ADDITION OF PHOSPHORUS PENTACHLORIDE TO UNSATURATED ORGANOSILICON COMPOUNDS

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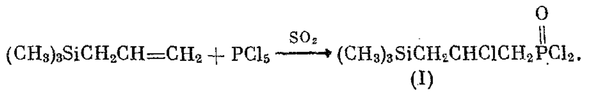
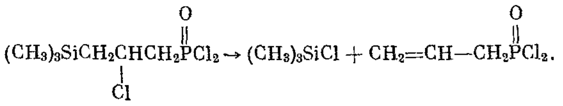
Phosphorus pentachloride reacts with allyltrimethylsilane at from −20 to −30° in accordance with the scheme [1]



$$(CH_3)_3SiCH_2CH{=}CH_2 + PCl_5 \xrightarrow{SO_2} \underset{(I)}{(CH_3)_3SiCH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2}. \qquad (1)$$

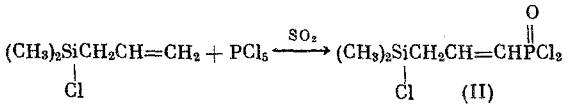
The [2-chloro-3-(trimethylsilyl)propyl]phosphonic dichloride (I) formed readily breaks down into chlorotrimethylsilane and allylphosphonic dichloride:



$$(CH_3)_3SiCH_2\underset{\underset{Cl}{|}}{CH}CH_2\overset{O}{\overset{\|}{P}}Cl_2 \rightarrow (CH_3)_3SiCl + CH_2{=}CH{-}CH_2\overset{O}{\overset{\|}{P}}Cl_2. \qquad (2)$$

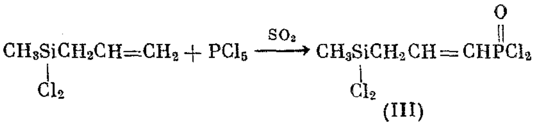
The addition of PCl_5 to unsaturated organosilanes and chloroorganosilanes is a general reaction. We have studied it for the case of allylchloromethylsilanes and chloromethyl(vinylphenyl)silanes.

Unlike allyltrimethylsilane, allylchlorodimethyl-, allyldichloromethyl-, and allytrichlorosilanes do not react with PCl_5 at −20°. At 0-5° in ether allylchlorodimethylsilane and allyldichloromethylsilane form adducts with PCl_5, which when treated with sulfur dioxide give [3-(chlorodimethylsilyl)propenyl]phosphonic dichloride (II)



$$(CH_3)_2\underset{\underset{Cl}{|}}{Si}CH_2CH{=}CH_2 + PCl_5 \xrightarrow{SO_2} (CH_3)_2\underset{\underset{Cl}{|}}{Si}CH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2 \;\; (II) \qquad (3)$$

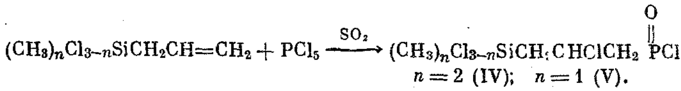
in 50% yield and [3-(dichloromethylsilyl)propenyl]phosphonic dichloride (III)



$$CH_3\underset{\underset{Cl_2}{|}}{Si}CH_2CH{=}CH_2 + PCl_5 \xrightarrow{SO_2} CH_3\underset{\underset{Cl_2}{|}}{Si}CH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2 \;\; (III) \qquad (4)$$

in about 25% yield.

It is not difficult to see that, unlike (1), reactions (3) and (4) go with the simultaneous dehydrochlorination of the addition product. If the process is conducted in benzene at 0 to −5° with the use of recrystallized PCl_5, dehydrochlorination can be avoided and [2-chloro-3-(chlorodimethylsilyl)propyl]phosphonic dichloride (IV) and [2-chloro-3-(dichloromethylsilyl)propyl]phosphonic dichloride (V) are obtained:



$$(CH_3)_nCl_{3-n}SiCH_2CH{=}CH_2 + PCl_5 \xrightarrow{SO_2} (CH_3)_nCl_{3-n}SiCH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2, \quad n=2\ (IV);\ n=1\ (V).$$

It may be supposed, therefore, that the addition of PCl_5 to allylsilanes at above 0° in polar solvents is accompanied by simultaneous dehydrochlorination with formation of propenylphosphonic derivatives. To confirm this we carried out the addition of PCl_5 to allyltrimethylsilane in ether at 0°.

