STRUCTURES OF PRODUCTS OF THE REACTIONS OF HALOTRIORGANOSILANES WITH TRIETHYL PHOSPHITE AND WITH SODIUM DIALKYL PHOSPHITES

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Information on the structure of products of the reactions of halotriorganosilanes with triethyl phosphite [1, 2] is contradictory. Thus, Arbuzov and Pudovik [1], who were the first to study the reactions of halotriorganosilanes with $P(OC_2H_5)_3$, supposed that reaction proceeds with formation of quinquevalent phosphorus derivatives containing an Si-P bond, i.e., in accordance with the scheme*

 $R_3SiX + P(OC_2H_5)_3 \rightarrow R_3SiPO(OC_2H_5)_2 + C_2H_5X$

in which R = alkyl or alkoxy and X = halogen.

In particular, to the product which they isolated in the reaction of $(C_2H_5)_3SiBr$ with $P(OC_2H_5)_3$ the authors of [1] assigned the structure of $(C_2H_5)_3SiPO(OC_2H_5)_2$ (I). Later, Malatesta [2] showed that Arbuzov and Pudovik had isolated not (I), but its isomer $C_2H_5PO[OSi(C_2H_5)_3]OC_2H_5$ (II). According to Malatesta, (II) could be formed in accordance to one of the schemes:

$$(C_{2}H_{5}O)_{3}P + (C_{2}H_{5})_{3}SiBr \rightleftharpoons (C_{2}H_{5}O)_{2}POSi(C_{2}H_{5})_{3} + C_{2}H_{5}Br \rightarrow C_{2}H_{5}PO/OSi(C_{2}H_{5})_{3}/OC_{2}H_{5} + C_{2}H_{5}Br \qquad (1)$$

$$(C_{2}H_{5}O)_{3}P + (C_{2}H_{5})_{3}SiBr \rightarrow C_{2}H_{5}PO(OC_{2}H_{5})_{2} + (C_{2}H_{5})_{3}SiBr \rightleftharpoons C_{2}H_{5}PO/OSi(C_{2}H_{5})_{3}/OC_{2}H_{5} + C_{2}H_{5}Br$$
(2)

Analysis of the reaction conditions of Arbuzov and Pudovik's (and also Malatesta's) experiment on the reaction of $(C_2H_5)_3$ SiBr with $P(OC_2H_5)_3$ enables us to give a priori preference to scheme (1). In [1, 2] the reaction between bromotriethylsilane and triethyl phosphite was conducted at 70°. This temperature is not sufficiently high for the rapid removal of the initially formed ethyl bromide from the reaction zone, which makes it possible for the ethyl bromide to take part in further reactions – with $(C_2H_5O)_2$ POSi $(C_2H_5)_3$, for example. Hence, the rapid removal of ethyl bromide from the reaction mixture (which can be achieved by raising the reaction temperature) should prevent, or at least diminish, the formation of (II).

In view of this we repeated the experiment on the reaction of $(C_2H_5)_3$ SiBr with $P(OC_2H_5)_3$, not at 70° as in [1, 2], but at 155-180° This indeed led to somewhat different results. In the first place, we could not isolate any (II). In the second place, although bromotriethylsilane and triethyl phosphite were taken in equimolecular proportions, the bromotriethylsilane reacted almost completely (92.1% of ethyl bromide was obtained), but the triethyl phosphite reacted only to the extent of 57%. In the third place, from the reaction mixture we isolated a compound corresponding to (II) in elemental analysis, but differing from (II) in physical properties.[†] Thus, according to [1] (II) has: b.p. 158-159° (10 mm); n_D²⁰ 1.4390; d₄²⁰ 0.9659. The compound which we isolated had: b.p. 95-97° (7 mm); n_D²⁰ 1.4333; d₄²⁰ 0.9332. Exactly the same properties were possessed by products obtained in the reactions of sodium triethylsilanolate with ClP(OC₂H₅)₂ and of chlorotriethylsilane with NaPO(OC₂H₅)₂:

$$(C_2H_5)_3SiONa + ClP(OC_2H_5)_2 \rightarrow (C_2H_5)_3SiOP(OC_2H_5)_2 + NaCl$$

 $(C_2H_5)_3SiCl + NaPO(OC_2H_5)_2 \rightarrow (C_2H_5)_3SiOP(OC_2H_5)_2 + NaCl$

* Until now in the literature it has been usual to consider that the reactions of R_3SiX with sodium dialkyl phosphites also lead to the formation of products containing an Si-P bond [1, 3-5]:

 $R_3SiX + NaPO(OR')_2 \longrightarrow R_3SiPO(OR')_2 + NaX.$

†It is interesting that a fraction containing this product [b.p. 104-125° (13 mm)] was also isolated in [1], but the authors did not investigate it in greater detail.

