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SYNTHESIS AND STUDY OF THE THERMAL STABILITY OF SILICON-CONTAINING ESTERS OF PHOSPHORUS ACIDS.

4. THERMAL REARRANGEMENT OF TRIMETHYLSILYLMETHYL ESTERS OF PHOSPHORUS ACIDS

M. I. Kabachnik, L. S. Zakharov, G. N. Molchanova, T. D. Drozdova, and P. V. Petrovskii

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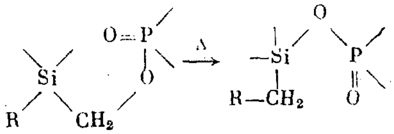
NMR spectroscopy has been used to study the thermal rearrangement of siliconeopentyl esters of phosphorus acids $Me_3SiCH_2OP(O)R_2$ (I, R = CF_3CH_2O, PhO, t-$BuCH_2O$, Bu). It has been established that in all cases the products of the rearrangement are the respective silyl esters $Me_2EtSiOP(O)R_2$ (II). The thermal rearrangement of $(Me_3SiCH_2O)_2P(O)OR'$ (III, R' = Ph, t-$BuCH_2$, Me_3SiCH_2) is similar. It has been shown that electronic and steric attributes of the substituents R and R' on the phosphorus atom are practically without effect on the extent of the thermal rearrangement. The presence of acidic additives, and initiators and inhibitors of radical reactions did not significantly influence the course of the rearrangement. It was concluded that this rearrangement apparently takes place as a result of heterolysis of the C—OP bond and simultaneous nucleophilic attack on the silicon atom by the phosphoryl part of the molecule.

We have previously described the thermal rearrangement of triorganosilylmethyl esters of phosphorus acids into the corresponding silyl esters:



It was shown that several other radicals behaved similarly to the methyl group in having a tendency to migrate from the silicon atom to the methylene carbon by a type of 1,2-shift. The effect of the type of radical on the silicon atom on the rate of the rearrangement was studied and it was suggested that the phosphoryl part of the molecule made a significant nucleophilic contribution to the rearrangement [1, 2].

In the present work experiments have been carried out to evaluate the effect of the substituents on the phosphorus atom on the course of the rearrangement. It should be noted here that the electronic influence of the substituent on the phosphorus atom can simultaneously affect both the strength of the CH_2—OP bond, i.e., its susceptibility to heterolytic cleavage, and also the nucleophilicity of the phosphoryl oxygen and accordingly its tendency

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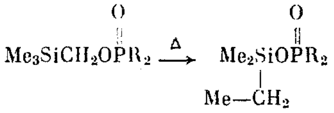
to nucleophilic attack on the silicon. This being so, the reaction rate must depend on both factors.

We have made a comparative study of the extent of the rearrangement of a series of monosiliconeopentyl esters of a phosphorus acid $Me_3SiCH_2OP(O)R_2$ (Ia-d) with a selection of substituents differing considerably in their electronic effect (in terms of the constant δ^{Φ}): R = CF_3CH_2O (0.51) (Ia), PhO (−0.06) (Ib), Me_3CCH_2O (0.29) (Ic), Bu (−1.22) (Id).

The esters (Ia, d) were prepared by phosphorylation of trimethylsilylmethanol by the corresponding phosphorus acid chloride in the presence of triethylamine. The preparation of the phosphates (Ib, c) and their thermal rearrangement was described in [1].

Thermolysis of the esters (Ia-d) was carried out under standard conditions [1] such as to produce quite a high degree of conversion (200°C, 5 h).

The phosphate (Ia) which contains the strong electron-accepting trifluoroethoxy group and the phosphinate (Id) with the strong electron-donating butyl radical underwent rearrangement in the thermolysis process in the same way as the previously studied phosphates (Ib, c) into the corresponding silyl esters (IIa-d):



$$Me_3SiCH_2O\overset{O}{\overset{\|}{P}}R_2 \xrightarrow{\Delta} \underset{\substack{|\\ Me-CH_2}}{Me_2Si}O\overset{O}{\overset{\|}{P}}R_2$$

(Ia—d) (IIa—d)

R = CF_3CH_2O (a), OPh (b), Me_3CCH_2O (c), Bu (d).

In the PMR spectrum of the pyrolysate of phosphate (Ia), in addition to the signals from the protons of the starting material there is a singlet from the protons of the methyl radical of the rearranged phosphate (IIa) in the region of 0.28 ppm and a characteristic signal for the ethyl group (0.92 ppm, m; 1.19 ppm, m). There is a corresponding reduction in the intensity of the proton signals from the $SiCH_2O$– and $(CH_3)_3Si$– groups. The ^{31}P spectrum of the pyrolysate of ester (Ia) also shows a signal from the initial phosphate (−1.07 ppm) and a signal at −11.32 ppm evidently corresponding to the rearrangement product (IIa).

