ADDITION OF HYPOPHOSPHOROUS ACID AND ITS SODIUM SALT TO ALLYL ALCOHOL

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Addition reactions of sodium hypophosphite and of hypophosphorous acid with olefins have been studied in fair detail [1-4]. They go in presence of peroxides with formation of dialkylphosphinic acids and their salts. The addition of these reagents to unsaturated compounds containing functional groups has received little investigation. The preparation of esters of phosphonosuccinic acid by prolonged reaction between hypophosphorous acid and maleic esters in absence of catalyst has been described [5]. There is also a brief reference in a patent to the formation of a cyclic ester by the reaction of sodium hypophosphite with 2-methyl-2-propen-1-ol [6]. However, these reactions are of undoubted practical interest, for they lead to the preparation of various derivatives containing a P—C bond and various functional groups.

We here report a study of the addition of sodium hypophosphite to allyl alcohol, allyl acetate, and allyl chloride and of crystalline hypophosphorous acid to allyl alcohol. The reaction of sodium hypophosphite with allyl alcohol was conducted in methanol in presence of t-butyl peroxide with heating in sealed tubes at 135-140° for 8-10 h. The crude product was hydrolyzed with hydrochloric acid, volatile products were removed in a vacuum, and as a result we isolated a mixture of (3-hydroxypropyl)phosphonic and bis(3-hydroxypropyl)phosphinic acids. The reaction of crystalline hypophosphorous acid with allyl alcohol was conducted also by heating the mixture of reactants in presence of t-butyl peroxide in sealed tubes at 120-135° for 12-14 h. As a result of this reaction an analogous mixture of acids was formed. The addition reactions of sodium hypophosphite with allyl acetate and with allyl chloride were carried out analogously.

Both in the additions of sodium hypophosphite to allyl alcohol and allyl acetate and also in the addition of pure hypophosphorous acid to allyl alcohol we were unable to isolate the individual products either by ordinary fractionation in a high vacuum, or by film distillation, or as their crystalline salts with aniline, barium, or lead. We were able to identify the products of addition to allyl alcohol only by their isolation as phosphonic dichlorides and phosphinic chlorides, obtained by treating the mixture of crude acids with PCl_5. The method which we used is at present used widely for the preparation of acid chlorides of a great variety of phosphonic and phosphinic acids. Thus, a method has been described for the preparation of bis(chloromethyl)phosphinic chloride [7] by the treatment of the product of the addition of sodium hypophosphite to formaldehyde with phosphorus pentachloride, and the synthesis of (3-alkoxy-3-chloropropenyl)phosphonic acid has also been described [8].

We studied the reaction of PCl_5 with the crude products obtained by the reaction of hypophosphorous acid or sodium hypophosphite with allyl alcohol, and we isolated (3-chloropropyl)phosphonic dichloride and bis(3-chloropropyl)phosphinic chloride. The chlorination of the crude product was conducted with PCl_5 in a medium of phosphoryl chloride at 5-7° with subsequent stirring of the reaction mixture, first at room temperature and then at 60°, until no more hydrogen chloride came off (1 h) (Table 1). We did not succeed in isolating products of the addition of sodium hypophosphite to allyl chloride and to allyl acetate in the form of the corresponding acid chlorides.

The (3-chloropropyl)phosphonic dichlorides and bis(3-chloropropyl)phosphinic chlorides which we obtained are reactive compounds. They can be used for the preparation of various derivatives and phosphorus-containing monomers and polymers. In a study of some of their chemical properties we carried out their reactions with methanol, ethanol, ethanethiol, phenol, and allyl alcohol. By the hydrolysis of the acid chlorides with water we prepared free (3-chloropropyl)phosphonic and bis(3-chloropropyl)phosphinic acids. In the treatment of the acids with aniline we isolated only anilinium hydrogen (3-chloropropyl)phosphonate. The constants of the substances obtained are given in Table 2.

