Chemistry

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Abstract

Full Text

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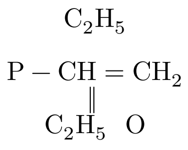
PHOSPHINE OXIDES CONTAINING A VINYL GROUP AT THE PHOSPHORUS ATOM

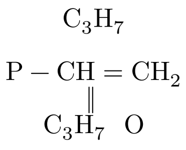
Recently, interest has greatly increased in organophosphorus compounds that can be used for obtaining nonflammable polymers. In particular, organophosphorus compounds containing unsaturated radicals at the phosphorus atom are attracting attention.

Whereas derivatives of vinylphosphinic acid have been the subject of numerous investigations (^{1}), phosphine oxides containing a vinyl group at the phosphorus atom have not yet been described.

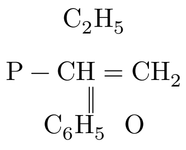
In the present work we obtained the following vinylphosphine oxides:



$$\overset{C_2H_5}{\underset{\substack{\| \\ C_2H_5\ \ O}}{P - CH = CH_2}}$$

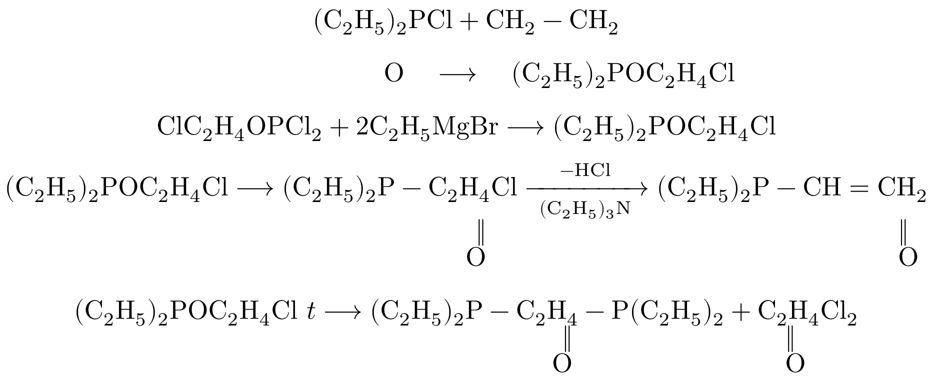


$$\overset{C_3H_7}{\underset{\substack{\| \\ C_3H_7\ \ O}}{P - CH = CH_2}}$$



$$\overset{C_2H_5}{\underset{\substack{\| \\ C_6H_5\ \ O}}{P - CH = CH_2}}$$

The synthesis was carried out according to the scheme:



$$(C_2H_5)_2PCl + \underset{O}{CH_2 - CH_2} \longrightarrow (C_2H_5)_2POC_2H_4Cl$$

$$ClC_2H_4OPCl_2 + 2C_2H_5MgBr \longrightarrow (C_2H_5)_2POC_2H_4Cl$$

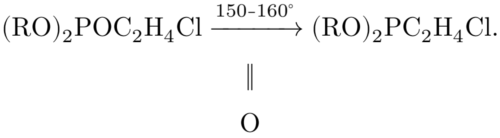
$$(C_2H_5)_2POC_2H_4Cl \longrightarrow (C_2H_5)_2\underset{\overset{\|}{O}}{P} - C_2H_4Cl \xrightarrow[(C_2H_5)_3N]{-HCl} (C_2H_5)_2\underset{\overset{\|}{O}}{P} - CH = CH_2$$

$$(C_2H_5)_2POC_2H_4Cl\ t \longrightarrow (C_2H_5)_2P - \underset{\overset{\|}{O}}{C_2H_4} - P(C_2H_5)_2 + \underset{\overset{\|}{O}}{C_2H_4}Cl_2$$

The reaction of addition of ethylene oxide to phosphorus trichloride, described by one of us and P. A. Rossiiskaya (^{2}) and later extended by a number of authors (^{3}–^{5}) to alkyl- and aryldichlorophosphines, was applied by us to obtain the β-chloroethyl ester of diethylphosphinous acid from diethylchlorophosphine, thereby confirming the generality of this reaction for compounds of the type PCl_3, $RPCl_2$, and R_2PCl.

The β-chloroethyl ester of diethylphosphinous acid was also prepared from β-chloroethyldichlorophosphite and ethylmagnesium bromide according to M. I. Kabachnik and E. N. Tsvetkov (^{6}).

