REACTIONS OF CHLORIDES, SOME ESTERS, AND AMIDES OF γ-CHLOROPROPYLPHOSPHONIC AND BIS-(γ-CHLOROPROPYL)PHOSPHINIC ACID WITH AMINES

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We have reported earlier on the synthesis of acid chlorides of γ-chloropropylphosphonic and bis(γ-chloropropyl)phosphinic acids and their reactions with alcohols [1]. Continuing the study of these acid chlorides we have investigated their reaction with amines and synthesized derivatives of aminopropylphosphonic and bis-(aminopropyl)phosphinic acids. The literature contains only data on the preparation of γ-aminopropylphosphonic acid [2], although such compounds are of interest as biologically active compounds, as intermediate products for the synthesis of other organophosphoric compounds, and as monomers [3].

The present communication describes reactions of γ-chloropropylphosphonic and bis-(γ-chloropropyl)-phosphinic acid chlorides with diethylamine, ethyleneimine, allylamine, and aniline, and also reactions of their esters and amides with diethylamine.

The reactions of acid chlorides with amines were carried out in absolute ether solutions in the presence of triethylamine. The amines obtained represented colorless liquids or crystalline compounds; their constants are given in Table 1. (I - IX). The synthesis of N-diethylaminopropylphosphonic and bis(N, N-diethylaminopropyl)-phosphinic acid derivatives was achieved by heating of the components in sealed tubes at 90-100°C for 6-8 h [4]. The synthesized compounds were transparent, slightly yellow liquids, easily distillable under vacuum (Table 1, X-XIV).

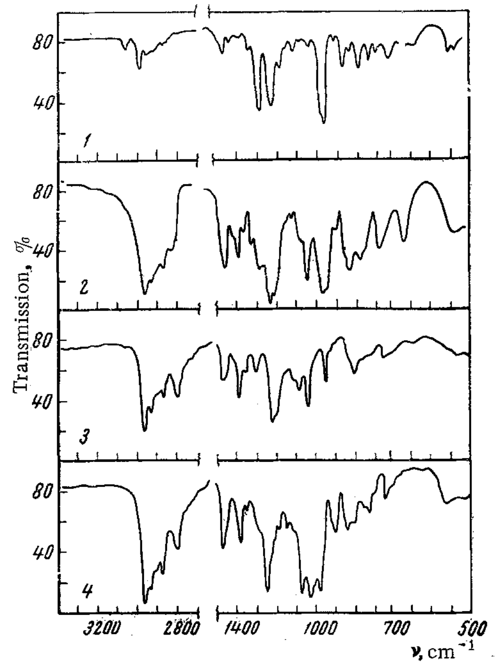

Fig. 1. IR-spectra of (1) γ-chloropropylphosphonic acid diethyleneimide, (2) bis(γ-chloropropyl)phosphinic acid diethylamide, (3) bis-(N, N-diethylaminopropyl)phosphinic acid diethylamide, and (4) N-diethylaminopropylphosphonic acid dibutylester.

The structure of the products was confirmed by IR spectral data. Figure 1 shows that the IR spectra of all four compounds contain a strong absorption band in the 1195-1300 cm^{-1} region. The frequency of the band maximum was 1195 cm^{-1} in spectrum (1), 1215 cm^{-1} in spectrum (2), 1210 cm^{-1} in spectrum (3), and 1255 cm^{-1} in spectrum (4). As known, the P = O valency vibration appears in this region. In the amide spectra (1-4) $\nu_{P=O}$ is shifted towards lower frequencies [5] relative to the absorption band in the spectrum of compound (XIV) due to increasing electron-donor properties of the substituent. The IR spectrum of γ-chloropropylphosphonic acid diethylenimide shows absorption bands at 940, 1265, and 3065 cm^{-1}, which are characteristic for the ethyleneimine rings adjacent to the P = O group [6]. In spectrum (4) of N-diethylaminopropylphosphonic acid dibutyl ester the well-known P — O — C bands at 1030 cm^{-1} are present, in accordance with its structure.

EXPERIMENTAL METHOD

Preparation of bis(γ-Chloropropyl)Phosphinic Acid Diethylamide. A solution of 15 g of bis(γ-chloropropyl)phosphinic acid chloride in 20 ml absolute ether was added dropwise at —5° to —3° with stirring and cooling to a solution of 4.6 g diethylamine and

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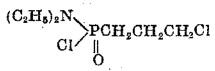
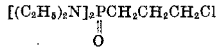
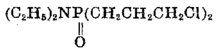
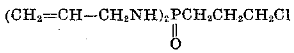
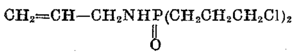
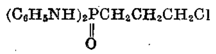
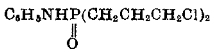
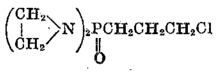
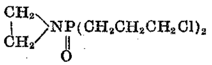
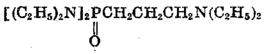
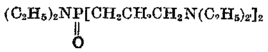
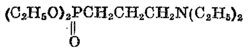
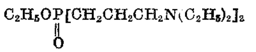
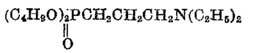
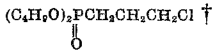
A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences, USSR. Translated from Izvestiya Akademii Nauk, SSSR, Seriya Khimicheskaya, No. 5, pp. 1163-1166, May, 1969. Original article submitted November 4, 1968.

