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Abstract

Full Text

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SYNTHESIS AND INVESTIGATION OF SOME VINYL ESTERS OF PHOSPHORUS ACIDS

The recently discovered unsubstituted vinyl esters of phosphorus acids were first synthesized by dehydrochlorination of the corresponding β-chloroethyl esters ([1]),

$$(RO)_2P(O) - OCH_2CH_2Cl \xrightarrow{-HCl} (RO)_2P(O) - OCH = CH_2^*$$

and somewhat later by the interaction of esters of trivalent phosphorus acids with chloroacetaldehyde ([3]) (according to Perkow ([4])).

$$(RO)_3P + ClCH_2CHO \rightarrow (RO)_2P(O) - OCH = CH_2 + RCl$$

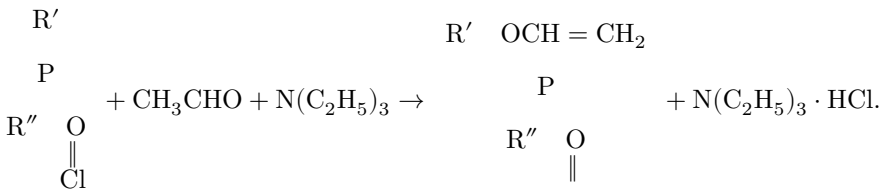
In the present article we describe a new method for the synthesis of vinyl esters of phosphorus acids, based on the interaction of the acid chlorides of these acids, acetaldehyde, and triethylamine. In developing it we proceeded from the following considerations:

Kabachnik and Shepeleva ([5–7]), having investigated the reaction of acid chlorides of trivalent phosphorus acids with aldehydes, came to the conclusion that in this process the first stage, occurring at low temperature, is the formation of α-chloroalkyl esters of the corresponding acids.

$$P - Cl + RCHO \rightarrow \quad P - OCHCl - R,$$

which at elevated temperature undergo further changes. The formation of products of aldehyde addition to phosphorus halide was confirmed by Faizulin and Trifonov ([7]) (in the example of benzaldehyde and phosphorus trichloride) by physicochemical methods of analysis.

We supposed that the addition to the aldehyde-phosphorus halide system of a strong organic base should direct the reaction toward the formation of vinyl esters of phosphorus acids according to the following scheme:



Experiment confirmed this assumption ([8]).

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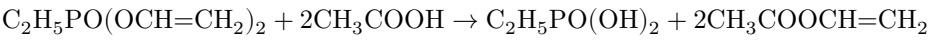
* Allen et al. ([2]), after unsuccessful attempts to reproduce these results, consider them erroneous.

The reaction was carried out by the action on the acid chlorides of phosphorus acids of an excess of acetaldehyde and triethylamine, with external cooling and vigorous stirring. In this process a white crystalline precipitate, reddening with time, separated. From the reaction flask a volatile fraction was distilled off (at 20-100 mm), and then, at 2-10 mm and with further heating, the vinyl ester of the corresponding phosphorus acid. The crystalline precipitate was sometimes filtered off before distillation; however, this did not affect the yields. To remove traces of triethylamine, the distilled product was mixed with several drops of phosphoric acid and, after some time, distilled a second time.

The structure of the vinyl esters of phosphorus acids was proved, in addition to analytical data, by saponification of some esters to the corresponding phosphorus acids and by their transesterification with acetic acid, leading to the formation of vinyl acetate



By the method described in the present communication we synthesized a series of new vinyl esters of substituted phosphorous and phosphinic acids, as well as trivinyl phosphate (Table 1).

Table 1

Formula	b.p., °C/mm	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.
$CH_3PO(OCH{=}CH_2)_2$	60–65/8	1.1097	1.4394	35.14	35.22
$C_2H_5PO(OCH{=}CH_2)_2$	60–61/5	1.0707	1.4409	39.99	39.84
	5.5				
$ClCH_2PO(OCH{=}CH_2)_2$	66–67/1	1.2458	1.4636	40.41	40.09
$CH_2{=}CHPO(OCH{=}CH_2)_2$	40–50/1–5	1.1020	1.4530	39.28	39.37
	2				
$CH_3P(=O)(OCH_2CH_2Cl)(OCH{=}CH_2)$	96–98/3–4	1.2361	1.4540	40.48	40.56
$CH_3P(=O)(OC_6H_5)OCH{=}CH_2$	63–65/2–3	1.0208	1.4278	44.89	44.92
$C_6H_5PO(OCH{=}CH_2)_2$	111/1.5–2	1.1589	1.5144	54.64	54.54
$(C_6H_5)(CH_3)P(=O)OCH{=}CH_2$	102–104/2	1.1166	1.5224	50.04	49.33
$o\text{-}C_6H_4O_2P{-}OCH{=}CH_2$	71–72/2–3	1.2306	1.5357	46.13	45.94
$(CH_2O)_2P{-}OCH{=}CH_2$	58–59/15	1.1672	1.4577	31.34	31.07
$PO(OCH{=}CH_2)_3$	84–85/10	1.1240	1.4314	40.60	40.50

Note. Analyses of the synthesized substances agree well with the calculated data.

