PREPARATION OF PHOSPHORYLATED CHLORAL HEMIACETALS, THEIR PROPERTIES AND REACTIONS

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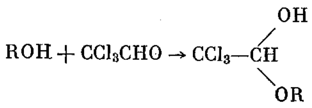
UDC 542.91+661.718.1+547.446.1

In the reactions of aldehydes with alcohols acetals are obtained, not usually hemiacetals. Only in rare cases has it been found possible to prepare stable hemiacetals when in the aldehyde the α-carbon atom is linked with a strongly electronegative atom or group of atoms. Under the influence of the electron-attracting group the reactivity of the carbonyl carbon increases to such an extent that such weak nucleophiles as alcohols are able to add readily with formation of stable hemiacetals. In the reactions of chloral with alcohols stable crystalline hemiacetals are obtained:



$$ROH + CCl_3CHO \rightarrow CCl_3{-}CH\begin{matrix}\diagup OH\\ \diagdown OR\end{matrix}$$

The hydroxy group in these compounds has an alcoholic character and undergoes reactions characteristic for alcohols. The IR spectra (Fig. 1) of chloral hemiacetals contain a strong hydroxyl absorption band at about 3400 cm^{-1}. The hydroxy group is also responsible for bands at 1290 cm^{-1} (δ_{OH} planar) and

TABLE 1

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	MR*	C, %	H, %	P, %	Cl, %
$(C_2H_5O)_2PO\underset{OCH_3}{\underset{\mid}{C}}HCCl_3$	58.0	126—128 (10)	1.4638	1.2880	64.12* 63.84	27.60* 28.05	4.58* 4.67	10.27* 10.35	34.92* 35.55
$(C_2H_5O)_2PO\underset{OC_2H_5}{\underset{\mid}{C}}HCCl_3$	61.7	126—128 (9)	1.4593	1.2557	68.25 68.46	30.40 30.62	5.04 5.10	10.07 9.88	33.54 33.97
$(C_2H_5O)_2PO\underset{OC_3H_7}{\underset{\mid}{C}}HCCl_3$	65.0	72—74 (0.03)	1.4596	1.2330	73.30 73.08	—	—	9.14 9.46	32.36 32.52
$C_2H_5O)_2PO\underset{OC_4H_9}{\underset{\mid}{C}}HCCl_3$	64.1	84—86 (0.03)	1.4594	1.1980	77.91 77.69	35.21 35.14	6.43 5.86	9.14 9.08	30.65 31.18
$(C_3H_7O)_2PO\underset{OCH_3}{\underset{\mid}{C}}HCCl_3$	50.0	79—81 (0.03)	1.4613	1.2311	73.04 73.07	32.35 32.97	5.20 5.50	9.62 9.47	—
$(C_3H_7O)_2PO\underset{OC_2H_5}{\underset{\mid}{C}}HCCl_3$	37.2	80—82 (0.025)	1.4605	1.2023	77.86 77.69	—	—	8.92 9.07	31.10 31.18
$(C_3H_7O)_2PO\underset{OC_3H_7}{\underset{\mid}{C}}HCCl_4$	54.1	84—86 (0.025)	1.4590	1.1810	82.28 82.31	—	—	9.01 8.72	—
$(C_3H_7O)_2PO\underset{OC_4H_9}{\underset{\mid}{C}}HCCl_3$	42.5	91—93 (0.03)	1.4580	1.1570	87.15 86.94	—	—	8.32 8.38	28.71 28.82
$(C_4H_9O)_2PO\underset{OCH_3}{\underset{\mid}{C}}HCCl_3$	59.5	95—97 (0.025)	1.4618	1.1849	82.45 82.31	—	—	8.62 8.72	—
$(C_4H_9O)_2PO\underset{OC_2H_5}{\underset{\mid}{C}}HCCl_3$	46.4	97—99 (0.025)	1.4598	1.1650	86.84 86.93	—	—	8.68 8.39	28.72 28.82
$(C_4H_9O)_2PO\underset{OC_3H_7}{\underset{\mid}{C}}HCCl_7$	61.8	92—94 (0.025)	1.4580	1.1465	91.28 91.55	—	—	7.86 8.08	27.95 27.77
$(C_4H_9O)_2PO\underset{OC_4H_9}{\underset{\mid}{C}}HCCl_3$	54.3	105—107 (0.03)	1.4595	1.1286	96.38 96.17	—	—	7.89 7.80	—