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TABLE 1

No.	Compound	bp, °C (p, mm)	n_D^{20}	d_4^{20}	*MR*		Yield, %	Found, %		Molecular formula	Calculated, %	
					found	calculated		P	Cl		P	Cl
I	$\mathrm{Cl_2\underset{\overset{\|}{O}}{P}CH_2CH_2CH_2Cl}$*	63—64 (0,04)	1,4982	1,4534	39,41	38,61	22,7	15,69	54,84	$C_3H_6Cl_3OP$	15,85	54,47
II	The same†	85—86 (0,06)	1,4984	1,4543	39,39	38,61	28	15,09	54,00	The same	15,85	54,47
III	$\mathrm{Cl\underset{\overset{\|}{O}}{P}(CH_2CH_2CH_2Cl)_2}$*	144—146 (0,04)	1,5142	1,3374	53,46	52,98	25		45,08	$C_6H_{12}Cl_3OP$		44,84
IV	The same†	150—152 (0,05)	1,5142	1,3357	53,51	52,98	12,5		45,20	The same		44,84

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* Obtained after the chlorination of the crude product of the reaction of sodium hypophosphite with allyl alcohol.

†Obtained after the chlorination of the crude product of the reaction of hypophosphorus acid with allyl alcohol.

For confirmation of the structure of the compounds obtained and their fuller characterization we determined their IR spectra, some of which are shown in Fig. 1. The IR spectra of the acid chlorides (a) and (b) contain the absorption bands (cm^{-1}): 500-600 (P–Cl), 1200-1300 (P = O), 660 (C–Cl). The IR spectrum of the ester (d) contains the bands (cm^{-1}): 1220 (P = O), 1040 (P–O–C), 650 (C–Cl).

EXPERIMENTAL

Reaction of Sodium Hypophosphite with Allyl Alcohol. A mixture of 30 g of sodium hypophosphite, 54 g of allyl alcohol, 60 ml of methanol, and 1.5 ml of t-butyl peroxide was heated in sealed tubes at 135-140° for 8-10 h. The salts obtained were hydrolyzed with HCl, NaCl was filtered off, and volatile components were driven off. We obtained 58 g of a mixture of unpurified acids.

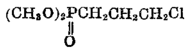
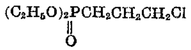
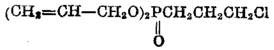
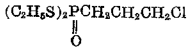
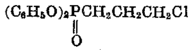
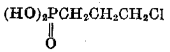
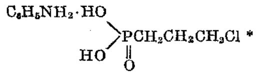
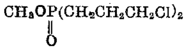
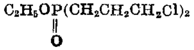
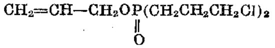
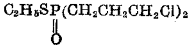
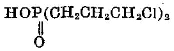
Preparation of (3-Chloropropyl)phosphonic Dichloride and Bis(3-chloropropyl)phosphinic Chloride. The 58 g of the mixture of unpurified acids was added with stirring and cooling to 3-7° to a suspension of 270 g of PCl_5 in 170 ml of $POCl_3$. When the whole of the mixture of acids had been added to the reaction mixture, the latter was stirred, first at room temperature, and then with cautious raising of the temperature in the bath to 60°; heating was continued at this temperature until no more HCl came off (1 h). Phosphoryl chloride was distilled off, unchanged PCl_5 was decomposed with dry SO_2, and the product was vacuum-fractionated. As a result of the fractionation we obtained (3-chloropropyl)phosphonic dichloride and bis(3-chloropropyl)phosphinic chloride. Physicochemical data are given in Table 1 [(I) and (III)].

Addition of Hypophosphorous Acid to Allyl Alcohol. A mixture of 29 g of crystalline hypophosphorous acid, 51 g of allyl alcohol, and 2 ml of t-butyl peroxide was heated in sealed tubes at 120-130° for 12-14 h. We obtained 69 g of a mixture of unpurified acids. (3-Chloropropyl)phosphonic dichloride and bis(3-chloropropyl)phosphinic chloride were prepared from the mixture as before [see Table 1, (II) and (IV)].

