<u>Tris(1,1,5-trihydroperfluoroamyl)</u> Phosphite (X). Under analogous conditions from 310 g (1.551 mole) of (II) and 68 g (0.494 mole) of PCl<sub>3</sub> was obtained 323 g (90.3%) of a colorless liquid, bp 114°C (1 mm);  $d_4^{2°}$  1.733;  $n_D^{2°}$  1.3355. Found: C 25.03; H 1.21; F 63.27; P 4.09%. C<sub>15</sub>H<sub>9</sub>F<sub>24</sub>O<sub>3</sub>P. Calculated: C 24.89; H 1.24; F 63.01; P 4.28%.

 $\frac{\text{Tris}(1,1,7-\text{trihydroperfluoroheptyl) Phosphite (XI).}{g (1.566 \text{ moles}) \text{ of (III) and 66 g (0.480 \text{ mole}) of PCl<sub>3</sub> was obtained 440 g (89.5%) of a colorless liquid, by 172-173°C (1 mm); <math>d_4^{2°}$  1.795;  $n_D^{2°}$  1.3320. Found: C 24.31; H 0.86; F 66.45; P 3.09%. C<sub>21</sub>H<sub>9</sub>F<sub>36</sub>O<sub>3</sub>P. Calculated: C 24.59; H 0.88; F 66.72; P 3.03%.

#### CONCLUSIONS

1. Transformations in  $PCl_3-\alpha, \alpha, \omega$ -trihydroperfluoroalkanol systems have a steplike, equilibrium character.

2. The stability of ester acid chlorides of phosphorous acid is sharply reduced in proportion to the introduction of  $\alpha, \alpha, \omega$ -trihydroperfluoroalkoxy groups to the phosphorus atom, which attests to the similar increase in its v-acceptor properties.

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# CERTAIN REACTIONS OF TRIS ( $\alpha, \alpha, \omega$ -TRIHYDROPERFLUOROALKYL) PHOSPHITES

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During the study of the reactions of  $\alpha, \alpha, \omega$ -trihydroperfluoroalkanols with  $P_4O_{10}$  and  $PCl_3$ , it was shown that the characteristic features of the reactions of these systems are determined by the increase in the v-acceptor properties of the P atom when  $\alpha, \alpha, \omega$ -trihydroperfluoroalkoxyl groups are introduced [1, 2]. This, in fact, explains the formation of trialkyl phosphates in the reactions of the above alcohols with  $P_4O_{10}$ , and the dismutation of the corresponding alkyldichloro phosphites, and in particular dialkylchloro phosphites.

In the present work we attempted to study certain properties of tris(1,1,3-trihydroperfluoropropyl) (I), tris(1,1,5-trihydroperfluoropentyl) (II), and tris(1,1,7-trihydroperfluoroheptyl) phosphites (III) to find the effects of the mutual influence of the  $\alpha, \alpha, \omega$ trihydroperfluoroalkoxyl groups and the P atom. The properties of the perfluorinated trialkyl phosphites, in particular those of tris( $\alpha, \alpha, \omega$ -trihydroperfluoroalkyl) phosphites, have scarcely been studied.

As expected, compounds (I) and (II) show no tendency to transformations by the Arbuzov reaction, and with CH<sub>3</sub>I they do not react, even when heated to 200°C. The products of the Arbuzov reaction are formed only when equimolecular amounts of the reagents are heated to 230-240°C in stainless-steel test tubes. A considerable part of the initial trialkyl phosphites is thus oxidized and pyrolyzed as the result of the reaction with the metal surface

