phonate (1 g.) in 10 ml. 20% hydrochloric acid was refluxed for 5 hr. and evaporated to dryness under reduced pressure. The oily residue was dissolved in ethanol and an excess benzylamine (1.3 g.) was added. The precipitated di(benzyl-ammonium)salt was separated by filtration and washed with ethanol (1.5 g.). Recrystallization from ethanol yielded white needles, m.p. 171°.

Anal. Calcd. for $C_{21}H_{28}N_3O_3P$: P, 7.7; N, 10.5. Found: P, 7.6; N, 10.4.

2-[6'-(2'-Methylpyridyl)]ethylphosphonic acid. A solution containing diethyl 2-[6'-(2'-methylpyridyl)]ethylphospho-nate (2 g.) in 20 ml. 20% hydrochloric acid was refluxed for 5 hr. The solution obtained was evaporated under reduced pressure. The residue was dissolved in small amount of water and evaporated *in vacuo.* This operation was repeated twice. Crude hydrochloride (1.8 g.) was dissolved in water (10 ml.)

and sodium bicarbonate (0.7 g.) was added. The solution was evaporated to dryness *in vacuo* and the acid extracted with hot absolute ethanol. The alcohol solution was concentrated to small volume. The solid acid was collected (1.1 g.) and recrystallized from ethanol. White, very hygroscopic small plates, m.p. 169–171°, appeared.

Diethyl 2-(4'-pyridyl)ethylphosphonate. A solution of sodium ethoxide in ethanol was added dropwise with stirring to a mixture of 4-vinylpyridine (21 g., 0.2 mole) and of diethyl phosphite (27.6 g., 0.2 mole). After 15 min. the temperature rose to 70°, and was kept at 50° by occasional cooling. The product was isolated in the usual manner, b.p. 117° at 0.2 mm., n_D^{25} 1.4935, n_D^{30} 1.4916, d_4^{25} 1.1267. Yield 39.3 g., 81%.

Lodz, Poland

Nitrogen Compounds of the Phosphoric and Phosphonic Acids. IV. Some Derivatives of Phenylphosphonamidic and Phenylphosphonamidothioic Acids

M. F. HERSMAN[1,2] AND L. F. AUDRIETH

Partial solvolysis of phenylphosphonic dichloride with an alcohol (or a phenol) in the presence of pyridine in ether or benzene leads to formation of the *O*-alkyl (aryl) phosphonochloridates. These intermediates can be converted by ammonolysis into the *O*-alkyl-*P*-phenylphosphonamidates, $C_6H_5PO(OR)(NH_2)$, where R = Me, Et, *n*-Pr, *n*-Bu, *n*-Am, Ph, and by aminolysis into the *O*-alkyl (aryl)-*P*-phenylphosphonamidates, $C_6H_5PO(OR)(NX_2)$, where R = C_6H_5 and NX_2 = —NHC_6H_5, —$N(CH_2)_4CH_2$, —$NC_2H_4OCH_2CH_2$, —$NHCH_2CH(CH_3)_2$, and R = C_2H_5 and NX_2 = —NHC_6H_5. Some typical *O*-alkyl (aryl)-*N*-alkyl (aryl)-*P*-phenylphosphonamidothioates, $C_6H_5PS(OR)(NX)_2$, were also prepared by partial solvolysis followed by aminolysis of the intermediate *P*-phenylphosphonochloridothioate, $C_6H_5PS(OR)Cl$. The *O*-alkyl phosphonochloridates undergo thermal decomposition to yield the corresponding alkyl chlorides and the *P*-phenyl metaphosphonate, $(C_6H_5PO_2)_x$.