Similarly, the PMR spectrum of the pyrolysate of the phosphinate (Id) shows, in addition to signals from the protons of the starting material, an additional signal from methyl protons in the 0.48 ppm region and proton signals from the ethyl group (0.94 ppm, m; 1.24 ppm, m) of the rearranged silylphosphinate (IId). In the ^{31}P NMR spectrum of the pyrolysate of ester (Id) a signal from the original phosphinate is also observed at 55.77 ppm together with a signal from the product of the rearrangement (IId) in the 46.36 ppm region.

Quantitative comparison of the extent of the conversion of the esters (Ia-d) from the results of PMR spectroscopy (Table 1) show that the difference in the rate of rearrangement of esters with different substituents on the phosphorus atom is relatively small, there being no correlation between the extent of the rearrangement and the electronic nature of the substituent on the phosphorus atom. In all probability this can be connected with the fact that the effect of the substituent on the strength of the C—OP bond and on the nucleophilicity of the phosphoryl oxygen approximately compensate each other. Some reduction in the rate of migration of the methyl group of phosphate (Ia) is probably explained by the fact that in the presence of acceptor trifluoroethoxy groups in the molecule the reduced tendency of the phosphoryl oxygen atom to nucleophilic attack on silicon determines the rate of the rearrangement to a greater extent than does the heterolysis of the C—OP bond; this also indirectly supports the hypothesis which we expressed previously on the significant role of nucleophilic assistance to the rearrangement by the phosphoryl part of the molecule.

TABLE 1. Thermolysis of Siliconeopentyl Esters of Phosphorus Acids $Me_3SiCH_2OP(O)R_2$ (Ia-d) and $(Me_3SiCH_2O)_2P(O)OR'$ (IIIa-c) (200°C, 5 h)

Extent of rearrangement from NMR results, %						
(Ia)	(Ib)	(Ic)	(Id)	(IIIa)	(IIIb)	(IIIc)
36	58	59	46	54*	59*	59*

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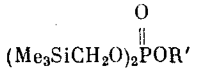
*Calculated on overall number of siliconeopentyl groups.

TABLE 2. Thermolysis of Diphenyl(trimethylsilylmethyl) Phosphate (Ib) in the Presence of 1 mole % of Different Additives (200°C, 5 h)

Medium	Additive	Extent of rearrangement from NMR results, %
Air	–	59
	H_3PO_4	56
Argon	–	58
	H_3PO_4	55
	Hydroquinone	58
	Azobisisobutyronitrile	57

It should also be noted that for compounds (IIIa-c)[*] which contain several siliconeopentyl substituents, the rate of migration of the methyl groups (Table 1) is practically independent of the number of quite bulky neopentyl and siliconeopentyl fragments in the molecule [cf. (Ib, c)]



$$(Me_3SiCH_2O)_2\overset{\overset{O}{\|}}{P}OR'$$

(IIIa–c)

$R' = Me_3SiCH_2$ (a), Ph (b), Me_3CCH_2 (c).

A heterolytic mechanism for the rearrangement would in principle permit acid catalysis. We examined the effect of H_3PO_4 on the thermolysis of the phosphate (Ib) which has only one siliconeopentyl group available for rearrangement. Thermolysis was carried out at 200°C in the presence of 1 mole % H_3PO_4 in air and in argon. However, we did not succeed, at least within the limits of accuracy of the NMR method, in recording any acid catalysis of the rearrangement; independently of the conditions of the thermolysis, the extent of the rearrangement remained practically the same (Table 2) – after 5 h, 55-59% rearranged phosphate (IIb) was formed.

Since the extent of the rearrangement was independent of electronic and steric attributes of the substituent on the phosphorus atom, and was not susceptible to acid catalysis, we were prompted to consider a homolytic route as a possible alternative mechanism. We have, however, established that rearrangement of the phosphate (Ib) in the presence of either an inhibitor or an initiator of free radical reactions (hydroquinone and azobisisobutyronitrile, respectively) proceeds at 200°C at approximately the same rate (within the limits of experimental error, ~5%) as in the absence of any additive (Table 2). Thus, in all cases, after a 5 h reaction 55-58% of the rearranged phosphate (IIb) was formed. The extent of the rearrangement was also independent of the medium (air or argon) in which the thermolysis was carried out (Table 2). From these results one can confidently exclude a free radical mechanism for the rearrangement.

Thus, on the basis of the results obtained, one can conclude that rearrangement of siliconeopentyl esters of phosphorus acids, consisting in migration of radicals from the silicon atom to the methylene carbon with the formation of the corresponding silyl ester, evidently proceeds by thermal heterolysis of the C–OP bond and simultaneous nucleophilic attack on silicon by the phosphoryl part of the molecule. In the course of the rearrangement, no significant effect is produced by the environment of the phosphorus atom, or by the presence of acidic additives, or initiators or inhibitors of free radical reactions.