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c				Chemical	l shifts, pp	E				
com-	Formula	Ģ	÷	ô,	ŵ	ð5	δ <sub>6</sub>	δ <sub>7</sub>	ð,	Spin-spin coupling constants J, Hz
(IV)	$\left(\mathrm{HCF}_{2}^{2}\mathrm{CF}_{2}^{3}\mathrm{CH}_{2}^{4}\mathrm{O}\right)_{2}^{5}\mathrm{P}\left(\mathrm{O}\right)\mathrm{CH}_{3}^{6}$	5,83	60,48	48,03	4,24		1,42			$J_{12} = 52,5, J_{13} = 5,2, J_{23} = 3,4, J_{24} = 1,4, J_{24} = 12,9, J_{45} = 8,2, J_{56} = 17,4$
(v)	$\left  \begin{array}{c} 1 & 2 \\ (\mathrm{HCF_2CF_2CH_2O})_{3}\mathrm{PO} * \end{array} \right $	5,93	61,89	48,45	4,41					$J_{12} = 52, 5, J_{13} = 3, 6, J_{24} = 1, 2, J_{34} = 12, 1, J_{45} = 7, 8$
(IV)	HCF2CF2CH2I	5,93	57,12	32,03	3,56					$J_{12} = 53,5, J_{13} = 2,7, J_{23} = 1,6, J_{24} = 1,2, J_{34} = 16,5$
(III)	$\frac{1}{\mathrm{HCF}_2\mathrm{CF}_2\mathrm{CH}_3}$	5,73	58,74	32,24	1,76					$J_{12} = 53,5, J_{13} = 2,6, J_{24} = 1,7, J_{34} = 19,2$
(1111)	<sup>1</sup> <sup>2</sup> <sup>3</sup> <sup>4</sup> <sup>5</sup> <sup>6</sup> <sup>7</sup> <sup>7</sup> <sup>7</sup> <sup>8</sup> <sup>8</sup> <sup>8</sup> <sup>7</sup> <sup>8</sup> <sup>8</sup> <sup>7</sup> <sup>8</sup>	6,02	60'09	52,29	47,48	43,17	4,43		1,53	$J_{1_2} = 52, 5, J_{1_3} = 5, 3, J_{56} = 13, 2, J_{67} = 8, 4, J_{78} = 18, 4$
(XI)	<sup>1</sup> (HCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO*	6,03	60,51	52,60	47,80	43,79	4,54			$J_{12} = 52, 5, J_{13} = 4, 6, J_{56} = 12, 8, J_{67} = 8, 2$
(X)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6,08	59,26	51,37	45,65	28,77	3,71			$I_{12}=52,5, I_{13}=5,0, I_{46}=1,6, I_{56}=17,3$
(IX)	$\frac{1}{14}CF_2CF_2CF_2CF=CH_2$	6,67	60,11	53,80	42,1	4				$J_{12} = 53,5, J_{13} = 5,5$

TABLE 1

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	č	opin spin coupling constants J, Hz	$J_{12}=52.5, J_{13}=3.8, J_{34}=12.0, J_{43}=8.2, J_{56}=4.6$	$I_{1_2=52,5,\ I_{1_3}=3,8,\ I_{2_3}=2,8,\ J_{2_4}=1,4,\ J_{3_4}=13,4$	$I_{12}=52,5, I_{13}=4,6, I_{78}=11,8, I_{88}=8,2$	$I_{1_2}=52,5, I_{1_3}=4,2, I_{2_4}=1,3, I_{3_4}=12,6, I_{1_5}=9,4$	$I_{1_2} = 52,5, I_{13} = 5,5, I_{56} = 13,5, I_{67} = 9,0$	$J_{1_{2}=52,5}, J_{1_{3}}=4,0, J_{2_{4}}=1,2, J_{3_{4}}=11,6, J_{4_{5}}=9,2, J_{5_{6}}=742,5$	$I_{12} = 52,5, I_{13} = 4,3, I_{23} = 3,4, I_{34} = 13,5$	$J_{12}=53,5, J_{13}=4,5, J_{45}=8,4, J_{56}=10,2$
		\$°			4,62	_				
		ô,			43,21					5,72
		Ô.	6,87		44,41		4,77	6,18		4,34
	mqq ,	ô <sub>5</sub>					42,78		2,01	
	ical shifts,	ţ,	4,42	3,95	45,6	4,47	47,38	4,37	4,35	4,68
	Chemi	ç,	47,42	43,35	51,80	47,43	52,18	47,60	47,26	45,57
		Ĝ2	60,26	60,75	59,84	60,05	59,83	60,05	61,08	58,73
		Ŷ	5,84	6,04	6,07	5,91	6,08	5,90	5,84	5.97
<pre>1 (continued)</pre>		Formula	$(HCF_2CF_2CH_2O)_2P(O)OCH=CCl_2$	HCF2CF2CH2CI	1 <sup>2</sup> <sup>3</sup> <sup>3</sup> <sup>5</sup> <sup>5</sup> <sup>5</sup> <sup>5</sup> <sup>7</sup> <sup>3</sup> <sup>9</sup> <sup>9</sup> <sup>9</sup> (HCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> C) <sup>3</sup> <sup>9</sup> <sup>9</sup>	$\left  \begin{array}{cc} 1 & 2 \\ (\mathrm{HCF_2CF_2CH_2O})_{3}\mathrm{PS} \end{array} \right $	(HCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> O) 3PS	$(HGF_2GF_2GH_2O)_2P(O)H$	<sup>1</sup> <sup>2</sup> <sup>3</sup> <sup>4</sup> <sup>4</sup> <sup>4</sup> <sup>5</sup> <sup>5</sup> <sup>5</sup>	$\left(\mathrm{HCF_{2}CF_{2}CH_{2}O}\right)_{2}^{5}\mathrm{P(O)CH(OH)CCI_{3}}$
TABLE	punc	dmoO	(IIIX)	(111X)	(XIV)	(XV)	(XVI)	(IIAX),	(IIIAX)	(XIX)