*The upper values were found, and the lower were calculated.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 593-602, March, 1968. Original article submitted July 3, 1967.

TABLE 2

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	*MR*	P, %	Cl, %	S, %
$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}O\overset{OCH_3}{\overset{|}{C}}HCCl_3$	63.0	84—86 (0.035)	1.4810	1.3406	70.37* 70.25	9.69* 9.25	32.42* 32.13	9.29* 9.65
$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}O\overset{OC_2H_5}{\overset{|}{C}}HCCl_3$	55.3	80—82 (0.025)	1.4766	1.3069	74.65 74.87	9.05 8.97	30.97 30.82	9.06 9.26
$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}O\overset{OC_3H_7}{\overset{|}{C}}HCCl_3$	53.7	92—94 (0.025)	1.4760	1.2767	79.41 79.48	8.44 8.62	30.30 29.62	8.83 8.90
$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}O\overset{OC_4H_9}{\overset{|}{C}}HCCl_3$	48.1	95—97 (0.025)	1.4745	1.2505	84.00 84.10	8.51 8.30	28.92 28.51	—

*The upper values were found, and the lower were calculated.

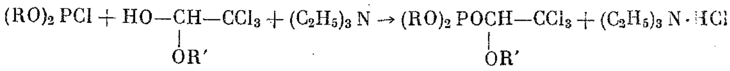
TABLE 3

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	*MR*	P, %	Cl, %
$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}O\overset{OC_2H_5}{\overset{|}{C}}HCCl_3$	48.8	80—81 (0.025)	1.4510	1.3148	67.48* 67.39	9.24* 9.41	32.45* 32.32
$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}O\overset{OC_4H_9}{\overset{|}{C}}HCCl_3$	57.7	87—88 (0.02)	1.4510	1.2549	76.71 76.61	8.58 8.67	30.32 29.79
$(C_4H_9O)_2\overset{O}{\overset{\|}{P}}O\overset{OC_3H_7}{\overset{|}{C}}HCCl_3$	45.4	108—109 (0.025)	1.4520	1.1888	90.66 90.47	7.65 7.75	27.20 26.66

*The upper values were found, and the lower were calculated.

650 cm^{-1} (δ_{OH} nonplanar). The presence of a C—O bond is confirmed by intense absorption at 1100 cm^{-1}, and also by a band at 1040 cm^{-1}. The strong doublet at 800 and 830 cm^{-1} must be assigned to the CCl_3 group. The presence of a $\geqslant$CH group may be indicated by the band of medium intensity at 1340 cm^{-1} [1].

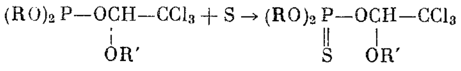
In presence of agents for the binding of hydrogen chloride (under suitable conditions) by reaction with dialkyl phosphorochloridites chloral hemiacetals give the corresponding phosphorous triesters:



$$(RO)_2PCl + HO-\underset{OR'}{\underset{|}{C}}H-CCl_3 + (C_2H_5)_3N \rightarrow (RO)_2PO\underset{OR'}{\underset{|}{C}}H-CCl_3 + (C_2H_5)_3N\cdot HCl$$

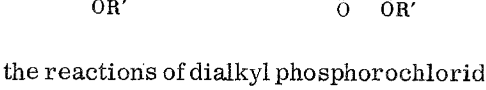
Since the compounds formed contain a complex radical (a 1-alkoxy-2,2,2-trichloroethyl group), the tervalence of the phosphorus present is in need of proof. A group containing halogen atoms could play the part of the alkyl halide in the Arbuzov reaction, especially at elevated temperatures. In distillation, for example, intramolecular rearrangement of phosphite into phosphonate might occur. With this object we carried out the addition of sulfur and oxidation.