EXPERIMENTAL

A Bruker WP 200SY instrument was used to obtain PMR and ^{31}P NMR spectra. The internal standard for the ^{31}P NMR spectra was 85% H_3PO_4.[†]

Di-(2,2,2-trifluoroethyl)(trimethylsilylmethyl)phosphate (Ia). To a mixture of 10.4 g (0.10 mole) trimethylsilylmethanol and 11.1 g (0.11 mole) Et_3N in 50 ml dry CCl_4 was added, with stirring and cooling in water, 28.0 g (0.10 mole) di-(2,2,2-trifluoroethyl)chlorophos-

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[*] Preparation and qualitative results will be found in [1].

[†] A positive value of the chemical shift denotes a shift of the signal downfield relative to the standard.

phate in 50 ml CCl_4. It was stirred for 2 h and left to stand for 12 h. The deposit of triethylamine hydrochloride was filtered off and washed with hexane and the filtrate passed through a layer of alumina. After distilling off the solvent and redistillation in vacuum, there was obtained 26.4 g (75.6%) (Ia), bp 66-67°C/1 mm, n_D^{20} 1.3660, d_4^{20} 1.2724. Found, %: C 27.5, H 4.4, F 32.5, P 8.9. $C_8H_{15}F_6O_4PSi$. Calculated, %: C 27.5, H 4.3, F 32.7, P 8.9. PMR spectrum ($CDCl_3$, δ, ppm): 0.08 s (CH_3), 3.77 d ($SiCH_2O$, J_{H-P} = 5.8 Hz), 4.28 m (CF_3CH_2, J_{H-P} = 8.1, J_{H-F} = 8.1 Hz). ^{31}P NMR spectrum (δ, ppm): −0.57 s.

Dibutyl(trimethylsilylmethyl)phosphinate (Id) was prepared in a similar manner to (Ia) from 3.4 g (0.033 mole) trimethylsilylmethanol, 5.9 g (0.030 mole) dibutylchlorophosphinate, and 3.3 g (0.033 mole) triethylamine in 50 ml dry CH_2Cl_2 to yield 2.5 g (31.5%) (Id), bp 103-105°C/1 mm, n_D^{20} 1.4472, d_4^{20} 0.9227. Found, %: C 54.4, H 11.0, P 11.5, Si 10.4. $C_{12}H_{24}O_2PSi$. Calculated, %: C 54.5, H 11.1, P 11.7, Si 10.6. PMR spectrum ($CDCl_3$, δ, ppm): 0.32 s (CH_3Si), 1.16 t (CH_3C), 1.66-1.80 m ($CH_2CH_2CH_2$), 3.83 d (OCH_2, J_{H-P} = 6.4 Hz). ^{31}P NMR spectrum (δ, ppm): 53.0 s.

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REACTIONS OF ORGANYLHALOSILANES WITH 1,1,3,3-TETRA- AND HEXAMETHYLDISILAZANE

S. V. Basenko, I. A. Gebel', D. D. Toryashinova,
V. Yu. Vitkovskii, R. G. Mirskov, and M. G. Voronkov

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Organylchlorosilanes, and also $SiCl_4$, decompose 1,1,3,3-tetra- and hexamethyldisilazanes with formation of hitherto unknown organylchlorosilazanes of general formulas $R_{4-n}SiCl_{n-1}NHSiH(CH_3)_2$ and $R_{4-n}SiCl_{n-1}NHSi(CH_3)_3$ (n = 2-4) in yields of 54-98%. The IR and mass spectra of the prepared compounds were studied.

Earlier we investigated the reaction of diorganyldifluoro and organyltrifluorosilanes with hexamethyldisilizane [1]. We have found that under the described conditions organylchlorosilanes are more reactive and enable one to prepare hitherto unknown organylchlorosilazanes (I)-(VII) in high yields (Table 1).

$$R_{4-n}SiCl_n + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow \underset{(I)-(VII)}{R_{4-n}SiCl_{n-1}NHSi(CH_3)_3} + ClSi(CH_3)_3$$

$$R = H;\ n = 3\ (I);\quad R = ClCH_2,\ CH_3,\ n = 2\ (II);$$
$$R = C_2H_5,\ n = 3\ \ (III);\quad R = CH_2{-}CH,\ n = 3\ \ (IV);$$
$$R = C_6H_5,\ n = 3\ \ (V);\quad R = ClCH_2,\ n = 3\ \ (VI);\quad n = 4\ (VII).$$

Substitution of a second chlorine atom for a $(CH_3)_3SiNH$ group proceeds more difficultly. Thus, $(C_6H_5)ClSi[NHSi(CH_3)_3]_2$ (VIII) is formed in the reaction of phenyltrichlorosilane with an excess of hexamethyldisilazane in a yield of only 5-7%.

On reacting hexamethyldisilazane with $BrSiCl_3$, reaction only takes place at the Si−Br bond.

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