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Abstract

Full Text

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SYNTHESIS OF CERTAIN ORGANOSILICON MONOMERS WITH A PHOSPHORUS-CONTAINING FUNCTIONAL GROUP

Compounds of the type $R_{nX_{3-n}}(\mathrm{CH_2})_{m}P(=O)X_2$, where R is an alkyl or aryl radical; X is a halogen or an alkoxy(aryloxy) group; n = 0-3; $m = 1, 2, 3, ...$, constitute a very interesting but little-studied class of organosilicon monomers. Patent reports ([1,2]) propose the use of these compounds as lubricating oils, or additives to them, plasticizers, and also insecticides. Their use is also possible as starting substances for obtaining phosphorus-containing silicones, which will combine the properties of both silicon-containing and organophosphorus polymers.

Several years ago, two of us ([3,4]) proposed a method for the synthesis of silicon-phosphorus organic monomers of the above-mentioned type by the interaction of alkylchlorosilanes with phosphorus trichloride and oxygen according to the scheme:

$$R_{nCl_{3-n}}SiC_{xH}y + 2PCl_3 + O_2 \rightarrow R_{nCl_{3-n}}SiC_{xH_{y-1}}P(=O)Cl_2 + POCl_3 + HCl.$$

However, by this method the yields of the target product did not exceed 15%, calculated on the starting alkylchlorosilane.

Recently, descriptions have appeared in the literature of several other methods for preparing the indicated monomers. One of them is based on the addition reaction of dialkylphosphinic acids to olefins. To obtain a silicon-phosphorus-containing compound, an olefin containing a silicon atom in the molecule is used:

$$\equiv Si(CH_2)_{nCH} = CH_2 + (RO)_2P(O)H \xrightarrow[140\text{-}150^\circ]{\text{peroxide}} \equiv Si(CH_2)_{n+2}P(O)(OR)_2.$$

This route was first proposed by Linville ([2]), and then used by others ([5]). The yields of the target products were 33-62%. Gilbert ([1]) proposed using the

Arbuzov rearrangement as a method for the synthesis of silicon-phosphorus organic monomers:

$$\equiv SiCH_2Cl + P(OC_2H_5)_3 \rightarrow \equiv SiCH_2P(O)(OC_2H_5)_2 + C_2H_5Cl.$$

Kieber, Post, and Fekete Frank ([6,7]), for the preparation of similar compounds, used the reaction of sodium salts of the type $NaP(O)(OR)_2$ with chloromethyltriorganosilanes:

$$\equiv SiCH_2Cl + NaP(O)(OR)_2 \rightarrow \equiv SiCH_2P(O)(OR)_2 + NaCl.$$

In the present study we propose a new route for the synthesis of acid chlorides of organochlorosilylalkylphosphinic acids, consisting in the addition of organochlorosilicon hydrides to allylphosphinic acid chloride in the presence of a catalyst—chloroplatinic acid:

$$R_{nCl_{3-n}}SiH + CH_2 = CHCH_2P(O)Cl_2 \xrightarrow{H_2PtCl_6 \cdot 6H_2O} R_{nCl_{3-n}}SiC_3H_6P(O)Cl_2.$$

Trichlorosilane, methyldichlorosilane, and ethyldichlorosilane were used as the silicon hydrides. The yields of the target products in all cas-

···parts amounted to 43-50%. The order of addition is currently being studied. It should be noted that attempts to use triethylsilane in this reaction were not successful. We also failed to add any chlorosilicon hydride to vinylphosphonic acid chloride anhydride,
CH_2=CH—P(O)Cl_2. In this case the reaction either did not occur at all, or the phosphorus-containing component was converted into a polymer.

Several new silicon-phosphorus-containing monomers were obtained by us by the above methods described in the literature. Thus, the reaction of addition of dialkylphosphinous acids to olefins was used for the synthesis of ethyl esters of β-triorganosilylethylphosphonic acids:

$$R_3SiCH{=}CH_2 + HP(O)(OC_2H_5)_2 \xrightarrow[140-150^\circ]{\text{tert.-}C_4H_9O)_2} R_3SiCH_2CH_2P(O)(OC_2H_5)_2,$$

where R = C_2H_5; $-OC_2H_5$.