TABLE 1

No.	Compound	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		Yield, %	Found, %		Brutto formula	Calculated, %	
					found	calculated		P	N		P	N
I	 $(C_2H_5)_2N(Cl)\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2Cl$	114—115 (0,05)	1,4878	1,1870	56,23	56,07	90,4	13,31	6,73	$C_7H_{16}Cl_2NOP$	13,36	6,03
II	 $[(C_2H_5)_2N]_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2Cl$	146—147 (0,04)	1,4810	1,0590	72,14	72,65	89,9	11,39	10,40	$C_{11}H_{26}ClN_2OP$	11,59	10,42
III	 $(C_2H_5)_2N\underset{\underset{O}{\|}}{P}(CH_2CH_2CH_2Cl)_2$	158—159 (0,04)	1,5075	1,1678	69,87	69,96	61,7	11,40	5,15	$C_{10}H_{22}Cl_2NOP$	10,31	5,11
IV	 $(CH_2{=}CH{-}CH_2NH)_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2Cl$	134—135 (0,04)	1,5233	1,1343	63,72	62,48	50	12,95	11,84	$C_9H_{18}ClN_2OP$	13,10	11,83
V	 $CH_2{=}CH{-}CH_2NH\underset{\underset{O}{\|}}{P}(CH_2CH_2CH_2Cl)_2$	Т. пл. 167—169	—	—	—	—	71,5	12,27	6,01	$C_9H_{18}Cl_2NOP$	12,01	5,42
VI	 $(C_6H_5NH)_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2Cl$ *	Т. пл. 116—118	—	—	—	—	31,5	9,80	9,05	$C_{15}H_{18}ClN_2OP$	10,05	9,08
VII	 $C_6H_5NH\underset{\underset{O}{\|}}{P}(CH_2CH_2CH_2Cl)_2$	170—171 (0,004)	—	—	—	—	40,5	10,61	4,80	$C_{12}H_{18}Cl_2NOP$	10,54	4,76
VIII		92—93 (0,005)	1,5085	1,2334	50,44	50,26	61,4	14,40	13,52	$C_7H_{14}ClN_2OP$	14,86	13,42
IX		135—136 (0,008)	1,5255	1,2699	58,98	58,52	47,3	12,81	5,70	$C_8H_{16}Cl_2NOP$	12,70	5,73
X	 $[(C_2H_5)_2N]_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2N(C_2H_5)_2$	140—141 (0,04)	1,4678	0,9472	89,50	89,91	64	9,81	14,02	$C_{15}H_{36}N_3OP$	10,16	13,77
XI	 $(C_2H_5)_2N\underset{\underset{O}{\|}}{P}[CH_2CH_2CH_2N(C_2H_5)_2]_2$	137—138 (0,002)	1,4778	0,9422	104,20	104,76	62	9,17	11,80	$C_{18}H_{42}N_3OP$	8,93	12,10
XII	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2N(C_2H_5)_2$	116—117 (0,004)	1,4441	0,9970	66,92	67,80	63,3	12,65	5,39	$C_{11}H_{26}NO_3P$	12,35	5,57
XIII	 $C_2H_5O\underset{\underset{O}{\|}}{P}[CH_2CH_2CH_2N(C_2H_5)_2]_2$	162—163 (0,006)	1,4709	0,9628	92,85	93,61	50	9,75	8,81	$C_{16}H_{37}N_2O_2P$	9,68	8,70
XIV	 $(C_4H_9O)_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2N(C_2H_5)_2$	152—153 (0,04)	1,4438	0,9512	85,69	86,27	76	10,03	4,63	$C_{15}H_{34}NO_3P$	10,09	4,59
XV	 $(C_4H_9O)_2\underset{\underset{O}{\|}}{P}CH_2CH_2CH_2Cl$ †	127—128 (0,05)	1,4482	1,0577	68,50	68,73	78	11,48	—	$C_{11}H_{24}ClO_3P$	11,54	—

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* Recrystallized from benzene.

† Found: C 49.01, H 8.92%. Calculated C 48.80, H 8.81%.

6.4 g triethylamine in 100 ml absolute ether. The reaction mixture was then kept 1 h at room temperature and the precipitate filtered off. The product obtained after two distillations was 10.7 g (61.7% of theory) bis(γ-chloropropyl)phosphinic acid diethylamide. The physicochemical constants are presented in Table 1 (III). The other amides were obtained in the same way.

Preparation of N-Diethylaminopropylphosphonic Acid Dibutylester. The constants of γ-chloropropylphosphonic acid dibutyl ester (XV) are given in Table 1. A mixture of 7 g (XV) and 10 g diethylamine was heated in a sealed tube for 6 h. The precipitate was filtered and the excess diethylamine distilled off. The product after two distillations was 6 g (76%) of N-diethylaminopropylphosphonic acid dibutyl ester (XIV). The other esters and amides of N-diethylaminopropylphosphonic and bis(N,N-diethylaminopropyl)phosphinic acids were obtained in the same way. Their constants are shown in Table 1.

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CONCLUSIONS

1. The reactions of γ-chloropropylphosphonic and bis(γ-chloropropyl)phosphinic acid chlorides with amines have been studied.

2. The reaction of diethylamine with esters and amides of γ-chloropropylphosphonic and bis(γ-chloropropyl)phosphinic acids gave the derivatives of N-diethylaminopropylphosphonic and bis(N,N-diethylaminopropyl)phosphinic acids.

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