A significant feature of compounds having a phosphorus-halogen linkage is their ability to undergo solvolytic reactions with compounds possessing a labile hydrogen atom. In alkyl (and aryl) phosphonic dichlorides, $(RPOCl_2)$, the presence of a phosphorus to oxygen bond imparts to the phosphorus-chlorine bond properties similar to those of the acid chlorides of the carbon family. Due to the electronegative character of the groups attached to the phosphorus atom, the latter becomes electron deficient and therefore prone to nucleophilic attack. The chlorine atoms of alkyl (and aryl) phosphonic dichlorides can, however, be made to react in a stepwise fashion. The second chlorine atom is much less reactive than the first. Partial solvolysis of the alkyl (aryl) phosphonic dichloride leads to formation of an intermediate ester-chloridate when reaction with an alcohol is allowed to take place. The oxygen atom thus in-

troduced as an alkoxy group into the molecule is electron rich and has a tendency to donate electrons instead of withdrawing them as is the case with chlorine atoms; it thereby serves to reduce the partial positive charge on the phosphorus atom and, in turn, to reduce the reactivity of the remaining halogen atom.
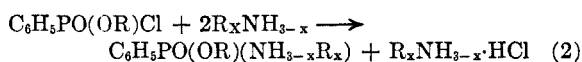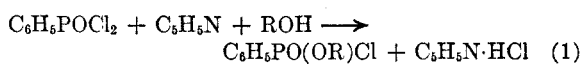
These considerations, however, are not meant to imply that the second chlorine atom will not undergo reaction under appropriate circumstances, but only that the replacement reaction takes place less vigorously. In the usual cases, most solvolytic reactions of alkyl (aryl) phosphonic dichlorides involve replacement of both chlorine atoms since an excess of the solvolytic agent is generally employed. Examples of stepwise reaction are relatively few.

The investigations described in the present publication are concerned with the preparation and characterization of some phenyl phosphonic and phosphonothioic acid derivatives containing both P—O (or P—S) and P—N linkages, such as C_6H_5-$PO(OR)(NX_2)$, where R = alkyl and aryl, and NX_2 = amide and primary, or secondary amine radicals. This study was undertaken initially to develop a new route to the preparation of the alkyl-

P-phenylphosphonamidates, $C_6H_5PO(NH_2)OR$, containing the urethane-like H_2NPOOR moiety. These substances had previously been prepared in this laboratory[3] by the partial alcoholysis of phenylphosphonic diamide. The new and improved synthesis of the ester-amide derivatives of phosphonic (and phosphonothioic) acids has been accomplished by a two-step procedure involving the reaction of the dichloride with an alcohol (or phenol) followed by reaction with ammonia, or an amine. The preparative procedures were carried out in either ether or benzene, using stoichiometric quantities of reactants and employing pyridine in the alcoholysis step of the reaction to take up liberated hydrogen chloride.

$$C_6H_5POCl_2 + C_5H_5N + ROH \longrightarrow$$
$$C_6H_5PO(OR)Cl + C_5H_5N \cdot HCl \quad (1)$$

$$C_6H_5PO(OR)Cl + 2R_xNH_{3-x} \longrightarrow$$
$$C_6H_5PO(OR)(NH_{3-x}R_x) + R_xNH_{3-x} \cdot HCl \quad (2)$$

The intermediate alkyl-*P*-phenyl phosphonochloridates could not be characterized as pure products since they were found to undergo decomposition during attempted isolation in accordance with Equation 3 to give the alkyl chlorides and *P*-phenyl metaphosphonate. The *P*-phenyl

$$XC_6H_5PO(OR)Cl \longrightarrow (C_6H_5PO_2)_x + XRCl \quad (3)$$
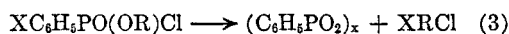
metaphosphonate was converted by slow hydrolysis into *P*,*P'*-diphenyldiphosphonic acid and eventually into phenyl phosphonic acid. The aryl-*P*-phenyl phosphonochloridates as well as the alkyl and aryl *P*-phenyl phosphonochloridothioates were much more stable to heating and could be isolated and characterized.

