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Abstract

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Synthesis of Dialkyl Triorganosilylmethoxymethylphosphinates and Their Hydrolytic Stability

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To date, several types of silicon-phosphorus-containing compounds have been synthesized in which silicon and phosphorus are linked either directly ([1]), or through atoms of oxygen ([2]), carbon ([3]), etc. ([4]). These compounds are recommended for practical use ([2]-[4]), but often the possibility of their use is limited by their insufficient hydrolytic stability ([5]). The only examples of compounds whose hydrolysis is not accompanied by significant destruction of the group linking silicon and phosphorus are certain compounds containing the bond Si—(CH_2) —P ([6], [7]).

In the present work we have synthesized a new class of silicon-phosphorus-organic compounds—esters of triorganosilylmethoxymethylphosphinic acids, in which silicon and phosphorus are linked by a simple ether group potentially resistant to hydrolysis. These compounds were obtained by the interaction of chloromethyltriorganosilanes with dialkyl sodium oxymethylphosphinates according to the general scheme:

$$(RO)_2P(O)CH_2ONa + ClCH_2SiR'R''_2 \longrightarrow$$

$$\longrightarrow (RO)_2P(O)CH_2OCH_2SiR'R''_2 + NaCl,$$

where R is alkyl, R′ is alkyl, and R″ is alkoxyl or alkyl.

When R″ is alkoxyl, the reaction is complete within 5-7 h and, at a 1:1 molar ratio of the starting reagents, gives the silicon-phosphorus-containing product in 50-55% yield. The reaction with trialkylchloromethylsilanes proceeds with greater difficulty and requires more prolonged heating for completion (10-15 h), while the yields of the target products are 35-55%; moreover, the starting silane must be taken in considerable excess. Replacement of the ethyl radicals in the ester groups of phosphorus by isopropyl radicals also lowers the product yield.

The compounds obtained are colorless liquids which distill without decomposition in vacuum. Their properties are given in Table 1.

Hydrolysis of dialkyl trialkylsilylmethoxymethylphosphinates by boiling with 18% hydrochloric acid for 20 h leads to formation of the corresponding trialkylsilylmethoxymethylphosphinic acids in 85–90% yield according to the following scheme:

$$(C_2H_5O)_2P(O)CH_2OCH_2SiR_3+2H_2O \xrightarrow{HCl} (HO)_2P(O)CH_2OCH_2SiR_3+2C_2H_5OH,$$

where R is alkyl.

The acids obtained as a result of hydrolysis form the upper organic layer and, after separation, washing free of chloride ions, and drying, are viscous colorless liquids readily soluble in ethanol and diethyl ether. Judging from analytical data, they are somewhat contaminated with silicon-containing products and do not form crystals. The acids, dissolved in alcohol, give crystalline salts with aniline,

Table 1

Dialkyl triorganosilylmethoxymethylphosphinates, trialkylsilylmethoxymethylphosphinic acids, and their anilinium salts

Compound	Yield, %	b.p., °C (mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % P	Found, % Si	Formula	Calc., % P	Calc., % Si
$(C_2H_5O)_2P(O)CH_2OCH_2Si(C_2H_5)_2CH_3$	52,5	140 (6)	0,9917	1,4401	75,06	75,17	10,92 10,98	9,81 9,70	$C_{11}H_{27}O_4PSi$	10,97	9,95
$(iso\text{-}C_3H_7O)_2P(O)CH_2OCH_2Si(C_2H_5)_2CH_3$	34,9	135 (5)	0,9404	1,4355	84,30	84,53	10,12 10,18	8,89 8,72	$C_{13}H_{31}O_4PSi$	9,98	9,05
$(C_2H_5O)_2P(O)CH_2OCH_2Si(C_2H_5)_3$	33,0	121 (3)	0,9883	1,4450	79,84	79,68	10,32 10,43	9,34 9,40	$C_{12}H_{29}O_4PSi$	10,45	9,47
$(C_2H_5O)_2P(O)CH_2OCH_2SiCH_3(OC_2H_5)_2$	50,0	120 (2)	1,0595	1,4282	76,37	76,93	9,90 9,91	8,76 8,71	$C_{11}H_{27}O_4PSi$	9,86	8,94
$CH_3(C_2H_5)_2SiCH_2OCH_2P(O)(OH)_2$	84,8	Non-distilling liquid					13,31 13,23	12,79 12,74	$C_7H_{19}O_4PSi$	13,61	12,36
$(C_2H_5)_3SiCH_2OCH_2P(O)(OH)_2$	86,3	Non-distilling liquid					12,54 12,52	12,58 12,75	$C_8H_{21}O_4PSi$	12,91	11,70

Compound	Yield, %	b.p., °C (mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % P	Found, % Si	Formula	Calc., % P	Calc., % Si
$CH_3(C_2H_5)_2SiCH_2OCH_2P(O)(OH)_2 \cdot C_6H_5NH_2$	—	m.p. 139,5—140,5 (from alcohol)					9,57 9,78	8,59 8,70	$C_{13}H_{26}NO_4PSi$	9,70	8,78
$(C_2H_5)_3SiCH_2OCH_2P(O)(OH)_2 \cdot C_6H_5NH_2$	—	m.p. 145—146° (from alcohol)					9,57 9,56	8,57 8,63	$C_{14}H_{28}NO_4PSi$	9,30	8,42

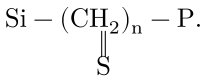
in which form they are convenient to identify. The properties of the acids and their anilinium salts are given in Table 1.

