12. C. T. Liu and B. E. Douglas, Inorg. Chem., 1356 (1964).

- 13. J. Blake and L. Folden, Biochem. J., 92, 136 (1964).
- 14. H. Wiesom and R. Canuam, J. Biol. Chem., <u>119</u>, 309 (1937).
- 15. A. Gordon and R. Ford, The Chemist's Companion, Wiley, New York (1973).

16. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).

SYNTHESIS AND STRUCTURE OF DIALKYL FLUOROFORMIMINO PHOSPHATES

I. V. Martynov, V. K. Brel', V. I. Uvarov, A. V. Yarkov, V. P. Novikov, L. A. Chepakova, and O. A. Raevskii

One of the simplest and easiest methods for the preparation of phosphorylated oximes is reaction of halonitrosoalkanes with acid [1], neutral [2], and halodialkyl phosphites [3]. Thereby derivatives of dihalo- and haloalkylformoximino phosphoric acids are formed. Monohaloformoximino phosphates have not been described in the literature because it is assumed that they are unstable [4].

UDC 542.91:541.6:547.26'118'161

This article describes the synthesis of the hitherto unknown fluoroformimino phosphates (I)-(IV) and the determination of their structure by means of IR and NMR spectroscopy. Reaction of fluorochloronitromethane with neutral phosphites in the ratio of 1:2 yielded phosphorylated oximes (I)-(IV) with trialkyl phosphates as byproducts.

 $\begin{array}{c} 2 (\mathrm{RO})_3 \mathrm{P} + \mathrm{ClCHFNO}_2 \rightarrow (\mathrm{RO})_2 \mathrm{PON} = \mathrm{CHF} + (\mathrm{RO})_3 \mathrm{PO} + \mathrm{RCl} \\ \mathrm{R} = \mathrm{CH}_3 \ (\mathrm{I}), \ \mathrm{C}_2 \mathrm{H}_5 \ (\mathrm{II}), \ n - \mathrm{C}_3 \mathrm{H}_7 \ (\mathrm{III}), \ n - \mathrm{C}_4 \mathrm{H}_9 \ (\mathrm{IV}). \end{array}$

Reactions were carried out at $0-10^{\circ}$ C without solvent. Each of the oximes (I)-(IV) produced was isolated by repeated vacuum distillation using an effective column. The dialkyl fluoro-formimino phosphates (I)-(IV) are mixtures of the syn (s) and anti (a) geometrical isomers (relative position of the 0 atom and the proton of the CHF group).

The structures and the compositions of (I)-(IV) were determined by means of ¹H, ¹⁹F, and ³¹P NMR spectroscopy, IR spectroscopy, and elemental analyses. In the PMR spectrum of the methyl ester of fluoroformimino phosphate (I) there are signals of the methyl group and the proton at the double bond. Analysis of the chemical shifts and the spin-spin coupling of the proton with the P and F nuclei makes it possible to unambiguously assign the signals to the syn (s) and anti (a) isomers. Thus, the O atom of the phosphoryl group exerts an influence on the syn proton H_s . The polar effect of the O atom causes deshielding of the H_s proton and its signal is at low field (δ 8.90 ppm) in comparison with the H_a proton of the anti isomer (δ 7.68 ppm). Moreover, the H_S proton, in contrast to the H_a proton, has a spin-spin coupling constant JH.P of 1.30 Hz, which points to the possibility of the formation of a hydrogen bond and to interaction with the P atom through the O atom of the phosphoryl group. In the IR spectrum there is an absorption band in the region 100 cm^{-1} , which can be explained as corresponding with a hydrogen bond. The intensity of the band does not change on dilution, which points to the intramolecular nature of the interaction of the H_s proton with the O atom of the phosphoryl group. Comparison of the recorded spectra with IR spectra of trimethyl phosphate [5] and with the spectra of oximes [6], and also analysis of the spectra of the prepared dialkyl fluoroformimino phosphates (I)-(IV) make it possible to reliably identify the bands of all the valence vibrations and to confirm the structures of oximes (I)-(IV) (Table 1). The splitting of the band of the stretching vibration vC=N is connected with the existence of syn and anti isomers. The relative intensities of the components of this doublet in solvents of different polarity (CCl₄ and CH₃CN) change only

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 857-860, April, 1987. Original article submitted September 6, 1985.

