[CONTRIBUTION FROM THE MELLON INSTITUTE[1]]

Synthesis and Hydrolytic Stability of Some Organosilicon Phosphonate Esters

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A series of organosilicon phosphonates has been synthesized by the peroxide-initiated addition of dialkyl phosphonates to substituted vinyl-, allyl-, and cyclohexenylethylsilanes. Hydrolysis with concentrated hydrochloric acid gave the corresponding phosphonic acids. No cleavage of silicon-carbon bonds was observed under either acid or alkaline conditions.

A series of diethyl esters of substituted silylmethylphosphonic acids was prepared by Gilbert and Precopio[2] through the use of the Michaelis-Arbuzov reaction. These esters containing one carbon between silicon and phosphorus were stated to undergo cleavage of the silicon-carbon bonds under both acidic and alkaline conditions when oxygen was present on silicon. When all of the remaining groups attached to silicon were alkyl, hydrolysis of the ester groups was the principal reaction and silicon-substituted phosphonic acids were apparently isolated. Keeber and Post[3] prepared dibutyl trimethylsilylmethylphosphonate as well as the corresponding acid, trimethylsilylmethylphosphonic acid. This paper also contains a summary of the literature on organosilicon-phosphorus compounds which will not be repeated here. Chernyshev[4] has since reported the compounds: $Cl_3Si(CH_2)_3P(O)Cl_2$, $CH_3Cl_2Si(CH_2)_3P(O)Cl_2$, and $(C_2H_5)SiCHClCH_2P(O)Cl_2$ resulting from reactions of phosphorus trichloride and oxygen with various propyl-, vinyl-, α-chloroethyl-, and β-chloroethylsilanes.

The preparation of the present series of organosilicon phosphonates followed procedures worked out by Stiles *et al.*[5] in preparing dialkyl alkylphosphonates through the addition of dialkyl phosphonates to various olefins using either peroxide or light as initiators. After the present work was completed, Linville[6] described in a patent a similar series of organosilicon phosphonates prepared by the same type of addition. Catalysts claimed were free-radical producing compounds such as the azonitriles and peroxides, as well as various potassium complexes, metallic potassium, and other potassium compounds. Only one of the resulting organosilicon phosphonates was duplicated in this work. Six new organosilicon phosphonates and six new organosilicon phosphonic acids are now reported.

DISCUSSION

The organosilicon phosphonates were of the general formula, $CH_{3n}(RO)_{3-n}Si(CH_2)_mP(O)(OR)_2$ where *n* was 0, 1, 2, or 3; *m* was 2 or 3; and R was ethyl or *n*-butyl. The following is a typical example of the reaction.

$$(CH_3)_2(C_2H_5O)SiCH{=}CH_2 + HP(O)(OC_2H_5)_2 \xrightarrow[(t\text{-}C_4H_9O)_2]{\Delta} (CH_3)_2(OC_2H_5O)SiCH_2CH_2P(O)(OC_2H_5)_2 \quad (1)$$

One example of a cyclohexenylethylsilane was also included in the group of olefins used. Table I lists the resultant adducts.

The reaction conditions used followed recommendations of Stiles.[5] A two to one molar ratio of dialkyl phosphonate to alkenylsilane was employed. The initiator was di-*t*-butylperoxide at a concentration of 5 mole % based on the dialkyl phosphonate. The reactions were carried out at 120°-150° for sixteen hours under a dry nitrogen atmosphere at atmospheric pressure whenever possible. Those with low-boiling components were run in sealed glass ampoules. The yields (with one exception) were 48-62%. Increasing the ratio of dialkyl phosphonate to alkenylsilane to three to one in one trial failed to improve the yield.

In order to prevent any possible interchange of unlike radicals, the alkoxy groups on silicon and the alkoxy groups on the phosphorus were the same in each reaction.

Substitution of an alkenylchlorosilane for an alkenylalkoxysilane in one experiment led to an undesirable side-reaction which eliminated chlorosilanes as suitable reactants. The products appeared to be as shown in Equation 2:

$$(CH_3)_2ClSi(CH_2)_4CH{=}CH_2 + HP(O)(OC_4H_9\text{-}n)_2 \longrightarrow n\text{-}C_4H_9Cl + CH_2{=}CH(CH_2)_4(CH_3)_2SiOPH(O)(OC_4H_9\text{-}n) \quad (2)$$

Siloxanes also proved to be undesirable for the isolation of pure esters. The reaction investigated was that of pentamethylvinylidisiloxane and di-*n*-butyl phosphonate. Addition to the olefinic double bond appeared to have taken place, but no constant-boiling material was isolated on distillation. Apparently, this was due to the siloxane linkage which appeared to be reactive under these conditions yielding a mixture of products.