Preparation of Diallyl (3-Chloropropyl)phosphonate. A solution of 11.3 g of (3-chloropropyl)phosphonic dichloride in 20 ml of ether was added dropwise to a solution of 8 g of allyl alcohol and 9.15 g of pyridine in 100 ml of dry ether at 5-7°. The mixture was then stirred for 2 h at room temperature and for 1 h at 35°. On the next day pyridine hydrochloride was filtered off and washed with ether. As a result of fractionation we obtained 7.05 g (51.1%) of diallyl (3-chloropropyl)phosphonate. Physicochemical data are given in Table 2 [(VII)]. The other dialkyl (3-chloropropyl)phosphonates and alkyl bis(3-chloropropyl)phosphinates were prepared analogously with small changes in the temperature schedules. The constants of the esters obtained are given in Table 2.

Preparation of (3-Chloropropyl)phosphonic Acid. With cooling and stirring 15 g of water was added cautiously dropwise to 7 g of (3-chloropropyl)phosphonic dichloride. Water was driven off, and the residue crystallized. After two crystallizations from benzene we obtained 4.4 g (86%) of (3-chloropropyl)phosphonic acid, mp 105-106°. Analytical data are given in Table 2 [(X)].

TABLE 2

No.	Compound	bp, °C (p, mm Hg) mp, °C	n_D^{20}	d_4^{20}	MR		Yield, %	Found, %			Molecular formula	Calculated,%		
					found	calculated		C	H	P		C	H	P
V	 $(CH_3O)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	74—75 (0,06)	1,4520	1,2368	40,70	41,01	64,5	31,96	6,23	16,02	$C_5H_{12}ClO_3P$	32,17	6,43	16,56
VI	 $(C_2H_5O)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	84—85 (0,04)	1,4460	1,1429	50,03	50,26	70,7	39,14	7,45	13,91	$C_7H_{16}ClO_3P$	39,16	7,45	14,45
VII	 $(CH_2{=}CH{-}CH_2O)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	102—103 (0,02)	1,4695	1,1462	58,06	58,56	51,1	44,76	6,80	13,01	$C_9H_{16}ClO_3P$	44,82	6,76	12,99
VIII	 $(C_2H_5S)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	121—122 (0,03)	1,5456	1,2089	64,69	65,09	71,8	34,06	6,45	12,20	$C_7H_{16}ClOPS_2$	34,07	6,49	12,57
IX	 $(C_6H_5O)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	172—173 (0,04)	1,5515	1,2441	79,77	80,00	76,8	58,09	5,09	9,79	$C_{15}H_{16}ClO_3P$	57,96	5,15	9,98
X	 $(HO)_2\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$	105—106	—	—	—	—	86	23,07	4,91	19,46	$C_3H_8ClO_3P$	22,71	5,04	19,55
XI	 $C_6H_5NH_2\cdot\begin{matrix}HO\\HO\end{matrix}\!>\!\underset{\overset{\Vert}{O}}{P}CH_2CH_2CH_2Cl$ *	151—152	—	—	—	—	80	—	—	12,48	$C_9H_{15}ClNO_3P$	—	—	12,32
XII	 $CH_3O\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	151—152 (0,05)	1,4942	1,2710	53,38	53,48	74,7	35,99	6,69	13,17	$C_7H_{15}Cl_2O_2P$	36,05	6,43	13,30
XIII	 $C_2H_5O\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	152—153 (0,05)	1,4871	1,2192	58,28	58,10	79,1	38,78	6,98	12,02	$C_8H_{17}Cl_2O_2P$	38,86	6,88	12,55
XIV	 $CH_2{=}CH{-}CH_2O\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	162—163 (0,05)	1,4998	1,2029	63,28	62,77	52,7	42,00	6,68	12,04	$C_9H_{17}Cl_2O_2P$	41,69	6,56	11,96
XV	 $C_2H_5S\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	172—173 (0,07)	1,5365	1,2268	66,85	66,04	65	36,90	6,45	11,28	$C_8H_{17}Cl_2OPS$	36,50	6,46	11,78
XVI	 $C_6H_5O\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	178—179 (0,03)	1,5370	1,2540	73,48	73,49	84,4	48,95	5,69	10,72	$C_{12}H_{17}Cl_2O_2P$	48,81	5,76	10,50
XVII	 $HO\underset{\overset{\Vert}{O}}{P}(CH_2CH_2CH_2Cl)_2$	64—66	—	—	—	—	62,3	32,62	5,93	13,93	$C_6H_{13}Cl_2O_2P$	32.87	5,93	14,17