The addition of sulfur goes with liberation of heat and formation of phosphorothioates:



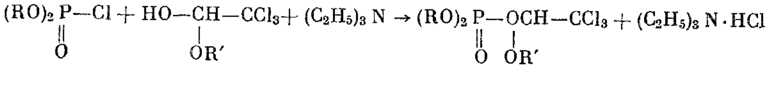
$$(RO)_2P-O\underset{OR'}{\underset{|}{C}}H-CCl_3 + S \rightarrow (RO)_2\underset{S}{\underset{\|}{P}}-O\underset{OR'}{\underset{|}{C}}H-CCl_3$$

Oxidation of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites with nitrogen dioxide leads to the corresponding phosphates:



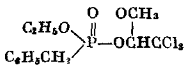
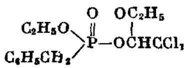
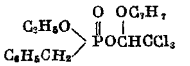
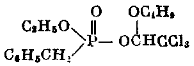
$$(RO)_2PO\underset{OR'}{\underset{|}{C}}H-CCl_3 + N_2O_4 \rightarrow (RO)_2\underset{O}{\underset{\|}{P}}-O\underset{OR'}{\underset{|}{C}}H-CCl_3$$

The same phosphates are obtained in the reactions of dialkyl phosphorochloridates with chloral hemiacetals [2]:



$$(RO)_2\underset{O}{\underset{\|}{P}}-Cl + HO-\underset{OR'}{\underset{|}{C}}H-CCl_3 + (C_2H_5)_3N \rightarrow (RO)_2\underset{O}{\underset{\|}{P}}-O\underset{OR'}{\underset{|}{C}}H-CCl_3 + (C_2H_5)_3N\cdot HCl$$

TABLE 4

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	MR	C, %	H, %	P, %	Cl, %	RX	Yield, %	Found, n_D^{20}
	45.8	118—120 (0.025)	1.5132	1.3451	80.81* 81.13	39.03* 39.83	4.92* 4.43	8.55* 8.57	29.95* 29,46	C_2H_5Br	73.7	1.4223†
	28.8	127 (0.035)	1.5070	1.3085	85.40 85.75	41.13 41.54	4.92 4.79	8.64 8.26	28.10 28.36	C_2H_5Br	66.7	1.4225
	42.0	122—123 (0.025)	1.5042	1.2861	89.71 90.36	—	—	7.79 7.96	27.38 27.34	C_2H_5Br	73.9	1.4230
	27.4	124—125 (0.025)	1.5018	1.2555	94.81 94.98	—	—	8.14 7.68	—	C_2H_5Br	71.9	1.4240

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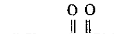
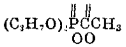
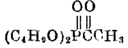
* The upper values were found, and the lower were calculated.

† [10] gives n_D^{20} 1.4239.

TABLE 5

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	C, %	H, %	P, %	RX	Yield, %	bp, °C (p, mm)	n_D^{20}
 $(C_2H_5O)_2\overset{O}{\overset{\|}{P}}\overset{O}{\overset{\|}{C}}CH_3$	45.5	101—102 (8)	1.4228	1.1036	40.37* 40.00	7.41* 7.22	17.02* 17.22	$CCl_3CH(Cl)OCH_3$ †	67.5	92—94 (20)	1.4830
 $(C_3H_7O)_2\overset{O}{\overset{\|}{P}}\overset{O}{\overset{\|}{C}}CH_3$	47.6	57—58 (0.025)	1.4285	1.0301	—	—	—	$CCl_3CH(Cl)OCH_3$	—	—	—
 $(C_4H_9O)_2\overset{O}{\overset{\|}{P}}\overset{O}{\overset{\|}{C}}CH_3$	57.1	137—138 (10)	1.4330	1.0290	—	—	—	$CCl_3CH(Cl)OC_2H_5$ ‡	—	67—68.5 (10)	1.4749

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* The upper values were found, and the lower were calculated.

