# OBTENTION OF DIALKYLAMIDES AND ETHYLENEAMIDES OF GLYCOLPHOSPHORIC ACIDS AND SOME OF THEIR PROPERTIES

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UDC 542.91+661.718.1+547.298.1

In our earlier publications [1, 2], we reported on the synthesis of ethyleneamides of glycolphosphorous acids and their interaction with amines and acetic acid. In this report, we shall describe the synthesis of dialkylamides and ethyleneamides of glycolphosphoric acids and some of their properties. Ethyleneimine and secondary amines react readily with glycolphosphorous acids and carbon tetrachloride in benzene solution at a temperature 0-5°, forming dialkylamides and ethyleneamides of the glycolphosphoric acids. When these compounds are distilled part of the product will polymerize; hence yields of end products vary between 20 and 77%. A higher yield is obtained for crystalline products which can be purified by recrystallizing (e.g., compound 5, Table 1) as against liquids which require distillation. The reaction will proceed in the presence of triethylamine if 1 M of the starter amine is introduced. Physical properties of the compounds obtained are shown in Table 1.

Ethyleneamides of 5-valent phosphorus acids are known to enter phosphonaminoethylation reactions with a number of organic compounds containing a mobile hydrogen atom [3]. This also applies to the ethyleneamides of glycolphosphoric acids. We opened the ethyleneimine ring with diethylamine and obtained a series of ( $\beta$ -diethylamino)ethylamides of glycolphosphoric acids whose physical properties are shown in Table 2.

Photos and analysis of the IR spectra of these compounds (spectra were determined for the compounds 1, 2, and 4, see Table 2) confirmed their structure and pointed towards opening of the ethyleneimine ring.

In all the spectra, we observed an intense absorption band at 3220 cm<sup>-1</sup> in the range of the NH group valence vibration. A similar reaction process was observed when the ethyleneamide of 1,3-propylene-glycol phosphoric acid was heated with thiophenol. The ethyleneimine ring opened, and the ( $\beta$ -mercapto-phenyl)ethylamide of 1,3-propyleneglycol phosphoric acid was formed.

$$\begin{array}{c|c} CH_2 & CH_2 & CH_2 & CH_2 \\ CH_2 & P - N & \\ CH_2 & O & \\ CH_$$

The IR spectrum of this compound also showed an absorption band at  $3220 \text{ cm}^{-1}$  in the range of valence vibration of the NH group.

### EXPERIMENTAL

Synthesis of the Dibutylamide of 1,3-Butyleneglycolphosphoric Acid. A benzene solution of 23.63 g dibutylamine was added dropwise to a benzene solution of 22.11 g CCl<sub>4</sub> and 15 g 1,3-butyleneglycolphosphorous acid under stirring and cooling. The reaction temperature was 0-5°. After all of the dibutylamine had been added, the reaction mixture was stirred for 1 h at room temperature and left to stand overnight. After removal of the hydrochloric dibutylamine, the solvent and CHCl<sub>3</sub>, the residue was distilled twice under vacuum. The fraction with a bp 119-120° (0.5 mm) was isolated; yield 16 g (42% of theoretical);  $d_4^{20}$  1.03457;  $n_D^{20}$  1.4566. Found %: P 11.37, 11.63; N 5.30, 5.49. MR 69.16.  $C_{12}H_{22}NO_3P$ . Calculated %: P 11.78; N 5.32. MR 69.62. Compounds 1, 6, 8, and 9 were obtained similarly (see Table 1).

Synthesis of the Ethyleneamide of 2,3-Butyleneglycolphosphoric Acid. A benzene solution of 2,3-butyleneglycolphosphorous acid was added dropwise under stirring and cooling

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2120-2123, September, 1967. Original article submitted February 26, 1967.

TADDE 1. DIAINYIAIIIUES AIN EM	ny remeaning o	Too f Too	orrdoorrd							
				W	В	Found,	do	Calculat	ed, %	%
Compound	bp (p. mm Hg)	$d_{4}^{20}$	<sup>72</sup> D	found	calcu- lated	Ч	z	đ	z	,blэiY
$ \overset{(CH_{3}-0)}{\leftarrow} \overset{(C_{4}H_{3}-1)_{3}}{\bigvee} $	$\frac{143-145\ (0.9-1)}{46-48\ *}$	I	I	1	1	13.10	5.31	13.19	5.95	33
$\operatorname{CH}_{d+2}^{-\operatorname{CH}} \xrightarrow{-\operatorname{CH}}_{0} \operatorname{CH}_{2}^{-\operatorname{CH}_{2}}$	9596 (0.06)	1,28285	1.4644	35.10	35.09	18.73	8.49	19.00	8,58	20
$CH_{3}-CH-O$ $CH_{3}-CH-O$ $CH_{3}-CH-O$	105106 (0.03)	1.09426	1 - 4679	58.68	59.45	12.88	5.71	13.42	6.06	51
CH <sub>a</sub> -CH-0 CH <sub>a</sub> -CH-0 CH <sub>a</sub> -CH-0 CH <sub>a</sub>	132 (0.09)	1.22333	1.4624	39.81	39.71	17.25	7.76	17.51	7.91	43
$_{\mathrm{CH}_2} \subset _{\mathrm{CH}_2 - 0} \subset _{\mathrm{H}_2 - 0} \subset _{\mathrm{H}_2} \subset _{\mathrm{CH}_3} \subset _{\mathrm{CH}_3}$	82—83 *	1	ļ	[	I	19.00	8.45	19.01	8.58	77
$CH_{a} \begin{pmatrix} CH_{a} - 0 \\ H_{a} & 0 \\ CH_{a} & 0 \end{pmatrix} = N(CH_{a} - CH = CH_{a})_{a}$	132—133 (0.8)	1,13632	1.4804	54.31	54,83	14.14	6.30	14.28	6.45	50
$\operatorname{CH}_{\mathcal{A}} \begin{pmatrix} \mathbf{I} & \mathbf{I} \\ \mathbf{CH}_{\mathbf{z}} & \mathbf{CH}_{\mathbf{z}} \\ \mathbf{CH}_{\mathbf{z}} & \mathbf{CH}_{\mathbf{z}} \end{pmatrix} = \mathbf{V} \begin{pmatrix} \mathbf{CH}_{\mathbf{z}} \\ \mathbf{CH}_{\mathbf{z}} \\ \mathbf{CH}_{\mathbf{z}} \end{pmatrix}$	126—127 (1)	1.25044	1.4739	39.79	39.71	17.02	8,16	17.51	7.94	42
CH <sub>5</sub> CH <sub>5</sub> O, CH <sub>2</sub> O, CH <sub>2</sub> CH <sub>3</sub> ),	133—134 (1)	1,09723	1.4770	59.50	59,45	12.95	6.24	13.42	6.06	40
$\operatorname{CH}_{CH_{2}} (\operatorname{CH}_{1} - 0) = \operatorname{CH}_{1} (\operatorname{C}_{H_{1}}) $	122124 (0.81)	1,03262	1.4570	69.34	69.61	11.63	5.30	11.78	5.32	42