It is known (^{7}) that β-chloroethyldiethyl phosphite isomerizes on heating, being converted into an ester of phosphinic acid:



$$\begin{array}{c}(RO)_2POC_2H_4Cl \xrightarrow{150\text{-}160^\circ} (RO)_2PC_2H_4Cl.\\ \|\\ O\end{array}$$

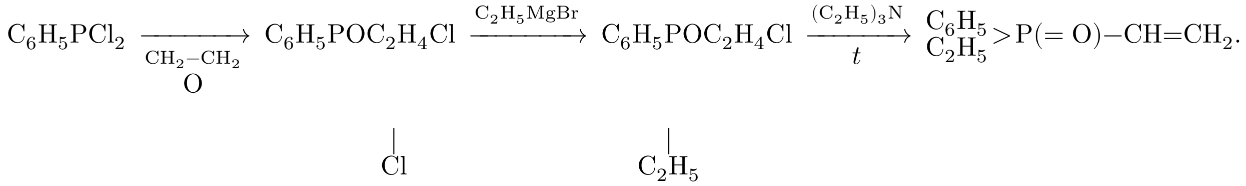
It was also shown (^{8}) that β-chloroethyl aryl esters of phosphorous acid, on heating, are likewise converted into compounds of penta-

of tervalent phosphorus, but in this case the rearrangement is accompanied by elimination of dichloroethane, and the reaction products are esters of ethylenediphosphinic acid.

We found that the β-chloroethyl ester of diethylphosphinous acid, on heating, undergoes analogous transformations; in this case it proved possible to isolate simultaneously both products of the Arbuzov rearrangement: β-chloroethyldiethylphosphine oxide and tetraethylethylenediphosphine dioxide. It should also be noted that the isomerization proceeds under considerably milder conditions (separation of crystals of tetraethylethylenediphosphine dioxide was observed already on storing the β-chloroethyl ester of diethylphosphinous acid at room temperature).

It may be assumed that the mechanism of the transformation is the same as in the case of aromatic esters of phosphorous acid (8): initially, intra- or intermolecular isomerization of the β-chloroethyl ester of diethylphosphinous acid takes place, and the β-chloroethyldiethylphosphine oxide formed then reacts as an alkyl halide with a second molecule of the β-chloroethyl ester of diethylphosphinous acid according to the scheme of the Arbuzov rearrangement. We carried out dehydrochlorination of β-chloroethyldiethylphosphine oxide by heating it in a sealed tube with triethylamine. It is more convenient to obtain diethylvinylphosphine oxide directly from the β-chloroethyl ester of diethylphosphinous acid by heating the latter with triethylamine, without isolation of the intermediately formed β-chloroethyldiethylphosphine oxide.

Similarly, the oxides of dipropylvinylphosphine and ethylphenylvinylphosphine were obtained. The synthesis scheme in the latter case is as follows:



$$C_6H_5PCl_2 \xrightarrow[\underset{O}{CH_2-CH_2}]{} C_6H_5\underset{\substack{|\\ Cl}}{P}OC_2H_4Cl \xrightarrow{C_2H_5MgBr} C_6H_5\underset{\substack{|\\ C_2H_5}}{P}OC_2H_4Cl \xrightarrow[t]{(C_2H_5)_3N} \begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}{>}P(=O)-CH=CH_2.$$

The structure of dipropylvinylphosphine oxide was confirmed by a mixed-melting test with the same substance obtained by M. I. Kabachnik, Chang Zhun-yu, and E. N. Tsvetkov by another method (9). The IR spectrum of diethylvinylphosphine oxide was recorded; it clearly shows bands at 1610 and 1175 cm^{-1}, characteristic of the vinyl and P=O groups.

Experimental Part

Reaction of diethylchlorophosphine (10) with ethylene oxide. To a solution of diethylchlorophosphine in abs. ether, an ethereal solution of ethylene oxide (10% excess) was added dropwise in a nitrogen atmosphere at −20°. After completion of the reaction, the ether was removed in vacuo and the residue was distilled. The β-chloroethyl ester of diethylphosphinous acid (I) was obtained—a colorless substance, rapidly oxidized in air, dissolving cuprous bromide on heating and reacting with phenyl azide. By its constants the substance is identical with that obtained by one of us and E. N. Tsvetkov from β-chloroethyldichlorophosphite and ethylmagnesium bromide (6).

Reaction of phenyldichlorophosphine (11) with ethylene oxide. It was carried out analogously, with the sole difference that the temperature of the reaction mixture was maintained at $\sim 10°$; the ratio of reagents was equimolar. The acid chloride of the mono-β-chloroethyl ester of phenylphosphinous acid (II) was obtained—a colorless liquid that changes on storage.