† [11] gives: bp 72-75° (22 mm); n_D^{25} 1.4820.

‡ [12] gives: bp 78° (12 mm); n_D^{20} 1.4755.

TABLE 6

Compound	Yield, %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	P, %	Cl, %	RX	Yield, %	bp, °C (p, mm)	n_D^{20}
$(C_2H_5O)_2P(O)OCH = CCl_2$	78.1	122—123 (10)	1.4490	1.3010	—	—	$CCl_3CH(Cl)OCH_3$ †	47.2	55—56 (10)	1.4835
$(C_2H_5O)_2P(O)OCH = CCl_2$	59.4	126—127 (13)	1.4520	1.2950	—	—	$CCl_3CH(Cl)OC_4H_9$	—	—	—
$(C_3H_7O)_2P(O)OCH = CCl_2$	72.7	142 (10)	1.4500	1.2265	11.06* 11.19	25.28* 25.63	$CCl_3CH(Cl)OC_2H_5$ ‡	83.3	70—75 (12)	—

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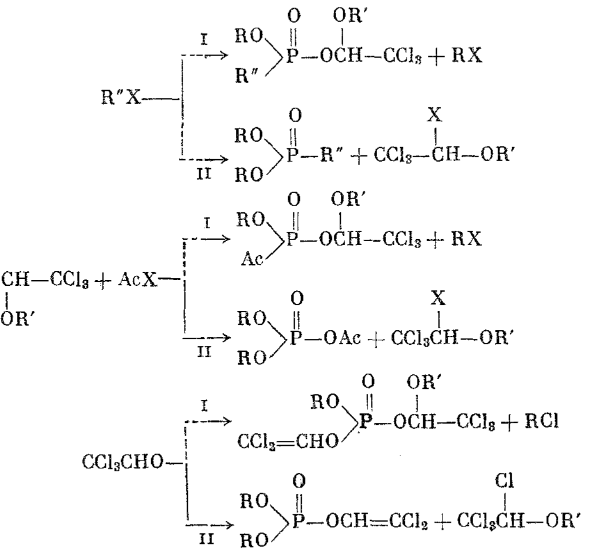
*The upper values were found, and the lower were calculated.

† [11] gives: bp 72-75° (22 mm); n_D^{20} 1.4820.

‡ [12] gives: bp 78° (12 mm); n_D^{20} 1.4755.

In the IR spectra the view that 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites are formed in the reactions of dialkyl phosphorochloridites with chloral hemiacetal is supported in the first place by the absence of the characteristic absorption of the P=O bond. A series of intense bands in the region 860-1050 cm^{-1} belongs to the vibrations of the C—O(P) group, and one of these (950 cm^{-1}) is sensitive to the valence state of phosphorus and usually lies higher (980-990 cm^{-1}) for phosphates. The so-called P—OC vibrations usually show up as a strong band at 755 cm^{-1}. The presence of the acetal group —C—O—C—O— is confirmed by intense absorption (4-5 bands) in the region 1050-1160 cm^{-1} and some complication of the absorption at about 1000 cm^{-1}. The band at 810-820 cm^{-1} associated with the vibrations of the CCl_3 group and present in the spectra of the original hemiacetals is preserved in these spectra. The spectra of O-(1-alkoxy-2,2,2-trichloroethyl) O,O-dialkyl phosphorothioates contain a P=S band at 630 cm^{-1}. The displacement in this case of the band at 950 cm^{-1} to 980 cm^{-1} confirms the transition of the phosphorus into the four-coordinated state. Also, the "P—OC" band is shifted toward the high frequencies to 800-830 cm^{-1}, where it merges with the CCl_3 band. We must mention that the spectra of the phosphites and phosphorothioates obtained contain weak absorption at about 1290 cm^{-1} indicative of the presence of small amounts of phosphate ($\nu_{P=O}$). This probably indicates that intramolecular rearrangement occurs, though to a limited extent.