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Analogously, the same product was obtained in the reactions

 $\begin{array}{l} (CH_3)_3SiONa + ClP(OC_2H_5)_2 \rightarrow (CH_3)_3SiOP(OC_2H_5)_2 + NaCl\\ (CH_3)_3SiBr + NaPO(OC_2H_5)_2 \rightarrow (CH_3)_3SiOP(OC_2H_5)_2 + NaBr \end{array}$

 $(C_{2}H_{5})_{3}SiOP(OC_{2}H_{5})_{2}$ and $(CH_{3})_{3}SiOP(OC_{2}H_{5})_{2}$, like trialkyl phosphites, readily combine with sulfur with formation of $(C_{2}H_{5})_{3}SiOPS(OC_{2}H_{5})_{2}$ and $(CH_{3})_{2}SiOPS(OC_{2}H_{5})_{2}$, respectively, and undergo Arbuzov reaction with alkyl halides. Thus, when $(C_{2}H_{5})_{3}SiOP(OC_{2}H_{5})_{2}$ and $(CH_{3})_{3}SiOP(OC_{2}H_{5})_{2}$ were heated with ethyl bromide in a sealed tube for 6 h at 150° we obtained II (32.5% yield) and $C_{2}H_{5}PO[OSi(CH_{3})_{3}]OC_{2}H_{5}$ (42.3% yield), respectively.

Our experimental results enable us to conclude that: 1) at high temperatures $(155-180^{\circ})$ the reaction of $(C_2H_5)_3SiBr$ with $P(OC_2H_5)_3$ goes mainly in accordance with the schemes

 $\begin{array}{c} (C_{2}H_{5})_{3}SiBr + P(OC_{2}H_{5})_{3} \rightarrow (C_{2}H_{5})_{3}SiOP(OC_{2}H_{5})_{2} + C_{2}H_{5}Br \\ (C_{2}H_{5})_{3}SiOP(OC_{2}H_{5})_{2} + (C_{2}H_{5})_{3}SiBr \rightarrow [(C_{2}H_{5})_{3}SiO]_{2}POC_{2}H_{5} + C_{2}H_{5}Br \\ [(C_{2}H_{5})_{3}SiO]_{2}POC_{2}H_{5} + (C_{2}H_{5})_{3}SiBr \rightarrow [(C_{2}H_{5})_{3}SiO]_{3}P + C_{2}H_{5}Br \end{array}$

i.e., with formation of tervalent phosphorus derivatives containing the Si-O-P link; 2) in a similar way, in the reaction of trialkylhalosilanes with sodium diethyl phosphite the products are not quinquevalent phosphorus derivatives containing the Si-P bond as the authors of [3, 4] supposed but are the isomeric tervalent phosphorus derivatives containing the Si-O-P link. There are clearly no grounds to doubt that the reactions of trialkoxyhalosilanes with sodium dialkyl phosphites [1, 5] proceed in an analogous way.

It is known that thionic organophosphorus compounds of the type $(RO)_3PS$ are isomerized into the thiol compounds $(RO)_2P(O)SR$ in presence of alkyl halides [6]. It was found that compounds of formula $R_3SiOPS(OC_2H_5)_2$ are also isomerized into the corresponding thiolic compounds, but the isomerization goes with great difficulty. When $(CH_3)_3SiOPS(OC_2H_5)_2$ was heated with a little ethyl bromide in a sealed tube for 70 h at 150°, we isolated the isomeric thiolic substance in 54.7% yield. In Fig. 1 we show the IR spectra of $(CH_3)_3SiOPS(OC_2H_5)_2$ and of its isomerization product. In the isomerization the P=S and P=O bonds of the starting compound are rearranged into the P-S and P=O bonds of the thiolic isomer. The P=O group is known to be characterized in the IR spectrum by an intense absorption band in the 1200-1300 cm⁻¹ region [7]. The P=S groups in compounds of the (RO)_3P=S type is characterized by an absorption band at about 610 cm⁻¹ [8]. It was in fact found that the IR spectrum of the isomerization product, while the spectrum of the isomerization product contains a band at 1220 cm⁻¹ (the intense absorption band at 1260 cm⁻¹, present in both spectra, must be assigned to the symmetrical vibrations of methyl groups attached to silic con [9]).

