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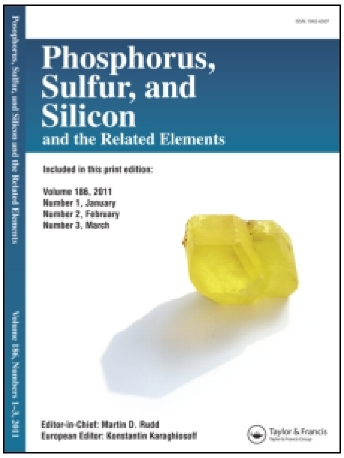

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS OF PHOSPHORUS AND SILICON CONTAINING MONOMERS AND OLIGOMERS WITH END PHOSPHONATE AND PHOSPHATE GROUPS

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SYNTHESIS OF PHOSPHORUS AND SILICON CONTAINING MONOMERS AND OLIGOMERS WITH END PHOSPHONATE AND PHOSPHATE GROUPS

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Phosphorus- and silicon-containing monomers are synthesized by the reaction of dealkylation of methyl esters of the phosphonic and phosphoric acids with dimethyl (and diphenyl) dichlorosilane. It is shown that the phosphorus- and silicon-containing monomers are condensed to oligomers with the evolution of the corresponding methyl esters of the phosphonic and phosphoric acid. It is established that at room temperature the addition of ethylene oxide occurs at the Si—O bonds.

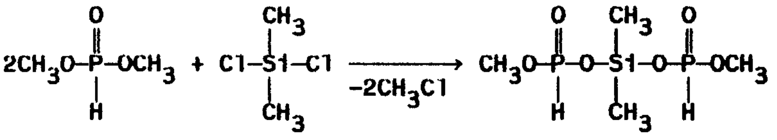
Key words: Dialkyl phosphonate; trialkyl phosphate; dialkyldichlorosilane; dealkylation.

I. INTRODUCTION

The present paper is a continuation of our investigation on the interaction of dialkyl phosphonates with dichlorodimethyl (or diphenyl) silanes.[1] The aim of this paper is to develop the synthesis of phosphorus- and silicon-containing oligomers with end phosphonate or phosphate groups by means of the reaction of dealkylation of the methyl esters of the phosphonic and phosphoric acids as well as their use as biologically active substances.

II. RESULTS AND DISCUSSION

The ^{1}H-NMR spectrum of the reaction product of dimethyl phosphonate (Equation 1, I) and dimethyldichlorosilane (Equation 1, II) at a molar ratio of 2:1 exhibits the signal: $\delta = 0.11$ ppm of the Si—CH$_3$ protons; 3.58 ppm, a doublet with a spin-spin interaction constant of 11,0 Hz, characteristic of P—OCH$_3$ protons; $\delta = 6.70$ ppm a doublet with a spin-spin interaction constant of 672.5 Hz, characteristic for P—H protons. These data characterize the product (Equation 1, III) obtained in the reaction of dealkylation of dimethyl phosphonate (**I**) by dimethyldichlorosilane (**II**):



$$2\mathrm{CH_3O}-\overset{\mathrm{O}}{\underset{\mathrm{H}}{\mathrm{P}}}-\mathrm{OCH_3} + \mathrm{Cl}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{Cl} \xrightarrow[-2\mathrm{CH_3Cl}]{} \mathrm{CH_3O}-\overset{\mathrm{O}}{\underset{\mathrm{H}}{\mathrm{P}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{O}}{\underset{\mathrm{H}}{\mathrm{P}}}-\mathrm{OCH_3} \qquad \text{(eq. 1)}$$

I II III

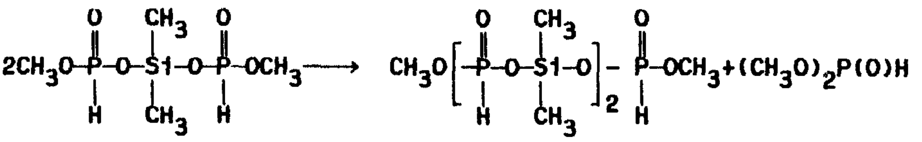
A second doublet at $\delta = 3.80$ ppm with a spin-spin interaction constant of 11,0 Hz, characteristic for P—OCH$_3$ protons, is observed in the ^{1}H-NMR spectrum of the reaction product. A second doublet is present also at $\delta = 6{,}80$ ppm with a spin-spin interaction constant of 710,0 Hz, characteristic for P—H protons. The J_{PH} constant (710,0 Hz) is characteristic for the phosphorus atom in the dimethyl phosphonate.[2]

The presence of dimethyl phosphonate is unexpected since the material balance of the reaction indicates that the dimethyl phosphonate has reacted completely.