The spectra of the phosphates, prepared by both methods, contain an intense band at 1290 cm^{-1} (P=O group). As in the case of the phosphorothioates the 950 cm^{-1} band is shifted to 980 cm^{-1}, and the so-called P—O(C) band is also shifted and becomes appreciably weaker. These changes correspond to the conversion of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites into the corresponding phosphates (see Fig. 1). In view of the fact that the phosphites being studied are mixed esters, it was of interest to study the reactions of these phosphites with alkyl halides, acyl halides, and chloral. The reactions of mixed phosphorous esters with halogen compounds can take two courses:



The course of reaction depends not only on the structures of the alcohol residues in the phosphite, but also on the nature of the

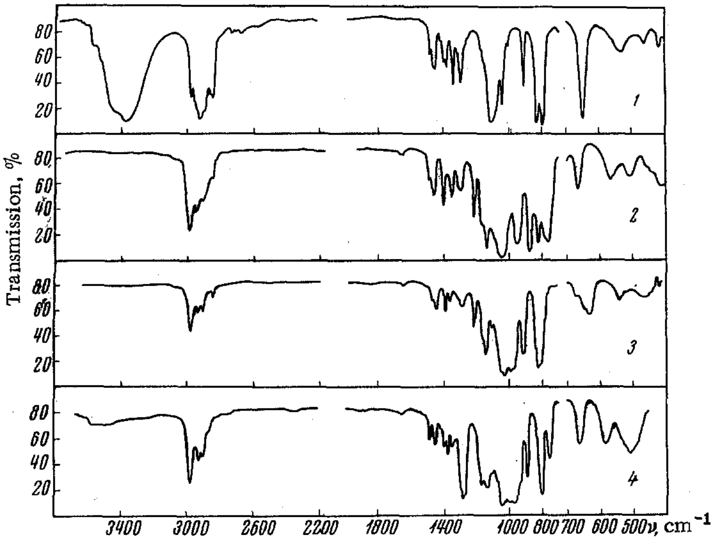


Fig. 1. IR spectra: 1) 2,2,2-trichloro-1-ethoxyethanol (mineral oil mull); 2) diethyl 2,2,2-trichloro-1-methoxyethyl phosphite; 3) O,O-diethyl O-(2,2,2-trichloro-1-methoxyethyl) phosphorothioate; 4) diethyl 2,2,2-trichloro-1-methoxyethyl phosphate.

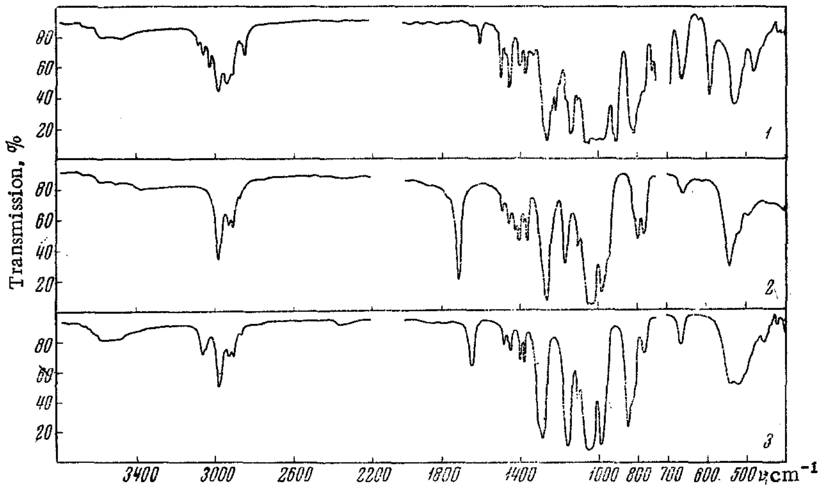


Fig. 2. IR spectra: 1) ethyl 2,2,2-trichloro-1-methoxyethyl benzylphosphonate; 2) diethyl acetylphosphonate; 3) 2,2-dichlorovinyl diethyl phosphate.

