halide to produce hydrogen chloride, since $NaPH_2$ was always in excess and no hydrogen chloride was ever noted in this reaction.

$$(CH_3)_3SiPH_2 + (CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_2PH + HCl$$

The phosphine reacted with diborane at room temperature to give the adduct, $(SiMe_3)_3P{\cdot}BH_3$, which split out trimethylsilane on heating giving a complex mixture. Treatment with methanol left a white crystalline powder that analyzed for the formula $[(SiMe_3)_2PBH_2]_x$ that is assumed to be the analog of Burg's phosphinoborines.[3] The material had an extended melting range and is presumed to be a mixture of different size rings. The material that reacted with methanol was found to be a highly cross linked polymer containing boron, phosphorus and trimethylsilyl groups. Heating split out more and more trimethylsilane until the product was a hard, brittle, infusible solid.

A similar product was formed with pentaborane-9. There was no reaction at room temperature, but on heating to 90° trimethylsilane, hydrogen and methane were evolved. It was noted in two experiments that the reaction ratio of $(SiMe_3)_3P/B_5H_9$ was 1.40 but the significance of this is not certain. No ring compounds were isolated; only the brown cross linked polymer was found.

It was expected that the phosphine would form complexes with transition metal halides, but with cobaltous chloride in tetrahydrofuran a black powder was formed that became stable to air only after first growing warm. Analysis showed this to be very finely divided Co_3P_2 which was formed by the reaction

$$2(SiMe_3)_3P + 3CoCl_2 \longrightarrow Co_3P_2 + 6SiMe_3Cl$$

This is similar to the results obtained by Scholder and Pattock[4] with phosphine and nickel chloride.

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(1) Presented in part at the 136th A.C.S. Meeting, Atlantic City N. J., September, 1959. We wish to thank the Office of Naval Research for partial support of this work.

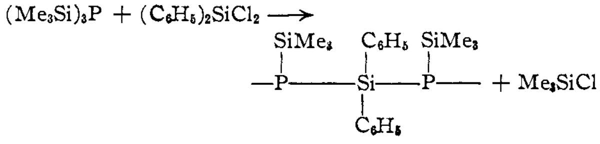
(2) G. W. Parshall and R. V. Lindsey, Jr., THIS JOURNAL, **81**, 6273 (1959). We wish to thank the author for a preprint of his paper.

(3) A. B. Burg and R. I. Wagner, *ibid.*, **75**, 3873 (1953).

Tris-trimethylsilylphosphine does not react with cold water, but at 100° hexamethyldisiloxane is produced. This reaction was not investigated further but is in agreement with Bagley[5] who reports that the hydrolysis of $[(CH_3)_3Si]_2PH$ produces hexamethyldisiloxane and PH_3.

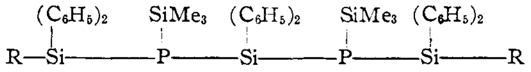
An attempt was made to determine the vapor pressure of the phosphine in a tensimeter, but the values obtained were always above those obtained during distillation. A sample was heated to 100° for 18 hours and a small amount of volatile material was found that showed the presence of trimethylsilyl groups but no Si–H in the infrared spectrum. When a sample was heated in the presence of triethylborane the volatile mixture had an average molecular weight of 124.5 (BEt_3 = 97.8). However, treatment of the non-volatile residue with phosphorus pentachloride at 200° gave no boron trichloride as would have been expected if there was any boron in the residue. It appears therefore that triethylborane only catalyzes the decomposition of the phosphine. The volatile material had the same infrared bands as hexamethyldisilane indicating that the reaction gives either $(SiMe_3)_2P$–$P(SiMe_3)_2$ or $[SiMe_3P]_4$. The non-volatile portion was not further investigated.

In an attempt to prepare polymers containing Si–P chains, tristrimethylsilylphosphine was treated with diphenyldichlorosilane. By refluxing the two at 400° for 3 hours approximately two-thirds of the trimethylchlorosilane expected from the reaction



$$(Me_3Si)_3P + (C_6H_5)_2SiCl_2 \longrightarrow -P(SiMe_3)-Si(C_6H_5)_2-P(SiMe_3)- + Me_3SiCl$$

was obtained. The resultant material consisted of a mixture of low molecular weight substances from which was isolated one compound with a Si/P ratio of $^5/_2$ and having the possible structure



$$R-Si(C_6H_5)_2-P(SiMe_3)-Si(C_6H_5)_2-P(SiMe_3)-Si(C_6H_5)_2-R$$

The nature of R was not determined but an infrared spectrum as a KBr disk showed the presence of OH groups indicating hydrolysis of the end-groups during handling.