A third type of P—H proton is found in the ^{1}H-NMR spectrum of the reaction mixture, a doublet at $\delta = 6{,}71$ ppm with $J_{PH} = 650{,}0$ Hz. This phosphorus atom is not bonded to a methoxy group, since signals of protons of both types of methoxy groups are observed in the spectrum.

The ^{31}P-NMR spectrum of the reaction product reveals signals for three types of phosphorus atoms: at $\delta = 11{,}40$ ppm a doublet of quartets with $J_{PH} = 690{,}0$ Hz. These data can be related to a phosphorus atom with the following environment —P(O)H(OCH$_3$); $\delta = 8{,}55$ ppm a doublet of septets with $J_{PH} = 696{,}4$ Hz. The latter are characteristic for the phosphorus atom in the dimethyl phosphonate; at $\delta = -15{,}30$ ppm a doublet with a spin-spin interaction constant of 621.26 Hz. These data can be referred to a phosphorus atom with O—Si groups on both sides.

A product with such a structure can be obtained if the monomer produced by the interaction of two phosphonate molecules with a molecule of dimethyldichlorosilane (Equation 1, III) is condensed according to the following scheme:



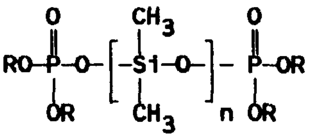
$$2CH_3O-\overset{O}{\underset{H}{P}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{O}{\underset{H}{P}}-OCH_3 \longrightarrow CH_3O\left[-\overset{O}{\underset{H}{P}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_2-\overset{O}{\underset{H}{P}}-OCH_3+(CH_3O)_2P(O)H$$

III IV (eq.2)

These assumptions are supported by the experimental results. On heating the reaction mixture at 140°C for 10 hours a distillate was evolved, the structure of which was confirmed by the ^{1}H-NMR spectra. The distillate evolved is dimethyl phosphonate in an amount of 45% with respect to that initially introduced.

The ^{1}H-NMR spectrum of the reaction product after its heating at 140°C (Equation 2, IV), exhibits signals for three types of P—H protons, but the ratio of the integrated intensities is different from that in the product before its heating. After heating the amount of the fragment where the phosphorus atom is bound with two O—Si— groups has strongly increased. The presence of oligomer product confirms the procedure of the thermal condensation.

M. Schmidt et al.[3] have established that polymers of the type

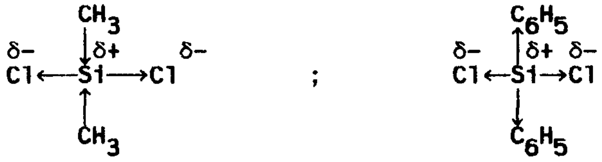


$$RO-\overset{O}{\underset{OR}{P}}-O-\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right]_n-\overset{O}{\underset{OR}{P}}-OR$$

undergo thermal condensation with the evolution of the trialkyl phosphate.

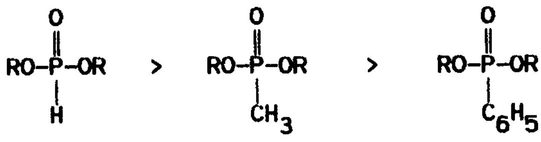
The preceding condensation makes possible the formation of oligomers with end phosphonate groups, structures which cannot be obtained by the dealkylation reaction.