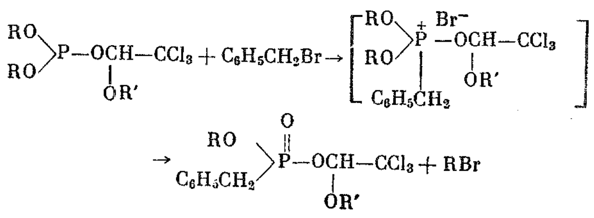
halogen compound. Investigations showed that in the case of alkyl halides reaction goes mainly by the course I, but in the case of acyl halides and chloral by the course II.

Reaction between a 1-alkoxy-2,2,2-trichloroethyl diethyl phosphite and benzyl bromide goes at 190-220°. The low-boiling fraction of the product was collected in a trap and found to be ethyl bromide. The high-boiling product corresponded in its physicochemical data to the 1-alkoxy-2,2,2-trichloroethyl ethyl benzylphosphonate. The IR spectra confirm the structure of the organophosphorus product. They contain (Fig. 2) absorption in the 1100-1200 cm^{-1} region characteristic for the acetal group and a band at 820 cm^{-1} due to the CCl_3 group. In the spectra of 1-alkoxy-2,2,2-trichloroethyl alkyl benzylphosphonates the $P{=}O$ band is displaced by 30 cm^{-1} toward the low frequencies relative to its position in the spectra of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphates. There is a strong band at 1460 cm^{-1} (skeletal vibrations of the phenyl nucleus [3]), and also bands associated with the vibrations of the phenyl ring {1500-1600 cm^{-1} ($C{=}C$), 3030-3080 ($=C{-}H$), 700 ($\delta_{=C-H}$), and 525 (nonplanar vibrations of ring [4])}.

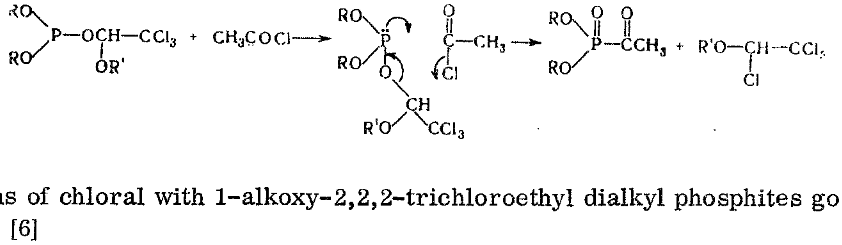
The products of reaction between 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites and acetyl chloride were alkyl 1,2,2,2-tetrachloroethyl ethers and dialkyl acetylphosphonates; their constants correspond to the reported values. The IR spectra of dialkyl acetylphosphonates contain a strong band due to C=O stretch at 1710 cm^{-1}. The absence of the above-described characteristic strong absorption of C—O—C—O and CCl_3 groups supports the formation of dialkyl acetylphosphonates and the selective elimination of the acetal fragment (see Fig. 2).