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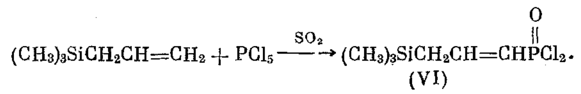
TABLE 1. Properties of Silyl Derivatives of Alkenylphosphonic Compounds

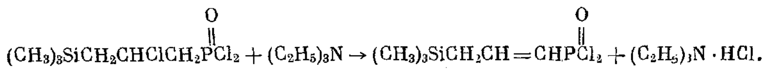
Compound		bp, °C (p, mm)	mp, °C	n_D^{20}	d_4^{20}	Yield, %	Found/Calculated, %				
No.	formula						C	H	Cl	Si	P
1	$\mathrm{(CH_3)_3SiCH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2}$	108—110 (2)	36	—	—	84	$\frac{27,4}{26,93}$	$\frac{5,3}{5,27}$	$\frac{40,0}{39,75}$	$\frac{9,6}{10,50}$	$\frac{11,3}{11,57}$
2	$\mathrm{(CH_3)_2\underset{\underset{Cl}{\|}}{Si}CH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2}$	118 (1,5)	32	—	—	34	$\frac{20,1}{21,85}$	$\frac{3,6}{3,85}$	$\frac{49\ 1}{50,24}$	$\frac{9,6}{9,75}$	$\frac{10,5}{10,75}$
3	$\mathrm{CH_3\underset{\underset{Cl_2}{\|}}{Si}CH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	105 (3)	—	1,4747	1,2935	20	$\frac{17,4}{17,66}$	$\frac{2,6}{2,59}$	$\frac{52,8}{51,14}$	$\frac{10,5}{10,33}$	$\frac{11,2}{11,39}$
4	$\mathrm{(CH_3)_2\underset{\underset{Cl}{\|}}{Si}CH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	102 (3)	—	1,4993	1,2806	30	$\frac{23,4}{23,87}$	$\frac{4,0}{4,01}$	$\frac{42,1}{42,28}$	$\frac{11,7}{11,17}$	$\frac{11,8}{12,31}$
5	$\mathrm{CH_3\underset{\underset{Cl_2}{\|}}{Si}CH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2}$	123 (1,5)	26	—	—	16	$\frac{15,2}{15,57}$	$\frac{6,2}{6.18}$	$\frac{57,1}{57,47}$	$\frac{9,6}{9,10}$	$\frac{10,3}{10,04}$
6	$\mathrm{(CH_3)_3SiCH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	85 (2)	—	1,4900	1,1472	50	$\frac{31,6}{30,45}$	$\frac{5,18}{5,72}$	$\frac{30,2}{30,07}$	$\frac{11,8}{12,26}$	$\frac{13,8}{13,57}$
7	$\mathrm{(CH_3)_3SiC_6H_4CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	138 (0,2)	46	—	—	70	$\frac{44,8}{45,06}$	$\frac{5,1}{5,16}$	$\frac{24,3}{24,18}$	$\frac{9,3}{9,58}$	$\frac{9,8}{10,56}$
8	$\mathrm{(CH_3)_2\underset{\underset{Cl}{\|}}{Si}C_6H_4CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	170 (0,5)	36	—	—	42	$\frac{38,1}{38,30}$	$\frac{3,9}{3,86}$	$\frac{33,5}{33,91}$	$\frac{9,1}{8,96}$	$\frac{9,7}{9,88}$
9	$\mathrm{CH_3\underset{\underset{Cl_2}{\|}}{Si}C_6H_4CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}$	145 (0,3)	38	—	—	23	$\frac{31,9}{32,33}$	$\frac{2,7}{2,72}$	$\frac{42,2}{42,45}$	$\frac{8,5}{8,41}$	$\frac{9,0}{9,27}$
10	$\mathrm{(CH_3)_3SiCH_2CH{=}CH\overset{O}{\overset{\|}{P}}(OC_2H_5)_2}$	96 (1)	—	1,4477	1,0028	49	$\frac{48,1}{47,97}$	$\frac{9,2}{9,19}$	$\frac{—}{—}$	$\frac{12,3}{11,66}$	$\frac{13,1}{12,37}$
11	$\mathrm{(CH_3)_3SiCH_2CH{=}CH\overset{O}{\overset{\|}{P}}(OH)_2}$	—	62	—	—	61	$\frac{40,6}{40,49}$	$\frac{8,5}{8,47}$	$\frac{—}{—}$	$\frac{15,9}{15,76}$	$\frac{17,2}{17,36}$
12	$\mathrm{(CH_3)_2\underset{\underset{OC_2H_5}{\|}}{Si}CH_2CH{=}CH\overset{O}{\overset{\|}{P}}(OC_2H_5)_2}$	122 (1)	—	1,4469	1,0133	22	$\frac{47,0}{47,12}$	$\frac{9,00}{8,99}$	$\frac{—}{—}$	$\frac{9,9}{10,02}$	$\frac{11,2}{11,04}$
13	$\mathrm{CH_3\underset{\underset{(OC_2H_5)_2}{\|}}{Si}CH_2CH_2CH{=}CH\overset{O}{\overset{\|}{P}}(OC_2H_5)_2}$	153 (1,5)	—	1,4448	1,0367	32	$\frac{46,7}{46,43}$	$\frac{8,7}{8,77}$	$\frac{—}{—}$	$\frac{9,2}{9,05}$	$\frac{9,8}{9,98}$
14	$\mathrm{(CH_3)_3SiC_6H_4CH{=}CH\overset{O}{\overset{\|}{P}}(OH)_2}$	—	126,5	—	—	30	$\frac{51,8}{51,54}$	$\frac{6,7}{6,69}$	$\frac{—}{—}$	$\frac{10,5}{10,96}$	$\frac{12,2}{12,09}$
15	$\mathrm{(CH_3)_3SiC_6H_4CH{=}CH\overset{O}{\overset{\|}{P}}(OC_2H_5)_2}$	162 (0,5)	—	1,5199	1,0492	29	$\frac{57,8}{57,66}$	$\frac{8,0}{8,06}$	$\frac{—}{—}$	$\frac{9,1}{8,99}$	$\frac{10,2}{9,91}$

