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Soviet-era science, translated into English

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1964

SovietRxiv

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**Abstract**

**Full Text**

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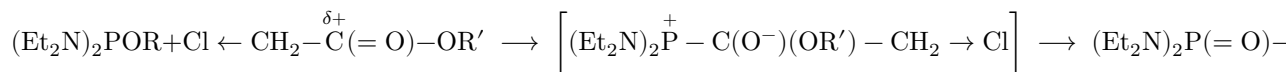
**REARRANGEMENT OF AMIDO ESTERS OF PHOSPHOROUS ACIDS IN REACTIONS WITH  $\alpha$ -HALOCARBONYL COMPOUNDS. ACTION OF ESTERS OF MONOCHLOROACETIC ACID ON DI-(DIETHYL)-AMIDOALKYL ESTERS OF PHOSPHOROUS ACID**

*(Presented by Academician B. A. Arbuzov on 26 IX 1963)*

Amidoalkyl esters of phosphorous acid, by their chemical nature, are analogous to full esters of phosphorous acid, and in their behavior in reactions they largely reproduce the reactions of phosphites. Thus amidoalkyl esters, like phosphites, add monohalide salts of copper; with alkyl halides they undergo the Arbuzov rearrangement <sup>(1)</sup>; and they react with aldehydes and ketones analogously to esters of phosphorous acid <sup>(2)</sup>.

Of particular interest is the reaction of amidoalkyl esters of phosphorous acid with  $\alpha$ -halo-substituted aldehydes and ketones. This reaction, like the reaction of phosphites with  $\alpha$ -halo-substituted aldehydes and ketones <sup>(3)</sup>, proceeds with rearrangement and leads to the formation of vinyl esters of amidophosphates <sup>(4)</sup>. It was to be expected that other  $\alpha$ -halo-substituted carbonyl compounds should react analogously. The investigation carried out by us showed that esters of monochloroacetic acid react with di-(diethyl)-amidoalkyl esters of phosphorous acid with evolution of heat and liberation of the alkyl halide corresponding to the ester radical of the di-(diethyl)-amidoalkyl phosphite.

As a result of the reaction,  $\alpha$ -alkoxyvinyl esters of di-(diethyl)-amidophosphates are obtained. The reaction of formation of the latter, by analogy with the reaction of chloral with phosphites, as interpreted by Karash and Bengelsdorf <sup>(5)</sup>, may be represented by the scheme:



OR

It must be assumed that in the course of the reaction intermediate formations are produced which split off a chlorine ion. The latter, attacking the radical of the ester group at phosphorus, gives the alkyl halide with simultaneous transformation of the remaining part of the molecule into the  $\alpha$ -alkoxyvinyl ester of di-(diethyl)-amidophosphate, which may also be regarded as mixed acetals of acrolein.

The  $\alpha$ -alkoxyvinyl esters of di-(diethyl)-amidophosphates obtained are colorless, readily mobile liquids, the constants of which are presented in Table 1.

Table 1

$\alpha$ -Alkoxyvinyl esters of di-(diethyl)-amidophosphates  $[(C_2H_5)_2N]_2P(O)O-C(OR)=CH_2$

Run No.	R	B.p., °C	Yield, %	$d_4^{20}$	$n_D^{20}$	$MR_D$ , found	$MR_D$ , calc.	Empirical formula	Phosphorus, % found	Phosphorus, % calc.
1	$CH_3$	176 — 177 (10)	50.0	1.0522	1.4675	69.69	70.76	$C_{11}H_{23}N_2O_3P$	11.69	11.74
2	$C_2H_5$	176 — 177 (7)	71.0	1.0312	1.4652	74.55	75.38	$C_{12}H_{27}N_2O_3P$	11.90	11.15
3	$C_2H_5$	177 — 178 (7)	78.0	1.0308	1.4648	74.53				
4	$n-C_3H_7$	180 — 182 (7)	63.0	1.0130	1.4620	79.24	79.99	$C_{13}H_{29}N_2O_3P$	10.59	10.61
5	iso- $C_3H_7$	175 — 176 (6)	57.0	1.0100	1.4600	79.23	79.99	$C_{13}H_{29}N_2O_3P$	10.58	10.61
6	$n-C_4H_9$	189 — 190 (7)	50.0	1.0075	1.4646	83.90	84.61	$C_{14}H_{31}N_2O_3P$	10.16	10.13
7	$n-C_4H_9$	189 — 190 (7)	60.0	1.0087	1.4652	83.90				
8	$n-C_5H_{11}$	194 — 196 (7)	60.0	1.0065	1.4680	88.51	89.23	$C_{15}H_{33}N_2O_3P$	9.46	9.68
9	iso- $C_5H_{11}$	192 — 194 (8)	69.0	1.9945	1.4619	88.47	89.23	$C_{15}H_{33}N_2O_3P$	9.50	9.68