In the reactions of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites with chloral rearrangement occurs. From the reaction mixtures we isolated alkyl 1,2,2,2-tetrachloroethyl ethers and dialkyl 2,2-dichlorovinyl phosphates. This was confirmed by elemental and spectral analysis, and also by data in the literature. The IR spectrum of 2,2-dichlorovinyl diethyl phosphate contains absorption bands due to the stretching vibrations of C=C and =C—C bonds at 1650 and 3070 cm^{-1} respectively. The formation of dialkyl 2,2-dichlorovinyl phosphates is confirmed by the appearance of a strong "PO—C" band at 1160 cm^{-1} instead of the characteristic group of bands due to —C—O—C—O—. The absence of an acetal grouping is indicated also by the simplification of the spectral picture at about 1000 cm^{-1}. The ratio of the intensities of the bands at 990 and 1290 cm^{-1}, which is the same for 2,2-dichlorovinyl diethyl phosphate as for 1-alkoxy-2,2,2-trichloroethyl diethyl phosphates, points to the unchanged number of ethoxy groups on the phosphorus atom. The appearance of a peak at 850 cm^{-1} and the diminution in the absorption intensity at 820 cm^{-1} correspond to the replacement of the CCl_3 by the CCl_2 group (see Fig. 2).

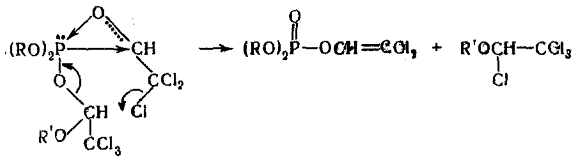
The different courses of the reactions of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites with benzyl bromide on the one hand and with acetyl chloride and chloral on the other suggest that two different reaction mechanisms operate. The reactions of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites with benzyl bromide pass through the intermediate formation of quasiphosphonium salts. As shown previously for the reactions of esters of tervalent phosphorus acids with alkyl halides, in the reactions of mixed phosphorous esters with alkyl halides it is usually the most highly electron-donating group which splits off in the second stage of the Arbuzov reaction [5]. For example, when both AlkO and ArO groups are present in the phosphite, in all cases without exception the alkyl chloride is eliminated; in 2-chloroethyl diethyl phosphite ethyl chloride, not 1,2-dichloroethane, is eliminated. In view of the fact that these transformations are described by the classical scheme of the Arbuzov rearrangement, we considered it possible to represent our reaction by the following scheme:



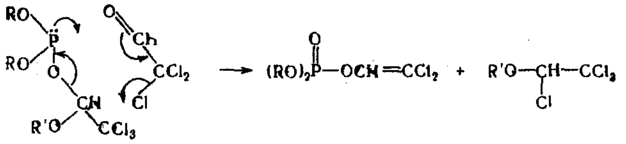
In the case of acetyl chloride and chloral, as the alkyl halide in the reactions with 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites the alkyl 1,2,2,2-tetrachloroethyl ether is eliminated. In view of the fact that the molecules of acetyl chloride and chloral, and also of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites, are strongly polarized, we considered that a cyclic reaction mechanism probably operates. For the reactions of acetyl chloride with 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites, as one of the possible variants we may propose transformation into the dialkyl acetylphosphonate via a five-center transition complex.



The reactions of chloral with 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites go by the cyclic mechanism proposed in [6]



or [7]



EXPERIMENTAL

IR spectra were determined with a UR-10 spectrophotometer with slit program 4 and with other conditions in accordance with the instructions with the instrument. Solid samples were prepared as mineral oil mulls.

1-Alkoxy-2,2,2-trichloroethyl Dialkyl Phosphites

The procedure for the preparation of trialkyl phosphites described in [8] was used. A four-necked flask fitted with stirrer, thermometer, reflux condenser, and dropping funnel was charged with an ethereal solution of 1 mole of the 1-alkoxy-2,2,2-trichloroethanol and 1 mole of the organic base (triethylamine). The mixture was cooled to between −10 and −15°, and with vigorous stirring 1 mole of the dialkyl phosphorochloridite was added dropwise at such a rate that the temperature of the mixture did not rise above −5°. The hydrochloride of the base was precipitated. To complete the reaction the mixture was left overnight. The precipitate was filtered off and washed several times on the filter with ether. The filtrate was vacuum-evaporated, and the residue was vacuum-distilled two or three times.