As a result we obtained [3-(trimethylsilyl)propenyl]phosphonic dichloride:



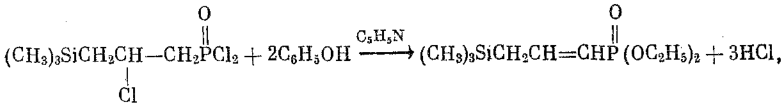
$$\mathrm{(CH_3)_3SiCH_2CH{=}CH_2 + PCl_5 \xrightarrow{SO_2} \underset{(VI)}{(CH_3)_3SiCH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2}}. \qquad (5)$$

To confirm the structure of (VI) we carried out the dehydrochlorination of (I) with triethylamine in ether at −20° and obtained (VI) in 84% yield:



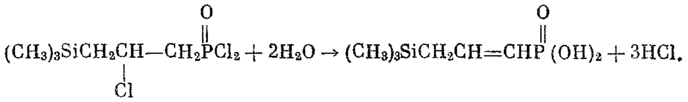
$$\mathrm{(CH_3)_3SiCH_2CHClCH_2\overset{O}{\overset{\|}{P}}Cl_2 + (C_2H_5)_3N \rightarrow (CH_3)_3SiCH_2CH{=}CH\overset{O}{\overset{\|}{P}}Cl_2 + (C_2H_5)_3N\cdot HCl}. \qquad (6)$$