Each of the classes of *P*-phenyl phosphonochloridates discussed in the preceding paragraph was subjected to ammonolysis (with liquid ammonia) and to aminolysis using various primary aliphatic amines and aniline, as well as a number of representative cyclic amines. The P—N linkages in such N-substituted compounds are easily cleaved in acid solution, thus offering a possible route to the preparation of the mono- esters of the *P*-phenyl phosphonic acids (achieved in the case of phenyl-*P*-phenyl phosphonic acid).

The *O*-alkyl derivatives of P-phenyl phosphonamidic acid reveal an increase in melting points (see Table I) from the methyl to the propyl derivatives and a decrease from the propyl to the amyl compounds. In the case of the derivatives from methyl to propyl this suggests dimer association through hydrogen bonding within the crystal lattice through formation of a six-membered ring, or an intermolecular type of bonding with increased contribution of a linear chain-type association. This effect was first observed by Bus-

well, Rodebush, and Roy[4] in their consideration of the structures of the carboxylic amides. For the homologs above the propyl derivative it is likely that the longer alkyl chain is oriented in such a manner as to effectively block this type of association or decrease it materially. This probably promotes an increased amount of intramolecular type of association. The corresponding derivative of phenol shows a much higher melting point than the amyl derivative which possesses about the same molecular weight. From stereochemical considerations the benzene nucleus would be expected to have the same steric effect as the *n*-propyl chain. On the other hand, the amyl derivative possessing a long zigzag chain could be expected to cause appreciable steric hindrance to hydrogen bonding. The benzene ring being planar in configuration would thus exhibit less interference with the hydrogen bonding of the molecule as a whole. This was found to actually be the case, the propyl derivative having a melting point of 135° and the phenyl derivative melting at 131–133°.

Hydrogen bonding ability is also indicated by the greater solubilities of these substances, especially the *N*-disubstituted derivatives, in chloroform than in carbon tetrachloride.[5] The simple phosphonamidates also reveal solubility in water, with solubility decreasing with an increase in molecular weight. The thioic acid derivatives have lower melting points than the corresponding oxygen analogs. This is to be expected due to the greater electro-negativity of the oxygen atom and the increased hydrogen bonding properties of oxygen compounds in general when compared with their thio analogs.

Attempts to resolve some of the simple phosphonamidates by adsorption on optically active quartz or lactose hydrate were unproductive of any evidence of successful resolution. The reactions with such adsorbents were carried out either by shaking solutions of compounds to be resolved with the adsorbent for various time intervals or by a column chromatographic procedure, but neither method gave positive results. Formation of internal diastereoisomers by reaction of pseudoephedrine with phenyl-*P*-phenylphosphonochloridate was not accomplished due to hydrolytic cleavage of the P——N bond and consequent formation of the amine salt of the corresponding acid. Even though these experiments were unsuccessful, the possibility of resolving compounds of this type is not in doubt and has been accomplished recently by VanderWerf and co-workers.[6,7]

(3) W. C. Smith and L. F. Audrieth, *J. Org. Chem.*, **22**, 265 (1957).

(4) A. M. Buswell, W. H. Rodebush and M. F. Roy, *J. Am. Chem. Soc.*, **60**, 2444 (1938).

(5) L. F. Audrieth and A. D. F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).

(6) D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **78**, 3061 (1956).

(7) K. L. Marsi, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **78**, 3063 (1956).

TABLE I

PROPERTIES AND ANALYTICAL DATA FOR SOME ALKYL P-PHENYL PHOSPHONAMIDATES

C_6H_5PO-(OR)(NH$_2$) where R =	M.P., °C.	Analyses					
		Carbon		Hydrogen		Nitrogen	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
CH$_3$	111	49.20	49.06	5.88	5.91	8.19	8.11
C$_2$H$_5$	127 (127)[a]	51.88	51.80	6.50	6.54	7.56	7.67
n-C$_3$H$_7$	135 (135)[a]	54.26	54.06	7.08	6.98	7.03	7.05
n-C$_4$H$_9$	103 (104)[a]	56.32	56.57	7.52	7.54	6.57	6.56
n-C$_5$H$_{11}$	83 (82)[a]	58.20	57.70	7.98	8.16	6.16	6.16
C$_6$H$_5$	131-133 (136.5-137.5)[b]	61.80	61.95	5.18	5.12	6.02	6.15

[a] Melting points as recorded by Smith and Audrieth.[3] [b] Reference 7.