Of the two possible structures of the isomerization product $-(CH_3)_3SiSPO(OC_2H_5)_2$ and $(CH_3)_3SiOPO \cdot (OC_2H_5)(SC_2H_5)$ – the latter is the more probable.

EXPERIMENTAL

Chlorotrimethyl-, bromotrimethyl-, chlorotriethyl-, and bromotriethyl-silanes were prepared by the procedure described in [10] from the corresponding siloxanes and had properties corresponding to those reported in the literature. Triethyl- and trimethyl-silanols (in admixture with hexamethyldisiloxane



Fig. 1. IR spectra of $(CH_3)_3SiOPS(OC_2H_5)_2$ (1) and its isomerization product (2).

in the second case) were prepared by the hydrolysis of chlorotriethyl- and chlorotrimethyl-silanes with 1 N NaOH [11]. $(C_2H_5)_3$ SiOH, b.p. 73° (23 mm); n_D^{20} 1.4342 (according to [12]: b.p. 153.5-154.5° at 753 mm; n_D^{20} 1.4341; d_4^{20} 0.8646). The mixture of $(CH_3)_3$ SiOH and $[(CH_3)_3$ Si]_2O had: b.p. 97-99° (749 mm); n_D^{20} 1.3845 (according to [12] pure trimethylsilanol has: b.p. 98-98.6° at 757 mm; n_D^{20} 1.3892; d_4^{20} 0.8139). $(C_2H_5O)_2$ POH, $(C_2H_5O)_2$ PCl, and $(C_2H_5O)_3$ P were prepared by the action of ethanol on phosphorus trichloride (in presence of pyridine in the second and third cases) and had the following properties: $(C_2H_5O)_2$ POH, b.p. 67° (8 mm); n_D^{20} 1.4080; d_4^{20} 1.0739 (according to [13]: b.p. 75° at 15 mm; n_D^{20} 1.4080; d_0^{20} 1.0742); $(C_2H_5O)_2$ PCl, b.p. 151-152° (748 mm); n_D^{20} 1.4352; d_4^{20} 1.0754 (according to [14]: b.p. 153-155°; n_D^{20} 1.4350; d_0^{20} 1.0747). The triethyl phosphite had properties agreeing with those reported in [13].

Preparation of $(C_2H_5)_3SiOP(OC_2H_5)_2$

From Bromotriethylsilane and Triethyl Phosphite. A Claisen flask was charged with 16 g of $(C_{2}H_{5})_{3}$. SiBr and 13.5 g of P(OC₂H₅)₃ and was heated for 30 min with gradual rise of temperature in the range 155 to 180°. 8.2 g (92.1%) of ethyl bromide, b.p. 37-38° (738 mm), was distilled off. In the distillation of the residue we obtained three fractions: 45-95° (6-7 mm) and n_{D}^{20} 1.4165 (7.8 g); 95-115° (6-7 mm) and n_{D}^{20} 1.4340 (3.9 g); and 115-175° (6-7 mm) and n_{D}^{20} 1.4460 (10.8 g). In the redistillation of the first fraction we isolated 5.8 g (43%) of P(OC₂H₅)₃, b.p. 45-47° (6 mm) and n_{D}^{20} 1.4135; from the second we obtained 3.1 g (15%) of (C₂H₅)₃SiOP(OC₂H₅)₂; b.p. 95-97° (7 mm), n_{D}^{20} 1.4333, d_{4}^{20} 0.9332. Found %: C 48.1, 48.3; H 10.0, 10.1; P+Si 23.4, 23.1. C₁₀H₂₅O₃PSi. Calculated %: C 47.8; H 9.93; P+Si 23.4. From the third fraction we were unable to isolate any individual product, but in view of the fact that sulfur readily dissolves in this fraction and (C₂H₅)₃SiOH and H₂PO₃ are formed on hydrolysis the fraction is probably mainly a mixture of $[(C_{2}H_{5})_{3}SiO]_{2}POC_{2}H_{5}$ and $[(C_{2}H_{5})_{3}SiO]_{3}P$.