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(1) Multiple Fellowship on Silicones sustained by Dow Corning Corporation and Corning Glass Works.

(2) A. R. Gilbert and F. M. Precopio, Abstracts of Papers Presented at the 125th Meeting, *Am. Chem. Soc.*, 16N (1954).

(3) W. H. Keeber and H. W. Post, *J. Org. Chem.* **21**, 509 (1956).

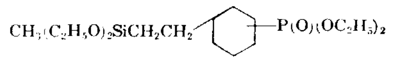
(4) E. A. Chernyshev, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* **1958**, (1) 96.

(5) A. R. Stiles, W. E. Vaughn, and F. F. Rust, *J. Am. Chem. Soc.* **80**, 714 (1958).

(6) R. G. Linville, U. S. Patent **2,843,615**, July 15, 1958.

TABLE I

ADDITION OF DIALKYL PHOSPHONATES TO ALKENYLSILANES

Organosilicon Phosphonate	Yield,[a] %	B.P.°	Mm	n_D^{25}	d_4^{25}	RD Obs.	RD Calcd.	Silicon, % Found	Silicon, % Calcd.	Phosphorus, % Found	Phosphorus, % Calcd.
$(CH_3)_3SiCH_2CH_2P(O)(OBu\text{-}n)_2$	55	128	1	1.4353	0.936	0.2789	0.2800	8.11[b]	9.54	10.4[b]	10.52
$(CH_3)_2(n\text{-}BuO)SiCH_2CH_2P(O)(OBu\text{-}n)_2$	59	157	1	1.4388	.954	.2756	.2758	8.9[b] 8.07[c]	7.96	8.2[b] 8.52[c]	8.79
$(CH_3)_2(C_2H_5O)SiCH_2CH_2P(O)(OC_2H_5)_2$	55	115	1	1.4299	.999	.2585	.2583	10.1[b] 10.87[c]	10.46	11.65[b] 11.2[c]	11.54
$(CH_3)_2(C_2H_5O)SiCH_2CH_2CH_2P(O)(OC_2H_5)_2$	62	120	1	1.4320	.986	.2630	.2620	9.80[c]	9.94	10.93[c]	10.90
$CH_3(C_2H_5O)_2SiCH_2CH_2P(O)(OC_2H_5)_2$[d]	48	124	2	1.4270	1.019	.2520	.2504	9.39[c]	9.41	10.43[c]	10.38
$(C_2H_5O)_3SiCH_2CH_2P(O)(OC_2H_5)_2$	33	141	2	1.4216	1.031	.2463	.2442	8.95[c]	8.55	8.83[c]	9.43
	52	198	2	1.4515	1.071	.2650	.2639	7.60[c]	7.38	7.85[c]	8.14

[a] Based on alkenylsilane. [b] By Analytical Department, Dow Corning Corporation. [c] By Galbraith Laboratories, Knoxville, Tennessee. [d] Ref. 6, b.p. 170–176° at 3–4 mm., n_D 1.4365 Phosphorus, found, 8.62%.

As phosphonates containing one carbon between silicon and phosphorus were cleaved under both acidic and alkaline conditions when oxygen was present on silicon, it was of interest to determine the behavior of analogous esters having two or more carbon atoms in the chain between silicon and phosphorus.

The organosilicon phosphonates were hydrolyzed to the phosphonic acids shown in Table II in essentially quantitative yields by refluxing with concentrated hydrochloric acid. No evidence for silicon-carbon cleavage was found in any of the hydrolyses.

$$2(CH_3)_2(OC_2H_5)SiCH_2CH_2P(O)(OC_2H_5)_2 + 5H_2O \xrightarrow{H^+} [(HO)_2(O)PCH_2CH_2(CH_3)_2Si]_2O \quad (3)$$

The neutral equivalents were determined by electrometric titration and were based on the first hydrogen only. From the titration curves, the pK_1 and pK_2 values were found, although the values must be considered only approximate. The low solubility of many of the acids in water required more dilute solutions than are usually used for such measurements, and in some cases considerable amounts of ethanol were employed to obtain solution. Comparison of these values with values reported for trimethylsilylmethylphosphonic acid and ethylphosphonic acid in the literature suggests that introduction of silicon into an alkyl chain attached to phosphorus decreases the acidity when the alkyl chain contains one or two carbons, but has little effect with three carbons present. Furthermore, when the silicon is bonded to two or three oxygen atoms, an increase in the acidity is observed. This effect is not observed, however, when the silicon is bonded to only one oxygen atom.