It is known ([8]) that the presence of ethoxyl groups at the silicon atom promotes polymerization of the corresponding vinylsilanes. Indeed, from triethoxyvinylsilane the target monomer was obtained in a yield of only 27%; together with the addition of diethylphosphinous acid to triethoxyvinylsilane, considerable polymerization of the latter was observed here. In the reaction with triethylvinylsilane, the yield of the desired product was 87.5%. A series of diethyl esters of

triorganosilylmethylphosphonic acids (compounds VI–IX in Table 1) was synthesized by us by means of the Arbuzov rearrangement:

$$R'_2R''SiCH_2Cl + P(OC_2H_5)_3 \rightarrow R'_2R''SiCH_2P(O)(OC_2H_5)_2 + C_2H_5Cl,$$

where $R' = CH_3$; $R'' = C_2H_5,\ OC_2H_5,\ OSi(CH_3)_2CH_2Cl$.

It turned out that replacement in chloromethyltriorganosilane of an ethyl radical by an ethoxyl group greatly facilitates the course of the reaction. Thus, when chloromethylethoxydimethylsilane was used, the target product (compound VII) was obtained in a yield of 63% after two hours' boiling of the reaction mixture, whereas from chloromethylethyldimethylsilane the corresponding silicon-phosphorus-containing compound (compound VI) was formed in a yield of 44% only after eleven hours' boiling of the mixture.

The formulas of the synthesized compounds and their properties are given in Table 1.

Table 1

No.	Compound	B.p., °C (mm)	n_d^{20}	D_4^{20}	Found, % C	Found, % H	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Cl	Yield, %
I	$(C_2H_5)_3SiCH_2P(O)(OC_2H_5)_2$	135–138(4)	1.4470*	1.0718*	51.2	10.5	—	51.5	10.3	—	87.5
II	$(C_2H_5)_3SiCH_2P(O)(OH)(OC_2H_5)$	138–141(2)	1.4530*	1.0337*	48.8	9.2	—	44.0	8.85	—	27
III	$Cl_3SiCH_2P(O)(OC_2H_5)_2$	142.5(6)	1.4985	1.5160	11.9	2.0	59.8	12.2	2.05	60.3	44
IV	$Cl_2(CH_3)SiCH_2P(O)(OC_2H_5)_2$	139(6)	1.4570	1.1041	17.6	3.6	50.1	17.7	3.3	50.6	49.5
V	$Cl_2(C_2H_5)SiCH_2P(O)(OC_2H_5)_2$	126(3)	1.4581	1.0818	18.2	3.4	48.8	18.5	3.4	49.3	43
VI	$C_2H_5(CH_3)_2SiCH_2P(O)(OC_2H_5)_2$	131.5(13)	1.4475	0.9900	46.5	9.5	—	45.5	9.65	—	44
VII	$C_2H_5(CH_3)_2SiCH_2P(O)(OC_2H_5)_2$	79–81(3)	1.4302	1.0060	42.4	9.1	—	42.6	9.05	—	63
VIII	$ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2P(O)(OC_2H_5)_2$	121(3–4)	1.4535	1.0778	36.6	7.3	10.6	36.1	7.8	10.7	22.5
IX	$\{(C_2H_5O)_2P(O)CH_2Si(CH_3)_2\}_2O$	157–160(3)	1.4525	1.0838	38.3	8.3	—	38.7	8.3	—	31

* n_D^{25}, d_4^{25}.

** Literature data ([5]): n_D^{25} 1.4216; d_4^{25} 1.031.

Experimental Part

Triethylvinylsilane and triethoxyvinylsilane were obtained in yields of 68.5% and 79%, respectively, by ethylation and ethoxylation of vinyltrichlorosilane and had the following properties: $(C_2H_5)_3SiCH{=}CH_2$, n_D^{20} 1.4347, d_4^{20} 0.7729; $(C_2H_5O)_3SiCH{=}CH_2$, n_D^{20} 1.3992, d_4^{20} 0.9042.

Allylphosphinic acid chloride was obtained in 55% yield by the method of Kinnear and Perren ([9]) and had the following properties: b.p. 77° (5 mm), n_D^{20} 1.4870, d_4^{20} 1.3783. $C_2H_5(CH_3)_2SiCH_2Cl$, $C_2H_5O(CH_3)_2SiCH_2Cl$, and $ClCH_2(CH_3)_2SiOSi(CH_3)_2CH_2Cl$ were obtained by ethylation, ethoxylation, and hydrolysis of $ClCH_2Si(CH_3)_2Cl$ in yields of 76%, 68%, and 98%, respectively, and had: $C_2H_5(CH_3)_2SiCH_2Cl$, b.p. 129–130° (750 mm), n_D^{20} 1.4298, d_4^{20} 0.8897; $C_2H_5O(CH_3)_2SiCH_2Cl$, b.p. 133–133.5° (750 mm), n_D^{20} 1.4190, d_4^{20} 0.9484; $ClCH_2(CH_3)_2Si{-}O{-}Si(CH_3)_2CH_2Cl$, b.p. 98° (21 mm), n_D^{20} 1.4365, d_4^{20} 1.0343.