EXPERIMENTAL[8]

Alkyl (aryl)-P-phenylphosphonochloridates and phosphonochloridothioates. Preparation of these substances was effected by adding an ether or benzene solution of equimolecular quantities of an alcohol (or phenol) and pyridine to a solution containing an equimolecular quantity of phenylphosphonic dichloride (or the thio analog)[9] in the same solvent. Rapid precipitation of pyridine hydrochloride was observed when the reaction between the alcohol and the phenylphosphonic dichloride was carried out at or below room temperature. In all other instances, the solutions were generally warmed on the steam bath and additional solvent added to replenish that lost by evaporation to effect the separation of the pyridine hydrochloride. The latter was removed by filtration, after which the filtrates were distilled fractionally under reduced pressure first to remove solvent, secondly to eliminate pyridine hydrochloride which appeared to possess some solubility in the chloridates and generally deposited in the condenser during the early stages of fractionation and finally, to isolate the desired compounds.

The alkyl P-phenyl phosphonochloridates were not isolated (see below). Solutions of these substances were used directly, after removal of precipitated pyridine hydrochloride, for conversion into the amidates and N-substituted derivatives by treatment with ammonia and amines.

Phenyl-P-phenylphosphonochloridate, $C_6H_5PO(OC_6H_5)Cl$. By addition of a solution containing 42 g. (0.447 mole) of phenol and 33.7 g. pyridine (0.426 mole) in 200 cc. of ether to a solution of 83 g. (0.43 mole) of $C_6H_5POCl_2$ in 200 cc. of ether. Treatment as described above for removal of pyridine hydrochloride, solvent, and a forerun of dissolved pyridine hydrochloride and final distillation under reduced pressure yielded 86 g. (78.5%) of product boiling at 121-125° at 0.025 mm., $n_D^{21.5}$ 1.5742.

Anal. Calcd. for $C_{12}H_{10}ClO_2P$: C, 57.2; H, 4.0. Found: C, 57.9; H, 4.25.

This compound had previously been prepared by Marsi, VanderWerf, and McEwen[7] by refluxing together equimolar quantities of phenylphosphoric dichloride and phenol. These authors give 152-155° (0.3 mm.) as the boiling point and $n_D^{31} = 1.5718$.

Phenyl-P-phenylphosphonochloridothioate, $C_6H_5PS(OC_6H_5)Cl$. By addition of a solution of 73.6 g. (0.784 mole) of phenol and 61.9 g. (0.784 mole) of pyridine in 100 cc. of ether to 165 g. (0.784 mole) of $C_6H_5PSCl_2$ in 100 cc. of ether. Product yield, 152.4 g. (74%), boiling at 131-135° at 0.45 mm.; $n_D^{21.5}$ 1.6197.

Anal. Calcd. for $C_{12}H_{10}ClOPS$: C, 53.6; H, 3.75. Found: C, 53.8; H, 3.84.

_____

(8) Melting points are uncorrected.

(9) The acid chlorides used in this investigation were kindly furnished by the Victor Chemical Works, Chicago, Ill.

Ethyl-P-phenylphosphonochloridothioate, $C_6H_5PS(OC_2H_5)Cl$. By interaction of 0.1-molar quantities of EtOH (4.43 g.) and pyridine (7.76 g.) in 20 cc. of ether with $C_6H_5PSCl_2$ (20.7 g.) in 20 cc. of ether. Product yield, 17.8 g. (83%) boiling at 90° at 0.32 mm.; $n_D^{21.5}$ 1.5700.

Anal. Calcd. for $C_8H_{10}ClOPS$: C, 43.60; H, 4.57. Found: C, 43.64; H, 4.76.

