properties, and analytical data of the phosphinates prepared in this manner are given in Table III and the major infrared absorption bands are listed in Table I.

**General Procedure for the Reaction of Phosphorus Trichloride with α-Acetylenic Alcohols (Phosphonates).**—The general procedure for the preparation of phosphine oxides given above was followed using 0.33 mole of phosphorus trichloride, 1 mole of acetylenic alcohol, 1.2 moles of pyridine, and 400 ml. of ether as solvent. The phosphonates prepared in this manner are described in Table IV (compounds 10 and 11), and the major infrared absorption bands are listed in Table I.

**General Procedure for the Reaction of 2-Chloro-4-methyl-1,3,2-dioxaphospholane (and Phosphorinane) with α-Acetylenic Alcohols (Phosphonates).**—Addition of the chloride (1 mole) in 100 ml. ether to the solution of acetylenic alcohol (1 mole), base (1.2 moles), and ether (400 ml.) was carried out in the usual manner. On warming the reaction mixture to room temperature, an exothermic reaction occurred when the temperature reached 20° and cooling was necessary to maintain a temperature below 30°. Since the products of this reaction were susceptible to hydrolysis, triethylamine was used as the base and the hydrochloride was separated by filtration. The filtrate was stripped of ether and unchanged triethylamine by heating to 50° at 5 mm. The residue was refiltered with suction and the product recovered as the filtrate. Yields, physical properties, and analytical data are given in Table IV and the major infrared absorption bands are given in Table I.

**Hydrogenation of Diphenyl(3-methyl-1,2-butadien-1-yl)-phosphine Oxide.**—A solution of 3.1 g. (0.012 mole) of diphenyl(3-methyl-1,2-butadien-1-yl)phosphine oxide in 60 ml. of absolute ethanol containing 1 g. of platinum oxide was hydrogenated at room temperature (4 hr.) under an initial pressure of 48 p.s.i.g. The catalyst was removed by filtration. Water (100 ml.) was added to the filtrate and this solution was extracted with three 50-ml. portions of ether. The ether extracts were combined, washed with two 100- ml. portions of water and dried over anhydrous potassium carbonate. The ether was removed by distillation leaving a white solid residue (3.0 g., 95% yield) which was recrystallized from petroleum ether (b.p. 60–90°), m.p. 95–96° (reported,[7] m.p. 96–97°). The infrared spectrum exhibited no absorption bands usually assigned to carbon-carbon unsaturation (allene or olefin).

**Acknowledgment.**—The authors are indebted to Mr. Harry Ferber and the members of his staff who performed the analytical determinations and to Mr. Lawrence Grieshammer and Miss Frances Judnick who assisted in the interpretation of the infrared spectra.

---

# A New Phosphorylation Reaction of Olefins. II. A Novel Synthesis of a Four-Membered Phosphorus-Containing Ring Compound[1,2]

J. J. McBRIDE, JR., ERIC JUNGERMANN,[3] J. V. KILLHEFFER,[4] AND R. J. CLUTTER

*Armour Industrial Chemical Co., Research Laboratories, McCook, Ill.*

*Received November 6, 1961*

Reaction of 2,4,4-trimethyl-2-pentene with phosphorus trichloride and aluminum chloride in methylene chloride at 0–5° followed by decomposition of the product with water gives 1,1,2,3,3-pentamethyltrimethylenephosphinic acid chloride in good yield. The conversions: acid chloride → acid → ester are readily accomplished by conventional reactions. Structure assignment is based on proton-NMR spectra, absence of unsaturation in the products, and evidence for the existence of *cis-trans* isomers in the esters. This four-membered ring is stable to several powerful reagents such as hot concentrated nitric acid, hot concentrated sulfuric acid, and refluxing concentrated aqueous sodium hydroxide.

The reaction of olefins with phosphorus trichloride and aluminum chloride is a new method for forming carbon-phosphorus bonds.[1,2,5] This paper reports the first detailed structural study of a product of this reaction.

Addition of 2,4,4-trimethyl-2-pentene (hereafter referred to as TMP) to a cold suspension of equimolar amounts of phosphorus trichloride and aluminum chloride in methylene chloride followed by partial hydrolysis with water or aqueous methanol gives a product (I) which contains phosphorus and chlorine in a 1:1 ratio. Further hydrolysis of I gives a chlorine-free acidic material (II). I also reacts with sodium methoxide in methanol to give a neutral phosphorus - containing material (III). Saponification of III followed by acidification regenerates the acid (II) and treatment of II with thionyl chloride gives I.