\*cf. [1].

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It is characteristic that even under these conditions, (I) undergoes no Arbuzov rearrangement during the reaction with 1,1,3-trihydroperfluoropropyl iodide and 1,1,3-trihydroperfluoropropyl benzenesulfonate. The transformations occur only as the result of the reaction of trialkyl phosphite with the oxide film of the metallic test tube surface

 $(I) + HCF_2CF_2CH_2X \rightarrow OP (OCH_2CF_2CF_2H)_3 + HCF_2CF_2CH_3 + HCF_2CF_2CH_2OH$ 

 $X = I, OSO_2 - \bigcirc$ 

The tendency of (I) to undergo the Arbuzov rearrangement sharply increases after the substitution of even a single 1,1,3-trihydroperfluoropropoxyl group for an alkoxyl group. Thus, the introduction of methanol into the reaction leads to transesterification, while in the presence of  $CH_3I$  at 150-180°C, the Arbuzov reaction takes place simultaneously. In general, no 1,1,3-trihydroperfluoropropyl iodide was observed

 $(I) + CH_3OH \rightarrow [(HCF_2CF_2CH_2O)_2 POCH_3 + HCF_2CF_2CH_2OH] \xrightarrow{CH_3I} (IV)$ 

When the reaction is carried out in a large excess of methanol, the limiting stage is the transesterification process, and not the isomeric transformations of the initially formed bis(1,1,3-trihydroperfluoropropyl)methyl phosphite, which in fact leads to the presence of bis(1,1,3-trihydroperfluoropropyl)methyl phosphonate in the reaction products in larger amounts than 1,1,3-trihydroperfluorodimethyl phosphonate and trimethyl phosphonate

 $(I) + CH_{3}OH \xrightarrow{CH_{3}I} (IV) + CH_{3}P \xrightarrow{OCH_{3}} + CH_{3}P (OCH_{3})_{2}$ 

It would appear probable that the low ability of (I), (II), and (III) to undergo the Arbuzov rearrangement is due to the decreased n-donor properties of the phosphorus atom in these compounds, and the difficulties involved in the hybrid rearrangement of the transition phosphite no complexes with alkyl halide. Our results confirm this for the reaction of (I) with chloral according to Perkov

The reaction takes place even at  $130^{\circ}$ C. It is probable that the relatively easy proceeding of the reactions, after Perkov, is due to the fact that the process takes place by a four-centered mechanism, including the nv and no interactions



A more ready rearrangement of pentacoordinated phosphorus compounds containing the  $\alpha, \alpha, \omega$ trihydroperfluoroalkoxyl groups does in fact take place, for example, in the reaction of 1,1,3-trihydroperfluoropropyldichloro phosphite with piperylene, as studied by us [2].

The electron-density deficiency on the P atom is also the reason why the phosphites studied are difficult to oxidize. Thus, the oxidation of (I) by  $H_2O_2$  into (V) is not accompanied by an exothermic effect, characteristic of the reactions of aliphatic phosphites. Thus, oxidation even under mild conditions  $(0-5^{\circ}C)$  is accompanied by exchange reactions with the separation of 1,1,3-trihydroperfluoropropanol, so that the yield of (V) does not exceed 30%. At the same time, (I), (II), and (III), in contrast to trialkyl phosphites in the aliphatic series, are quantitatively oxidized by  $N_2O_4$  in the absence of solvents into the corresponding trialkyl phosphates

 $[\mathrm{H} (\mathrm{CF}_{2})_{n} \mathrm{CH}_{2}\mathrm{O}]_{3}\mathrm{P} + \mathrm{N}_{2}\mathrm{O}_{4} \xrightarrow{-\mathrm{N}_{2}\mathrm{O}, \mathrm{NO}} [\mathrm{H} (\mathrm{CF}_{2})_{n} \mathrm{CH}_{2}\mathrm{O}]_{3} \mathrm{PO}$  $n = 2 (\mathrm{V}), 4 (\mathrm{IN}), 6 (\mathrm{XIV})$ 