Alkyl (aryl) P-phenylphosphonamidates, $C_6H_5PO(OR)(NH_2)$. As noted above and discussed in detail below isolation of the alkyl-P-phenylphosphonochloridates was not effected. The synthesis solutions, prepared by using equimolar quantities of the alcohol, pyridine, and $C_6H_5POCl_2$, were used directly after removal of precipitated pyridine hydrochloride for conversion into the amides by treatment with liquid ammonia. The preparation of a representative example of this group of compounds is described. Melting points and analytical data for members of this series of compounds are given in Table I.

Methyl-P-phenylphosphonamidate, $C_6H_5PO(OCH_3)(NH_2)$. A solution containing 0.11-molar quantities of methanol (3.42 g.) and pyridine (8.5 g.) was added dropwise with mechanical stirring to 20.8 g. (0.11 mole) of $C_6H_5POCl_2$ in 50 cc. of ether. Stirring was continued for an additional 5 min. after which the precipitated pyridine hydrochloride was removed by filtration. The filtrate containing the methyl-P-phenylphosphonochloridate was added dropwise to a mixture of 50 cc. of ether and 50 cc. of liquid ammonia. The ether and ammonia were allowed to evaporate from the reaction mixture; the residue was extracted with two 300-ml. portions of hot $CHCl_3$. The solvent was removed by evaporation on the steam bath under reduced pressure to give 13.2 g. (72.5%) of the desired product. Recrystallization from 10/1:CCl_4/EtOH yielded a product melting at 111°. See Table I for analytical data. The compound is soluble in H_2O, $CHCl_3$, C_5H_5N, $HCON(CH_3)_2$, MeOH, EtOH, $(CH_3)_2$-CO, dioxane, and boiling xylene; slightly soluble in benzene, high boiling petroleum ether, CS_2 and hot CCl_4, but insoluble in low boiling petroleum ether and $(C_2H_5)_2O$.

Yields obtained in the preparation of the alkyl (aryl) phosphonamidates listed in Table I averaged around 75%. Solubilities of the amidates in water were found qualitatively to decrease with increasing molecular weights; in diethyl ether the reverse was observed.

In several instances recrystallization of the product from a high boiling solvent, in contact with the atmosphere, caused extensive hydrolysis to occur. By keeping a hot solution of the n-amyl derivative in xylene in contact with the atmosphere complete conversion was effected to the corresponding ammonium salt, $C_6H_5PO(OC_5H_{11})OH\cdot NH_3$, melting at 136-138°.

Anal. Calcd. for $C_{11}H_{20}NO_3P$: C, 53.80; H, 8.16; N, 5.72. Found: C, 52.61; H, 7.98; N, 6.20.

Alkyl (aryl)-N-alkyl (aryl)-P-phenylphosphonamidates, $C_6H_5PO(OR)(NX_2)$ (where NX_2 represents a primary or secondary amine group). Aminolysis of the alkyl (aryl)-P-

TABLE II

ALKYL (ARYL)-N-ALKYL (ARYL)-P-PHENYLPHOSPHONAMIDATES, $C_6H_5PO(OR)(NX_2)$
(WHERE NX_2 = PRIMARY OF SECONDARY AMIDE GROUP)

$C_6H_5PO(OR)(NX_2)^a$		M.P., °C.	Analyses					
			Carbon		Hydrogen		Nitrogen	
where R =	NX_2 =		Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5	—NHC$_6$H$_5$	147	70.2	70.1	4.92	5.31	4.6	4.5
C_6H_5	—N(CH$_2$)$_4$CH$_2$	82	67.8	67.8	6.7	7.0	4.7	4.5
C_6H_5	—NC$_2$H$_4$OCH$_2$CH$_2$	134	63.5	64.5	6.0	6.0	4.6	4.5
$C_6H_5{}^c$	—NHCH$_2$CH(CH$_3$)$_2$	83	66.5	66.4	7.0	6.8	4.9	4.7
$C_2H_5{}^b$	—NHC$_6$H$_5$	131^d	64.5	64.2	6.2	6.0	5.4	5.4

