

REACTION OF TRIALKYL (OR ARYL) SILANOLS WITH
(ETHOXYMETHYLSILYL) METHYL DIMETHYLPHOSPHINATES

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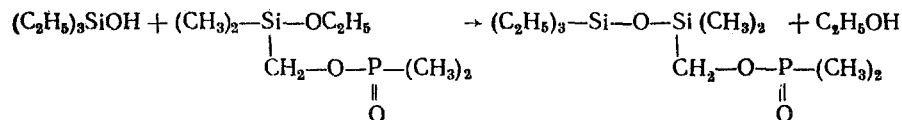
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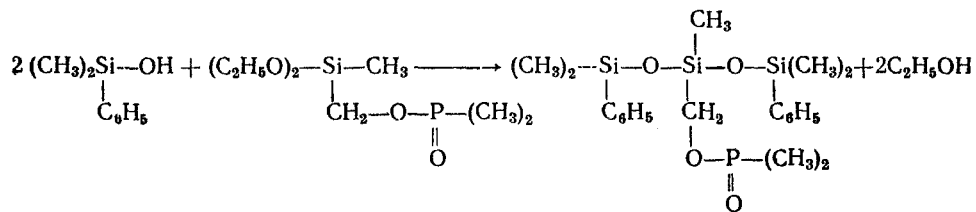
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In Smith's papers it was shown that an ethoxy group attached to silicon in alkoxysilanes reacting with alkylsilanols in presence of sodium [1] or sodium alkoxide [2] as catalyst, is replaced by an alkylsiloxo group. It was of interest to study the replacement of an alkoxy group in various organosilicon compounds containing dimethylphosphinic acid residues among their terminal groups. In carrying out the replacement of ethoxy groups attached to silicon by trialkyl (or aryl) siloxy groups, we have opened up great possibilities for the synthesis of new compounds containing two or more silicon atoms as well as phosphorus.

Investigation of the reaction of (ethoxydimethylsilyl) methyl dimethylphosphinate with triethylsilanol at a ratio of 1 : 1 showed that heating of the reaction mixture at 140-150° leads to the liberation of ethanol and the formation of (3, 3, 3-triethyl-1, 1-dimethyldisiloxanyl) methyl dimethylphosphinate in 60% yield in accordance with the scheme:



In the reaction of (ethoxydimethylsilyl) methyl dimethylphosphinate with dimethylphenylsilanol and with methyldiphenylsilanol we obtained, respectively, (1, 1, 2, 3-tetramethyl-3-phenyldisiloxanyl) methyl dimethylphosphinate. This reaction is of general significance; it occurs with the replacement not only of one, but also of two silicon-attached ethoxy groups. Thus, in the reaction of dimethylphenylsilanol with (diethoxymethylsilyl) methyl dimethylphosphinate at a ratio of 2 : 1 we obtained [1-(dimethylphenylsiloxy)-1, 3, 3-trimethyl-3-phenyldisiloxanyl] methyl dimethylphosphinate:



Analogous reactions were carried out with triethylsilanol and with methyldiphenylsilanol. In all cases the reactions were carried out without a catalyst. The ethanol formed in the reaction was distilled off in the course of the experiment and identified by its boiling point and refractive index. As a result of the reactions carried out we obtained previously undescribed organosilicon compounds containing two or three silicon atoms and a dimethylphosphinic acid group. The products are colorless liquids which may be distilled in a vacuum and are readily soluble in organic solvents. The properties of the products are presented in the table.

No.	Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
					Found	Calc.
I	$ \begin{array}{c} (C_2H_5)_3Si-O-Si-(CH_3)_2 \\ \\ C-H_2-O-P(O)(CH_3)_2 \\ \\ CH_3 \end{array} $	117—118(2)	1,4409	0,9609	81,48	81,87
II	$ \begin{array}{c} (CH_3)_2C_6H_5-Si-O-Si-CH_3 \\ \\ CH_2-O-P(O)(CH_3)_2 \end{array} $	155—157(2)	1,4820	1,0329	87,40	88,10
III	$ \begin{array}{c} CH_3(C_6H_5)_2-Si-O-Si-(CH_3)_2 \\ \\ CH_2-O-P(O)(CH_3)_2 \end{array} $	172—174(0,15)	1,5275	1,0780	108,00	108,30
IV	$ \begin{array}{c} (C_2H_5)_3Si-O-Si-O-Si-(C_2H_5)_3 \\ \\ CH_2-O-P(O)(CH_3)_2 \end{array} $	153—156(1—1,5)	1,4442	0,9634	114,20	114,58
V	$ \begin{array}{c} CH_3 \quad CH_3 \quad CH_3 \\ \quad \quad \\ C_6H_5-Si-O-Si-O-Si-C_6H_5 \\ \quad \quad \\ CH_2 \quad CH_2 \quad CH_3 \\ \quad \quad \quad \\ \quad \quad \quad CH_2-O-P(O)(CH_3)_2 \end{array} $	147—150(0,15)	1,5034	1,0615	126,40	126,90
VI	$ \begin{array}{c} CH_3 \quad CH_3 \quad C_6H_5 \\ \quad \quad \\ CH_3-Si-O-Si-O-Si-CH_3 \\ \quad \quad \\ C_6H_5 \quad CH_2-O-P(O)(CH_3)_2 \end{array} $	250(1·10 ⁻⁴)	1,5580	1,1178	166,5	167,2

EXPERIMENTAL

Dimethylphenylsilanol and methyldiphenylsilanol were prepared by the method of Andrianov and Delazari [3]. The preparation of (ethoxydimethylsilyl) methyl dimethylphosphinate and (diethoxymethylsilyl) methyl dimethylphosphinate were described by us in a previous communication [4].