From Chlorotriethylsilane and Sodium Diethyl Phosphite. The reaction and all succeeding operations were conducted in an atmosphere of dry oxygen-free nitrogen. 15 g of chlorotriethylsilane was added drop-wise with vigorous stirring to a solution of $(C_2H_5O)_2P(O)$ Na prepared from 2.3 g of sodium and 14 g of $(C_2H_5O)_2POH$ in 100 ml of dry ether. Stirring was continued further for 1 h, the precipitate was filtered off and washed with two 25-ml portions of dry ether, ad after the removal of ether the filtrate was vacuum-distilled. We obtained 13.4 g (53.4%) of $(C_2H_5)_2SiOP(OC_2H_5)_2$, b.p. 105-106° (10 mm), nD²⁰ 1.4332, d₄²⁰ 0.9340.

From Sodium Triethylsilanolate and Diethyl Phosphorochloridite. The reaction was conducted in an atmosphere of nitrogen. With stirring and cooling to between -20 and -30° , 20.3 g of $(C_2H_5O)_2PCI$ was added dropwise to a solution of $(C_2H_5)_3SiONa$ prepared from 3 g of sodium and 17.2 g of $(C_2H_5)_3SiOH$ in 100 ml of dry ether. The mixture was stirred for 1 h at room temperature, the precipitate was filtered off andwashed with two 25-ml portions of dry ether, and the filtrate, after removal of solvent, was vacuum-distilled. We obtained 19 g (58%) of $(C_2H_5)_2SiOP(OC_2H_5)_2$, b.p. 105-106° (10 mm), n_D^{20} 1.4332, d_4^{20} 0.9338. The IR spectra and the constants of the compounds prepared by the three methods agreed completely.

Preparation of $(CH_3)_3 SiOP (OC_2H_5)_2$

<u>From Bromotrimethylsilane and Sodium Diethyl Phosphite.</u> The reaction and all succeeding operations were conducted in an atmosphere of dry oxygen-free nitrogen. 22 g of bromotrimethylsilane was added dropwise with vigorous stirring to a solution of $(C_2H_5O)_2P(O)$ Na prepared from 3.35 g of sodium and 20 g of $(C_2H_5O)_2POH$ in 150 ml of dry ether. Stirring was continued further for 1 h, the precipitate was filtered off and washed with two 30-ml portions of dry ether, solvent was driven off, and the residue was vacuum-distilled. We obtained 16.8 g (55.2%) of $(CH_3)_3SiOP(OC_2H_5)_2$, b.p. 60-62° (11 mm), n_D^{20} 1.4116; d_4^{20} 0.9485. Found %: C 40.0, 40.2; H 9.02, 9.21; P+Si 27.7, 27.9. $C_7H_{19}O_3PSi$. Calculated %: C 40.1; H 9.05; P+Si 28.1.

<u>From Sodium Trimethylsilanolate and Diethyl Phosphorochloridite.</u> The reaction was conducted in an atmosphere of nitrogen. With stirring and cooling to between -20 and -30° , 7.85 g of ClP(OC₂H₅)₂ was added dropwise to a solution of $(CH_3)_2SiONa$ prepared by the gradual addition of a mixture of $(CH_3)_3SiOH$ and $[(CH_3)_3Si]_2O$ to 1.15 g of sodium in 100 ml of dry ether until complete solution occurred. The mixture was stirred for 1 h at room temperature, the precipitate was filtered off and washed with two 25-ml portions of dry ether, solvent was driven off, and the residue was vacuum-fractionated. We obtained 5.6 g (53.4%) of $(CH_3)_3SiOP(OC_2H_5)_2$, b.p. 59-61° (11 mm), nD²⁰ 1.4115, d4²⁰ 0.9493. The IR spectra of the compounds prepared by the two methods were identical.