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* Found: N 5.39%; calculated N 5.56%.

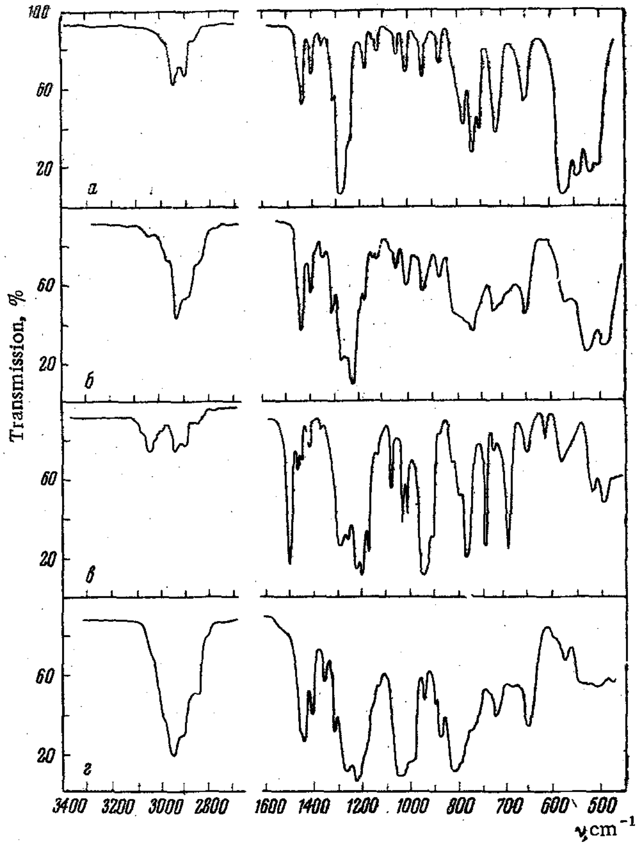

Fig. 1. IR spectra: a) (3-chloropropyl)phosphonic dichloride; b) bis(3-chloropropyl)phosphinic chloride; c) diphenyl (3-chloropropyl)phosphonate; d) methyl bis(3-chloropropyl)phosphinate.

Bis(3-chloropropyl)phosphinic acid was prepared analogously [see Table 2, (XVII)].

Preparation of Anilinium Hydrogen (3-Chloropropyl)phosphonate. To a solution of 1 g of the acid in methanol 1.46 g of aniline was added with stirring. After a few minutes crystallization set in. Recrystallization from CCl_4 gave 1.2 g (80%) of the salt, mp 151-152°. Analytical data are given in Table 2 [(XI)].

We thank L.I. Kulakova for determining the IR spectra.

CONCLUSIONS

1. The reactions of hypophosphorous acid and its sodium salt with allyl alcohol were studied.

2. A method was developed for the preparation of (3-chloropropyl)phosphonic dichloride and bis(3-chloropropyl)phosphinic chloride, and the reactions of these acid chlorides with alcohols and water were studied.

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