Thus, the exothermic effect decreases appreciably with increase in the molecular weight of the initial trialkyl phosphite. At the same time, the relative amount of NO also markedly increases. Sulfur adds to (I) and (II) with greater difficulty than to unsubstituted aliphatic phosphites. Even during prolonged boiling of (I) with an excess of sulfur in dioxane (catalyzed by  $Et_3N$ ), the conversion into the corresponding thiophosphate is inappreciable. This process proceeds unequivocally and quantitatively without a solvent and in the absence of traces of moisture in a sealed glass tube at 200-230°C

$$[\mathrm{H} (\mathrm{CF}_2)_n \mathrm{CH}_2\mathrm{O}]_3 \mathrm{P} + \mathrm{S} \rightarrow [\mathrm{H} (\mathrm{CF}_2)_n \mathrm{CH}_2\mathrm{O}]_3 \mathrm{PS}$$
$$n = 2 (\mathrm{XV}), 4 (\mathrm{XVI})$$

The uniqueness of the properties of trialkyl phosphites (I), (II), and (III) is especially noticeable in their reactivity towards hydroxyl-containing compounds. As already noted, they fairly readily enter the alcoholysis reaction with methanol. In the presence of a large excess of the latter, compounds (I), (II), and (III) convert into trimethyl phosphite

$$[H (CF_2)_n CH_2O]_3 P + CH_3OH \xrightarrow{i} (CH_3O)_3 P + H (CF_2)_n CH_2OH$$
  
$$n = 2, 4, 6$$

However, with carboxylic acids, the polyfluorinated phosphites, as we showed on the example of (I), react at >90°C only, with the formation of the corresponding dialkyl phosphites

$$(I) - CH_{3}COOH \rightarrow (HCF_{2}CF_{2}CH_{2}O)_{2} P + CH_{3}C + CH_{$$

At the same time, the reaction of (I) with chloral hydrate, even at  $\sim 20^{\circ}$ C, leads to bis(1,1,3-trihydroperfluoropropy1)-1-hydroxy-2,2,2-trichloroethyl phosphonate (XIX), whose formation assumes an intermediate conversion of (I) into dialkyl phosphite (XVII)

(I) + CCl<sub>3</sub>CHO · H<sub>2</sub>O 
$$\rightarrow$$
 (HCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub> PCHCCl<sub>3</sub> + HCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH  
(XIX)  $\parallel$   
OOH

The formation of (XIX) from chloral and (XVII) was confirmed directly by the experiment

$$(XVII) + CCl_3CHO \rightarrow (XIX)$$

Thus, an examination of the properties of  $tris(\alpha, \alpha, \omega-trihydroperfluoroalkyl)$  phosphites convincingly shows that for these compounds the reactions based on the n-donor ability of the tricoordinated phosphorus atom, are considerably impeded, while reactions related to the v-acceptor properties are facilitated.

#### EXPERIMENTAL

The NMR spectra were run on the "Hitachi K-20" apparatus (60 MHz). The chemical shifts were determined with reference to HMDS and  $CF_3COOH$ , using solutions of the compounds in CHCl<sub>3</sub> during the measurements. The data on the NMR spectra are listed in Table 1.

Gas—liquid chromatography was carried out on a "Varian Aerograph, Series 1700" apparatus, using a capillary column (55 m) with KhE-60 as the stationary phase, flame-ionization detector, and carrier gas He, and on an LKhM-8MD chromatograph, using a column (3 m  $\times$  3 mm), Chromaton N-AW-DMCS with 5% SE-30; column (1 m  $\times$  3 mm), Chezasorb AW-HMDS with 5% XE-60; carrier gas He.

Reaction of Tris(1,1,3-trihydroperfluoropropyl) Phosphite (I) with  $CH_3I$ . A 60-g (0.141 mole) portion of (I) and 23 g (0.162 mole) of  $CH_3I$  were heated for 4 h in a metallic test tube at 220-230°C. Yield,  $\sim 0.8$  g of a liquid in a trap (-78°C) and 81.5 g of a liquid from which 22.5 g (49.3%) of (IV), 4.3 g (6.9%) of (V), and 27.1 g (79.5%) of (VI) were obtained by fractional distillation. The liquid in the trap is compound (VII).