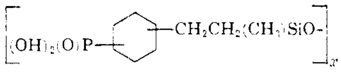
The phosphonic acids varied in appearance from viscous liquids to brittle resins as the number of silicon-oxygen bonds increased from one to three. One exception was (2-trimethylsilyl)ethylphosphonic acid which was a white, crystalline solid containing one molecule of water of hydration based on the neutral equivalent.

The organosilicon phosphonates were also hydrolysed by refluxing with 0.9*N* aqueous sodium hydroxide solutions for twenty-four hours. It was expected that the phosphorus grouping would be converted to the monosodium salts by such treatment, but it was found that the hydrolysis was not that specific. Electrometric titrations of the hydrolysis mixtures indicated that some of the phosphorus was always present as the unchanged diester and some also as the totally-changed disodium salt. No pure compounds were isolated from the alkaline hydrolyses even in the simplest example—di-*n*-butyl (2-trimethylsilyl)ethylphosphonate—with no functionality on silicon.

It was, however, possible to show that little if any silicon-carbon cleavage took place under alkaline conditions by further investigation of the mixtures. The mixtures were acidified, extracted

TABLE II

PHOSPHONIC ACIDS DERIVED FROM ACID HYDROLYSIS

Acid	Neut. Equiv. Found	Neut. Equiv. Calcd.	pK_1	pK_2	Remarks
$(CH_3)_3SiCH_2CH_2P(O)(OH)_2$	200[c]	182	3.4	8.4	White cryst. solid, m.p. 147°
$[(HO)_2(O)PCH_2CH_2(CH_3)_2Si]_2O$	176	177	3.4	8.5	Viscous liquid
$[(HO)_2(O)PCH_2CH_2CH_2(CH_3)_2Si]_2O$	182	189	2.5	8.3	Viscous liquid
$[(HO)_2(O)PCH_2CH_2(CH_3)SiO-]_x$	163	168	2.4	7.7	Stiff, tacky resin
$[(HO)_2(O)PCH_2CH_2SiO_3/_2]_x$	169	161	2.5	7.6	Dry, brittle resin
	255	250	3.1	8.4	Dry, foam-type resin
$(CH_3)_3SiCH_2P(O)(OH)_2$[a]			3.2	8.7	
$C_2H_5(O)(OH)_2$[b]			2.45	7.85	

[a] Ref.[3]. [b] P. Rumpf and V. Chavane, *Compt. Rend.*, **224,** 919 (1947). [c] A molecule of water of hydration is indicated. Repeated efforts to eliminate it by heating above the melting point failed.

with benzene, and the acidic products isolated by evaporation of the benzene. The experimental evidence considered on such products was: the weight balance, electrometric titration data, and the nuclear magnetic resonance spectra. The argument presented in the Experimental shows this evidence to be in good agreement only with a structural formula based on an assumption of no silicon-carbon cleavage. It was also observed during the initial reflux period with the alkali that there was no weight loss, thus eliminating any possibility of cleavage to yield a gas such as ethylene.

The organosilicion phosphonates containing two and three carbons between silicon and carbon and the one example containing the cyclohexylethyl-grouping all proved to be stable to cleavage of the silicon-carbon bond under both acidic and alkaline conditions regardless of the number of oxygens bonded to silicon. Linville[6] has stated a similar conclusion: "The presence of at least two carbon atoms between the phosphorus atom and the silicon atom, . . . unexpectedly lends marked stability in the presence of strong alkali or acids." However, he gave no experimental support for this statement.

EXPERIMENTAL

Materials. Diethyl phosphonate and *di-n-butyl phosphonate* were obtained from Virginia-Carolina Chemical Corp., and *di-t-butylperoxide* from Shell Corp., *vinyltriethoxysilane* and *vinylmethyldiethoxysilane* were obtained from Peninsular Chemresearch, and *vinyltrimethylsilane* from Metal and Thermit Corp. These reagents were used without further purification.

