CHEMISTRY

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Fig. 1 and Fig. 2 chromatograms

Figure 1: Fig. 1 and Fig. 2 chromatograms

Abstract

Full Text

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INTERACTION OF DIALKYLAMIDES OF DIALKYLPHOSPHOROUS ACID WITH ALDEHYDES

(Presented by Academician M. I. Kabachnik on 14 XI 1964)

Studies of recent years show that derivatives of trivalent phosphorus containing a P—N bond are acquiring considerable interest as starting materials for the synthesis of substances containing tri- and pentavalent phosphorus (^{1}-^{4}).

In the present work the interaction of dialkylamides of dialkylphosphorous acid with aldehydes was studied. In considering this reaction

Fig. 1

Fig. 2

Fig. 1. Chromatogram of O,O-dipropyl diethylaminomethylphosphonate: *1* —obtained by the reaction under study, R_f 0.395; *2* —obtained according to (^{9}), R_f 0.402. Support: Al_2O_3; mobile phase —absolute ether; developer —iodine; temperature 20°.

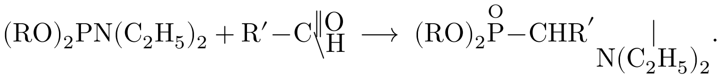
Fig. 2. Chromatogram of O,O-dipropyl-α-diethylaminoheptylphosphonate: *1* —obtained by the reaction under study in the presence of water, R_f 0.641; *2* —obtained according to (^{8}), R_f 0.655; *3* —obtained by the reaction under study, R_f 0.655. Chromatogram of O,O-dipropyl-α-oxyheptylphosphonate: *4* —obtained by the reaction under study in the presence of water, R_f 0.072; *5* —obtained according to (^{10}), R_f 0.072. Support: Al_2O_3; mobile phase —absolute ether; developer —iodine; temperature 23°.

it could be assumed that ether-amides would react with aldehydes in the same way as full esters of phosphorous acid, i.e., with the formation of α-alkoxyphosphinic acids (^{5}), or by addition of the aldehyde molecule, as is observed in the case of the use of hexaalkyltetramide of phosphorous acid (^{6}), or with formation of the corresponding phosphate and olefin (^{7}).

Experiments showed that when a mixture of an amide of phosphorous acid and an aldehyde, for example heptanal, is heated to 100–110°, the reaction mixture spontaneously heats to 160–180°. In the reaction products there was found a low-boiling fraction (about 15%) containing no nitrogen, probably consisting mainly of trialkyl phosphite, since after treatment with sulfur a trialkyl thiophosphate was isolated in 56% yield, and a high-boiling fraction containing nitrogen and soluble in acids.

In the IR spectrum an absorption band is observed in the region of 1250 cm^{-1}, characteristic of the phosphoryl bond. Potentiometric titration gives a molecular-weight value in satisfactory agreement with that calculated for α-dialkylaminophosphonates. For example, for O,O-dipropyl α-diethylaminoheptylphosphonate the molecular weight found was 343, 346; calculated, 335.

On the basis of the data obtained, it could be assumed that the reaction of dialkyl esters of dialkylamides of phosphorous acid with aldehydes indeed proceeds with formation of α-aminophosphonates



$$(\mathrm{RO})_2\mathrm{PN}(\mathrm{C}_2\mathrm{H}_5)_2 + \mathrm{R}'-\mathrm{C}\begin{matrix}\|\mathrm{O}\\ \backslash\mathrm{H}\end{matrix} \longrightarrow (\mathrm{RO})_2\overset{\mathrm{O}}{\mathrm{P}}-\underset{\mathrm{N}(\mathrm{C}_2\mathrm{H}_5)_2}{\mathrm{CHR}'}.$$

Fig. 3. IR spectrum (NaCl) of O,O-dipropyl-(α-diethylaminoheptyl)-phosphonate

In order to prove the structure of the substances obtained, we carried out a counter-synthesis of these products by (^{8,9}). The identity of the compounds obtained was established by thin-layer chromatography on aluminum oxide ($\mathrm{Al}_2\mathrm{O}_3$ —neutral, activity grade II, passed through a 100-mesh sieve) (Figs. 1 and 2) and by comparison of their IR spectra, which coincided completely (Fig. 3). In addition, for formaldehyde derivatives the identity was confirmed by comparison of the melting points of their oxalates.