β-Chloroethyl ester of phenylethylphosphinous acid (III). To a solution of 0.1 mole of the acid chloride of the mono-β-chloroethyl ester of phenylphosphinous acid and 0.22 mole of pyridine in 100 ml of ether, an ethereal solution of ethylmagnesium bromide, prepared from 0.11 mole of ethyl bromide and 0.11 gram-atom of magnesium in 50 ml of ether, was added dropwise with stirring in a nitrogen atmosphere; the reaction temperature ···

Table 1

No.	Compound	b.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	C, %, found	C, %, calc.	H, %, found	H, %, calc.	P, %, found	P, %, calc.	Cl, %, found	Cl, %, calc.	Yield, %
I	C_2H_5 C_2H_5 $>P-OC_2H_4Cl$ *	29–30/2	1.4670	1.0144	46.12	45.96							20.7	21.0	37
II	C_6H_5 Cl $>P-OC_2H_4Cl$	99–100/1	1.5645	1.2896	56.30		42.8 42.9	43.1	4.3 4.2	4.1	13.7 13.6	13.9	31.2 31.5	31.8	68
III	C_6H_5 C_2H_5 $>P-OC_2H_4Cl$	81–82/1	1.5430	1.1116	61.44		55.7 55.7	55.5	6.9 6.8	6.5	14.3 14.6	14.3	16.2 16.6	16.4	56
IV	C_3H_7 C_3H_7 $>P-OC_2H_4Cl$	49–50/2	1.4675	0.9825	55.59	55.20	49.4 49.3	48.9	8.9 9.0	9.2	15.4 15.7	15.7	17.7 18.1	18.0	40
V	C_2H_5 C_2H_5 $>P(=O)-C_2H_4Cl$	100–101/1 m.p. 33–34°	1.4855	1.1154	43.36	43.40	42.7 42.6	42.7	8.3 8.4	8.4	18.1 18.0	18.4	21.2 21.3	21.0	70
VI	C_2H_5 C_2H_5 $>P(=O)-C_2H_4P(=O)<$ C_2H_5 C_2H_5	m.p. 122–123°	–	–	–	–	50.5 50.4	50.4	10.3 10.4	10.1	25.7 25.8	26.0	None		15
VII	C_2H_5 C_2H_5 $>P(=O)-CH=CH_2$	62–63/2 m.p. 35–36°	–	–	–	–	54.4 54.6	54.5	9.8 9.7	9.9	23.4 23.0	23.4	None		50
VIII	C_3H_7 C_3H_7 $>P(=O)-CH=CH_2$ **	77–78/1 m.p. 36–37°	–	–	–	–									46

No.	Compound	b.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	C, %, found	C, %, calc.	H, %, found	H, %, calc.	P, %, found	P, %, calc.	Cl, %, found	Cl, %, calc.	Yield, %
IX	$\begin{matrix}C_6H_5\\C_2H_5\end{matrix}>P(=O)-CH=CH_2$	112 113/1 m.p. 43–44°	–	–	–	–	66.56 66.4	66.7	7.3 7.4	7.3	16.91 16.8	17.2	None		58

* Literature data (6): b.p. 27–28°/2 mm, n_D^{20} 1.4678; d_4^{20} 1.0143.

** Literature data (9): b.p. 89–89.5°/2 mm; m.p. 36–37°.

the reaction mixture was maintained at −60 to −65°. After addition of 150 ml of petroleum ether, the precipitate was filtered off, the solvent was removed in vacuo, and the residue was distilled.

β-Chloroethyl ester of dipropylphosphinous acid (IV). Obtained under the same conditions from 0.1 mole of β-chloroethyldichlorophosphite (2) and propylmagnesium bromide, prepared from 0.22 mole of propyl bromide and 0.22 g-at. of magnesium, in the presence of 0.44 mole of pyridine.

Isomerization of the β-chloroethyl ester of diethylphosphinous acid. A solution of the β-chloroethyl ester of diethylphosphinous acid in dry toluene (weight ratio 1 : 2) was refluxed in a nitrogen atmosphere for 4 hr. After removal of the solvent in vacuo, 70% of β-chloroethyldiethylphosphine oxide (V) was distilled off—a colorless liquid readily crystallizing on cooling; the solid residue in the distillation flask was recrystallized from chloroform with ether; 15% of tetraethylethylenediphosphine dioxide (VI) was obtained—hygroscopic crystals. The yield of β-chloroethyldiethylphosphine oxide upon heating without solvent at 100-110° for 1.5 hr was 49%; the residue contained tetraethylethylenediphosphine dioxide; a certain amount of dichloroethane was distilled off; the starting β-chloroethyl ester was not isolated.

Preparation of oxides of tertiary monovinylphosphines (VII-IX). A mixture of the β-chloroethyl ester of a dialkyl- or alkylarylphosphinous acid and triethylamine (20% excess) was heated in a sealed ampoule at 120° for 5 hr; crystals of triethylamine hydrochloride separated. After treatment of the reaction mixture with abs. ether, filtration, blowing off the solvent, and distillation, the oxide of the corresponding monovinylphosphine was obtained—low-melting hygroscopic crystals*.

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* Formation of a small amount of diethylvinylphosphine oxide was also observed upon heating the β-chloroethyl ester of diethylphosphinous acid without triethylamine in a sealed ampoule to 120°.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.