Preparation of the diethyl ester of β-triethylsilylphosphinic acid. A round-bottom flask equipped with a reflux condenser with a calcium chloride tube, a stirrer, and a thermometer was charged with 27.6 g (0.2 mole) of $(C_2H_5O)_2P(O)H$, 14.2 g (0.1 mole) of $(C_2H_5)_3SiCH{=}CH_2$, and 2 ml of tri-*tert*-butyl peroxide. At 140–150° the mixture was stirred for 11 h (the reaction is so exothermic that during the first 2 h the heating must be reduced). Distillation gave 13.2 g of $(C_2H_5O)_2P(O)H$ and 24.5 g of $(C_2H_5)_3SiCH_2CH_2P(O)(OC_2H_5)_2$. Yield 87.5%. Under analogous conditions, from 19 g (0.1 mole) of $(C_2H_5O)_3SiCH{=}CH_2$, 27.6 g (0.2 mole) of $(C_2H_5O)_2P(O)H$, and 2 ml of tri-*tert*-butyl peroxide, 8.9 g of $(C_2H_5O)_3SiCH_2CH_2P(O)(OC_2H_5)_2$ was obtained (yield 27%), with 12 g of polymer remaining in the residue.

Preparation of trichlorosilylpropylphosphinic acid chloride. In the apparatus described in the first example, 40.2 g (0.25 mole) of allylphosphinic acid chloride and 2 ml of a 0.1 *M* solution of chloroplatinic acid in isopropyl alcohol were placed. To the mixture, 51 g (0.39 mole) of trichlorosilane was gradually added. After addition of approximately one-fifth of the total amount of trichlorosilane, rapid heating of the mixture was observed. Cooling of the reaction mixture and the rate of addition of trichlorosilane were adjusted so that the temperature did not rise above 50°. After all the trichlorosilane had been added, the mixture was kept at 40° for another 2 h. Distillation gave 15.8 g of unreacted allylphosphinic acid chloride and 32.6 g (0.11 mole) of trichlorosilylpropylphosphinic acid chloride. Yield 44.0% based on the initial acid chloride. Compounds IV were obtained analogously (the temperature of the reaction mixture was maintained within 60–65°), yield 49.5%, and V (the temperature of the reaction mixture was maintained within 60–100°), yield 43%.

Preparation of $C_2H_5(CH_3)_2SiCH_2P(O)(OC_2H_5)_2$ (VI). The reaction was carried out in a two-necked flask with a thermometer immersed in the reaction mixture and a reflux condenser connected through a side arm to a Tishchenko

bottle containing concentrated H_2SO_4. The reaction was conducted until evolution of C_2H_5Cl ceased. The flask was charged with 13.7 g (0.1 mole) of $C_2H_5(CH_3)_2SiCH_2Cl$ and 16.6 g (0.1 mole) of $P(OC_2H_5)_3$, and the mixture was boiled for 11 h. During this time the boiling temperature of the mixture rose from 142° to 173°. Distillation yielded 10.5 g of VI. Yield 44%.

In an analogous apparatus, from 15.3 g (0.1 mole) of $C_2H_5O(CH_3)_2SiCH_2Cl$ and 16.6 g (0.1 mole) of $P(OC_2H_5)_3$, on boiling the mixture for 2 h (the temperature of the reaction mixture rose from 140° to 190°), 16 g of VII was obtained. Yield 63%.

Analogously, from 23.1 g (0.1 mole) of $[ClCH_2(CH_3)_2Si]_2O$ and 33.2 g (0.2 mole) of $P(OC_2H_5)_3$, on boiling the mixture for 3 h (the boiling temperature of the mixture rose from 156° to 215°), 7.5 g (22.5%) of VIII and

3.5 g (8.0%) of IX. After distillation, a considerable amount of brittle dark-brown polymer remained in the flask.

Hydrolysis of $C_2H_5O(CH_3)_2SiCH_2P(O)(OC_2H_5)$ (VII). Into a three-necked flask equipped with a reflux condenser, stirrer, and dropping funnel were placed 14 g (0.55 mole) of VII and 100 ml of ether; the mixture was heated to boiling, and 5 ml of water was added with stirring. The mixture was stirred under reflux for 20 hr. Distillation gave 3.7 g of product IX with b.p. 157–160° (3 mm), n_D^{20} 1.4425, $d_4^{20} = 1.0805$. Yield 31%.

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Note: Figure translations are in progress. See original paper for figures.

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