These interconversions are those to be expected of an acid chloride and the corresponding acid and methyl ester.

Neither I, II, nor III decolorizes bromine water or permanganate. This stability suggests the absence of unsaturation and of P—H bonds. II is recovered unchanged after treatment with boiling concentrated nitric acid and prolonged refluxing with concentrated aqueous sodium hydroxide; this confirms the absence of P—O—C bonds in this compound. Infrared spectra support these conclusions; a band near 8 μ in all three compounds indicates P → O to be present.

Potentiometric titration indicates II to be a strong monobasic acid. Elemental analyses agree best with the formulas $C_8H_{16}PO_2H$, $C_8H_{16}POCl$, and

---

(1) E. Jungermann, J. J. McBride, Jr., R. Clutter, and A. Mais, *J. Org. Chem.*, **27**, 606 (1962).

(2) Presented at 140th American Chemical Society Meeting, Chicago, Ill., September, 1961.

(3) Present address: Armour Soap Division, 1355 West 31st Street, Chicago 31, Ill., to whom inquiries should be addressed.

(4) Present address: Dept. of Chemistry, Northwestern University, Evanston, Ill.

(5) E. Jungermann and J. McBride, Jr., *J. Org. Chem.*, **26**, 4182 (1961).

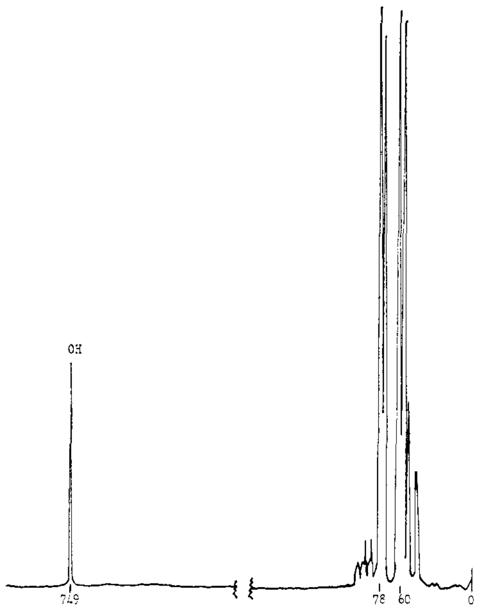
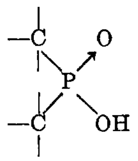


Fig. 1.—60 Mc. proton NMR spectrum of TMP-2 acid; $CCl_4$ solvent; internal standard $(CH_3)_4Si$ (0 c.p.s.)

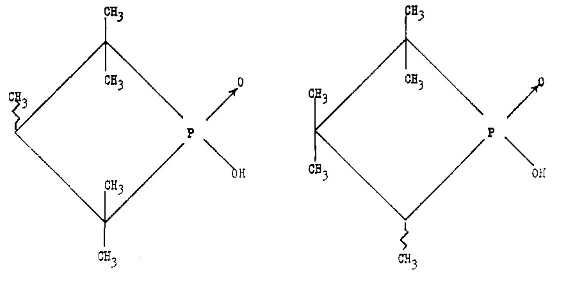
$C_8H_{16}PO_2CH_3$ for the acid, the chloride, and the ester, respectively. The neutralization equivalent of the acid and the saponification equivalent of the ester are both in excellent agreement with these formulas. Ebullioscopic molecular weight determinations indicate the ester to be a monomer and the acid to be somewhat associated ($n = 1.7$). The data are summarized in Table I.

**Structure.**—The best fit to the data given in Table I seemed to be a disubstituted phosphinic acid:



The absence of unsaturation is in agreement with this formulation. Attachment of two alkyl groups to phosphorus would require cleavage of the carbon chain into two fragments, a most unlikely occurrence; the other alternative is that one divalent radical is attached to phosphorus.

