

which are used in the synthesis of thieno[2,3-b]pyridine and thiazolo[3,2-a]pyridinium cations.

2. The structure of 2,2'-bis[6-(2,4-dimethoxyphenyl)-3-cyanopyridine-2] disulfide has been established unequivocally by an x-ray diffraction study. The molecule is structured from two approximately planar fragments joined by a disulfide bridge with CSSC torsion angle = 83.5(2)° and S-S bond length = 2.015(1) Å.

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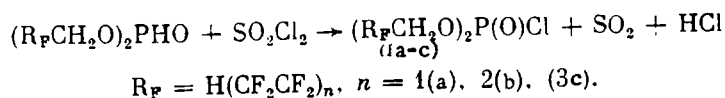
#### SYNTHESIS OF $\alpha, \alpha, \omega$ -TRIHIDROPOLYFLUOROALKYL CHLOROPHOSPHATES BY THE REACTION BETWEEN $\alpha, \alpha, \omega$ -TRIHIDROPOLYFLUOROALKYL PHOSPHITES AND SULFURYL CHLORIDE

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Polyfluoroalkyl chlorophosphates are key compounds in the synthesis of practically useful derivatives of polyfluoroalkylphosphoric acids. Their preparation by alcoholysis of  $\text{POCl}_3$  under severe conditions and in the presence of catalysts [1-4] results in the formation of mixtures of products. More efficient methods are the reactions of tris(polyfluoroalkyl) phosphites and polyfluoroalkyl dichlorophosphites [5] with chlorine [6] and nitrogen oxides [5, 7]. In order to obtain chlorophosphates, we here describe the reaction of  $\alpha, \alpha, \omega$ -trihidropolyfluoroalkyl phosphites (and chlorophosphites) with the preparatively more convenient reagent sulfuryl chloride, which behaves towards three-coordinated phosphorus compounds as both a chlorinating agent [8, 9] and an oxidant [10].

It has been found that bis( $\alpha, \alpha, \omega$ -trihidropolyfluoroalkyl) phosphites are chlorinated by sulfuryl chloride at 20-30°C in the same way as their hydrogen analogs [9], being uniquely converted into the bis( $\alpha, \alpha, \omega$ -trihidropolyfluoroalkyl) chlorophosphates (Ia-c).



In an analogous reaction,  $\alpha, \alpha, \omega$ -trihidropolyfluoroalkyl dichlorophosphites give only the oxidation products,  $\alpha, \alpha, \omega$ -trihidropolyfluoroalkyl dichlorophosphates (IIa-c).

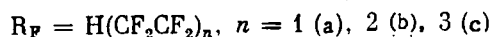
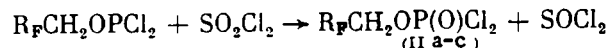
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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 1, pp. 146-149, January, 1988. Original article submitted April 28, 1986.

TABLE 1.  $\alpha, \alpha, \omega$ -Trihydrodipolyfluoroalkyl Chlorophosphates  $[H(CF_2CF_2)_n CH_2O]_m P(O)Cl_{3-m}$

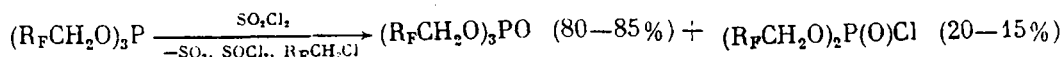
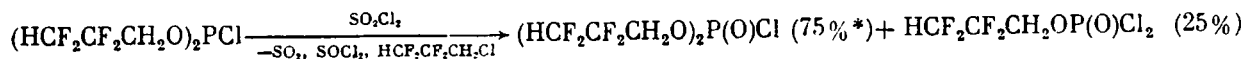
Compound	n	m	Yield, %	Bp, °C (mm)	n <sub>D</sub> <sup>20</sup>	Found, %			Calculated, %			$\delta$ p, ppm
						C	H	Cl	C	H	Cl	
(Ia)	1	2	81.2	101(1*)	1.3584	20.76	1.62	10.00	20.90	1.74	10.30	4.52
(Ib)	2	2	77.3	127(1)	1.3571	22.15	1.12	6.76	22.81	1.14	6.75	4.77
(Ic)	3	2	85.2	180(3*)	1.3398	...	...	...	...	...	...	4.95
(IIa)	1	1	88.2	60(1*)	1.3306	17.26	0.86	21.41	17.29	0.86	21.29	7.85
(IIb)	2	1	83	89(2)	1.3699	18.93	0.65	15.70	18.71	0.67	15.81	8.25
(IIc)	3	1	80	101(3)	1.3581	...	...	...	...	...	...	8.51

\*cf. [4].