Vinyldimethyl-n-butoxysilane was prepared by the direct reaction of the corresponding chlorosilane (Dow Corning Corp.) with *n*-butanol. *Dimethylethoxyvinylsilane* and *(2-cyclohex-3-enylethyl)methyldiethoxysilane* were prepared from the reaction of the corresponding chlorosilanes with ethyl orthoformate.[7] The chlorosilane for the latter reaction was prepared by the addition of methyldichlorosilane to 4-vinylcyclohexene with a chloroplatinic acid catalyst.[8] Allyldimethylethoxysilane[9] was prepared in a two-step procedure in poor yield. The addition of dimethylchlorosilane to allylmagnesium chloride yielded the intermediate, allyldimethylsilane, which was then converted to the desired product with sodium ethoxide in ethanol. *Hex-5-enyldimethylchlorosilane* was isolated from the addition of one mole of dimethylchlorosilane to 1,5-hexadiene using a chloroplatinic acid catalyst. *Pentamethylvinyldisiloxane* was prepared by cohydrolysis of *vinyldimethylchlorosilane* and trimethylchlorosilane.

General procedure for the additions. The alkenylsilane, phosphonate, and catalyst were thoroughly mixed in a three necked flask equipped with a nitrogen inlet tube, thermometer, and condenser, and placed in an oil bath thermostatically controlled at 120°. Trimethylvinylsilane (b.p. 55°) was treated in a sealed glass ampoule. Two olefins required temperatures higher than 120° to react: vinyltriethoxysilane (130°) and (2-cyclohex-3-enylethyl)methyldiethoxysilane (150°). In most cases, the reaction was quite exothermic during the first hour, the temperature rising above that of the bath, and it was necessary to remove the flask temporarily and cool with an air stream. In no case was the reaction vigorous after the first hour, although reaction continued to take place during the 16-hr. period allowed. The progress of the reaction could be determined at any time by titration,[5] or qualitatively by refractive index rise.

The reaction mixtures were distilled through a small Podbielniak column at 1–2 mm. in order to minimize thermal decomposition. Resultant data are compiled in Table I.

Hex-5-enyldimethylchlorosilane and di-n-butyl phosphonate. This mixture was sealed in a glass ampoule for reaction. Upon distillation, a low-boiling fraction collected in the Dry Ice trap appeared to be *n*-butyl chloride, 2.7 g. (theory: 2.7 g.), n_D^{25} 1.3983 (lit. n_D^{20} 1.4015). A fraction obtained in the range expected for adduct (123°/1 mm.) in approximately 30% yield (if desired product) was examined by NMR spectra. The H^1 spectrum revealed, however, that both H—P and C=C were present in large amounts and in approximately a 1 to 1 molar ratio.

Pentamethylvinyldisiloxane and di-n-butyl phosphonate. The general procedure was used in this reaction. Conversion, based on titration, was 73%, but no constant-boiling material was obtained on distillation.

Hydrolysis with hydrochloric acid. Mixtures of the organosilicon phosphonate and a ten-fold excess, by volume, of concd. hydrochloric acid were refluxed for 24 hr., after which time all of the mixtures were homogeneous; some were so initially. The volume of the mixture was then reduced 50% by distillation. No organic layer was observed in any of the aqueous distillates. The concentrated solutions were evaporated to dryness several times on a steam bath to re-

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(7) L. M. Shorr, *J. Am. Chem. Soc.*, **76,** 1390 (1954).

(8) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79,** 974 (1957).

(9) J. Swiss and C. E. Arntzen, U. S. Patent **2,595,729,** May 6, 1952.

move residual hydrogen chloride. The resulting phosphonic acids were dried to constant weight at 100°, under vacuum when necessary. The one crystalline solid acid was recrystallized three times from cyclohexane and appeared to contain one molecule of water of hydration.

Hydrolysis with alkali. A typical example of an alkaline hydrolysis follows: $(n\text{-}C_4H_9O)(CH_3)_2SiCH_2CH_2P(O)(OC_4H_9\text{-}n)_2$, 10.56 g., 0.03 mole, was refluxed for 24 hr. with a 0.9*N* NaOH solution. The acidified hydrolysis mixture was extracted with benzene from which the product was isolated on evaporation of the benzene. The product weighed 5.0 g. and an electrometric titration gave neutral equivalents of 279 and 211 for one hydrogen and both hydrogens, respectively. Assuming no cleavage, the titration values would be satisfied by an overall structural formula of:

