PREPARATION AND REARRANGEMENT OF DIALKYL AND DIARYL 1-METHYL-1-(TRICHLOROMETHYL)PROPYL PHOSPHITES

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The reactions of chlorine-substituted t-alkyl alcohols with phosphorus trichloride have been little studied. Descriptions have been given of the reactions of 1,1,1-trichloro-2-methyl-2-propanol [1-3], 1-(trichloromethyl)cyclopentanol [4], and 1-(trichloromethyl)cyclohexanol [5] with phosphorus trichloride. In these papers it was shown that in the reaction of three moles of the chlorine-substituted tertiary alcohol with one mole of phosphorus trichloride in presence of pyridine, instead of the expected phosphorus triester the phosphorochloridous diester is obtained. The third chlorine atom in the phosphorochloridous diester can be replaced by a primary or secondary alkoxyl or by phenoxyl, but it cannot be replaced by a tertiary-alcohol residue.

Only one paper [6] has appeared on the rearrangement of dialkyl chlorinated-t-alkyl phosphites. We have studied the reaction of 1,1,1-trichloro-2-methyl-2-butanol, prepared by a known method [7], with phosphorus trichloride. By the reaction of one or two moles of this alcohol with one mole of phosphorus trichloride we obtained good yields of 1-methyl-1-(trichloromethyl)propyl phosphorodichloridite and bis[1-methyl-1-(trichloromethyl)propyl] phosphorochloridite. We were unable to prepare tris[1-methyl-1-(trichloromethyl)propyl] phosphite.

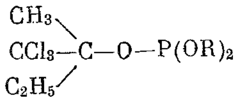
In this paper we describe the synthesis and rearrangement of dialkyl and diaryl 1-methyl-1-(trichloromethyl)-propyl phosphites. By the reaction of 1-methyl-1-(trichloromethyl)propyl phosphorodichloridite (I) with normal and branched primary alcohols, secondary alcohols, and phenol in presence of triethylamine we obtained the corresponding mixed esters (II), the constants of which are given in Table 1. All the esters obtained are thick colorless liquids which can be vacuum-distilled without decomposition, dissolve in organic solvents (ether, acetone, benzene, alcohol), but are insoluble in water.

From the products of the reaction of one mole of (I) and two moles of 1,1,1-trichloro-2-methyl-2-propanol in presence of two moles of pyridine we isolated 1-methyl-1-(trichloromethyl)propyl 2,2,2-trichloro-1,1-dimethylethyl phosphorochloridite (III) together with unchanged 1,1,1-trichloro-2-methyl-2-propanol and pyridine. We were unable to obtain the phosphorus triester with three t-alkyl groups, probably because of steric factors. In presence of triethylamine the phosphorodichloridite reacts with 2,3-dimethyl-2,3-butanediol with formation of the corresponding cyclic tetramethylethylene ester (IV). The ease with which this ester is formed may be explained by the sterically favorable cyclic structure of the ester.

All the mixed phosphorous esters obtained (see Table 1) react exothermically with cuprous chloride [8] and give the corresponding complex compounds (V) in the form of crystals or thick sirups.

We have shown previously [6] that the rearrangement of alkyl bis(2,2,2-trichloro-1,1-dimethylethyl) phosphites with methyl iodide and with benzyl bromide goes with the elimination of the light unsubstituted alkyl. We carried out the rearrangement of our dialkyl 1-methyl-1-(trichloromethyl)propyl phosphites (II) with allyl bromide. As a result we obtained a number of allylphosphonic esters (VI), the constants of which are given in Table 3. Hence, the rearrangement of dialkyl 1-methyl-1-(trichloromethyl)propyl phosphites with allyl bromide goes with the elimination of the light unsubstituted alkyl in accordance with the scheme (see the structure below Table 2). All the mixed allylphosphonic esters obtained (VI) (Table 3) are sirupy liquids which can be vacuum-distilled without decomposition. Diphenyl and dimethyl 1-methyl-1-(trichloromethyl)propyl phosphites react with allyl bromide in a complicated way; no individual substances could be isolated from the reaction products.