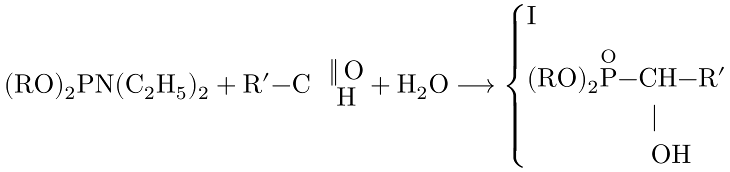
Thus, it may be asserted that the reaction of dialkylamides of dialkylphosphorous acid with aldehydes leads not to the products obtained by V. Abramov (^{5}) or W. Mark (^{6}), but to the formation of α-aminophosphonates.

However, the synthesis of the latter in the reaction under consideration might occur not through direct interaction of the aldehyde and the amidophosphite, but as a result of traces of water entering the reaction mass and the consequent hydrolysis of the dialkyl phosphite and dialkylamine. In this case, the synthesis of aminophosphonates could proceed by the method of M. I. Kabachnik (^{8}):

$$(\mathrm{RO})_2\mathrm{POH} + \mathrm{HN}(\mathrm{C}_2\mathrm{H}_5)_2 + \mathrm{R}'\mathrm{C}\begin{matrix}\|\mathrm{O}\\ \backslash\mathrm{H}\end{matrix} \longrightarrow \mathrm{I} + \mathrm{HOH}.$$

This assumption was ruled out by specially designed experiments. Thus, in the reaction of the dialkylamide of dialkylphosphorous acid with heptanal in the presence of 0.5-equimolar or equimolar amounts of water, a sharp decrease (almost twofold) in the yield is observed···

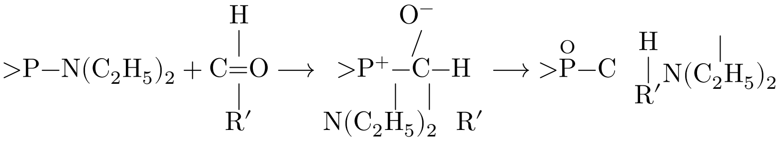
hydrolysis of the aminophosphonate and the simultaneous formation of the α-hydroxyethylphosphonate:



$$(RO)_2PN(C_2H_5)_2 + R'-C\overset{O}{\underset{H}{\|}} + H_2O \longrightarrow \begin{cases} I \\ (RO)_2\overset{O}{P}-\underset{\underset{OH}{|}}{CH}-R' \end{cases}$$

The constants, as well as the data from chromatography on aluminum oxide, for the latter agreed well with those for the α-hydroxyethylphosphonate obtained by a known method (10).

The formation of α-aminophosphonates in the reaction of dialkylamides of dialkylphosphorous acid with aldehydes can be represented by the following scheme:



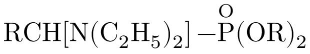
$$>P-N(C_2H_5)_2 + \overset{\overset{H}{|}}{\underset{\underset{R'}{|}}{C}}=O \longrightarrow >P^+-\overset{\overset{O^-}{/}}{\underset{\underset{R'}{|}}{C}}-H \longrightarrow >\overset{O}{P}-C\overset{H}{\underset{R'}{|}}N(C_2H_5)_2$$

It is not excluded that the first step of the reaction may be interaction at the free electron pair of nitrogen.

The constants and analytical data for the aminophosphonates obtained are presented in Table 1.

Table 1

α-Aminophosphonates of the type



$$RCH[N(C_2H_5)_2]-\overset{O}{P}(OR)_2$$

No.	R	R′	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Yield, %
1	C_3H_7	H	83-84 (1)	1.4370	–	–	–	9

No.	R	R′	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Yield, %
2	C_3H_7	C_3H_7	58-59 (0.03)	1.4421	0.9539	81.61	81.66	36
3	C_3H_7	C_6H_{13}	83-84 (0.05)	1.4464	0.9386	95.12	95.51	50
4	C_4H_9	C_6H_{13}	93-95 (0.05)	1.4466	0.9306	104.66	104.75	53
5	C_3H_7	C_6H_5	90-91 (0.04)	1.4929	1.0251	92.62	91.91	29