Synthesis of (3, 3,3-Triethyl-1, 1-dimethyldisiloxanyl) methyl Dimethylphosphinate (I). A mixture of 4.2 g (0.02 mole) of (ethoxydimethylsilyl)methyl dimethylphosphinate and 2.65 g (0.02 mole) of triethylsilanol was prepared in a Claisen flask fitted with thermometer, stirrer, and condenser with receiver set for distillation. With vigorous stirring the reaction mixture was heated at 140–150° for 4.5 hours. In the course of the experiment 0.7 g (75%) of alcohol, b.p. 78° and n_D^{20} 1.3625, was distilled off. The residue was vacuum fractionated. We obtained 3.5 g (60%) of product; b.p. 117–118° (2 mm); n_D^{20} 1.4409; d_4^{20} 0.9609; found MR 81.48; calculated MR 81.87. Found: C 44.55; H 9.89%. $C_{11}H_{20}O_3PSi_2$. Calculated: C 44.55; H 9.86%.

Synthesis of (1, 1, 3, 3-Tetramethyl-3-phenyldisiloxanyl) methyl Dimethylphosphinate (II). Similarly, from 4.21 g (0.02 mole) of (ethoxydimethylsilyl) methyl dimethylphosphinate and 3.05 g (0.05 mole) of dimethylphenylsilanol we obtained 20 g (about 30%) of product; b.p. 155–157° (2 mm); n_D^{20} 1.4820; d_4^{20} 1.0329; found MR 87.37; calculated MR 88.13. Found: C 48.9; H 7.94; Si 17.9%. $C_{13}H_{25}O_3PSi_2$. Calculated: C 49, 3; H 7.96; Si 17.8%.

Synthesis of (1, 1, 3-Trimethyl-3, 3-diphenyldisiloxanyl) methyl Dimethylphosphinate (III). From 4.21 g (0.02 mole) of (ethoxydimethylsilyl) methyl dimethylphosphinate and 4.28 g (0.02 mole) of methyldiphenylsilanol we obtained 5 g (65%) of product; b.p. 172–174° (0.15 mm); n_D^{20} 1.5275; d_4^{20} 1.0780; found MR 108.0; calculated MR 108.3. Found C 57.09; H 7.4; ash 50.49%. $C_{18}H_{27}O_3PSi_2$. Calculated: 57.10; H 7.2; ash 50.63%.

Synthesis of [3, 3, 3-Triethyl-1-methyl-1-(triethylsiloxy) disiloxanyl] methyl Dimethylphosphinate (IV). Similarly, on heating 7.2 g (0.03 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate with 7.95 g (0.06 mole) of triethylsilanol at 140–150° for five hours, we distilled off 2.7 g (75%) of ethanol. On fractionation of the residue we collected a fraction of b.p. 153–156° (1–1.5 mm); yield 7.6 g (70%); n_D^{20} 1.4442; d_4^{20} 0.9634; found MR 114.2; calculated MR 114.58. Found: C 46.69; H 10.07; Si 20.5%; mol. wt. 413.0. $C_{16}H_{41}O_4PSi_3$. Calculated: C 46.60; H 10.01; Si 20.4%; mol. wt. 413.0.

Synthesis of [1-(Dimethylphenylsiloxy)-1, 3, 3-trimethyl-3-phenyldisiloxanyl] methyl Dimethylphosphinate (V). Similarly, from 7.2 g (0.03 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate and 9.15 g (0.06 mole) of dimethylphenylsilanol we obtained 8.0 g (60%) of product; b.p. 147-150° (0.15 mm); n_D^{20} 1.5034; d_4^{20} 1.0615; found MR 126.4; calculated MR 126.9. Found: C 53.41; H 7.50; S 18.72%. $C_{20}H_{33}O_4PSi_3$. Calculated: C 53.1; H 7.40; S 18.63%.

Synthesis of [1, 2-Dimethyl-1-(methyldiphenylsiloxy)-3, 3-diphenyl-disiloxanyl] methyl Dimethylphosphinate (VI). Similarly, from 2.4 g (0.01 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate and 4.28 g (0.02 mole) of methyldiphenylsilanol we obtained 1.8 g (30%) of product; b.p. 250° ($1 \cdot 10^{-4}$ mm); n_D^{20} 1.5580; d_4^{20} 1.1178; found MR 166.5; calculated MR 167.2. Found: C 62.3; H 6.50; Si 14.20; ash 43.33%. $C_{30}H_{37}O_4PSi_3$. Calculated: C 62.4; H 6.50; Si 14.61; ash 43.55%.

SUMMARY

1. An investigation was made of the reaction of trialkyl (or aryl) silanols with (ethoxymethylsilyl) methyl dimethylphosphinates; it can serve as a method of synthesizing organosilicon compounds containing the dimethylphosphinic acid group.
2. New compounds containing phosphorus and two or more silicon atoms were synthesized and characterized.

LITERATURE CITED

1. B. Smith, Svensk Kem. tidskr. 65, 101 (1953); Chem. Abstrs 48, 9907 (1954).
2. B. Smith, Svensk. kem. tidskr. 67, No. 9, 421 (1955); RZhKhim. No. 10, 29058 (1956).
3. K. A. Andrianov and N. Delazari, Dokl. AN SSSR 122, 3, 393 (1958).
4. K. A. Andrianov and I. K. Kuznetsova, Izv. AN SSSR. Otd. khim. n. 1961, 1454.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