TABLE 1. Dialkyl and Diaryl 1-Methyl-1-(trichloromethyl)propyl Phosphites



$$CCl_3-\overset{CH_3}{\underset{C_2H_5}{C}}-O-P(OR)_2$$

(II)

R	B. p., °C (p, mm)	d_4^{20}	n_D^{20}	Found*			Calculated			Yield, %
				MR	Cl, %	P, %	MR	Cl, %	P, %	
CH_3	78—79(0,1)	1,3130	1,4857	61,96	37,59	11,02	62,25	37,51	10,92	90,0
C_2H_5	89—90(0,18)	1,2430	1,4768	70,82	34,26	10,24	71,49	34,13	9,94	74,4
C_3H_7	112—113(0,24)	1,1880	1,4748	80,46	31,29	9,20	80,72	31,35	9,12	88,0
i-C_3H_7	82(0,08)	1,1824	1,4703	80,19	32,00	8,78	80,72	31,35	9,12	74,0
C_4H_9	110(0,07)	1,1516	1,4738	89,76	29,07	8,64	89,95	28,94	8,43	90,1
i-C_4H_9	116—117(0,16)	1,1451	1,4711	89,78	29,05	8,51	89,95	28,94	8,43	71,2
s -C_4H_9	108(0,2)	1,1618	1,4737	89,00	29,51	8,00	89,95	28,94	8,43	56,5
i-C_5H_{11}	120(0,1)	1,1195	1,4718	98,95	27,04	8,00	99,19	26,88	7,83	76,2
C_6H_5	158(0,09)	1,3040	1,5645	101,60	25,51	7,40	101,22	26,09	7,60	92,0

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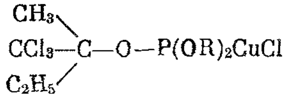
* The chlorine and phosphorus contents are means of two determinations.

TABLE 2. Complex Compounds of Dialkyl and Diaryl 1-Methyl-1-(trichloromethyl)propyl Phosphites



$$CCl_3-\overset{CH_3}{\underset{C_2H_5}{C}}-O-P(OR)_2CuCl$$

(V)

R	M.p., °C	Found*, %		Calculated, %	
		Cl	P	Cl	P
CH_3	107—108	37,39	8,12	37,08	8,09
i-C_3H_7	128—129	32,71	7,28	32,33	7,06
s -C_4H_9	134—135	30,37	6,85	30,28	6,63
C_6H_5	93	27,78	6,28	27,99	6,11

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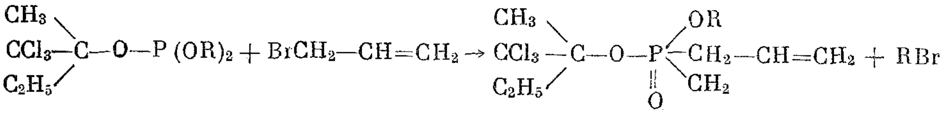
* The chlorine and phosphorus contents are means of two determinations.



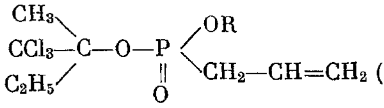
$$CCl_3-\overset{CH_3}{\underset{C_2H_5}{C}}-O-P(OR)_2 + BrCH_2-CH=CH_2 \rightarrow CCl_3-\overset{CH_3}{\underset{C_2H_5}{C}}-O-\underset{O}{\overset{OR}{P}}\!-CH_2-CH=CH_2 + RBr$$