(continued)

No.	Found, % C	Found, % H	Found, % P	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % P	Calculated, % N
1	–	–	–	–	–	–	–	–	–
2	57.60	10.83	10.35	4.64	$C_{14}H_{32}NO_3P$	57.35	10.92	10.57	4.78
2	57.46	10.99	10.46	4.55	$C_{14}H_{32}NO_3P$	57.35	10.92	10.57	4.78
3	60.60	11.10	9.43	4.44	$C_{17}H_{38}NO_3P$	60.9	11.3	9.26	4.18
3	60.7	11.07	9.51	4.44	$C_{17}H_{38}NO_3P$	60.9	11.3	9.26	4.18
4	63.21	11.94	8.30	3.95	$C_{19}H_{42}NO_3P$	62.9	11.56	8.53	3.86
4	62.92	11.70	8.26	4.03	$C_{19}H_{42}NO_3P$	62.9	11.56	8.53	3.86
5	62.18	9.31	9.76	4.15	$C_{17}H_{30}NO_3P$	62.4	9.17	9.5	4.28
5	62.26	9.37	9.83	5.0	$C_{17}H_{30}NO_3P$	62.4	9.17	9.5	4.28

Experimental Part

1. O,O-Dialkyl-α-diethylaminoalkyl-(aryl)-phosphonates. Typical procedure. A mixture of equimolar amounts of the amidophosphite and aldehyde is heated for 15-20 min* at 100-120°; the light fraction (15%) is distilled off, the residue is dissolved in a small excess of 10% HCl solution, the solution is washed with ether, made alkaline with 10% KOH, the separated oil is extracted with ether, the extract is dried over $MgSO_4$, the ether is removed, and the residue is distilled.

2. Reaction of dipropyl amidophosphite with heptanal in the presence of water. The procedure is analogous to that described above. From the extract of the acidic solution, O,O-dipropyl-α-hydroxyheptylphosphonate is obtained. Yield 20%. B.p. 98° (0.001), n_D^{20} 1.4430, d_4^{20} 1.0044.

$C_{13}H_{29}O_4P$. Found, %: C 55.3; 56.23; H 10.70; 10.68; P 10.68
Calculated, %: C 55.75; H 10.35; P 11.0

In parallel, O,O-dipropyl-α-hydroxyheptylphosphonate was obtained by the usual method from dipropyl phosphite and heptanal. B.p. 98° (0.001), n_D^{20} 1.4426.

From the extract of the alkaline solution, O,O-dipropyl diethylaminoheptylphosphonate is obtained. Yield 30%.

3. Oxalate of O,O-dipropyl-(diethylaminomethyl)-phosphonate. To 1.63 g of O,O-dipropyl-(diethylaminomethyl)-phosphonate in 5 ml of abs. ether is added a solution of 0.59 g of anhydrous oxalic acid in 5 ml of abs. ether. The precipitate formed is triturated several times with fresh portions of absolute ether and kept at 0–3° for about 60 h. This gives 1.55 g (70%) of a substance with m.p. 61–63°. Oxalate from the aminophosphonate obtained according to (9): m.p. 62–64°. Mixed sample: m.p. 62–64°.

$C_{13}H_{28}NO_7P$. Found, %: C 45.01; H 8.35; P 8.46; N 3.88
Calculated, %: C 45.65; H 8.22; P 9.08; N 4.11

4. Tripropyl thiophosphate. To 10.0 g of the light fraction obtained in the reaction of diethylamide of dipropylphosphorous acid with heptanal, 1.54 g of powdered sulfur is added and, after self-heating ceases, the mixture is heated for a further 2 h at 100–130° and distilled. This gives 6.45 g (56%) of substance. B.p. 85° (1 mm), n_D^{20} 1.4510.

Found, %: C 45.70; 45.74; H 9.53; 9.22; P 12.31; 12.54; S 13.33; 13.04
Calculated, %: C 45.15; H 8.95; P 12.9; S 13.35

Lit. (11): b.p. 123.5–124.5° (10 mm), n_D^{20} 1.4502.

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* In the case of paraform, heating is continued until the latter dissolves; in the case of benzaldehyde, heating is carried out for several hours until the n_D^{20} of the reaction mass no longer changes.

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

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