PROPERTIES OF ETHYLENAMIDES OF GLYCOL PHOSPHITES

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The ethylenamides of some glycol phosphites were synthesized by us [1]; as derivatives of trivalent phosphorus these compounds display the reactions usual for them. Previously we had shown [2] that the ethylenamides of pentavalent phosphorus acids enter into the phosphonaminoethylation reaction with a number of organic compounds possessing a labile hydrogen atom (amines, acids, mercaptans, etc.), certain other compounds, for example, halo derivatives, and also with inorganic compounds, acids, halides, etc.

Under analogous conditions, the ethylenamides of the glycol phosphites react in a different manner with some of the enumerated compounds.

In attempting to open the ethylenimine ring in the amides of some glycol phosphites (Table 1) using various amines, we observed in all cases the liberation of free ethylenimine and the formation of a new glycol phosphite amide, i. e., the transamination reaction. This shows the very low strength of the nitrogen-phosphorus bond. At times the transamination reaction can serve as a method for the preparation of glycol phosphite amides. The yields of the new amides in the transamination are small; this phenomenon is apparently explained by the simultaneous amonolysis of the aliphatic bonds.

In all of the studied cases where the ethylenamides of glycol phosphites were reacted with acetic acid (Table 2), we isolated two compounds: the free glycol phosphite and the ethylenamide of acetic acid. The quite high yields of the cyclic phosphorus acids (60-70% of theory) make it possible to propose the deamination reaction as a convenient method for their preparation. The results of our studies on the ethylenamides of glycol phosphites are found to be in complete agreement with the data of R. Burgada, who recently published a comprehensive paper [3] on the transformations of various amides of trivalent phosphorus acids.

EXPERIMENTAL SECTION

The transamination of the ethylenamides of glycol phosphites was run in sealed tubes by heating equimolar amounts of the reagents at 70-100° for 10-18 h. The starting materials and the transamination products are given in Table 1. The deamination of the amides of glycol phosphites with acetic acid was run in benzene solution at $0-5^{\circ}$. The flask with the solution was kept overnight at room temperature. Fractional distillation of the mixture gave the ethylenamide of acetic acid and the glycol phosphites, characterized in Table 2.

SUMMARY

1. Transamination occurs when the ethylenamides of glycol phosphites are reacted with amines.

2. When the ethylenamides of glycol phosphites are treated with acetic acid they are deaminated to give the ethylenamide of acetic acid and the free ethylene glycol phosphites.

Glycol Phosphites
of
Ethylenamides
of
Reaction
Transamination
TABLE 1.

			B. p., °C			IWI	~	Found	%	Calc.	0/0	
Amine	Reaction	product	(p, mm of Hg)	n_D^{20}	d_4^{20} f	ound	calc.	 А	z	 д	z	Y leid
2-Methy azetidin	e CH ₂ -0	CH ₂ -N CH CH CH CH	60-62(1,5)	1,4845	1,0873	46,09	45,45	17,85	7,98 8,12	17,77	8,00	36,6
Diethyl- amine	сн, Сн–0 Сн ₂ –0 Сн ₂ –0	$N(C_2H_6)_2$	43,5-44,5 (0,5)	1,4652	1,0426	46,99	47,66	17,19	8,26	17,51	7,91	53,0
Morpholi	ne cHP		76—77 (0,8)	1,4932	1,1439	52,11	51,65	15,00	6,60	15,12	6,82	27,0
	CH ₂ —Ó The same, counter sy	СН2СН2 obtained by nthesis	99-100 (2,0)	1,4933	1,1450	52,07	51,65	14,84	6,85	1	I	1

TABLE 2.	Deamination	of Ethy	lenamides	of Gl	ycol Phosp	hites with	Acetic	Acid
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	Obtained acids	В. р., °С (р,	Р,	Yield,	
Ethylenamide		mm of Hg)	found	calc.	%
$\begin{array}{c} \hline \\ CH_3-CH-O \\ CH_3-CH-O \\ CH_2 \\ \end{array} \\ \begin{array}{c} P-N \\ CH_2 \\ CH_2 \\ \end{array}$	CH ₃ -CH-0 CH ₃ -CH-0 POH	95—96 (1)	22,30	22,79	_
$CH_2 \langle CH_2 \rightarrow O \rangle P - N \langle I \rangle CH_2 \rangle P - N \langle I \rangle CH_2$	$CH_2 \xrightarrow{CH_2 \to 0} POH$	122-123 (1) B. p. 29.5-30.5	24,89	25,42	70
$CH_2 \begin{pmatrix} CH_2 - O \\ CH_2 - O \end{pmatrix} P - N \begin{pmatrix} CH_2 \\ I \\ CH_2 \end{pmatrix}$	CH ₂ CH ₂ -0 POH	116—121 (2—2,5) B. p. 49—50,5 *	22,36	22,79	60
$CH_{3}CO-N \begin{pmatrix} CH_{2} \\ CH_{2} \end{pmatrix}$	CH ₃	56,5—57 (37) †	d_4^{20} 0,9946	n_D^{20} 1,4380	63 —65

*Literature data [4]: b. p. 138-140° (3 mm); 150-155° (10-11mm); b. p. 49-50°; 48-50°, †Literature data [5]; b. p. 38-39° (17 mm); n_D^{20} 1.4378; d_4^{20} 0.9923.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.