$\alpha$ -Ethoxyvinyl ester of di-(diethyl)-amidophosphate is obtained from ethyl chloroacetate and from both di-(diethyl)-amidoethyl ester (I) and di-(diethyl)-amidobutyl ester of phosphorous acid (II) (runs Nos. 3 and 2); and  $\alpha$ -butoxyvinyl ester of di-(diethyl)-amidophosphate is obtained from butyl chloroacetate from both I and II (runs Nos. 6 and 7), respectively. The preparation of one and the same substance from different esters confirms the proposed reaction scheme.

$\alpha$ -Alkoxyvinyl esters of di-(diethyl)-amidophosphates readily add bromine quantitatively in the cold. The addition products are heavy, glycerol-like liquids.

The reactivity of the compounds obtained is being studied.

## Experimental Part

The action of mono-chloroacetic acid esters on di-(diethyl)-amidoalkyl esters of phosphorous acid.

0.05 gram-mole of a monochloroacetic ester was slowly added to an equimolecular amount of a di-(diethyl)-amidoalkyl ester of phosphorous acid. The latter reacts with methyl and ethyl monochloroacetates with an increase in temperature. With an increase in the alkyl radical of the esters, the intensity of the reaction decreases. After addition, the reaction mixture was heated on a water bath, in different experiments at 60–95° for 2–4 h. Then, at ordinary pressure, the alkyl halide was distilled off, and the residue was distilled under vacuum.

The properties of the  $\alpha$ -alkoxyvinyl esters of di-(diethyl)-amidophosphates obtained are presented in Table 2, and the experimental data are summarized.

Table 2

Run No.*	$[(C_2H_5)_2N]_2P(O)R$ R	$[(C_2H_5)_2N]_2P(O)R'$ g	$[(C_2H_5)_2N]_2P(O)R''$ R'	$[(C_2H_5)_2N]_2P(O)R'''$ g	Temperature rise on mixing, °C	Heating, °C	Heating, duration, h	Yield, g
1	$C_4H_9$	12.4	$CH_3$	5.4	20–50	–	–	6.8
2	$C_4H_9$	12.4	$C_2H_5$	6.2	20–30	60–70	3	10.2
3	$C_2H_5$	11.0	$C_2H_5$	6.2	20–40	60–70	3	10.9
4	$C_4H_9$	12.4	$C_3H_7$	6.8	insignificant	80–90	3	9.4
5	$C_4H_9$	12.4	iso- $C_3H_7$	6.8	«	80–90	2	8.5

Run No.*	$[(C_2H_5)_2P(O)R]_2CO_2R'$ g	$[(C_2H_5)_2P(O)R]_2CO_2R'$ g	$[(C_2H_5)_2P(O)R]_2CO_2R'$ g	Temperature rise on mixing °C	Heating, °C	Heating, duration, h	Yield, g
6	$C_4H_9$	12.4	$C_4H_9$	7.5	« 80–95	3	7.9
7	$C_2H_5$	11.0	$C_4H_9$	7.5	« 60–70	3	9.2
8	$C_4H_9$	12.4	$C_5H_{11}$	8.2	« 90–95	3	9.8
9	$C_2H_5$	11.0	iso- $C_5H_{11}$	8.2	« 70–85	3	11.0

In the fourth and eighth experiments, butyl chloride was isolated with constants satisfactorily coinciding with those in the literature, and in yields of 40 and 45%, respectively.

On the basis of the foregoing, the following conclusions may be drawn: di-(dialkyl)amidoalkyl esters of phosphorous acid readily enter into reaction with esters of monochloroacetic acid and form  $\alpha$ -alkoxyvinyl esters of di-(dialkyl)amidophosphates or mixed acetals of acrolein. A scheme for their formation has been proposed. New mixed acetals of acrolein, presented in Table 1, have been obtained.

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Received  
10 VII 1963

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

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