NMR spectra were obtained on the acid II and its methyl ester III. The spectrum of the acid is shown in Fig. 1. The single signal at 749 c.p.s. is from the hydroxyl proton and using this as a standard area equivalent to one proton, the other groups of signals may be integrated to 7.1 and 8.9 protons. In the aliphatic region of the spectrum almost all the intensity is seen as tall sharp signals characteristic of methyl groups; there are indications of only one CH proton. The group of lines to the extreme right of the spectrum is assigned to three methyl groups; the group just to the left of this (78 c.p.s.) is assigned to the other two methyl groups plus the lone CH hydrogen. Any structures with hydrogen directly bonded to phosphorus are ruled out since no doublet signal with a large spin coupling is observed.



IIa IIb

Figure 2

Fig. 3.—Gas chromatograph of TMP methyl ester; Apiezon L column, 100 ft. × 0.01 in. i.d.; column temp. 55°

In the spectrum of the ester, the methoxy signal appeared at 218 and 228 c.p.s. as a doublet by spin coupling to the phosphorus. Using these two signals as being equivalent to 3.0 protons, integration of the remaining signals gave areas equivalent to 7.2 and 9.3 protons.

Two possible structures which agree with both the integral information and the numbers of methyl and CH hydrogens are IIa and IIb (Fig. 2).

IIa is favored by us for mechanistic reasons (see following page).

Either of the ring structures proposed above would seem to require that the ester exhibit *cis-trans* isomerism. Evidence supporting the presence of two isomers was obtained by high resolution gas chromatography. A highly purified sample of the ester III showed only one peak when chromatographed on a 6-ft. analytical column; the same sample, however, showed two distinct peaks when put through a 100-ft. capillary column (Fig. 3).

TABLE I

IONIZATION CONSTANTS OF PHOSPHINIC ACIDS[a]

| A. Open Chain Acids, $R_2PO_2H$ | | B. Cyclic Acids $(CH_2)_nPO_2H$ | |
|---|---|---|---|
| R | *pK* | *n* | *pK* |
| $CH_3$— | 3.08 | 3 | 3.07 |
| $C_2H_5$— | 3.29 | 4 | 2.51 |
| *i*-$C_3H_7$ | 3.46 | 5 | 2.73 |

[a] G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957).

TABLE II

| Physical Character | I, Neutral Solid | II, Acidic Solid | III, Neutral Solid |
|---|---|---|---|
| Elemental analysis | $C_8H_{16}POCl$ | $C_8H_{16}PO_2H$ | $C_8H_{16}PO_2CH_3$ |
| C found/calcd. | 49.80/49.36 | 54.89/54.53 | 56.97/56.82 |
| H | 8.45/ 8.29 | 9.72/ 9.73 | 9.28/10.07 |
| P | 15.90/15.92 | 16.07/17.58 | 17.32/16.29 |
| Cl | 18.20/18.22 | ......... | ......... |
| O (by difference) | 7.65/ 8.22 | 19.32/18.16 | 16.43/16.82 |
| Neut. equiv. | ......... | 176.0/176.2 | ......... |
| Sapon. equiv. | ......... | ......... | 190.6/190.2 |
| Melting point | 74–75° | 75–76° | 35–36° |
| *pK'* | | 2.85 | |
| $n^{20}D$ (supercooled liquid) | | | 1.4634 |
| $d^{20}$ (supercooled liquid) | | | 1.009 |
| Mol. wt. (ebullioscopic in acetone) | | 302/176 | 201/190.2 |

The cyclic structure is also supported by the observed *pK* of the acid II which was determined to be 2.85. The ionization constants of the only nonaromatic cyclic phosphinic acids reported were measured by Kosolapoff and Struck and compared with open chain members as shown in Table I.

The refractive index and the density of the methyl ester III are unusually high for an open chain structure[6,7] and are more consistent with a compact ring structure.

The acid shows remarkable stability to attack by a number of powerful reagents. It is recovered unchanged from treatment with a) boiling concentrated nitric acid, b) concentrated sulfuric acid or 15% oleum, c) boiling bromine–carbon tetrachloride with or without ferric chloride, d) boiling concentrated aqueous potassium hydroxide, and e) sulfuryl chloride in refluxing carbon tetrachloride in the presence of benzoyl peroxide.

