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N. A. RAZUMOVA, A. A. PETROV

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Abstract

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CHEMISTRY

N. A. RAZUMOVA, A. A. PETROV

CONDENSATION OF ACID CHLORIDES OF GLYCOLPHOSPHOROUS ACIDS WITH α,β-UNSATURATED KETONES

(Presented by Academician M. I. Kabachnik on 23 IV 1964)

Acid chlorides of 1,2- and 1,3-glycolphosphorous acids condense with diene hydrocarbons to form cyclic 1,4-adducts, which usually isomerize into β-chloroalkoxyphospholine oxides ([1,2]). In those cases where the Arbuzov rearrangement is impossible, the 1,4-adducts are the final products of the reaction ([3]). Similar condensations may also proceed with the participation of acid chlorides of thio- and dithioglycolphosphorous acids ([4]).

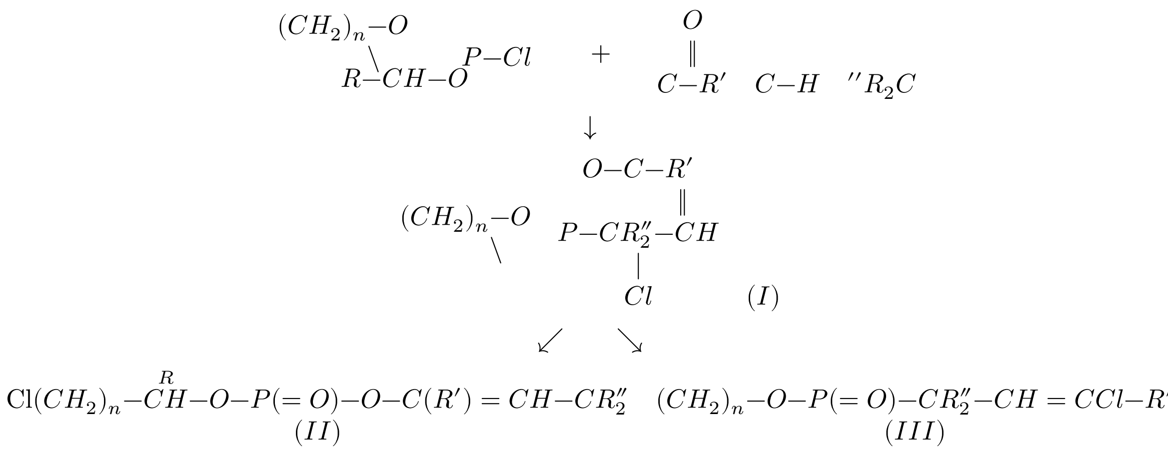
Continuing the study of cyclization reactions involving acid chlorides of glycolphosphorous acids, we have shown that they are capable of adding in the 1,4-position to α,β-unsaturated ketones with the formation of cyclic systems containing two heteroatoms—isoxaphospholines.

As a result of the condensation of acid chlorides of ethylene-, propylene-, and 1,3-butyleneglycolphosphorous acids with methyl vinyl ketone and mesityl oxide, products containing pentavalent phosphorus were obtained. They did not add oxygen or sulfur. The atomic refraction of phosphorus corresponded to the value characteristic of a pentavalent phosphorus atom (4.27). In the IR spectra of the condensation products, intense absorption was observed in the region of 1260 cm^{-1}, characteristic of the P = O group. Thus, it was established that the reaction proceeded with an Arbuzov rearrangement.

It could be assumed that the condensation proceeds with the formation of adducts of formula (I), which subsequently rearrange into products (II) or (III).

IR spectra

Figure 1: IR spectra



where $n = 1$ or 2, $R = H$ or CH_3, $R' = CH_3$, $R'' = H$ or CH_3.

The IR spectra spoke rather in favor of formula (II) than (III), since the bands of the valence vibrations of the double bond had frequencies too high to permit assuming the formation of compounds with a chlorine atom at the double bond (Fig. 1).

Fig. 1. IR spectra (layer thickness 20 μ): 1 —1-(2-chloroethoxy)-3-methylisoxaphospholine 3-oxide-1; 2 —1-(2-chloro-1-methylethoxy)-3-methylisoxaphospholine 3-oxide-1; 3 —1-(2-chloroethoxy)-3,5,5-trimethylisoxaphospholine 3-oxide-1; 4 —1-(2-chloro-2-methylethoxy)-3,5,5-trimethylisoxaphospholine 3-oxide-1.

Table 1

Substance	$(CH_3)_2C$	$CH_3-(CH)$	$CH_3-C=$	CH_2-P	CH_2-Cl	CH_2-O	$CH-O$	$CH=$
$CH_2Cl-CH_2-O-P(=O)(O-C(CH_3)-CH_2-CH=$	–	–	2,8	2,1 (2)	1,0 (3)	0,4 (3)	–	–0,9
$CH_2Cl-CH(CH_3)-O-P(=O)(O-CH_3)-CH_2-CH=$	–	3,4 (2)	3,0	2,3 (2)	1,0 (2)	–	0,2	–0,8
$CH_2Cl-CH_2-CH(CH_3)-O-P(=O)(O-C(CH_3)-CH_2-CH=$	–	3,5 (2)	2,9	2,25 (2)	1,1 (3)	–	0,2	–0,8
$CH_2Cl-CH_2-O-P(=O)-O-C(CH_3)=C(CH_3)_2-CH$	3,6 (2)	–	2,9	–	1,0 (3)	0,4 (3)	–	–0,7
$CH_2Cl-CH(CH_3)-O-P(=O)-O-C(CH_3)=C(CH_3)_2-CH$	3,5 (2)	3,4 (2)	2,9	–	1,1 (2)	–	0,2	–0,6

Fig. 2. NMR spectra

Figure 2: Fig. 2. NMR spectra

Substance	$(CH_3)_2C$	$CH_3-(CH)$	$CH_3-C=$	CH_2-P	CH_2-Cl	CH_2-O	$CH-O$	$CH=$
$CH_2Cl-CH_2-CH(CH_3)-O-P(=O)-O-C(CH_3)=C(CH_3)_2-CH$	3,5 (2)	3,4 (2)	2,8		1,1 (3)		0,2	−0,6

The final conclusion on the structure of the condensation products was made possible by proton magnetic resonance spectra. These spectra (Fig. 2) allow only one structure (II). The assignment of the chemical shifts is given in Table 1.