Reaction of Tris(1,1,5-trihydroperfluoropentyl) Phosphite (II) with  $CH_3I$ . A 61.2-g (0.0845 mole) portion of (II) and 12 g (0.0845 mole) of  $CH_3I$  were heated for 5 h in a metallic tube at 230-240°C. Yield, 72 g of liquid, from which 17 g (38.4% of (VIII), 12.8 g (20.5%) of (IX), 12.7 g (46.7%) of (X), and 3.2 g of (XI) were isolated by fractionation.

	-										
			Found	aju		-			Calculate	d, 95	
		н ———		<u>ج</u>	£	Empirical formula	IJ	н		£	୍ୟ 
1,356	55 25,	79 2,7	ي ا	50,12	9,71	$C_7H_9F_8O_3P$	25,03	2,78	1	46,91	9,57
1,343	38 24,	83 2,0	۲ ۱	52,13	7,15	$\mathrm{C_9H_9F_{12}O_4P}$	24,55	2,05	1	51,82	7,05
1,395	55 15,	03 1,1	7 (52,75)	31,82	1	C <sub>3</sub> H <sub>3</sub> F <sub>4</sub> I	14,88	1,24	(52,48)	31,41	1
, <b>1</b>	31,	27 3,2	- 6	65,77	. 1	$C_3H_4F_4$	31,04	3,45	1	65,52	1
1,34(	55 25,	32 1,8		57,83	6,13	C <sub>11</sub> II,F <sub>16</sub> O <sub>3</sub> P	25,19	1,72	1	58,02	5,92
1,335	31 23,	98   1,2	4 -	61,47	4,21	$\mathbf{C}_{15}\mathbf{H}_{9}\mathbf{F}_{24}\mathbf{O_{4}}\mathbf{P}$	24,32	1,22	I	61, 62	4,19
1,374	17, E	91 0,6	5 (36,87)	44,20	I	$C_5 \Pi_3 F_8 I$	17,54	0,88	(37,14)	44,44	1
1,302	23 30,	93   1,2	۱ 6	68,15	ļ	$C_5 H_3 F_7$	30,61	1,53	1	67,86	1
1,381	9 22,	83 1,7	4 16,99	36,50	7,30	$C_8H_7Cl_2F_8O_4P$	22,80	1,66	16,87	36,11	7,36
1,329	9 24,	17 2,0	4 23,81	50,19	1	$C_3 \Pi_3 C \Pi F_4$	23,92	1,99	23,59	50,50	1
1,328	39 24,	07 0,5	1	66,49	2,95	C21H9F36O4P.	24,23	0,87	I	66,77	2,98
1,367	78 23,	67 1.9	2 [6,78]	49,79	7,02	C <sub>9</sub> H <sub>9</sub> F <sub>12</sub> O <sub>3</sub> PS	23,68	1,97	[7,02]	50,00	6,80
1,345	8 24,	13 1,2	1 [4,51]	60,12	4,33	$C_{15}H_9F_{24}O_3PS$	23,81	1,19	[4,23]	60, 32	4,10
1,352	23,	33 2,3	ي در	49,10	9,79	$C_6H_7F_8O_sP$	23,23	2,26	I	49,03	10,00
1,34(	0 34,	78 3.5	ا حو	43,33	l	$C_5H_6F_4O_2$	34,48	3,45	I	43,68	I
1	20,	77   1,8	2 23,16	33,15	6,51	C <sub>8</sub> H <sub>8</sub> Cl <sub>3</sub> F <sub>8</sub> O <sub>4</sub> P	20,98	1,75	23,28	33,22	6,78
	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$d_{a^{a}}$ $n_{a}^{20}$ $r_{a}^{20}$ $r_{a}^{20}$ Empirical         C. a Loutare $d_{a^{a}}$ $n_{a}^{20}$ $c$ H $c_{a}^{(1)}$ $p$ $c_{a}^{(1)}$ $c$	$u_{1}^{20}$ $u_{1}^{20}$ $r_{1}^{20}$

TABLE 2

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Bis(1,1,3-trihydroperfluoropropy1)methyl Phosphonate (IV). A mixture of 10.6 g (0.025 mole) of (I), 0.9 g (0.028 mole) of methanol, and 5 g (0.0352 mole) of  $CH_3I$  was heated for 12 h in a sealed tube at 170-180°C. By fractional distillation, 6.5 g (80.2%) of (IV) were isolated.