\* Melting point

TABLE 1. Dialkylamides and Ethyleneamides of Glycolphosphoric Acids

Compound	bp (p, mm Hg)	$d_4^{20}$	$n_{D}^{20}$	MR		Found, %		Calc., %		
				found	calcu- lated	Р	N	р	N	Yield, %
$\begin{array}{c} \mathbf{CH}_{3}-\mathbf{CH}=0\\ \mathbf{H}_{3}-\mathbf{CH}=0\\ \mathbf{CH}_{3}-0\\ \mathbf{R}\end{array}$	$  \begin{array}{c} 141 - 142 \\ (0,07) \end{array}  $	1.10528	1.4659	59.13	59.70	12.77	12.00	13.13	11.86	34
CH <sub>s</sub> -CH-O CH <sub>s</sub> -CH-O	129—130 (0.05)	1.08326	1.4643	63.74	64.32	12.25	10.79	12.40	11.20	20
$CH_2 < CH_2 - O CH_2 - O R$	139—140 (0.06)	1.11078	1 4734	59.64	59.70	13.10	11.77	13.13	11.86	22
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	128—130 (0.04)	1.09781	1.4700	63,52	64.32	12.08	11.03	12.40	11.20	30

TABLE 2. ( $\beta$ -Diethylamino)ethylamides of Glycolphosphoric Acids

to a benzene solution of 2.5 g ethyleneimine, 6.8 g (excess) triethylamine and 9 g CCl<sub>4</sub> that had been cooled to 0°. After the acid had been added, the reaction mixture was stirred for 1 h at room temperature and left to stand overnight. After removal of the hydrochloric triethylamine, the solvent and the chloroform, the residue was distilled twice under vacuum. The fraction with a bp 132° (0.1 mm) was isolated; yield 4.45 g (43%);  $d_4^{20}$  1.22333;  $n_D^{20}$  1.4624. Found %: P 17.02, 17.25; N 7.76, 7.65. MR 39.81. C<sub>6</sub>H<sub>12</sub>NO<sub>3</sub>P. Calculated %: P 17.51; N 7.90. MR 39.71. The compounds 2, 3, 4, 5, and 7 were obtained in the same way (see Table 1).

Interaction of the Ethyleneamide of 1,2-Propyleneglycolphosphoric Acid with Diethylamine (a typical test). A mixture of the above ethyleneamide (7.3 g), an excess of diethylamine (10 g) and ~ 0.1 g ammonium chloride were heated in a sealed tube for 11 h at 90-100°. The excess of amine was distilled off under vacuum. The residue obtained after two distillations was 3.6 g (34%) of a very thick fluid, boiling at 141-142° (0.07 mm);  $d_4^{20}$  1.10528;  $n_D^{20}$  1.4659. Found %: P 12.77, 12.64; N 12.00, 12.08. MR 59.13.  $C_9H_{21}N_2O_3P$ . Calculated %: P 13.13; N 11.86. MR 59.70.

Interaction of the Ethyleneamide of Propyleneglycolphosphoric Acid with Thiophenol. A mixture of 6.5 g ethyleneamide and 4.31 g thiophenol was heated for 8 h at 70-80° under stirring. The reaction mixture crystallized on the following day. The crystals were dissolved in benzene and precipitated with petrol ether: mp 99.5-101°, yield 7.56 g (70%). Found %: P 11.04, 11.03; N 5.45, 5.38.  $C_3H_{16}NO_3PS$ . Calculated %: P 11.43; N 5.16.

The IR spectra were obtained and analyzed by R. P. Shagidullin and L. Maslenkova, co-workers at our institute; the authors wish to thank them for their help.

#### CONCLUSIONS

1. Dialkylamides and ethyleneamides of glycolphosphoric acids were obtained by the interaction of secondary amines and ethyleneimine with glycolphosphorous acids and carbon tetrachloride.

2. Reactions of ethyleneamides of glycolphosphoric acids with diethylamine and thiophenol were studied.

## LITERATURE CITED

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