^{a} Product yields, except for (b) and (c) exceeded 90% of theory. ^{b} The solution obtained by interaction of $C_6H_5POCl_2$ with ethanol-pyridine was subjected directly, after removal of precipitated pyridine hydrochloride, to reaction with aniline. Yield was 77%. ^{c} Yield was 62%. ^{d} This compound had presumably been prepared previously by Michaelis (*Ann.*, **407**, 290 (1915)) who states that it "schmiltzt gegen 105°."

TABLE III

O-ALKYL (ARYL)-N-ALKYL (ARYL)-P-PHENYLPHOSPHONAMIDOTHIOATE, $C_6H_5PS(OR)(NX_2)$
(WHERE NX_2 = PRIMARY OR SECONDARY AMIDE GROUP)

$C_6H_5PS(OR)(NX_2)$		M.P., °C.	Analyses					
			Carbon		Hydrogen		Nitrogen	
where R =	NX$_2$ =		Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_6H_5^-$	—NC$_2$H$_4$OCH$_2$CH$_2$	87	60.3	60.2	5.7	5.8	4.4	4.2
$C_2H_5^-$	—NC$_2$H$_4$OCH$_2$CH$_2$	81	53.2	53.2	6.7	6.4	5.3	5.1
$C_6H_5^-$	—NHC$_6$H$_5$	103	66.5	66.8	5.0	5.2	4.3	4.2

phenylphosphonochloridates can be effected readily in ether or benzene solution. Two to one molar ratios of amine to chloridate are employed. The amine hydrochlorides precipitate from the reaction mixtures; the desired products are recovered from the solvent. The products are soluble in a wide variety of organic solvents, but insoluble in water. The preparation of the N-phenyl derivatives is described in detail as illustrative of the procedure employed for the isolation of representative examples of this class of compounds. The melting points and analytical data are presented in Table II.

Phenyl-N-phenyl-P-phenylphosphonamidate, $C_6H_5PO(O-C_6H_5)(NHC_6H_5)$. A solution of 18.6 g. (0.2 mole) of aniline and 25 cc. of benzene was added dropwise with stirring to a solution consisting of 25 g. (0.1 mole) of phenyl-P-phenylphosphonochloridate and 15 cc. of benzene. After completion of the reaction an additional 100 cc. of benzene was added, stirring continued for 5 min. after which the white precipitate consisting of aniline hydrochloride and product was removed by filtration. The residual solution was concentrated to crystallization. The precipitate was extracted with benzene to remove product from the aniline hydrochloride. A total yield of 30.2 g. (98%) was recovered. Purification for analysis was effected by crystallization from acetone to give a product melting at 147–149°.