EXPERIMENTAL

Preparation of 1-Methyl-1-(trichloromethyl)propyl Phosphorodichloridite (I). A mixture of 121 g of phosphorus trichloride and 500 ml of dry ether was prepared in a 1-liter four-necked flask with ground joints carrying a mechanical stirrer, a dropping funnel, a thermometer, and a reflux condenser protected by a calcium chloride tube, the flask was cooled externally with ice and salt, and 153.2 g of 1,1,1-trichloro-2-methyl-2-butanol was added. 63.3 g of pyridine was then added dropwise at such a rate that the temperature inside the flask did not rise above 0°. The mixture was stirred at room temperature for 4 h, heated at the boiling point of ether for 1 h, and left overnight. On the next day pyridine hydrochloride was filtered off, ether was removed in a vacuum, and the residue was distilled. We isolated 194 g (83%) of (I), b. p. 121-122° (8 mm); d_4^{20} 1.4913; n_D^{20} 1.5262; Found: P 10.50; Cl 60.21% MR 60.17. $C_5H_8OCl_5P$. Calculated: P 10.60; Cl 60.63%; MR 60.20.

Preparation of Bis[1-methyl-1-(trichloromethyl)propyl] Phosphorochloridite. A mixture of 68.67 g of phosphorus trichloride and 500 ml of ether was prepared in the apparatus described above, the flask was cooled externally with salt and ice, and 191.5 g of 1,1,1-trichloro-2-methyl-2-butanol was added. With cooling and stirring 79.1 g of

TABLE 3. Mixed Allylphosphonic Esters


(VI)

R	B. p., °C (p, mm)	d_4^{20}	n_D^{20}	Found*			Calculated			Yield, %
				MR	Cl, %	P, %	*MR*	Cl, %	P, %	
C_2H_5	99(0,13)	1,2682	1,4826	73,00	33,11	9,50	73,38	32,83	9,57	47,5
C_3H_7	111—112(0,15)	1,2380	1,4808	77,60	31,72	9,20	78,00	31,50	9,17	60,2
i-C_3H_7	112(0,2)	1,2361	1,4783	77,36	32,07	8,88	78,00	31,50	9,17	50,1
C_4H_9	130(0,18)	1,2135	1,4808	82,43	30,60	8,71	82,62	30,25	8,81	67,1
i-C_4H_9	112(0,15)	1,2096	1,4785	82,36	30,68	9,07	82,62	30,25	8,81	60,0
s -C_4H_9	119(0,12)	1,2170	1,4797	82,08	30,18	8,86	82,62	30,25	8,81	60,4
i-C_5H_{11}	120(0,09)	1,1922	1,4787	87,00	29,64	8,32	87,24	29,09	8,47	74,2

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* The chlorine and phosphorus contents are means of two determinations.

pyridine was added dropwise at such a rate that the temperature within the flask did not rise above 0°. On the next day pyridine hydrochloride was filtered off, ether was removed in a vacuum, and the residue was distilled. We isolated 152.5 g (68.5%) of product, b. p. 162° (0.14 mm); d_4^{20} 1.4683; n_D^{20} 1.5310. The product was a thick fuming liquid which rapidly solidified to crystals; m. p. 69-70°. Found: P 6.80; Cl 54.96%; MR 94.27. $C_{10}H_{16}O_2Cl_7P$. Calculated: P 6.92; Cl 55.47%; MR 94.29.

Preparation of Dialkyl (Diphenyl) 1-Methyl-1-(trichloromethyl)propyl Phosphites (II). A mixture of 0.3 mole of the alcohol (phenol), 0.3 mole of triethylamine, and 250 ml of dry ether was prepared in a 500-ml four-necked flask assembled as described above. With external cooling of the flask with salt and ice 0.15 mole of the phosphorodichloridous ester was added at such a rate that the temperature inside the flask remained below 0°. The cooling bath was removed, and the mixture was stirred at room temperature. On the next day triethylamine hydrochloride was filtered off, ether was removed in a vacuum, and the residue was vacuum-distilled. The corresponding phosphorous esters (II) were obtained; their constants and yields are given in Table 1.