TABLE 1. Physical Properties of Dialkyl Fluoroformimino Phosphates (I)-(IV)

Com- pound	Yield, %	bp, °C (mm Hg)	d_{4}^{20}	n_{D}^{20}	Found, %			Empirical	Calculated, %		
					F	N	Р	formula	F	N	P
(I) (II) (III)	18 11 25	$ \begin{array}{c} 75(3) \\ 85(2) \\ 64(2) \end{array} $	1,3124 1,3004 1,1271	1,4047 1,4130 1,4168	11,08 9,15 8,02	8,03 6,79 5,94	18,33 15,74 13,82	C3H7FNO4P C5H11FNO4P C7H15FNO4P	11,11 9,50 8,37	8,12 7,03 6,17	18,13 15,56 13,66

TABLE 2. NMR and IR Spectra of Dialkyl Fluoroformimino Phosphates (I)-(IV) (δ , ppm; J, Hz)

Contracting and a second s		PMR spectrum			¹⁹ F NMR	³¹ P NMR		IR spectrum, V, cm ⁻¹	
Compound		ði	$J_{ m HF}$	J_{HP}	δ	$J_{ m PF}$	δ	C=N	P=0
(I) sy a	yn nti	$8,50 \\ 7,50$	96,70 91,10	1,30	-21,91 7,78	3,50 6,85	1,78	1649 1667	1287
(II) sy ar	yn nti	$8,63 \\ 7,42$	95,88 91,00	1,05	$\left \begin{array}{c} -22,24\\ 7,56\end{array}\right $	3,61 7,00	-0,45	1651 1667	1278 1296
(III) sy ai	yn nti	8,90 7,68	96,40 91,00	1,25	-23,55 7,34	4,58 7,51	-0,18	$1647 \\ 1663$	1250 1283
(IV) sy ai	yn nti	$8,75 \\ 7,50$	97,20 91,55	1,18	$\begin{vmatrix} -23,04\\7,21 \end{vmatrix}$	$4,51 \\ 6,88$	-0,30	1648 1664	1249 1280

for dimethyl fluoroformimino phosphate (I). The presence of the double vC=N bond at 1650 cm^{-1} suggests the existence of a great barrier between the syn and anti forms, and therefore we relate the changes in the relative intensities of the components to the presence of a conformational equilibrium in the molecule, which arises from internal rotation around the P-O bond. In (I) this is also found in the bands of the valence vibrations vP=0 and vPC. The absence in the spectra of (II)-(IV) may be explained by stabilization of one of the conformers because of the steric hindrance of the bulkier groups C_2H_5 , C_3H_7 , and C_4H_9 as compared to CH3. These conclusions are also supported by investigation of the temperature dependence of the relative intensities of the pairs of the stretching vibrations $vCN(I_1/I_2)$ and the spectra of cooled dimethyl fluoroformimino phosphate (I). The dependence of $\log (I_1/I_1)$ I_2) from 1/T is not linear in nature, which is characteristic of equilibria of the type A \neq C in a narrow temperature interval. This is an indication of the presence of a very complicated equilibrium: each band pertains to two different conformers, the ratio of which changes with the temperature. At low temperatures the ratio of the integrated intensities of the vCN doublet approaches a constant value, equal to the ratio of the most stable conformers of the syn and anti isomers. These same conformers also remain on cooling of (I), whereas for an equilibrium A \neq C with a low barrier usually one form remains on freezing. Thus, the facts mentioned allow one to assume that the conformational mobility relative to the P-O bond is the cause of the change in the ratio of the intensities of the components of the ν C=N vibration bands of oxime (I).

Spectral and physicochemical data of (I)-(IV) are summarized in Table 2.

EXPERIMENTAL

¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a CXP-200 spectrometer from CDCl₃ solutions relative to TMS, CF₃COOH, and H₃PO₄, and operating at 200, 188, and 81 MHz, respectively. IR spectra of liquid samples were taken in CH₃CN, CCl₄, and C₂Cl₄ on a Bruker IFS-113 Fourier spectrometer in the region 4000-400 cm⁻¹ with a resolution of 2 cm⁻¹. The temperature dependence of the IR spectra of compound (I) in tetrachloroethylene was studied in the region of -10 to +110°C. The valence vibrations vC=N were separated into two components of the Lorentz type by the method of the least squares. The intensity integrals obtained were used for plotting the temperature dependence of log (I₁/I₂) from 1/T.

Fluorochloronitromethane was synthesized according to [7].