As can be seen from the data in this table, the signals in the spectra of all six substances strictly correspond to formula (II). In the spectra of the isoxaphospholines obtained from mesityl oxide, two signals are observed for the methyl groups of the isopropenyl grouping, owing to their nonequivalence. One of the peaks of the methyl-group signal in the ether residue is superimposed on the peak of the signal of the methyl groups of the isopropenyl grouping. The signals of methylene and methine groups bonded to oxygen are split owing to interaction with neighboring protons and the phosphorus atom (through oxygen). The splitting of the signals of the CH_2 groups bonded to phosphorus is due to their nonequivalence and to the influence of the phosphorus atom and of the neighboring proton.

The structure of the condensation products as isoxaphospholine derivatives was confirmed by converting one of them (obtained from mesityl oxide) by the action of PCl_5 into the previously described 1-chloroisoxaphospholine oxide (IV).

$$Cl-P(=O)\genfrac{}{}{0pt}{}{-O-C-CH_3}{-C(CH_3)_2-CH} \qquad \| \qquad (IV)$$

The substance was identified by its boiling point and by conversion into a crystalline anilide with the known melting point (124°).

1-Chloroisoxaphospholine-3-oxide (IV) was obtained as early as 1884 by Michaelis by the action of PCl_5 on acetone in the presence of $AlCl_3$; however, an incorrect formula was assigned to it ([5]). Later the formation of the same substance was observed upon treatment with acetic anhydride of the products of the reaction of PCl_3 with mesityl oxide ([6]). The structure and identity of the substances obtained by both methods were established by Anschütz ([7]).

Fig. 2. N.m.r. spectra: **1** –1-(2-chloroethoxy)-3-methylisoxaphospholine-3-oxide-1, **2** –1-(2-chloro-1-methylethoxy)-3-methylisoxaphospholine-3-oxide-1, **3** –1-(3-chloro-1-methylpropoxy)-3-methylisoxaphospholine-3-oxide-1, **4** –

1-(2-chloroethoxy)-3,5,5-trimethylisoxaphospholine-3-oxide-1, **5** —1-(2-chloro-3-methylethoxy)-3,5,5-trimethylisoxaphospholine-3-oxide-1, **6** —1-(3-chloro-1-methylpropoxy)-3,5,5-trimethylisoxaphospholine-3-oxide-1.

Experimental Part*

The acid chlorides of glycolphosphorous acids were obtained by the usual methods ([8], [9]). Their reaction with unsaturated ketones was carried out in sealed —

* With the participation of A. Kh. Voznesenskaya and M. V. Zolotarevskaya.

Table 2

Substance	bp, °C	Pressure, mm	d_4^{20}	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Found, % P	Found, % Cl	Formula	Calculated, % C	Calculated, % H	Calculated, % P	Calculated, % Cl
1-(2-Chloroethoxy)-3-methylisoxaphospholin-3-oxide-1	78–79	0.08	1.3086	1.4825	53.29	53.00	36.96	5.62	13.70	15.72	$C_6H_{13}O_3ClP$	36.66	5.61	13.73	15.76	18.04
1-(2-Chloro-1-methylethoxy)-3-methylisoxaphospholin-3-oxide-1	64–66	0.06	1.2547	1.4762	57.42	57.59	40.14	5.96	12.50	16.58	$C_7H_{15}O_3ClP$	39.92	6.13	12.74	14.71	16.84
1-(3-Chloro-1-methylpropoxy)-3-methylisoxaphospholin-3-oxide-1	67–69	0.07	1.2098	1.4765	62.40	62.21	43.43	6.29	13.48	13.66	$C_8H_{17}O_3ClP$	42.77	6.12	13.78	13.79	

Substance	bp, °C	Pressure, mm	d_4^{20}	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Found, % P	Found, % Cl	Formula	Calculated, % C	Calculated, % H	Calculated, % P	Calculated, % Cl
1-(2-Chloroethoxy)-3,5,5-trimethylisoxaphospholin-3-oxide-1	159–161	10	1.2023	1.4765	52.48	52.21	42.68	6.22	13.61	13.20	$C_8H_{14}ClO_3P$	42.77	6.28	13.79	
1-(2-Chloro-3-methylethoxy)-3,5,5-trimethylisoxaphospholin-3-oxide-1	72–73	0.2	1.1669	1.4697	56.99	56.83	45.19	6.53	13.05	13.31	$C_9H_{16}ClO_3P$	45.29	6.76	12.98	
1-(3-Chloro-1-methylpropoxy)-3,5,5-trimethylisoxaphospholin-3-oxide-1	67–68	0.07	1.1424	1.4696	61.87	61.45	47.28	6.74	12.22	12.39	$C_{10}H_{18}ClO_3P$	47.07	7.11	12.25	14.02

tubes, with heating on a water bath until the decrease in volume ceased. In experiments with methyl vinyl ketone the reaction was completed within 4–6 h, and in experiments with mesityl oxide, within 8–12 h. The condensation products were distilled in a high vacuum. The yields were 30–50% (higher with mesityl oxide). Resinified polymers remained in the residue. The constants and analytical data for the condensation products are given in Table 2.

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