The interaction between dimethyl phosphonate and diphenyldichlorosilane proceeds at a considerably higher temperature of 60°C. The substitution of the donor methyl groups at the silicon atom with the acceptor phenyl groups is evidently the reason for the observed reduction in the reactivity of the dealkylation agent:

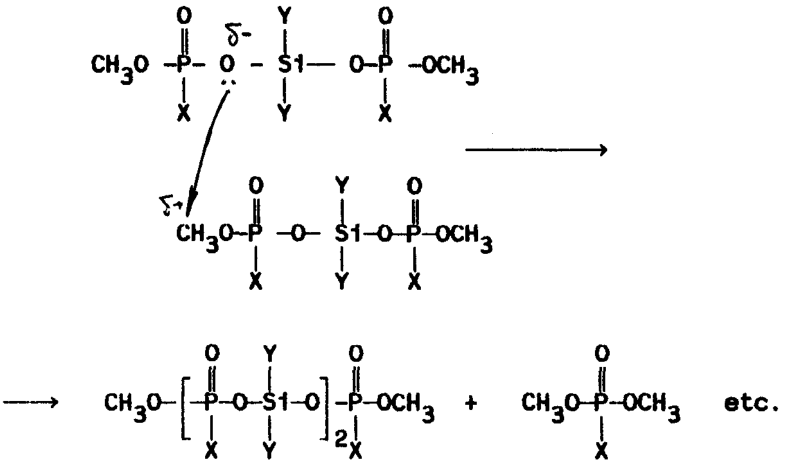


The methyl groups contribute to the increase in the electron density of the chlorine atoms, whereas the phenyl groups will cause a reduction of the electron density of the chlorine atom, thus decreasing the electron density of silicon.

It was established that the thermal condensation decreases in the order hydrogen, methyl- and phenylphosphonic acids:

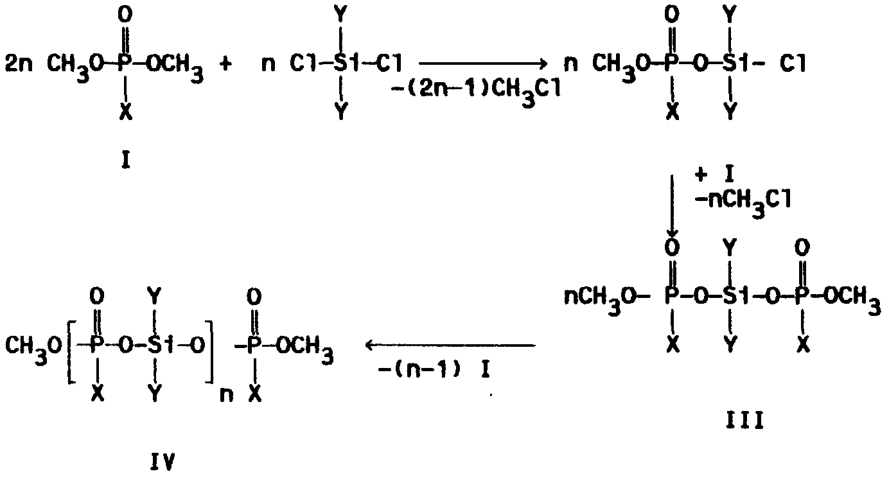


The above order of reactivity can be explained by the assumption that the thermal condensation proceeds by a nucleophilic substitution, whereby the oxygen atom at the —Si—O— bond, which is 50% ionic, acts as a nucleophile, while the α-carbon atom of the alkoxy group serves as an electrophile center:



The experimental data show that the rate of the thermal condensation reaction depends on the nature of the substituents at the phosphorus atom. The electron acceptor substituents bring about a higher rate of thermal condensation, while donor substituents retard it. The observed reduction in the rate of the condensation with a phenyl group as substituent can be explained by the assumption that due to the lower electron density of the phosphorus atom, it is possible to realize the interaction between the free electron pairs of oxygen and the free d-orbitals of phosphorus. The existence of such an interaction will reduce the strength of the nucleophile.

The following most likely scheme for the interaction between esters of the phosphonic and phosphoric acids and dimethyl (or diphenyl) dichlorosilane can be accepted on the basis of the available experimental data:

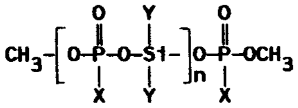


The data from IR spectra confirm the structure of the reaction product: where X=H, $Y=CH_3$ the IR spectra of the reaction product shows the following absorptions at: 1010 cm^{-1} for P—O—Si groups; 1094 cm^{-1} for $P—OCH_3$ group; 1265 cm^{-1} for P=O group; 2438 cm^{-1} P—H group; 2964 cm^{-1} for $Si—CH_3$ group; where $X=CH_3$, Y=Ph the IR spectra of the reaction product shows the following absorptions at: 1009 cm^{-1} for Si—O—P group; 1129 cm^{-1} for $P—OCH_3$ group; 1200 cm^{-1} for P=O group; 1315 cm^{-1} for $P—CH_3$ group; 1590 cm^{-1} for Si—Ph group; where X=Ph, Y=Ph the IR spectra of the reaction product shows the following absorptions: 1029 cm^{-1} for $P—OCH_3$ group; 1216 cm^{-1} for P=O group; 1438 cm^{-1} for P—Ph group; 1591 cm^{-1} for Si—Ph group; where $X=OCH_3$, Y=Ph the IR spectra of the reaction product shows the following absorptions at: 1014 cm^{-1} for $P—OCH_3$ group; 1224 cm^{-1} for P=O group; 1590 cm^{-1} for Si—Ph group.