The oxidation of the phosphine was accomplished by allowing air to diffuse slowly into the vessel.

Experimental

Preparation of Tris-trimethylsilylphosphine.—A dispersion of 24.8 g. of sodium in 125 ml. of toluene was prepared using a Waring blender by heating to 108° and agitating at high speed for 10 minutes under a slow stream of nitrogen. The dispersion was allowed to cool, transferred to a 500-ml. 3-neck flask equipped with a stirrer, condenser, and gas inlet tube, and 125 ml. of Ansul 141 ether dried over Na was added. PH_3 was generated by adding water to magnesium aluminum phosphide[6] and the gas dried first with NaOH and then P_2O_5. This was passed with nitrogen into the Na dispersion through the gas inlet tube and as the reaction progressed the mixture grew warm. There is an interesting series of color changes during the course of the reaction starting from a tan of the original dispersion and passing through black, dark green, yellow, and in some cases almost white stages. The nature of the stages is not understood although it was noted that the hydrogen is only slowly evolved and a loose complex between the Na and PH_3 may be part of the reaction. It was noted that Ansul 141, $CH_3O(C_2H_4O)CH_2$, is more effective than Ansul 121, $CH_3OC_2H_4OCH_3$, in promoting this reaction apparently due to the complexing action with Na or PH_3. At the conclusion, the $NaPH_2$ settles and is no longer dispersed.

To the $NaPH_2$ was added dropwise 106 g. of $(CH_3)_3SiCl$ and the reaction allowed to proceed until the PH_3 was completely evolved. The resultant mixture was transferred under nitrogen pressure to centrifuge bottles, centrifuged, the solid slurried with toluene, and recentrifuged. The combined liquid was distilled to yield 33.3 g. of $[(CH_3)_3Si]_3P$, 40% yield, b.p. 102° (16 mm.), d. $\sim 0.87^{20}$. *Anal.* Calcd. P, 12.3; Si, 33.8; C, 43.2. Found: P, 12.4; Si, 33.8; C, 42.0.

An attempt was made to obtain a vapor pressure curve using an immersible tensimeter as described by Sanderson[7]; a vapor pressure of 37.65 mm. at 104.5° was observed showing that there is a slow decomposition in the vapor phase.

Oxidation of Tris-trimethylsilylphosphine.—A sample of the phosphine was allowed to stand for several weeks with slow diffusion of air. The resultant liquid was odorless and air stable. Analysis showed it was the phosphate, $[(CH_3)_3SiO]_3PO$, and this was confirmed by infrared spectrum; $[(CH_3)_2SiO]_3PO$, d^{20}_4 0.928, n^{30}_D 1.4023. *Anal.* Calcd. for $[(CH_3)_2SiO]_3PO$: P, 8.92; Si, 26.8; C, 34.4; H, 8.60. Found: P, 9.13; Si, 27.1; C, 35.52; H, 8.81.

Reaction of Tris-trimethylsilylphosphine and Diborane.—The initial reaction is the formation of the crystalline adduct $[(CH_3)_2Si]_3P \cdot BH_3$ as reported in the literature.[2] Heating of the crystalline adduct to 135° for 14 hours split out $SiMe_3H$ leaving a yellowish liquid. This was treated with MeOH and there was a vigorous evolution of gas and all of the material went into solution except a small amount of white crystalline material. The solid was filtered and air-dried. *Anal.* Calcd. for $([(CH_3)_3Si]_2PBH_2)_x$: P, 16.35; Si, 28.5; B, 5.7. Found: P, 16.09; Si, 29.0; B, 4.7. The melting range of a sample recrystallized from MeOH was 140–205°, indicating that different ring sizes are present.

An examination of the untreated oil by infrared as a 20% solution in CCl_4 showed a P–H bond and the spectrum strongly resembled $[(CH_3)_3Si]_2PH$ as described by Bagley.[5] However, the vapor pressure at room temperature was less than 1 mm. Upon heating, it split out more CH_3SiH, solidified, and resembled the product obtained from B_5H_9 described below.