Upon interaction with 18% hydrochloric acid (boiling for 20 h), diethyl methyldiethoxysilylmethoxymethylphosphinate undergoes not only hydrolysis at the alkoxyl groups bonded to the silicon and phosphorus atoms, but also, to a considerable extent, cleavage of the $P-C-O-C-Si$ grouping, which leads to the formation of a cross-linked siloxane polymer insoluble in organic solvents and in water. The polymer contains 23-24% silicon and 3-4% phosphorus. Under milder hydrolysis conditions (boiling with 6% hydrochloric acid for 9 h), cleavage of the silicon-phosphorus-containing grouping occurs to a lesser extent, and the polymer formed (insoluble in benzene and water, but soluble in ethanol) contains 14-15% silicon and 10.5-11.5% phosphorus (for $[-O-Si-]_n$, 15.22% Si and 16.82% P were calculated).

$$H_3C \quad CH_2OCH_2P(O)(OH)_2$$

Thus, in compounds containing alkoxyl groups at the silicon atom, cleavage of the grouping linking silicon and phosphorus occurs considerably more readily than in trialkylsilyl derivatives. It should be noted that comparison of literature data on the hydrolysis of compounds containing the $Si-C-P$ bond reveals the same dependence ([7,8]).

On the basis of the results of this work and literature data on the hydrolysis of other silicon-phosphorus-containing compounds, it may be concluded that the $P-C-O-C-Si$ grouping is considerably more resistant to hydrolysis than the groupings $Si-O-P$ (^{2}), $Si-C-O-P$ (^{8}), $Si-C-O-P$ (^{8}), and approaches in stability the grouping



$$\mathrm{Si}-\underset{\overset{\|}{\mathrm{S}}}{(\mathrm{CH}_2)}{}_{\mathrm{n}}-\mathrm{P}.$$

Experimental Part

Diethyl methyldiethylsilylmethoxymethylphosphinate. To a solution of diethyl sodium oxymethylphosphinate, obtained from 13.8 g (0.1 mole) of diethyl phosphite, 2.3 g (0.1 g-atom) of sodium, and 3.0 g (0.1 mole) of paraform in 60 ml of ether, 37.6 g (0.25 mole) of chloromethylmethyldiethylsilane was added dropwise with stirring over 30 min. The reaction mixture was then heated in an apparatus with a reflux condenser with stirring for 10 h, after which sodium chloride was separated by filtration and the solvent was distilled off. Fractional distillation of the residue gave 26.2 g (69.6% of the starting amount) of unreacted chloromethylmethyldiethylsilane, b.p. 155–156°/760 mm, n_D^{20} 1.4370, and 11.3 g (16%, calculated on the starting amount, and 52.5% on the chloromethylmethyldiethylsilane that had entered into reaction) of diethyl methyldiethylsilylmethoxymethylphosphinate $(C_2H_5O)_2P(O)CH_2OCH_2Si(C_2H_5)_2CH_3$, b.p. 140°/6 mm.

Other dialkyl triorganosilylmethoxymethylphosphinates were obtained by an analogous procedure; the ratio of the starting materials in the case of chloromethylmethyldiethoxysilane was 1 : 1.

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REFERENCES

1. A. J. Leffer, E. G. Teach, J. Am. Chem. Soc., **82**, 2710 (1960).
2. E. Feher, K. Lippert, Chem. Ber., **94**, 2437 (1961).
3. K. C. Frisch, H. Lyons, J. Am. Chem. Soc., **75**, 4078 (1953).
4. M. L. Galanshina, M. V. Sobolevskii, K. A. Andrianov, Author' s Certificate 140061, Byull. Izobr., No. 15, 19 (1961).

5. A. D. Abbot, J. R. Wright et al., J. Chem. Eng. Data, **6**, 437 (1961).

6. H. P. David, G. H. Barness, J. Org. Chem., **25**, 1191 (1960).

7. E. A. Chernyshev, E. F. Bugerenko, A. D. Petrov, DAN, **148**, 875 (1963).

8. M. L. Galanshina, M. V. Sobolevskii, T. P. Alekseeva, *Plasticheskie massy*, No. 1, 18 (1965).

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

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