By the of dealkylation of the methyl ester of alkyl- and phenylphosphonic and phosphoric acids phosphorus- and silicon-containing compounds with end phosphonate and phosphate groups (Table I) were synthesized. The structure of the products was revealed by ^{1}H-NMR and ^{31}P-NMR spectrographic investigations and elemental analysis.

TABLE I

Phosphorus and silicon containing monomers and oligomers with a general formula



$$CH_3-\left[O-\overset{O}{\underset{X}{\overset{\|}{\underset{|}{P}}}}-O-\overset{Y}{\underset{Y}{\overset{|}{\underset{|}{Si}}}}-\right]_n O-\overset{O}{\underset{X}{\overset{\|}{\underset{|}{P}}}}-OCH_3$$

Starting monomers[a]		Degree of Completion of the Reaction[b]	Degree of Completion of the Condensation the Monomer III(n=1)	Quantity of the distilate[c]	Composition of the Reaction Product Monomers	 Oligomers	Degree of Condensation	Yield		C,%		H,%	
X	Y	%	%	g	%	%	n	g	%[d]	found	calc.[e]	found	calc.[e]
H	CH_3	100	90	10,2	10	90	2	14,6	58,5	17,24	17,56	5,65	5,14
CH_3	C_6H_5	100	27	1,7	73	27	2	18,3	91,5	54,81	54,21	5,09	4,98
C_6H_5	C_6H_5	100	68	6,3	32	68	2	19,6	75,8	60,27	61,50	4,83	4,90
OCH_3	C_6H_5	100	49	3,4	51	49	2	17,9	83,6	48,49	48,43	5,04	4,77
H	C_6H_5	100[f]											

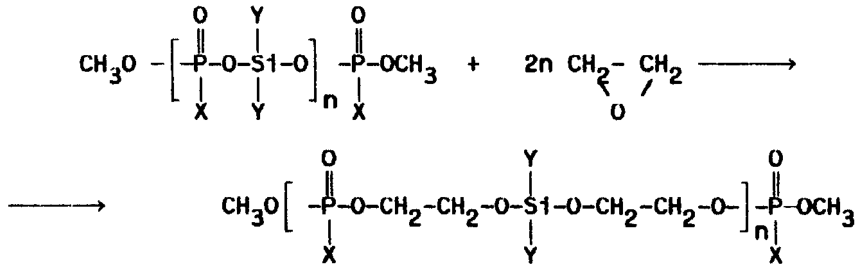
a–molar ratio 2:1;
b–calculated by the amount of CH_3Cl evolved;
c–see experimental section;
d–calculated with respect to chlorosilane;
e–calculated on the base of the content in percentage of the monomer III and oligomers (elementary unit);
f–to the reaction product is added ethylene oxide;

The data from the GPC reveal that the products have the following molecular weight:

$X=CH_3$, $Y=Ph$ - $\bar{M}_w=454$; PDI=1,1
$X=Ph$, $Y=Ph$ - $\bar{M}_w=693$; PDI=1,1
$X=OCH_3$ $Y=Ph$ - $\bar{M}_w=553$; PDI=1,2

The content of the monomeric(III) and oligomeric(IV) products in the reaction mixture was calculated on the base of the amount of the phosphorus monomer evolved.