**Mechanism.**—The following mechanism is suggested for the formation of the proposed cyclic structure (Fig. 4).

The most important features of this mechanism are: 1) Formation of the electrophilic species, $PCl_2^+$ by an acid-base reaction between aluminum chloride and phosphorus trichloride. 2) Attack of the positive species, $PCl_2^+$, at the 2- position rather than the 3- position of the olefin; it is suggested that for steric reasons, the bulky $PCl_2^+$ ion preferentially attacks the 2-position rather than the neopentyl-type 3-position. 3) Shift of a methyl group from C-4 to C-3 converting the initially formed secondary carbonium ion into the more stable tertiary carbonium ion. 4) Cyclization of the rearranged ion in preference to loss of a proton. 5) Reaction of the cyclic cation with a solvent anion to form a neutral species followed by loss of hydrogen chloride to give the observed product.

This mechanism places the lone ring proton opposite the phosphorus atom and results in a product having structure IIa rather than IIb. It is difficult to visualize a mechanism for formation of IIb that does not involve at least two methyl group shifts.

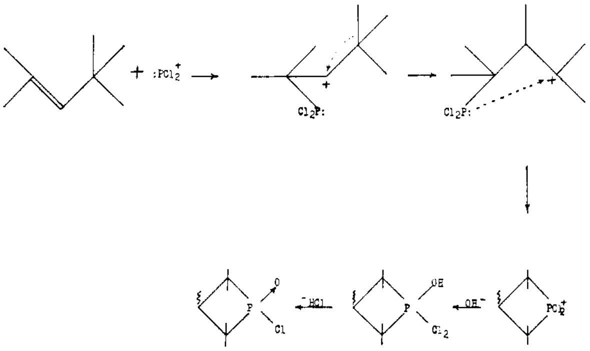


Figure 4

It is perhaps surprising that cyclization apparently occurs exclusively in preference to loss of a proton; the geometry of the intermediate must be especially favorable to ring closure, since the cyclic product is obtained in high yield.

## Experimental

**2,4,4-Trimethyl-2-pentene (TMP)** was obtained from Phillips Petroleum Co., Special Products Division, and was technical grade, 95 mole % min. purity.

**Phosphorylation of TMP.**—A 1-l., three-neck flask, fitted with stirrer, reflux condenser, and dropping funnel was charged with 300 ml. of methylene chloride, 68.8 g. (0.50 mole) of phosphorus trichloride, and 66.6 g. (0.50 mole) of anhydrous aluminum chloride. The mixture was cooled to 0–10° and 56.0 g. (0.50 mole) of TMP was added over about 20 min. The aluminum chloride dissolved as the addition proceeded. After addition was complete, the temperature and stirring was continued for an additional hour. Three hundred milliliters of water was then added dropwise with cooling to keep the temperature below 25°. The organic phase was separated, washed, dried, and stripped *in vacuo*, leaving 85 g. white solid. On recrystallization from petro-

---

(6) B. A. Arbuzov and N. I. Rizpolozhenskii, *Izvest. Akad. Nauk. U. S. S. R., Otdel, Khim. Nauk.*, 253 (1955); *Chem. Abstr.*, **50**, 3270f (1956).

(7) A. I. Razunov and O. A. Mukhocheva, *Trudy Kazan, Khim. Tekhnol Inst. in S. M. Kirova*, **42**, No. 18 (1953); *Chem. Abstr.*, **51**, 56887g (1957).

leum ether (b.p. 60–68°) there was obtained 60.0 g. (62%) of the acid chloride I, m.p. 72–75°. Concentration of the filtrate yielded 19.0 g. (0.11 mole) of the acid II, m.p. 72–74°.

**1,1,2,3,3-Pentamethyltrimethylenephosphinic Acid (II).**—Refluxing the acid chloride I with water for 2 hr. gives a quantitative yield of the acid II as its dihydrate; white shiny platelets, m.p. 54–58°; calcd. for $C_8H_{16}PO_2H \cdot 2H_2O$, neut. equiv. 212; found, neut. equiv. 216. Drying in a vacuum desiccator or heating above its melting point converts the hydrate to the anhydrous acid II, m.p. 72–74°.

**Methyl Ester of II.**—A solution of 98.0 g. (0.50 mole) of the acid chloride I in 150 ml. of methanol was added dropwise with stirring to a solution of sodium methoxide made from 18.2 g. (0.55 g.-atom) of sodium in 500 ml. of methanol. After standing for 20 hr., the methanol was stripped off *in vacuo.* The solid remaining was taken up in water and this solution was extracted several times with methylene chloride. After drying and removal of the solvent, distillation gave 89.1 g. (94%) of ester III, b.p. 66–69°/0.2 mm.