2,2-Dichlorovinylbis(1,1,3-trihydroperfluoropropyl) Phosphate (XII). A mixture of 21 g (0.0496 mole) of (I) and 7.2 g (0.0489 mole) of chloral was heated for 8 h in a sealed tube at 190-210°C. Fractionation yielded 14.4 g (70.2%) of (XII) and 5.1 g (69.4%) of (XIII).

<u>Tris(1,1,3-trihydroperfluoropropyl)</u> Phosphate (V). a. Vapors of 3 g (0.0326 mole) of N<sub>2</sub>O<sub>4</sub> were bubbled at 10-20°C with a stream of dry N<sub>2</sub> through 24 g (0.0567 mole) of (I). The excess of N<sub>2</sub>O<sub>4</sub> was removed by blowing dry N<sub>2</sub>. Yield, 23.2 g (93.1%) of (V).

b. A 20-ml portion of 15% H<sub>2</sub>O<sub>2</sub> was added dropwise with stirring and at  $15-20^{\circ}$ C to an emulsion of 26 g (0.0614 mole) of (I) in 10 ml of water. The mixture was stirred for another 2.5 h. The organic layer was then separated, diluted with dry CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub> and distilled. Yield, 7.6 g (28.1%) of (V).

<u>Tris(1,1,5-trihydroperfluoropentyl)</u> Phosphate (IX). Under similar conditions, 43.1 g (93.7% of (IX) were obtained from 45 g (0.0623 mole) of (II) and 3.2 g (0.0348 mole) of  $N_2O_4$ .

<u>Tris(1,1,7-trihydroperfluoroheptyl)</u> Phosphate (XIV). Under similar conditions, 48.5 g ( $\sqrt{100\%}$ ) of (XIV) were obtained from 48 g (0.0468 mole) of tris(1,1,7-trihydroperfluoroheptyl) phosphite (III) and 3 g (0.0276 mole) of N<sub>2</sub>O<sub>4</sub>.

<u>Tris(1,1,3-trihydroperfluoropropyl)</u> Thiophosphate (XV). A 12-g (0.0283 mole) portion of (I) and 4 g (0.125 mole) of sulfur were heated for 8.5 h in a sealed tube at 190-210°C. Fractionation of the liquid phase yielded 12.3 g (95.4%) of (XV).

 $\frac{\text{Tris}(1,1,5-\text{trihydroperfluoropentyl}) \text{ Thiophosphate (XVI)}}{\text{g (83.1\%) of (XVI) were obtained from 20 g (0.0277 mole) of (II) and 6 g (0.187 mole) of sulfur.}$ 

<u>Bis(1,1,3-trihydroperfluoropropyl)</u> Phosphite (XVII). A mixture of 35.2 g (0.083 mole) of (I) and 6.3 g (0.105 mole) of glacial CH<sub>3</sub>COOH was heated for 7 h at 160-170°C. Fraction-ation yielded 21.3 g (82.9%) of (XVII) and 13.6 g (94.4%) of (XVIII).

Bis(1,1,3-trihydroperfluoropropy1)-1-hydroxy-2,2,2-trichlorophosphonate (XIX). a. A 12.5-g (0.0403 mole) portion of (XVII) and 5.6 g (0.0379 mole) of chloral were held for 3 h at 20°C and for 30 min at 120-130°C. The product was recrystallized from a mixture of 1,1,3-(trichloro-trifluoroethane-benzene (3:1). Yield 16.1 g (91%) of (XIX).

b. A mixture of 15 g (0.0354 mole) of (I) and 5.9 g (0.0356 mole) of chloral hydrate in 15 ml of CHCl<sub>3</sub> was held with periodic stirring for 5 days at 20°C, and for 3 h at the boiling point. The volatile products were removed under 1 mm Hg vacuo at 90-100°C. The residue was recrystallized from a mixture of 1,1,3-(trichloro)-trifluoroethane-benzene (3: 1). Yield, 15.3 g (92.6%) of (XIX).

The properties and results of elementary analysis of the synthesized compounds are listed in Table 2.

### CONCLUSIONS

Certain properties of tris(1,1,3-trihydroperfluoropropyl), tris(1,1,5-trihydroperfluoropentyl), and tris(1,1,7-trihydroperfluoroheptyl) phosphites were studied, and it was shown that the presence of the  $\alpha, \alpha, \omega$ -trihydroperfluoroalkoxyl groups determines their behavior as the result of an increase in the v-acceptor and decrease in the n-donor ability of the phosphorus atom.

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