It was established that the above synthesized phosphorus- and silicon-containing monomers and oligomers can add ethylene oxide:



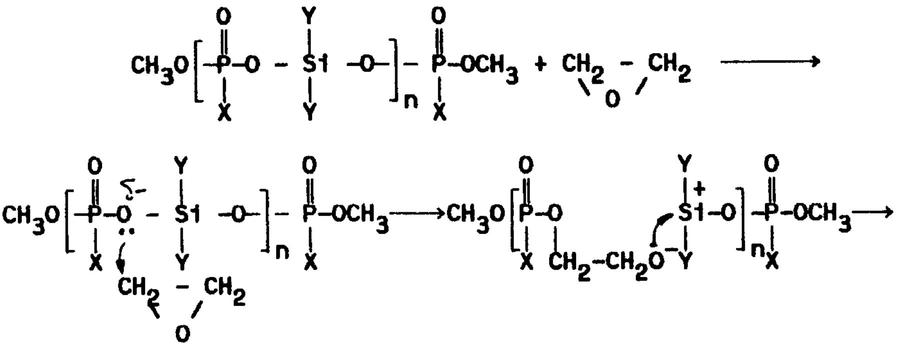
where: X = H,; OCH_3; Y = CH_3, C_6H_5; n = 2.

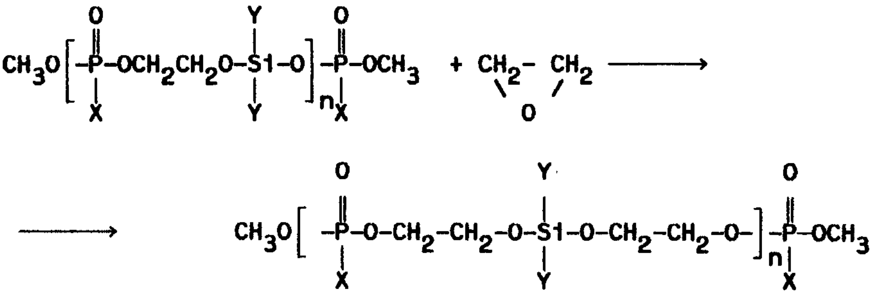
where: X = H,; OCH_3; Y = CH_3, C_6H_5; $n = 2$.

The addition of ethylene oxide was confirmed with the aid of ^{1}H-NMR spectroscopic investigations. The spectrum reveals new signals: at $\delta = 4.16$ ppm, a multiplet, which can be assigned for the $POCH_2$ protons with a splitting constant of $J_{POCH} = 5.2$ Hz and at $\delta = 3.77$ ppm, a triplet, which can be assigned for the Si—OCH_2 protons.[2]

It was found that the amount of ethylene oxide bound is close to the theoretically estimated for two Si—O bonds. It is likely that the strong polar character of the —Si—O bond makes possible the addition of ethylene oxide.

It can be accepted that the addition of ethylene oxide to phosphorus and silicon containing monomers and oligomers proceeds by the following scheme:





The reactivity of the phosphorus- and silicon-containing monomers and oligomers with Si—O bonds with respect to ethylene oxide reveals new possibilities for the synthesis of new compounds with the use of alkylene oxide. Being bifunctional (with end alkyl- or phenylphosphonate groups) and polyfunctional (with end phosphonate groups) and being also monomers and oligomers containing a labile hydrogen atom, the synthesized phosphorus- and silicon-containing compounds are of interest for organic synthesis as well as biologically active substances.

EXPERIMENTAL

Starting compounds: dimethyl phosphonate, dimethylmethyl phosphonate, dimethylphenyl phosphonate, trimethyl phosphate, dimethyldichlorosilane, diphenyldichlorosilane, ethylene oxide.

The infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer.

The ^{1}H-NMR spectra were measured on a Bruker WM 50/250 spectrometer, at 13 MHz ^{1}H/, with DMSO-d$_6$ and CDCl$_3$ as solvents.

The ^{31}P-NMR spectra were recorded on a Bruker WM 250 spectrometer, with CH$_3$Cl as solvent.

The GPC were measured on a Waters 244 with columns of 100, 100, 500 and 1000 Å, calibrated with PS standards and THF as solvent.

A. Interaction between methyl esters of phosphonic and phosphoric acids with dimethyl (or diphenyl) dichlorosilane.

Example 1. 22.7 g (0.2 moles) of dimethyl phosphonate and 12.27 g (0.1 moles) of dimethyldichlorosinale are introduced in a three-neck flask, provided with a capillary for argon bubbling, a thermometer and a reflux condensor. The reaction is carried out at 25–30°C for 10 hours. After the completion of the reaction, (controlled by the amount of CH$_3$Cl evolved) the reaction mixture is vacuum distilled at 140°C and at a residual pressure of 0.1–0.15 mm Hg to a constant weight. 10.2 g of a distillate with n_D^{20} = 1.4020 are evolved. The product is a colourless viscous liquid with a specific odor, soluble in CH$_3$Cl, C$_6$H$_6$, THF etc. Yield 14.62 g.