Saponification of the methyl ester with aqueous base followed by acidification regenerates the acid II as its dihydrate. The anhydrous acid is readily converted to the acid chloride by short refluxing with thionyl chloride in benzene.

The analytical data on compounds I, II, and III are summarized in Table II.

---

# 5,10-Dihydrosilanthrene Derivatives

HENRY GILMAN, ERNEST A. ZUECH, AND WALTER STEUDEL

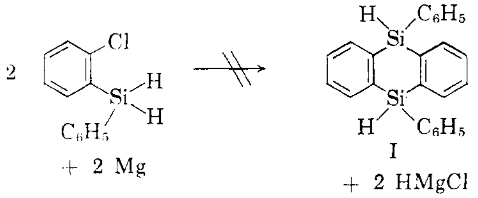
*The Chemical Laboratory of Iowa State University, Ames, Iowa*

*Received October 24, 1961*

5,10-Dihydrosilanthrene derivatives have been prepared by the intermolecular sodium coupling of *o*-chlorophenyl silicon compounds containing a silicon-hydrogen grouping In the appropriately substituted derivatives, a separation of the *cis-trans* isomers has been accomplished Attempts to treat *o*-chlorophenylsilane with magnesium in tetrahydrofuran were unsuccessful.

The 5,5,10,10-tetraphenyl and 5,5,10,10-tetrabenzyl derivatives of 5,10-dihydrosilanthrene have recently been prepared by treating *o*-phenylenedilithium with dichlorodiphenylsilane and with dibenzyldichlorosilane, respectively.[1] Those derivatives were the first members of a new cyclic organosilicon system, the silicon analog of 9,10-dihydroanthracene. We now wish to report the syntheses of 5,10-dihydrosilanthrene derivatives by new procedures, which involved intermolecular Wurtz-type coupling reactions.

The initial approach in this investigation was concerned with the preparation and possible intermolecular cyclization of *o*-chlorophenylphenylsilane. Two attempts to prepare *o*-chlorophenylphenylsilane by treating phenylsilane[2] with *o*-chlorophenylmagnesium bromide were unsuccessful, but the compound was obtained in fair yield by the interaction of the Grignard reagent and phenylbromosilane. In light of the recent successes in the preparation of Grignard reagents from aryl chlorides[3] and in the reactions of Grignard reagents with silicon hydrides[2] through the use of tetrahydrofuran as the solvent, reactions of *o*-chlorophenylphenylsilane with magnesium in tetrahydrofuran were attempted in an effort to obtain 5,10-diphenyl-5,10-dihydrosilanthrene (I). However, this aryl chloride could not be induced to react with magnesium, probably because of steric reasons.



Attention was subsequently turned to Wurtz-type coupling reactions as a means of preparing 5,10-dihydrosilanthrene compounds. Clarke[4] had shown that *o*-chlorophenyltrimethylsilane and chlorotrimethylsilane could be readily coupled upon treatment with molten sodium in refluxing toluene to give *o*-phenylenebis (trimethylsilane). Also, Benkeser and Foster[5] found that organosilicon compounds such as triphenylsilane were unaffected by molten sodium metal. It therefore seemed desirable to investigate the possible intermolecular cyclization by sodium of certain *o*-chlorophenyl silicon derivatives containing a silicon-hydrogen grouping.

Treatment of *o*-chlorophenylphenylsilane with phenylmagnesium bromide in refluxing tetrahydrofuran gave *o*-chlorophenyldiphenylsilane in good yield. A toluene solution of this *o*-chlorophenyl derivative was then added to a suspension of molten sodium in refluxing toluene to afford 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (II), which was shown to be identical with the material obtained by the interaction of *o*-phenylenedilithium and dichlorodiphenylsilane.[1] In addition, lesser amounts

---

[1] H. Gilman and E. A. Zuech, *Chem. & Ind.*, 120 (1960); *J. Am. Chem. Soc.*, **82**, 3605 (1960).

[2] For the reactions of organometallic compounds with silicon hydrides, see H. Gilman and E. A. Zuech, *ibid.*, **81**, 5925 (1959).

[3] H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); H. Normant, *Compt. rend.*, **239**, 1510 (1954), and, particularly, pp. 1–65 in "Advances in Organic Chemistry," Interscience Publishers, New York, 1960.

[4] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

[5] R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).