Reaction Tris-trimethylsilylphosphine and Pentaborane-9.—A mixture of the phosphine (0.9382 g., 3.75 mmoles) and pentaborane (4.66 mmoles) in a 200-ml. sealed tube was heated for 20 hours at 90° and then opened to the vacuum system. There was produced 0.57 mmole of non-condensible material and 5.30 mmoles of $SiMe_3H$ together with 1.975 mmoles of unreacted B_5H_9. The non-volatile product was a low melting resin that evolved more $SiMe_3H$ plus non-condensibles when heated with a yellow flame. The total $SiMe_3H$ was 5.66 mmoles and the resin was not unmeltable, stable in air, and insoluble in water and methanol. Analysis showed 15.8% B, 19.5% Si, and 17.2% P for a ratio of P:Si:B of 1:1.25:2.63. Another sample weighing 0.0582 g. was heated to 344° for 5 hours *in vacuo* and lost 0.0015 g. The amount of $SiMe_3H$ produced depends on the thermal treatment of the product and has reached a ratio of $SiMe_3H$ to $(SiMe_3)_3P$ of 1.51 indicating removal of one-half of the silyl groups. An infrared spectrum of a sample of the meltable resin showed that the B_5H_9 bridge and skeletal frequencies were missing indicating that the product is a cross linked polymer of unknown structure.

Reaction of Tris-trimethylsilylphosphine and $CoCl_2$.—Anhydrous $CoCl_2$ was prepared from the hexahydrate by reaction with $SOCl_2$ as described by Brauer.[8] A suspension of 2 g. of $CoCl_2$ in 50 ml. of dry tetrahydrofuran was treated with 6.0 ml. of the phosphine in 50 ml. of tetrahydrofuran to yield a colloidal black precipitate. Approximately two-thirds of the solvent was evaporated under a stream of

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(4) R. Scholder and K. Pattock, *Z. anorg. allgem. Chem.*, **220**, 250 (1934).

(5) G. Bagley, Thesis, University of Pennsylvania, 1959.

(6) Available from Rocky Mountain Research, Inc.

(7) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 84.

(8) G. Brauer, "Preparative Anorganische Chemie," Ferdinand Enke Verlag, Stuttgart, p. 1131.

nitrogen and the remaining suspension centrifuged. The residue was washed twice with 30–60° petroleum ether and dried under a stream of nitrogen. Because of the very fine particle size, great difficulty was encountered in collecting the solid and no yield was determined. The product was a black powder that smoked on initial exposure to air and then was stable even when heated with a torch. *Anal.* Calcd. for Co_3P_2: P, 26.9. Found: P, 27.7.

Thermal Decomposition of Tris-trimethylsilylphosphine.—A mixture of 3.0464 g. of the phosphine and 1.4606 of triethylborine was heated in a 100-ml. sealed bulb for 19 hours at 108°. The bulb was opened to the vacuum system and no non-condensibles were found. Fractionation through a $-63°$ trap yielded a trace of PH_3 and C_2H_4. The material in the $-63°$ trap, 1.0534 g., was examined by infrared and was found to be a mixture of BEt_3 and a trimethylsilyl-containing group, of average molecular weight of 124.5, equivalent to 4.0 mmoles of Si_2Me_6. Comparison of the spectrum and an authentic spectrum of Si_2Me_6 showed bands at 3.35, 3.43, 7.95, 8.80 and 12.0 μ and the other bands in the mixture were attributed to the BEt_3. The non-volatile residue was heated with excess PCl_5 in a sealed tube at 200° for 10 hours to convert all of the BEt_3 to BCl_3 and EtCl and the Si–P residue to $SiMe_3Cl$ and PCl_3. Fractionation of the material through $-63°$, $-126°$ and into $-196°$ traps separated out the HCl and only $SiMe_3Cl$ was found in the $-126°$ trap. This indicated no BCl_3 and hence no BEt_3 in the non-volatile residue. Therefore, BEt_3 did not take part in the reaction but only catalyzed the decomposition of the phosphine. Heating of the phosphine in a 200-ml. bulb at 100° for 18 hours yielded only a very small amount of volatile $SiMe_3$ containing material showing the catalytic effect of the BEt_3.