Example 2. 12.4 g (0.1 moles) dimethylmethyl phosphonate and 2.6 g of diphenyldichlorosilane (0.05 moles) are reacted in the conditions described in Example 1 at 100–105°C during 3 hours. After the completion of the reaction (controlled by the amount of CH$_3$Cl evolved) the reaction mixture is vacuum distilled at 150–155°C and at a residual pressure of 0.1–0.15 mm Hg to a constant weight. 1.68 g of a distillate with n_D^{20} = 1.4120 are evolved. The synthesized product is light yellow viscous liquid with a specific odor, soluble in CHCl$_3$, C$_6$H$_6$, THF etc. Yield 18.28 g.

Example 3. 18.7 g (0.1 moles) of dimethylphenyl phosphonate and 12.3 (0.05 moles) diphenyldichlorosilane are reacted in the conditions described in Example 1 at 85–90°C during 10 hours. After the completion of the reaction (controlled by the amount of CH$_3$Cl evolved) the reaction mixture is vacuum distilled at 170–173°C and at a residual pressure of 0–1.15 mm Hg to a constant weight. 6.32 g of a distillate with n_D^{20} = 1.5132 are evolved. The product is a very viscous yellow liquid, soluble in CHCl$_3$, C$_6$H$_6$, THF etc. Yield 19.84 g.

Example 4. 14 g (0.1 moles) of trimethyl phosphate and 12.4 g (0.05 moles) of diphenyldichlorosilane are reacted in the conditions described in Example 1 at 90–95°C during 6 hours. After the completion of the reaction (controlled by the amount of CH$_3$Cl evolved) the reaction mixture is vacuum distilled at 160–165°C and at a residual pressure of 0.1–0.15 mm Hg to a constant weight. 3.44 g of a distillate with n_D^{20} = 1.3970 are evolved. The synthesized product is a light-yellow liquid with a specific odor, soluble in CHCl$_3$, C$_6$H$_6$, THF etc. Yield 17.89 g.

B. Interaction of phosphorus- and silicon-containing monomerrs and oligomers with ethylene oxide.

Example 5. 6.34 g phosphorus- and silicon-containing oligomer, obtained by the interaction of dimethyl phosphonate and dimethyldichlorosilane (Example 1) are introduced in a three-neck flask, provided with a magnetic stirrer, thermometer and a capillary for the introduction of ethylene oxide. The ethylene oxide is introduced at room temperature. The reaction is exothermal and the temperature is raised to 55°C. After 3 hours the reaction product is vacuum distilled at room temperature in an argon medium to a constant weight. The amount of the bound ethylene oxide is 2.6 g. The product is a colourless viscous liquid with a specific odor, soluble in $CHCl_3$, C_6H_6 et al.

Example 6. 17.82 g of the product obtained by the interaction of dimethyl phosphonate and diphenyldichlorosilane (non distilled) with ethylene oxide are reacted in the conditions described in Example 5 at 25–30°C. The interaction is exothermal and the temperature rises at 40°C. After 5 hours the reaction product is vacuum distilled in an argon atmosphere to a constant weight. The amount of the ethylene oxide bound is 4.0 g. The product is a colourless viscous liquid with a specific odor soluble in $CHCl_3$, C_6H_6 et al.

Example 7. 9.015 g of the product obtained by the interaction of trimethyl phosphate and diphenyldichlorosilane and ethylene oxide are reaction in the conditions described in Example 5 at 25–30°C. The reaction is exothermal and the temperature rises to 40°C. After 7 hours the reaction product is vacuum distilled at 60°C in an argon atmosphere to a constant weight. The amount of ethylene oxide bound is 1.44 g. The product is a colourless viscous liquid with a specific odor, soluble in $CHCl_3$, C_6H_6 et al.

REFERENCES

1. K. Troev and G. Borisov, *Phosphorus and Sulphur,* **29**, 129 (1987).
2. The Sadtler Handbook of Proton NMR Spectra, **1931**, 1229 (1978).
3. M. Schmidt and H. Schmidbaur, *Angew. Chem.*, **71**, 553 (1959).