Preparation of $C_2H_5PO[OSi(C_2H_5)_3]OC_2H_5$

A mixture of 12.6 g of $(C_2H_5)_3$ SiOP $(OC_2H_5)_3$ and 5.5 g of C_2H_5 Br was heated in a sealed tube at 150° for 6 h. In the fractionation of the reaction mixture we isolated 4.1 g (32.5%) of C_2H_5 PO $[OSi(C_2H_5)_3]OC_2H_5$, b.p. 117-121° (2 mm), n_D^{20} 1.4394, d_4^{20} 0.9678 (according to [1]: b.p. 158-159° at 10 mm, n_D^{20} 1.4390, d_4^{20} 0.9659). Found %: C 48.2, 48.4; H 10.1, 10.0; P+Si 23.9, 23.7. $C_{10}H_{25}O_3$ PSi. Calculated %: C 47.8; H 9.93; P+Si 23.4.

Preparation of $C_2H_5PO[OSi(CH_3)_3]OC_2H_5$

A mixture of 8.5 g of $(CH_3)_3SiOP(OC_2H_5)_2$ and 3 g of C_2H_5Br was heated in a sealed tube at 150° for 6 h. The tube was opened, and its contents were fractionated. We obtained 3.6 g (42.3%) of $C_2H_5PO[OSi(CH_3)_3] \cdot OC_2H_5$, b.p. 85-88° (11 mm), n_D^{20} 1.4155, d_4^{20} 0.9947. Found %: C 39.8, 40.1; H 9.19, 9.10; P+Si 27.9, 27.7. $C_7H_{19}O_3P$. Calculated %: C 40.1; H 9.05; P+Si 28.1.

Preparation of $(C_2H_5)_3$ SiOPS $(OC_2H_5)_2$

In an atmosphere of nitrogen 1.6 g of sulfur powder was added in portions to a solution of 12.6 g of $(C_2H_5)_3SiOP(OC_2H_5)_2$ in 50 ml of dry petroleum ether, and the mixture was stirred until solution was complete. Petroleum ether was driven off, and the residue was vacuum-distilled. We obtained 13 g (91.5%) of $(C_2H_5)_3SiOPS(OC_2H_5)_2$, b.p. 89-90° (2 mm), n_D^{20} 1.4540, d_4^{20} 1.0129. Found %: C 42.2, 42.0; H 9.06, 9.16; S 11.9, 11.7. $C_{10}H_{25}O_3PSSi$. Calculated %: C 42.3; H 8.81; S 11.3.

Preparation of $(CH_3)_3 SiOPS (OC_2H_5)_2$

By the procedure of the preceding experiment from 10.5 g of $(CH_3)_3SiOP(OC_2H_5)_2$ and 1.6 g of sulfur we obtained 10.5 g (87%) of $(CH_3)_3SiOPS(OC_2H_5)_2$, b.p. 56-57° (1.5 mm), n_D^{20} 1.4433, d_4^{20} 1.0261 (according to [15]: b.p. 96-97° at 12 mm, n_D^{20} 1.4430, d_4^{20} 1.027). Found %: S 13.6, 13.4. $C_7H_{19}O_3PSSi$. Calculated %: S 31.2.

Isomerization of (CH_3) SiOPS $(OC_2H_5)_2$

A mixture of 11.5 g of $(CH_3)_3 SiOPS_3 (OC_2H_5)_2$ and about 2 g of C_2H_5Br was heated in a sealed tube at 150° for 70 h. In the fractionation we isolated 4.9 g of unchanged $(CH_3)_3 SiOPS (OC_2H_5)_2$ and 6.3 g (54.7%) of the isomerization product, b.p. 118.5–119.5° (14 mm), n_D^{20} 1.4495, d_4^{20} 1.0505. Found %: S 13.1, 13.5. $C_7H_{19}O_3PSSi$. Calculated %: S 13.2.

CONCLUSIONS

1. The reaction of bromotriethylsilane with triethyl phosphite at high temperatures (155-180°) goes with formation mainly of silyl-substituted tervalent phosphorus derivatives, which readily combine with sulfur and undergo Arbuzov reaction with ethyl bromide.

2. In the reactions of trialkylhalosilanes with sodium diethyl phosphite the products are not quinquevalent phosphorus compounds containing the Si-P bond as was supposed earlier, but the isomeric tervalent phosphorus compounds containing the Si-O-P link.

3. The thione-thiol isomerization of Si-P was effected in presence of ethyl bromide.

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