<u>Reaction of trimethyl phosphite with fluorochloronitromethane</u>. A three-necked flask was charged with 12.4 g of trimethyl phosphite and with stirring under an argon atmosphere 6.7 g of fluorochloronitromethane was added dropwise at 0-10°C. The reaction mixture was then kept for 2 h at 50°C. Vacuum distillation in 16 h yielded 1 g (18%) of dimethyl fluoroimino phosphate (I).

Compounds (II)-(IV) were prepared in the same way; spectral and physicochemical constants are summarized in Table 2.

CONCLUSION

1. On reaction of trialkyl phosphites with fluorochloronitromethane hitherto unknown dialkyl fluoroformimino phosphates were obtained.

2. Evidence is given of the presence of a conformational equilibrium in the molecule of dimethyl fluoroformimino phosphate due to internal rotation around the P-O bond.

LITERATURE CITED

- 1. I. V. Martynov, N. F. Privezentseva, and Yu. L. Kruglyak, Zh. Obshch. Khim., <u>39</u>, 1730 (1969).
- I. V. Martynov, Yu. L. Kruglyak, and N. F. Privezentseva, Zh. Obshch. Khim., <u>37</u>, 1125 (1967).
- I. V. Martynov, Yu. L. Kruglyak, and N. F. Privezentseva, Zh. Obshch. Khim., <u>37</u>, 1130 (1967).
- 4. J. Allen, J. Am. Chem. Soc., <u>79</u>, 3071 (1957).
- 5. F. Marsault-Kerail, J. Chim. Phys. Phys., <u>68</u>, 274 (1971).
- 6. L. Bellamy, The Infrared Spectra of Complex Molecules, 2nd ed., Methuen, London (1958).
- 7. I. V. Martynov, Yu. L. Kruglyak, A. V. Fokin, and I. L. Knunyants, "Method for the preparation of fluorinated hydrogen containing nitromethanes," Author's Certificate No. 159821; Byull. Izobr. (1962).

REACTIONS OF VINYLIDENEDIPHOSPHONIC ACID WITH NUCLEOPHILES.

COMMUNICATION 3. ADDITION OF THIOLS

UDC 542.955:547.1'118:547.269.1

I. S. Alfer'ev, N. V. Mikhalin, I. L. Kotlyarevskii, and L. M. Vainer

The reactions of aliphatic amines, NH_3 and N_2H_4 with vinylidenediphosphonic acid (I) have been reported previously [1, 2]. Thiols are, as a rule, highly active in similar nucleophilic addition reactions [3]. In the case of (I) and its salts, reaction with thiols is complicated by the mutual immiscibility of the components, resulting in low yields of addition products.

We have found suitable conditions for reacting various aliphatic and aromatic thiols with (I) and obtaining different 2-alkyl- and 2-arylthioethylidene-1,l-diphosphonic acids (IIa- ℓ) with high yields. In order to do this the thiols were reacted with the triethyl-ammonium salt of (I) obtained in anhydrous AcOH

 $\begin{array}{c} \text{CH}_2 = & \text{C}(\text{PO}_3\text{H}_2)_2 \xrightarrow[\text{Et_3N, ACOH}]{\text{RSH}} \text{RSCH}_2\text{CH}(\text{PO}_3\text{H}_2)_2 \\ (\text{I}) & (\text{IIa} \rightarrow 1) \end{array}$

$$\begin{split} &R = C_{3}H_{7}(II^{a}); \ C_{4}H_{9}(II^{b}); \ (CH_{3})_{2}CHCH_{2}(II^{c}); \ C_{6}H_{5}CH_{2}(II^{d}); \ \alpha-C_{10}H_{7}(CH_{2})_{4} \\ &(II_{e}); \ \alpha-C_{10}H_{7}O(CH_{2})_{3} \ (II_{f}); \ \alpha-C_{10}H_{7}O(CH_{2})_{5} \ (II_{g}); \ \alpha-C_{10}H_{7}O(CH_{2})_{6} \ (II^{b}); \\ &\alpha-C_{10}H_{7}O(CH_{2})_{7} \ (II^{i}); \ \beta-C_{10}H_{7} \ (II^{i}); \ p-CH_{3}C_{6}H_{4} \ (II^{k}); \ (CH_{3})_{3}CCH_{2}C(CH_{3})_{2} \\ &(II^{k}). \end{split}$$

Novosibirsk Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 860-864, April, 1987. Original article submitted July 11, 1985.