The dehydrochlorination of (2-chloro-3-silyl)phosphonic dichlorides always occurs in attempts to convert them into esters in presence of pyridine (Table 1)



$$(CH_3)_3SiCH_2\underset{\underset{Cl}{|}}{C}H-CH_2\overset{\overset{O}{\|}}{P}Cl_2 + 2C_6H_5OH \xrightarrow{C_5H_5N} (CH_3)_3SiCH_2CH{=}CH\overset{\overset{O}{\|}}{P}(OC_2H_5)_2 + 3HCl, \quad (7)$$

and in their hydrolysis

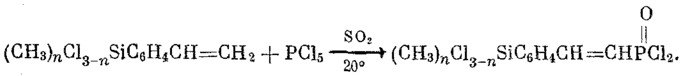


$$(CH_3)_3SiCH_2\underset{\underset{Cl}{|}}{C}H-CH_2\overset{\overset{O}{\|}}{P}Cl_2 + 2H_2O \rightarrow (CH_3)_3SiCH_2CH{=}CH\overset{\overset{O}{\|}}{P}(OH)_2 + 3HCl. \quad (8)$$

Regardless of the solvent used, the addition of PCl_5 to allylmethylsilanes at room temperature leads to the breakdown of the initially formed compound (I), (IV), or (V). Chlorotrimethylsilane, dichlorodimethylsilane, or trichloromethylsilane, respectively, is then isolated together with allylphosphonic dichloride [Eq. (2)]. This confirms that the initial stage of the reaction includes the addition of a chlorine atom in the β-position relative to silicon. Unlike allylchloromethylsilanes, allyltrichlorosilane does not combine with PCl_5 even after prolonged contact at room temperature: PCl_5 acts as a chlorinating agent:

$$Cl_3SiCH_2CH{=}CH_2 + PCl_5 \rightarrow Cl_3SiCH_2CHClCH_2Cl + PCl_3. \quad (9)$$

Hence, as the methyl groups in allyltrimethylsilane are replaced successively by chlorine atoms the ability of the compound to combine with PCl_5 diminishes. We carried out the reactions of PCl_5 with chloromethyl(p-vinylphenyl)silanes at a relatively high temperature (room temperature), and as would be expected, addition was accompanied by dehydrochlorination. After the sulfur dioxide treatment of the adducts we isolated (p-silylstyryl)phosphonic dichlorides:



$$(CH_3)_nCl_{3-n}SiC_6H_4CH{=}CH_2 + PCl_5 \xrightarrow[20^\circ]{SO_2} (CH_3)_nCl_{3-n}SiC_6H_4CH{=}CH\overset{\overset{O}{\|}}{P}Cl_2. \quad (10)$$

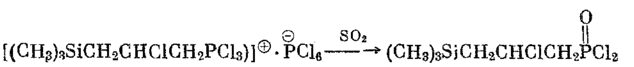
As in the case of allylmethylsilanes, the activity of methyl(p-vinylphenyl)silanes in this reaction falls as the Si-methyl groups are replaced by chlorine atoms. The reactions of PCl_5 with methyl(p-vinylphenyl)silanes give [p-(trimethylsilyl)styryl]phosphonic dichloride (VII) in 69% yield, [p-(chlorodimethylsilyl)styryl]phosphonic dichloride (VIII) in 41% yield, and [p-(dichloromethylsilyl)styryl]phosphonic dichloride (IX) in 23% yield. Phosphorus pentachloride does not add to trichloro(p-vinylphenyl)silane. Thus, the activities of alkenylsilanes in this reaction fall uniformly as the number of Si-methyl groups diminishes, i.e., as the electron-donor character of the silyl group and the nucleophilic character of the double bond weaken, which allows us to regard this reaction as the electrophilic addition of PCl_5 to double bonds.