$$[(n\text{-}C_4H_9O)_{0.93}(HO)_{1.07}P(O)CH_2CH_2(CH_3)_2Si]_2O \quad (A)$$

with 24 mole % of the phosphorus present with 2(—OH), 59 mole % with 1($—OC_4H_9\text{-}n$) and 1(—OH), and 17 mole % with 2($—OC_4H_9\text{-}n$). The 5.0 g. of product isolated represents a 73% yield based on formula A. A second structural formula in agreement with the titration data, but in which cleavage to yield dimethylsiloxy-units is assumed, would be:

$$[(n\text{-}C_4H_9O)_{0.70}(HO)_{1.30}P(O)CH_2CH_2(CH_3)_2SiO_{1/2}]_{1.00}\cdot(CH_3)_2SiO_{0.80} \quad (B)$$

with 30 mole % of the phosphorus present with 2(—OH), 70 mole % with 1($—OC_4H_9\text{-}n$), and 1(—OH), and none with 2($—OC_4H_9\text{-}n$). The 5.0 g. of product would then represent a 120% yield; this was the first evidence against formula B. The H^1 NMR spectra were obtained on the product diluted to 50% in carbon tetrachloride and on the product diluted to 25% by addition of benzene to the carbon tetrachloride solution. Only one methyl-silicon peak was found in each spectrum. The benzene solvent was chosen because a single peak is often split into two peaks by benzene if two different groups are present but give superimposed resonances. Only one methyl-silicone peak is consistent with formula A, but two peaks would be expected for formula B. Also, from these spectra, the ratio of $—CH_2O—$ to —OH groups estimated from the area under the respective peaks to be 0.85. The ratio calculated for formula A is 0.87 and for formula B 0.54. Thus, all of the evidence available is in agreement with the product having structural formula A rather than B.

Analyses. The phosphorus bond refraction values used in this work were calculated from organophosphorus compounds found in the literature, and agreed favorably with values recently reported by Gillis *et al.*[10] Their data included only one value for the P=O bond refraction in either phosphate or phosphonate structures, whereas our data indicated that two different values were necessary as listed in Table III.

TABLE III

BOND REFRACTION (CC.$^{-1}$)

Bond	Gillis	Our Values
P—O	3.18	3.14
P=O in phosphates	−1.22	−1.07
P=O in phosphonates		−1.42
P—C	3.60	3.66

Both silicon and phosphorus were determined gravimetrically following a sodium peroxide fusion in a Parr peroxide bomb. Considerable difficulty was encountered in this procedure by both analytical laboratories.

A Beckman *p*H meter, model H 2, was used for the electrometric titrations.

Acknowledgment. The NMR spectra and interpretations thereof were performed by Mr. P. C. Lauterbur of this laboratory.

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(10) R. G. Gillis, J. T. Horwood, and G. L. White, *J. Am. Chem. Soc.*, **80**, 2999 (1958).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Some Derivatives of Tribenzylsilane

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A series of compounds containing the tribenzylsilyl group has been prepared from tribenzylsilane and the appropriate organolithium reagent. One of these compounds, tetrakis(*p*-tribenzylsilylphenyl)silane, is apparently the highest molecular weight compound containing only carbon, hydrogen, and silicon. Compounds containing the tribenzylsilyl group are characteristically low-melting solids or liquids and are thermally stable.

The unusual stability of tetrabenzylsilane[1] and tribenzylsilane[2] prompted the preparation of a series of tetrasubstituted silanes containing the tribenzylsilyl group.

The tribenzylsilyl derivatives were prepared by treatment of tribenzylsilane with the appropriate aryllithium reagent, a method which has been used for the synthesis of tetrasubstituted silanes.[3]

$$(C_6H_5CH_2)_3SiH + ArLi \longrightarrow (C_6H_5CH_2)_3SiAr + LiH$$

The aryllithium reagents were obtained by reaction of the organic halide with lithium metal, by halogen-metal interconversion reactions, and by metalation reactions. The new tribenzylsilyl derivatives and their physical properties are listed in Table I.

In the preparation of *p*-bromophenyltribenzylsilane from *p*-bromophenyllithium[4] and tribenzyl-

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(1) A. Polis, *Ber.*, **19**, 1012 (1886).

(2) H. Gilman, R. A. Tomasi, and D. Wittenberg, *J. Org. Chem.*, **24**, 821 (1959).

(3) H. Gilman and S. P. Massie, Jr., *J. Am. Chem. Soc.*, **68**, 1128 (1946); R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946); H. Gilman and H. W. Melvin, *J. Am. Chem. Soc.*, **71**, 4050 (1949); H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959).