Reaction of Tris-methylsilylphosphine with Diphenyldichlorosilane.—A mixture of 12.6 ml. of diphenyldichlorosilane, 17.6 ml. of tris-trimethylsilylphosphine and 50 ml. of Amsco Odorless Mineral Spirits was refluxed under nitrogen overnight. Only 2.1 g. of chlorosilane collected in a Dry Ice trap connected to the system indicating that more vigorous conditions were necessary for reaction. Therefore, the solvent was distilled away and the flask heated to 400° for 3 hours; 5.8 g. more of the chlorosilane was produced. The residue was a semi-solid from which a solid was isolated by dissolving the liquid in a 30–60° petroleum ether–Et_2O mixture and filtering the solid. After two recrystallizations from benzene the solid melted 265–269° and analyzed 18.7% Si, 8.3% P, and less than 0.1% Cl. This is a Si/P ratio of 5/2 indicating that it cannot have a ring structure as might be expected from analogy to silicon oxygen compounds and shows good agreement with the formula: $(R)(Si(C_6H_5)_2)[P(SiMe_3)Si(C_6H_5)_2]_2\text{-}R$ where R could be OH or CH_3. Calcd. Si, 17.8; P, 7.95 for R = OH.

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

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. V. Phosphorus-containing Dienes[1]

BY K. DARRELL BERLIN[2] AND GEORGE B. BUTLER

RECEIVED OCTOBER 6, 1959

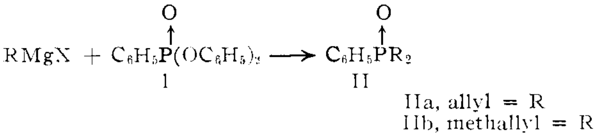
Diallylphenylphosphine oxide and dimethylallylphenylphosphine oxide have been synthesized. Both phosphine oxides polymerized in free radical systems to yield soluble polymers. A soluble polymer was isolated from the polymerization of allylphenyl allylphosphonate. Intrinsic viscosity measurements indicate the polymers are of low molecular weight. The polymerizations are examples of cyclic polymerization involving an intramolecular–intermolecular propagation step.

Cyclic polymerization was originally suggested by Butler and Angelo to explain the formation of soluble polymers when quaternary ammonium salts containing two allyl groups polymerized.[3] The mechanism involves an intramolecular–intermolecular propagation step which, in the case of a 1,6-diene system, would lead to linear chains composed of alternating six-membered rings (saturated) and methylene groups. Symmetrical and unsymmetrical 1,6-dienes, as well as dienes capable of forming rings containing more than six atoms, have been reported to undergo polymerization *via* cyclization.[4]

In this study the reaction was extended to include dienes which contained a phosphorus atom. The use of tertiary phosphine oxides of the type shown in the formula seemed particularly inviting since, in general, such compounds are thermally stable,[5] a characteristic which might be inherited by the polymers.

$$(CH_2{=}CHCH_2)_2(R)P{\rightarrow}O$$

An examination of the literature revealed, however, that tertiary phosphine oxides substituted with two allyl groups were unknown. Diallylphenylphosphine oxide (IIa) was first synthesized by condensation of diphenyl phenylphosphonate (I) with the allyl Grignard reagent as shown in the equation. In like manner dimethallylphenylphosphine oxide (IIb) was realized. The reaction is similar to that used to prepare di-*p*-tolylmethylphosphine oxide.[6]



$$RMgX + C_6H_5\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2 \longrightarrow C_6H_5\overset{\overset{O}{\uparrow}}{P}R_2$$

I II

IIa, allyl = R
IIb, methallyl = R

Although these dienes take up bromine, a quantitative determination of unsaturation failed to give consistent results.[7] Several attempts were made to hydrogenate diallylphenylphosphine oxide quantitatively over platinum at atmospheric pressure, but in all trials the residual oil contained considerable unsaturation as indicated by infrared analysis. Hydrogenation of diallylphenylphosphine oxide could, however, be accomplished under pressure. Di-*n*-propylphenylphosphine oxide, the reduction product, was made by an alternative

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[2] Post-doctoral Fellow, 1958–1960.

[3] G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).

[4] Many pertinent references can be found in: M. D. Barnett, A. Crawshaw and G. B. Butler, *ibid.*, **81**, 5946 (1959).

[5] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 98.

[6] P. W. Morgan and B. C. Herr, THIS JOURNAL, **74**, 4526 (1952).

[7] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 69; see also ref. 4 for additional details of procedure.