It is known that PCl_5 solutions may contain the ion pair $^+PCl_4\cdot{}^-PCl_6$ [2]. It may be supposed that the double bond of the alkenylsilane is subjected to electrophilic attack:

$$(CH_3)_3SiCH_2CH{=}CH_2 + \overset{+}{P}Cl_4\cdot\overset{-}{P}Cl_6 \rightarrow [(CH_3)_3SiCH_2CHCH_2PCl_4]^+PCl_6^-. \quad (11)$$

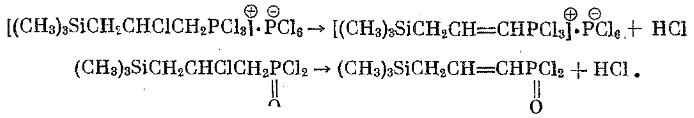
However, the breakdown which we have observed in the complex formed, leading to chlorosilanes, suggests the presence of chlorine in the β-position relative to silicon and the conversion of the ion pair $[(CH_3)_3\cdot$ $\cdot\, SiCH_2CHCH_2PCl_4]^+PCl_6^-$ into $[(CH_3)_3SiCH_2CHClCH_2PCl_3]^+\cdot PCl_6^-$.

The action of sulfur dioxide leads to the breakdown of the complex with formation of a derivative of (2-chloropropyl)phosphonic dichloride:



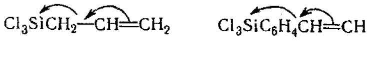
$$[(CH_3)_3SiCH_2CHClCH_2PCl_3)]^{\oplus}\cdot\overset{\ominus}{P}Cl_6 \xrightarrow{SO_2} (CH_3)_3SiCH_2CHClCH_2\overset{\overset{O}{\|}}{P}Cl_2$$

Both the complex formed and its derivative can undergo dehydrochlorination with formation of vinylphosphonic dichlorides:



$$[(CH_3)_3SiCH_2CHClCH_2PCl_3\overset{\oplus}{]}\cdot\overset{\ominus}{P}Cl_6 \rightarrow [(CH_3)_3SiCH_2CH{=}CHPCl_3\overset{\oplus}{]}\cdot\overset{\ominus}{P}Cl_6 + HCl$$
$$(CH_3)_3SiCH_2CHClCH_2\underset{\underset{O}{\|}}{P}Cl_2 \rightarrow (CH_3)_3SiCH_2CH{=}CH\underset{\underset{O}{\|}}{P}Cl_2 + HCl. \quad (12)$$

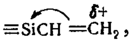
Unlike chloromethylsilyl groups, the trichlorosilyl group is probably an electron acceptor, which leads to a shift in electron density toward the silicon atom:



This explains the nonformation of PCl_5-addition products with allyltrichlorosilane and trichloro(vinylphenyl)silane.

Confirmation is provided by data in [3] on the addition of hydrogen bromide to allylsilanes. To allyltrichlorosilane hydrogen bromide adds only in the direction contrary to that required by the Markovnikov rule, whereas the reverse is true for allylchloromethylsilanes. A similar situation is found in the addition of hydrogen bromide to chloromethyl(vinylphenyl)silanes [4]. To trichloro(vinylphenyl)silane hydrogen bromide adds in the direction contrary to that required by the Markovnikov rule.

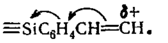
We found also that PCl_5 does not add to vinylsilanes (trimethyl-, chlorodimethyl-, dichloromethyl-, and trichlorovinylsilanes). This is in good accord with views [5] on the possibility of the delocalization of the π-electrons of the vinyl group into the d-orbitals of silicon



$$\equiv \mathrm{SiCH}{=}\overset{\delta+}{\mathrm{CH}_2},$$

which reduces the nucleophilicity of the double bond.