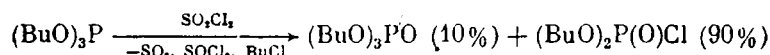


The starting phosphites are accessible [5, 7, 11], and this method therefore provides a convenient route to  $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl chlorophosphates (Table 1).

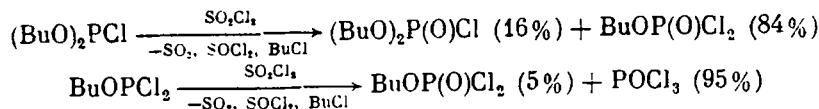
The reaction of bis(1,1,3-trihdropolyfluoroalkyl) chlorophosphite and tris-( $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl) phosphites with sulfuryl chloride at 20-30°C also results preferentially in oxidation. The formation of chlorination products has however also been observed, and when  $n = 2$  the reaction temperature (-10-+90°C) has virtually no effect on the product ratios.



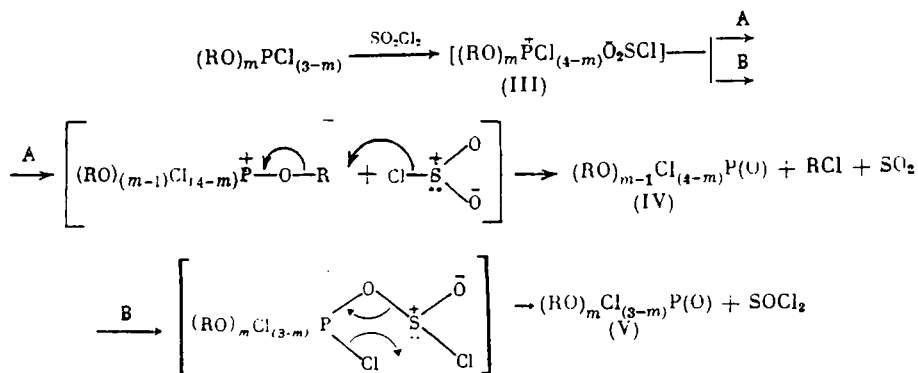
It is noteworthy that sulfuryl chloride reacts with the H-analogs differently. For example, tributyl phosphite at 20-30°C is preferentially chlorinated to dibutyl chlorophosphate, containing, according to our findings, only trace amounts of oxidation product.



Dibutyl chlorophosphite and butyl dichlorophosphite react with sulfuryl chloride similarly, i.e., the course of reaction of the three-coordinated organophosphite with this reagent is controlled by the type of organic radical rather than by the nucleophilicity of the organophosphite.



The overall pathway of this reaction includes electrophilic attack on the alkyl phosphite by the chlorine of the sulfuryl chloride to give the quasiphosphonium salt (III), which is then either converted by nucleophilic substitution at carbon (step A) into the chlorination product (IV), or by nucleophilic substitution at phosphorus (step B) into the oxidation product (V).

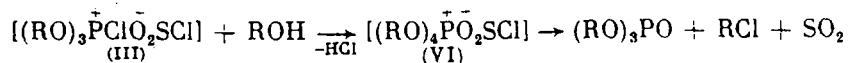


$$m = 1-3.$$

Fluorination of the group R increases its electronegativity and hinders heterolysis of the R-O bond (step A), which should favor the alternative step B. A reduction in the number of RO groups attached to phosphorus (the statistical factor) should also favor this. The follow-

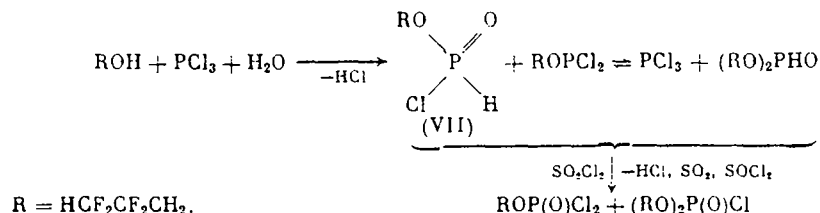
\*Here and subsequently, the  $^{31}P$  NMR molar percentages in the reaction mixture are given.

ing observations are also in accordance with the proposed pathway. Reaction of tris-(1,1,5-trihydrooctafluoropentyl) phosphite with sulfuryl chloride in the presence of 1,1,5-trihydrooctafluoropentyl alcohol at 20-30°C gives the triphosphate only. 1,1,5-Trihydrooctafluoropentyl alcohol does not react with sulfuryl chloride and bis-(1,1,5-trihydrooctafluoropentyl) chlorophosphate under these conditions, and therefore the absence of the latter from the reaction mixture explains the rapid alcoholysis of the salt (III),  $m = 3$ ,  $R = HC_4F_8CH_2$ , followed by the relatively slow dealkylation of the resulting salt (VI).