This compound was presumably first prepared by Michaelis[10] by the action of phenol upon a product mixture obtained from $C_6H_5POCl_2$ and $C_6H_5NH_2$·HCl, believed to contain N-phenyl-P-phenylphosphonamidochloridate, $C_6H_5PO(NHC_6H_5)Cl$. The melting point is recorded as 83° and is believed to be in error.
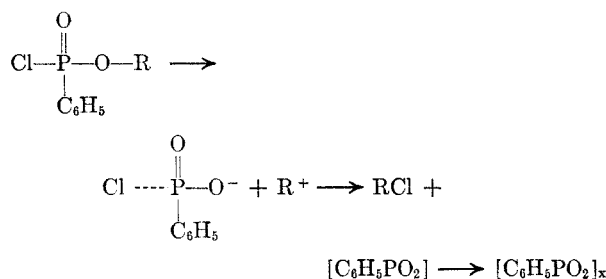
Alkyl (aryl)-N-alkyl (aryl)-P-phenylphosphonamidothioates, $C_6H_5PS(OR)(NX_2)$ (where NX_2 = a primary or secondary amine group). Typical examples of this class of compounds were prepared by the interaction of purified alkyl (aryl) P-phenylphosphonochloridothioate with the various amines, both dissolved in ether or benzene, in a 1:2 molar ratio. Procedures for recovery and isolation of the desired products did not differ materially from those used for the analogous phosphonic compounds. Melting points and analytical data are summarized in Table III.
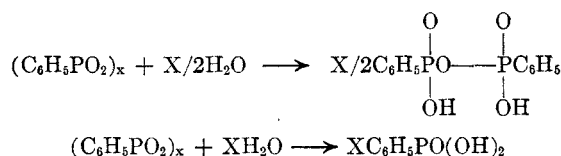
Thermal decomposition of the alkyl P-phenylphosphonochloridates. Attempted isolation of the alkyl derivatives of P-phenylphosphonochloridic acid from the synthesis solutions, by removal of solvent, led invariably to the formation of a resinous product which on long standing changed to a white amorphous powder. When solutions containing the isoamyl derivative were subjected to distillation the same residual product was obtained, together with isoamylchloride. It thus became obvious that displacement of the chloride ion by the alkoxide oxygen had occurred to give the alkyl chloride and a benzene metaphosphonate polymer by a mechanism such as illustrated by the following processes:

(10) A. Michaelis, *Ann.*, **293**, 193 (1896).
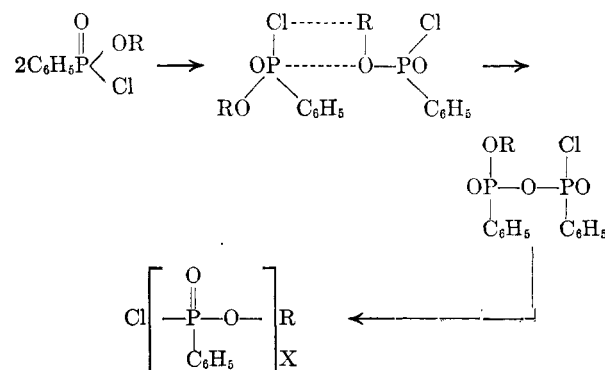
It is also conceivable that such a process might occur through ionization of an alkyl radical with inter- or intra-molecular reaction to form the alkyl chloride and an unstable monomer of $C_6H_5PO_2$ which would then undergo stabilization by polymerization.

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{Cl}\text{---}\text{P}\text{---}\text{O}\text{---}\text{R} \longrightarrow \\ \mid \\ \text{C}_6\text{H}_5 \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{Cl}\text{----}\text{P}\text{---}\text{O}^- + \text{R}^+ \longrightarrow \text{RCl} + \\ \mid \\ \text{C}_6\text{H}_5 \end{array}$$

$$[C_6H_5PO_2] \longrightarrow [C_6H_5PO_2]_x$$

The identity of the polymetaphosphonate with the product which was first prepared by Michaelis[11] was verified by analysis and by reaction with water (a) at room temperature to yield P,P'-diphenyl diphosphonic acid recently described by Anschütz[12] and (b) by complete hydrolysis in boiling water to yield benzene phosphonic acid.

$$(C_6H_5PO_2)_x + X/2H_2O \longrightarrow \begin{array}{c} \text{O} \quad\quad \text{O} \\ \parallel \quad\quad \parallel \\ X/2C_6H_5PO\text{----}PC_6H_5 \\ \mid \quad\quad \mid \\ \text{OH} \quad\quad \text{OH} \end{array}$$

$$(C_6H_5PO_2)_x + XH_2O \longrightarrow XC_6H_5PO(OH)_2$$

A solution consisting of equimolar quantities (0.21 mole) of pyridine (16.8 g.) and isoamyl alcohol (18.7 g.) and 60 cc. of ether was added dropwise with mechanical stirring to a solution of 41.4 g. (0.21 mole) of $C_6H_5POCl_2$ diluted with 50 cc. of ether. After an additional 15 min. of stirring the precipitated pyridine hydrochloride was removed by filtration. The ether solvent was removed by warming the solution under vacuum on the steam bath. The residual product

---

(11) A. Michaelis and F. Rothe, *Ber.*, **25**, 1747 (1892).