It should be noted that in this reaction methyl(vinylphenyl)silanes are less reactive than allylsilanes, and the replacement of methyl groups by chlorine atoms has a smaller effect in the case of methyl(vinylphenyl)silanes than in the case of allylsilanes in spite of the greater distance of the reaction center from the silicon atom. In benzene at 0° the yield of (IV) attains 74%, whereas even at room temperature the yield of (VIII) does not exceed 45%. This is probably also explained by the possibility of the interaction of the π-electrons of the phenyl nucleus with the d-orbitals of silicon:



$$\equiv \mathrm{SiC_6H_4CH}{=}\overset{\delta+}{\mathrm{CH}}.$$

Table 1 gives the properties of the organosilicon–phosphorus compounds synthesized by the addition of PCl_5 to alkenylsilanes and by the alcoholysis and hydrolysis of these silyl-substituted alkenylphosphonic dichlorides.

EXPERIMENTAL

Reactions of Phosphorus Pentachloride

With Allylchlorodimethylsilane in Ether at 0°. A flask fitted with stirrer, dropping funnel, and thermometer was charged with 103 g of PCl_5 and 300 ml of ether. The mixture was cooled at 0°, and allylchlorodimethylsilane was added dropwise with stirring at such a rate that the reaction temperature was kept between 0 and 5°. After the addition of 30 g of allylchlorodimethylsilane the mixture was stirred for 1.5 h at 0°, and dry sulfur dioxide was passed until the precipitate had dissolved completely. Solvent was vacuum-evaporated, and the residue was fractionated. The main fraction came over at 98-110° (3 mm). After redistillation we isolated 16 g of [3-(chlorodimethylsilyl)propenyl]phosphonic dichloride.

Analogously, from 103 g of PCl_5 and 34.5 g of allyldichloromethylsilane in 300 ml of ether we obtained 12 g of [3-(dichloromethylsilyl)propenyl]phosphonic dichloride (compound 3, Table 1). Also, from 150 g of PCl_5 and 40 g of allyltrimethylsilane in 600 ml of ether at −5 to −10° we obtained 40 g of [3-(trimethylsilyl)propenyl]phosphonic dichloride.

With Allylchlorodimethylsilane in Benzene at 0 to −5°C. A stirred mixture of 101 g of PCl_5 and 200 ml of benzene was cooled to −5° (the benzene began to freeze), and 47.4 g of allylchlorodimethylsilane was added slowly dropwise. The mixture was stirred for 0.5 h, and dry sulfur dioxide was passed until the precipitate had dissolved completely. Solvent was vacuum-evaporated, and the residue was fractionated. The main fraction came over at 118-122° (1.5 mm). After redistillation we isolated 35 g of [2-chloro-3-(chlorodimethylsilyl)propyl]phosphonic dichloride.

Analogously, from 41.5 g of allyldichloromethylsilane and 125 g of PCl_5 in 300 ml of benzene we obtained 12.7 g of [2-chloro-3-(dichloromethylsilyl)propyl]phosphonic dichloride.

With Chloromethyl(p-vinylphenyl)silanes in Benzene at Room Temperature. To a stirred mixture of 59.6 g of PCl_5 and 300 ml of benzene we added 24 g of trimethyl(p-vinylphenyl)silane. The mixture was left overnight, and then sulfur dioxide was passed until the precipitate had dissolved completely. Solvent was driven off, and vacuum distillation gave 27.5 g of [p-(trimethylsilyl)styryl]phosphonic dichloride (compound 7, Table 1).

Analogously, from 22 g of PCl_5 and 9.7 g of chlorodimethyl(p-vinylphenyl)silane in 150 ml of benzene we obtained 6.2 g of [p-(chlorodimethylsilyl)styryl]phosphonic dichloride (compound 8). From 30 g of PCl_5 and 15 g of dichloromethyl(p-vinylphenyl)silane in 200 ml of benzene we obtained 5.2 g of [p-(dichloromethylsilyl)styryl]phosphonic dichloride (compound 9).