The yields in this reaction are relatively small. Under all variations of the synthesis conditions they did not exceed 30–35% of theory. A large residue always remained in the distillation flask, decomposing upon further heating. It is absolutely necessary to use carefully purified starting substances, as well as an excess of aldehyde and amine; otherwise the yields drop sharply, sometimes to zero. As regards the mechanism of formation of vinyl esters of phosphorus acids, one may suggest that an α-chlorinated ester is first formed, which with triethylamine gives an unstable

$$\left[\begin{array}{c} R' \\ | \\ P{-}O{-}CH{-}CH_3 \\ | \quad\quad | \\ R'' \quad N^+(C_2H_5)_3 \\ \quad\quad \| \\ \quad\quad O \end{array}\right] Cl^-$$

complex (when triethylamine was replaced by trimethylamine, a complex of this kind was isolated and analyzed). Decomposition of the complex leads to the formation of the vinyl ester of phosphoric acid and triethylamine hydrochloride (and other unidentified products contained in the non-distilling residue). Sladkov and Petrov [10], who carried out an analogous reaction in the carbon series, suppose that the aldehyde first isomerizes into the corresponding vinyl alcohol,

which then reacts with the acid chloride. This assumption seems unlikely to us, in view of the extremely weak tendency of acetaldehyde to enolization.

The vinyl esters of phosphorus acids obtained are characterized by a capacity for polymerization, as shown by some preliminary experiments described below. Polymerization was carried out in carefully washed glass ampoules; the initiator was benzoyl peroxide, recrystallized from chloroform. After the initiator and the substance had been placed in the ampoule, the latter was kept for 10–15 min at a residual pressure of 15–20 mm, after which it was sealed under vacuum and placed in a thermostat, the temperature of which was gradually raised from 50 to 70–80°, or kept constant. The polymerization conditions and the nature of the polymers are given in Table 2.

Table 2

Polymerization of vinyl esters of phosphorus acids

Formula	Benzoyl peroxide, %	Polymerization temperature, °C	Time, h	Nature of polymer
$CH_3P(=O)(OC_4H_9)(OCH=CH_2)$	1.0–1.5	50–70	200	Light-yellow liquid
$CH_3P(=O)(OCH_2CH_2Cl)(OCH=CH_2)$	1.5	50–70	150	Yellow, soft. Swells in chloroform and slowly dissolves
$(C_5H_5)(CH_3)P(=O)OCH=CH_2$	1.0	50–80	200	Dark-yellow viscous liquid
[[unclear : cyclic aromatic phosphate]]$-OCH=CH_2$	0.9	50–70	120	Yellow, soft. Swells in chloroform
[[unclear : cyclic ethylene phosphate]]$-OCH=CH_2$	1.3–1.4	50–70	200	Dark, soft. Swells in chloroform and slowly dissolves
$CH_3PO(OCH=CH_2)_2$	1.4–1.9	50	50	Light-yellow, hard, non-flammable, insoluble

Formula	Benzoyl peroxide, %	Polymerization temperature, °C	Time, h	Nature of polymer
$C_2H_5PO(OCH{=}CH_2)_2$	1.3	50–70	100	Light-yellow, hard, non-flammable, insoluble
$ClCH_2PO(OCH{=}CH_2)_2$	0.67	50	30	Yellow, hard, non-flammable, insoluble
$C_6H_5PO(OCH{=}CH_2)_2$	1.2	50	150	Black, hard, non-flammable, insoluble
$CH_2{=}CHPO(OCH{=}CH_2)_2$	0.7	70	30	Yellow, hard, non-flammable, insoluble
$PO(OCH{=}CH_2)_3$	1	50–70	5	Yellow, hard, non-flammable, insoluble
$PO(OCH{=}CH_2)_3$	1	50–70	100	Yellow, hard, non-flammable, insoluble

From the data given in Table 2, it may be concluded that esters containing one double bond form comparatively low-molecular-weight substances of linear structure.

Ethers containing two and three double bonds polymerize considerably faster, and in doing so form spatially cross-linked polymers that are insoluble in organic solvents.

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