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Abstract

Full Text

Chemistry

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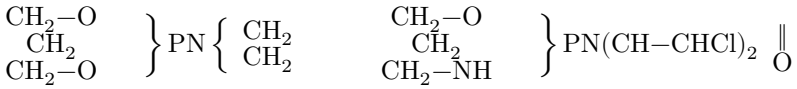
Ethyleneamides of Glycol Phosphorous Acids

(Presented by Academician A. E. Arbuzov, 25 V 1962)

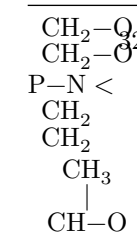
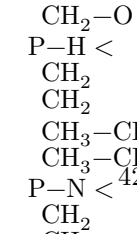
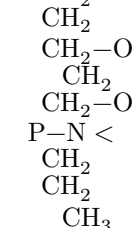
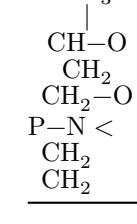
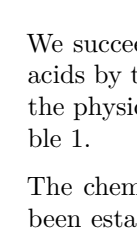
Esters of glycol phosphorous and phosphinous acids are now quite accessible and well-studied compounds. In a number of works, chiefly by A. E. Arbuzov and his students ([1]–[15]), a large number of such compounds were described and their properties studied. The authors of the works cited succeeded in showing that esters of glycol phosphorous acids undergo the Arbuzov rearrangement either with opening of the ester ring or without it; it was also observed that some esters are capable of polymerizing. Later both of these reactions were used for the preparation of phosphorus-containing polymers ([16], [17]).

Amides of glycol phosphorous acids have been studied much less ([13], [19]), although such compounds are undoubtedly of theoretical and practical interest, especially from the point of view of studying their physiological activity. In particular, it seemed to us very interesting to study the cytostatic properties of the previously unstudied ethyleneamides of glycol phosphorous acids and their derivatives with pentavalent phosphorus, in connection with the presence of the ethyleneimine ring and by a certain analogy with di-(β-chloroethyl)amides of cyclic amido-esters of phosphorus acids of the cytoxan type (B-518) ([20]) and others, whose cytostatic properties are well known:



Undoubtedly, the presence of the reactive ethyleneimine ring lends additional interest to the study of the chemical properties of ethyleneamides of glycol phosphorous acids.

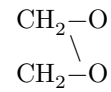
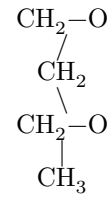
Table 1

Compound	b.p., °C, mm	d_4^{20}	n_D^{20}	MR, found	MR, calc.	P, %, found	P, %, calc.	Yield, %
	32-35/1	1.2348	1.4932	31.29	31.54	22.97	23.31	55
	35-36/1	1.1683	1.4810	35.81	36.16	20.94	21.09	45
	41-42/0.5	1.1215	1.4778	40.51	40.68	19.11	19.25	55
	44-45/1	1.1729	1.4910	36.39	36.16	21.01	21.09	50
	72-73/6	1.1263	1.4800	40.60	40.88	19.20	19.21	55

We succeeded in synthesizing a series of ethyleneamides of glycol phosphorous acids by the action of ethyleneimine on acid chlorides in the presence of a base; the physicochemical characteristics of the compounds obtained are given in Table 1.

The chemical properties of the compounds obtained are being studied; it has been established that they, like all compounds of trivalent phosphorus, readily add sulfur, forming ethyleneamides of glycol thiophosphoric acids (Table 2).

Table 2

Compound*	m.p., °C	H, % found	H, % calc.	C, % found	C, % calc.	P, % found	P, % calc.
	61–62	5.02	4.84	28.92	29.09	18.50	18.78
	76–77	6.40	6.21	37.26	37.30	16.21	16.06

* Yield almost quantitative.

These compounds are also of interest as potential cytostatic agents.

When this work was being prepared, a communication appeared in the literature[21] on the synthesis of the ethyleneamide of glycol thiophosphoric acid from ethylene glycol thiophosphoric acid chloride and ethyleneimine; as already stated, we obtained this compound by addition of sulfur to the corresponding acid chloride. The melting points determined by us and those reported in the cited work are identical. The cytostatic properties of the compounds described will be studied; further investigation of their chemical transformations, for example, the Arbuzov rearrangement, ring opening, etc., is continuing.

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

original.