With Allylchloromethylsilanes in Ether at Room Temperature. A mixture of 50 g of PCl_5 and 150 ml of ether was stirred with 11.4 g of allyltrimethylsilane. The mixture turned red, and the precipitate formed initially partially dissolved. After the passage of sulfur dioxide the solvent, which contained 7.1 g of chlorotrimethylsilane (identified chromatographically) was distilled off. The residue was vacuum-fractionated. We isolated 8.2 g of allylphosphonic dichloride, bp 58° (2 mm); n_D^{20} 1.4868; d_4^{20} 1.3783* [[6] gives: bp 77° (5 mm); n_D^{20} 1.4870; d_4^{20} 1.3783]. Found: C 22.5; H 3.2; Cl 44.7; P 19.5%. $C_3H_5Cl_2PO$. Calculated: C 22.67; H 3.12; Cl 44.61; P 19.48%.

Under similar conditions, from 50 g of PCl_5 and 13.4 g of allylchlorodimethylsilane in 150 ml of ether we isolated 8.1 g of dichlorodimethylsilane and 7 g of allylphosphonic dichloride. From 50 g of PCl_5 and 15.5 g of allyldichloromethylsilane in 150 ml of ether we isolated 9.0 g of trichloromethylsilane and 6.1 g of allylphosphonic dichloride.

With Allyltrichlorosilane in Benzene at Room Temperature. A mixture of 60 g of PCl_5, 120 ml of benzene, and 25.3 g of allyltrichlorosilane was stirred for 5 days. Sulfur dioxide was passed until the precipitate had dissolved completely, solvent was driven off, and the residue was vacuum-fractionated. We isolated 18.1 g of a fraction with bp 98-100° (25 mm), which was shown chromatographically to contain trichloro(2,3-dichloropropyl)silane. In the fractionation of the fraction we isolated a product with bp 208-209°; n_D^{20} 1.4870; d_4^{20} 1.4725 [[7] gives: bp 208.4° (747 mm); n_D^{20} 1.4868; d_4^{20} 1.4720). Found: C 14.2; H 2.0; Cl 72.1; Si 11.6%. $C_3H_5Cl_5$. Calculated: C 14.62; H 2.05; Cl 71.94; Si 11.40%.

Reactions of Ethanol and Pyridine

With [2-Chloro-3-(trimethylsilyl)propyl]phosphonic Dichloride. A flask fitted with stirrer, dropping funnel, and thermometer was charged with 3 g of absolute alcohol, 7 g of dry pyridine, and 50 ml of dry benzene, the mixture was cooled to 0°, and slowly with stirring 7.9 g of the acid chloride was added at such a rate that the reaction temperature remained between 0 and – 5°. The mixture was left overnight. The precipitate was filtered off and washed with benzene. Benzene was driven from the filtrate, and the residue was vacuum-fractionated. We isolated a fraction with bp 95-96° (1 mm). By redistillation we isolated 3.5 g of diethyl [3-(trimethylsilyl)propenyl] phosphonate (compound 10).

Analogously, from 4.7 g of alcohol, 11.1 g of pyridine, 50 ml of benzene, and 11.7 g of (IV) we obtain 2.8 g of diethyl [3-(diethoxymethylsilyl)propenyl]phosphonate (compound 12).

From 2.5 g of alcohol, 5.2 g of pyridine, 50 ml of benzene, and 3.5 g of (V) we obtained 1.3 g of diethyl [3-(diethoxymethylsilyl)propenyl]phosphonate (compound 13).

Preparation of Silyl-Substituted Alkenylphosphonic Acids

A flask fitted with stirrer and dropping funnel was charged with 8 g of (I) and 50 ml of benzene, and 50 ml of water was added with stirring. The organic layer was washed, solvent was driven off, and the crystals precipitated were melted and vacuum-dried at 100° to constant weight. We obtained 3.3 g of [3-(trimethylsilyl)propenyl]phosphonic acid (compound 11).

Under the conditions of the preceding experiment 6.9 g of (VII) was hydrolyzed. We obtained 1.8 g of white crystalline [p-(trimethylsilyl)styryl]phosphonic acid. The acid was recrystallized from aqueous alcohol (compound 14).