These postulated reactions of (III) have analogies in phosphorus chemistry, since step A is similar to the second step in the Arbuzov reaction [12], and step B is the final stage in the reaction of chlorophosphoranes with  $SO_2$  [13].

We have assessed the accessibility of chloro-(1,1,3-trihydrotetrafluoropropyl)phosphite (VII), which is a possible intermediate in the preparation of 1,1,3-trihydrotetrafluoropropyl dichlorophosphate. It has been found that on heating a mixture of bis-(1,1,3-trihydrotetrafluoropropyl) phosphite with  $PCl_3$ , or on reacting 1,1,3-trihydrotetrafluoropropanol with equimolar amounts of water and  $PCl_3$ , mixtures are obtained which contain, in addition to the phosphite (VII) ( $\delta_p$  6.6 ppm,  $J_{HP} = 730$  Hz), bis(1,1,3-trihydrotetrafluoropropyl) phosphite ( $\delta_p$  8.6 ppm,  $J_{HP} = 754$  Hz), 1,1,3-trihydrotetrafluoropropyl dichlorophosphate ( $\delta_p$  181.5 ppm), and  $PCl_3$ . Treatment of these mixtures of phosphites with sulfuryl chloride gives mixtures of chlorophosphates, the composition of which indicates that chlorination of the phosphite (VII) is preferred under these conditions.



#### EXPERIMENTAL

The reactions were carried out under dry nitrogen. The purity of the starting phosphites and reaction products, and the composition of the reaction mixtures were established by  $^{31}P$ - $^1H$  NMR (Bruker HX-90) from 85%  $H_3PO_4$  as external standard.

Bis-( $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl) Chlorophosphates (General Method). To 0.1 mole of the bis-( $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl) phosphite was added dropwise with vigorous stirring and cooling to 20-30°C 0.1 mole of sulfuryl chloride, and the mixture stirred until evolution of gas ceased, followed by fractionation. The properties of the products are given in Table 1.

$\alpha, \alpha, \omega$ -Trihdropolyfluoroalkyl dichlorophosphates were obtained by oxidizing  $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl dichlorophosphites with sulfuryl chloride in a similar manner, but with the order of addition of the reagents reversed, and the second product of the reaction with sulfuryl chloride isolated by trapping in a trap cooled to -78°C, with fractionation. The properties of the products are given in Table 1.

Reactions of organic phosphites with sulfuryl chloride in order to measure spectroscopically the ratios of chlorination to oxidation products in the reaction mixtures, they were carried out similarly. The results are given in the text.

#### CONCLUSIONS

An efficient method for the synthesis of  $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl chlorophosphates is by reacting  $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl dichlorophosphites and bis-( $\alpha, \alpha, \omega$ -trihdropolyfluoroalkyl) phosphites with sulfuryl chloride. It has been found that in three-coordinated polyfluoroalkyl phosphites, the high electronegativity of the polyfluoroalkyl groups hinders cleavage of the latter on reaction with sulfuryl chloride, thereby facilitating the formation of oxidation products.

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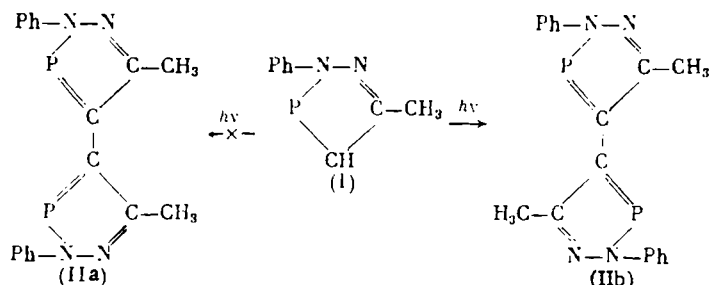
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STRUCTURE OF 4,4'-DIDEHYDROBIS(5-METHYL-2-PHENYL-1,2,3-DIAZAPHOSPHOLA)  
AND 4,4'-DIDEHYDROBIS(2-PHENYL-5-R-1,2,3-DIAZAARSOLES)

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We have previously shown [1-3] that UV irradiation of 5-methyl-2-phenyl-1,2,3-diazaphosphole (I) affords a crystalline product, which according to its PMR,  $^{31}\text{P}$  NMR, and mass spectra was assigned the structure (IIa) or (IIb) [3].



A final choice between (IIa) and (IIb) was made from an x-ray diffraction study, in favor of (IIb), 4,4'-didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaphosphole), which contains the 1,4-diphosphabuta-1,3-diene fragment with the S-trans configuration, and two-coordinated phosphorus atoms.

UV irradiation of 2,5-diphenyl-1,2,3-diazaarsole (III) and 5-methyl-2-phenyl-1,2,3-diazaarsole under similar conditions did not give the corresponding 4,4'-didehydrobis(diazaarsoles).

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