The physicochemical constants of the phosphites so obtained are given in Table 1.

Addition of Sulfur. A mixture of 12.2 g of diethyl 2,2,2-trichloro-1-methoxyethyl phosphite and 1.31 g of sulfur powder was prepared in a flask with a reflux condenser. The mixture was heated. When the temperature reached 90°, it suddenly rose spontaneously to 150° and the sulfur dissolved completely; the liquid became slightly yellow. After two distillations we obtained 9 g (63%) of O,O-diethyl O-(2,2,2-trichloro-1-methoxyethyl) phosphorothioate, bp 84-86° (0.035 mm). All the other phosphorothioic esters were prepared similarly. Their physicochemical constants are given in Table 2.

Oxidation. The oxidation of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites was conducted by the procedure proposed in [9]. Physicochemical data for the phosphates obtained are presented in Table 3.

Rearrangement with Benzyl Bromide

A mixture of 11.8 g of diethyl 2,2,2-trichloro-1-methoxyethyl phosphite and 6.8 g of benzyl bromide was prepared in a flask fitted with a Dean-Stark trap and a reflux condenser. The mixture was heated in an oil bath. At a bath temperature of 190° the temperature of the mixture rose sharply to 205°, and the liquid started to boil. Ethyl bromide collected in the trap. The bath temperature was kept at 225°, and in the course of 1.5 h 2.8 ml (73.7%) of ethyl bromide collected. The liquid stopped boiling. The product, which had turned yellow, was vacuum-distilled twice. We obtained 6.5 g (45.8%) of product, bp 118-120° (0.025 mm).

All the remaining 1-alkoxy-2,2,2-trichloroethyl alkyl benzylphosphonates were prepared analogously (Table 4).

Rearrangement with Acetyl Chloride

Acetyl chloride (13.8 g) was added dropwise with vigorous stirring to 52.7 g of the 1-alkoxy-2,2,2-trichloroethyl diethyl phosphite at such a rate that the temperature of the reaction mixture did not rise above 30°. The mixture was then heated in a water bath for 20-30 min to complete the reaction. As a result of fractionation we obtained 23.5 g (67.5%) of methyl 1,2,2,2-tetrachloroethyl ether, bp 92-94° (20 mm), and 15.4 g (45.5%) of diethyl acetylphosphonate, bp 101-102° (8 mm). The rearrangement of the other phosphites was conducted under similar conditions. Physicochemical constants of the products are given in Table 5.

Rearrangement with Chloral

A four-necked flask fitted with stirrer, thermometer, reflux condenser, and dropping funnel was charged with 7.7 g of diethyl 2,2,2-trichloro-1-methoxyethyl phosphite. Chloral (3.8 g) was added dropwise with vigorous stirring. The reaction went with liberation of heat, and the reaction temperature was kept in the range 35-40° by varying the rate of dropping and by cooling. By fractionation we isolated 2.4 g (47.2%) of methyl 1,2,2,2-tetrachloroethyl ether, bp 55-56° (10 mm), and 5 g (78.1%) of 2,2-dichlorovinyl diethyl phosphate, bp 122-123° (10 mm). The rearrangement of the other phosphites was conducted under similar conditions. Physicochemical constants of the products are given in Table 6.

CONCLUSIONS

1. Reactions of chloral hemiacetals with dialkyl phosphorochloridites were studied. They lead in high yields to phosphorylated chloral hemiacetals containing tervalent phosphorus.

2. By the addition of sulfur and by oxidation the corresponding phosphorothioates and phosphates were obtained.

3. The reactions of 1-alkoxy-2,2,2-trichloroethyl dialkyl phosphites with benzyl chloride and with acetyl chloride and chloral take different courses. Possible mechanisms for these reactions are proposed.

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