IR Spectra (cm^{-1}) of Silyl Derivatives of Alkenylphosphonic Compounds

1. 412 w, 487 m, 550 s, 625 s, 787 m, 825 m, 937 m, 987 m, 1074 w, 1112 w, 1187 w, 1212 w, 1275 s, 1387 s, 1425 w, 1637 w, 2900 w, 2962 w, 3025 w, 3087 w.

4. 479 s, 512 s, 563 m, 631 m, 717 m, 758 m, 808 s, 850 s, 975 m, 1008 w, 1037 m, 1058 m, 1142 m, 1183 w, 1208 m, 1275 s, 1346 w, 1400 m, 1608 m, 2900 w, 2958 m.

5. 446 m, 483 s, 555 s, 646 m, 685 s, 725 m, 775 s, 796 s, 825 s, 867 s, 975 m, 1008 m, 1042 s, 1067 s, 1183 m, 1212 m, 1275 s, 1342 w, 1396 m, 1608 w, 2900 m, 2958 w.

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* The allylphosphonic dichloride isolated by us previously [1] evidently contained impurities.

6. 506 m, 556 s, 592 m, 614 m, 667 m, 700 m, 750 m, 779 s, 852 s, 942 w, 987 m, 1042 m, 1121 s, 1275 s, 1308 m, 1417 m, 1600 s, 2896 m, 2950 m, 3025 w.

7. *450 w, 506 w, 529 s, 567 s, 642 m, 692 w, 696 w, 758 s, 792 s, 842 s, 992 s, 1108 s, 1183 m, 1250 s, 1329 m, 1396 m, 1546 m, 1608 s, 2892 m, 2950 s, 3008 m, 3058 m.

10. 446 w, 510 m, 554 m, 548 w, 621 m, 675 m, 648 m, 758 m, 783 m, 848 s, 967 s, 1045 s, 1100 m, 1137 m, 1167 m, 1250 s, 1367 w, 1392 m, 1446 w, 1483 w, 1621 m, 2900 m, 2950 s, 2983 s.

11. 467 m, 612 s, 700 m, 762 m, 825 m, 925 s, 970 s, 1012 s, 1075 s, 1100 s, 1150 s, 1200 s, 1387 m, 1425 m, 1650 m, 2250 s, 2577 s.

12. 450 w, 508 m, 556 m, 623 w, 696 m, 758 s, 827 s, 967 s, 1050 s, 1108 s, 1150 s, 1167 s, 1262 s, 1400 m, 1458 m, 1492 w, 1633 m, 2733 w, 2767 w, 2900 s, 2929 s, 2975 s, 3420 w.

13. 558 s, 627 w, 786 s, 833 s, 867 s, 967 s, 1050 s, 1167 s, 1254 s, 1392 s, 1450 m, 1483 m, 1625 s, 2733 s, 2900 s, 2925 s, 2975 s, 3418 m.

14. 421 w, 475 m, 521 m, 540 m, 621 w, 721 m, 758 m, 792 m, 837 m, 950 s, 992 m, 1021 m, 1208 m, 1146 m, 1212 m, 1258 m, 1387 s, 1475 s, 1625 m, 2725 m, 2908 s.

15. 400 w, 537 s, 612 m, 662 w, 700 m, 762 s, 812 s, 850 s, 975 s, 1025 s, 1062 s, 1112 s, 1162 m, 1187 m, 1250 m, 1325 w, 1375 m, 1400 m, 1450 m, 1475 w, 1550 w, 1625 m, 2900 m, 2950 s, 2975 s, 3050 w.

CONCLUSIONS

1. The addition of phosphorus pentachloride to unsaturated organosilicon compounds was studied.

2. The activities of alkenylsilanes in this reaction rise with increase in the number of Si-methyl groups.

3. Phosphorus pentachloride does not add to trichloroallylsilane, trichloro(p-vinylphenyl)silane, and vinylsilanes.

4. Fifteen new organosilicon–phosphorus compounds were isolated and characterized.

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* In CCl_4.