(12) L. Anschütz and H. Wirth, *Chem. Ber.*, **89**, 688 (1956).

was then distilled yielding isoamyl chloride, boiling at 98°.

Anal. Calcd. for $C_5H_{11}Cl$: C, 56.40; H, 10.42. Found: C, 56.38; H, 10.33.

A brown glassy mass remained in the still pot. When an attempt was made to distill the high boiling resin at low pressures, (0.5 mm.), foaming took place and the whole mass solidified. When heated with water this product was converted into phenylphosphonic acid, melting at 161°. Formation of the latter was verified by comparison of the infrared spectrum with that of an authentic sample (melting point, 158°), by the titration curve with sodium hydroxide[13] as well as by analysis.

Anal. Calcd. for $C_6H_5PO(OH)_2$: C, 45.57; H, 4.43. Found: C, 45.74; H, 4.60.

If the polymeric material, obtained as residue after distillation of solutions of any of the alkyl-P-phenyl phosphonochloridates, is allowed to stand in contact with water for about 12 hr., there is obtained a fluffy white solid, melting at 78°. Analyses of products so obtained [from solutions originally containing the methyl(I) and ethyl(II) phosphonochloridates] demonstrate that the primary hydrolysis product consists of P,P'-diphenyl diphosphonic acid.

Anal. Calcd. for $[C_6H_5PO(OH)]_2O$: C, 48.32; H, 4.02. (I) Found: C, 47.65; H, 4.20. (II) Found: C, 47.92; H, 4.32.

The uncorrected melting point given by Anschütz[12] for this compound is 79.5–80°. Further heating in all cases with water caused hydrolysis to benzene phosphonic acid.

The original glassy residue becomes more and more brittle when allowed to stand under anhydrous ether. If ground, and stored under high vacuum, it was found to melt between 105–107°. The melting point given for phenyl metaphosphonate by Michaelis[11] is 100°. Analytical results obtained by Michaelis are compared with those obtained in the present study.

Anal. Calcd. for C_6H_5PO: C, 51.43; H, 3.57. Found: C. 51.68; H, 5.80. Michaelis:[11] C, 51.42; H, 4.0.

The product is very hygroscopic and is moderately soluble in benzene, but insoluble in ether.

URBANA, ILL.

---

(13) Product furnished by Victor Chemical Works Research Laboratory, Chicago Heights, Ill.

Preparation and Properties of Styrenyl-Substituted Organosilicon Compounds

DANIEL W. LEWIS

The preparation and physical properties of five p-styrenyl-substituted silane monomers and one disiloxane are described.

There are two references in the literature to the preparation of styrenyl-substituted silanes; Bunnell and Hatcher[1] described the preparation of trichloro(p-styrenyl)silane and Winslow[2] describes the preparation of trialkyl(p-styrenyl)silanes. However, few data are given on the physical properties of these compounds.

In the preparation of reactive silicone casting

resins, five p-styrenyl-substituted silane monomers and one disiloxane were prepared. The silanes range in functionality from zero to three, with respect to siloxane condensation, *i.e.*, the number of hydrolyzable groups attached to silicon ranges from zero to three. The monomers were, trimethyl-(p-styrenyl)silane, methoxydimethyl(p-styrenyl)-silane, dimethoxymethyl(p-styrenyl)silane, trimethoxy(p-styrenyl)silane and trichloro(p-styrenyl)silane. The latter was prepared according to the method of Bunnell and Hatcher.[1] Also prepared was tetramethyl-1,3-bis(p-styrenyl)disiloxane.

---

(1) D. B. Bunnell and R. H. Hatcher, U. S. Patent 2,469,154.

(2) F. H. Winstow, U. S. Patent 2,642,415.