Reaction of One Molecular Proportion of the Phosphorodichloridous Ester (I) with Two Molecular Proportions of 2,2,2-Trichloro-1,1-dimethylethanol. A mixture of 33.7 g of 2,2,2-trichloro-1,1-dimethylethanol, 15.03 g of pyridine, and 250 ml of dry ether was prepared in a 500-ml four-necked flask assembled as in the preceding experiments. With external cooling of the flask with a mixture of salt and snow 27.8 g of the phosphorodichloridous ester (I) was added dropwise at such a rate that the temperature inside the flask remained below 0°. The cooling bath was removed, and the mixture was stirred at room temperature and then left overnight. On the next day pyridine hydrochloride was filtered off. The weight of the pyridine hydrochloride was 11 g. Ether was removed in a vacuum. From the head fraction (bath temperature 120°, p = 10 mm) we isolated 10.7 g of 2,2,2-trichloro-1,1-dimethylethanol in the form of the hydrate $2C_4H_7Cl_3O \cdot H_2O$ and 5 g of pyridine. The main reaction product—1-methyl-1-(trichloromethyl)propyl 2,2,2-trichloro-1,1-dimethylethyl phosphorochloridite—was a thick fuming liquid; b. p. 132° (0.1 mm); d_4^{20} 1.4963; n_D^{20} 1.5293. Found: Cl 57.01; P 7.31%; MR 89.33. $C_9H_{14}O_2Cl_7P$. Calculated: Cl 57.27; P 7.14%; MR89.68. Yield 36 g (88%).

Reaction of the Phosphorodichloridous Ester (I) with 2,3-Dimethyl-2,3-butanediol. A mixture of 30.36 g of triethylamine, 17.73 g of 2,3-dimethyl-2,3-butanediol, and 200 ml of dry ether was prepared in a four-necked flask assembled as described above. The flask was cooled externally with a mixture of snow and salt, and 43.86 g of the phosphorodichloridous ester was added dropwise. The formation of triethylamine hydrochloride began only at room temperature. On the next day 41 g of crude triethylamine hydrochloride was filtered off. Ether was removed in a vacuum, and the main product did not distill over a narrow range of temperatures; we isolated only 8 g (15.8%) of product; b. p. 102° (0.2 mm); d_4^{20} 1.2471; n_D^{20} 1.4878. Found: Cl 30.93; P 9.52%; MR 78.00. $C_{11}H_{20}Cl_3O_3P$. Calculated: Cl 31.50; P 9.17%; MR 78.52. In analysis and constants the product corresponded to (IV).

Preparation of Mixed Allylphosphonic Esters (VI). A mixture of 0.03 mole of the mixed ester (II) and excess (0.045 mole) of allyl bromide was sealed in a tube. The tube was heated at 120° for 10-24 h. The tube was cooled and opened, and the reaction products were fractionated. The head fraction consisted of a mixture of excess of allyl bromide and the alkyl bromide, which we did not succeed in separating. By vacuum distillation of the residue we obtained mixed allylphosphonic esters—colorless sirupy liquids whose constants are given in Table 3.

Preparation of Complex Compounds of the Mixed Esters (II) with Cuprous Chloride. To 1.5-3 g of the mixed ester (II) contained in a test tube we added an equimolecular amount of cuprous chloride. The mixture was stirred with a thermometer. The temperature usually rose by 18-32°. To complete reaction the mixture was heated to 120-150°. The reaction products were cooled and dissolved in chloroform, and the solution was filtered through filter paper. Methanol was added to the filtrate until a turbidity appeared. When warmed slightly, the solution became clear again. The solution was set aside, and the complex compounds (VI) were precipitated as white crystals or as thick sirups. The constants of the crystalline products (VI) are given in Table 2.

SUMMARY

1. In presence of triethylamine 1-methyl-1-(trichloromethyl)propyl phosphorodichloridite reacts with two molecular proportions of a primary or secondary alcohol or a phenol with formation of the corresponding mixed esters. Under these conditions chlorine-substituted tertiary alcohols can react with replacement of only one of the chlorine atoms of the phosphorodichloridous ester.

2. Rearrangement of dialkyl 1-methyl-1-(trichloromethyl)propyl phosphites with allyl bromide goes with the elimination of the unsubstituted alkyl group and leads to the formation of mixed allylphosponic esters.

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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-to-cover English translations appears at the back of this issue.**