ORGANOPHOSPHORUS COMPOUNDS

X. PHOSPHORISOCYANATIDIC DIFLUORIDE AND CHLORIDE FLUORIDE. PREPARATION OF ALKYL CARBAMATOPHOSPHORODIFLUORIDATES AND UREIDOPHOSPHORODIFLUORIDATES[1, 2]

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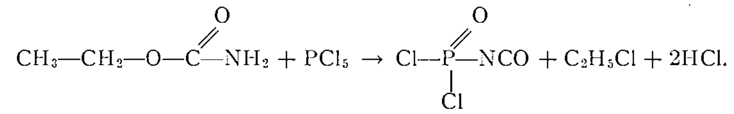
ABSTRACT

Phosphorisocyanatidic difluoride and phosphorisocyanatidic chloride fluoride were prepared. Addition reactions with alcohols (phenol) and amines were investigated, leading to carbamatophosphorodifluoridates and ureidophosphorodifluoridates.

Phosphorus oxyhalides are used as starting materials for the preparation of many organophosphorus compounds. The reactive halogens can be easily replaced by alkoxy, amido, mercapto groups, etc. The replacement of one of the halogens with an isocyanate group in the phosphoryl halides increases the versatility of these compounds and enables the preparation of many new groups of organophosphorus compounds.

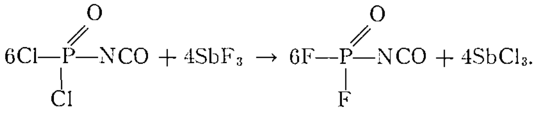
Phosphorisocyanatidic dichloride was prepared by Kirsanov (2) by the interaction of ethylcarbamate and phosphorus pentachloride:



$$CH_3\text{—}CH_2\text{—}O\text{—}\overset{O}{\overset{/\!\!/}{C}}\text{—}NH_2 + PCl_5 \rightarrow Cl\text{—}\underset{Cl}{\underset{|}{\overset{O}{\overset{/\!\!/}{P}}}}\text{—}NCO + C_2H_5Cl + 2HCl.$$

Phosphorisocyanatidic dichloride partially decomposes when distilled at atmospheric pressure or when stored at room temperature over long periods of time. It was hoped that by preparing the corresponding difluoridate or chlorofluoridate more stable compounds would be obtained. These could be useful new polyfunctional reagents for the preparation of derivatives of fluorophosphoric acid (3).

Phosphorisocyanatidic dichloride readily reacts with antimony trifluoride, in the absence of catalyst, to give a 90% yield of the corresponding difluoride, without interacting with the isocyanate group:



$$6Cl\text{—}\underset{Cl}{\underset{|}{\overset{O}{\overset{/\!\!/}{P}}}}\text{—}NCO + 4SbF_3 \rightarrow 6F\text{—}\underset{F}{\underset{|}{\overset{O}{\overset{/\!\!/}{P}}}}\text{—}NCO + 4SbCl_3.$$

The reaction is fast and exothermic; therefore the antimony trifluoride is added in small portions to the phosphorisocyanatidic dichloride. The lower-boiling difluoride distills out from the reaction vessel as it forms. Phosphorisocyanatidic difluoride is a colorless liquid which fumes if exposed to moist air. It boils at atmospheric pressure at 68–68.5°.

It is readily soluble in solvents like methylene chloride, chloroform, carbon tetrachloride, benzene.

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[1] *Contribution No. 64.*
[2] *For Part IX, see reference 1.*

The infrared spectrum shows maxima at 2247, 1458, 1351, 952, 905, 752 cm^{-1}, indicating the presence of the isocyanate group and P—F bonds. (See Fig. 1.)

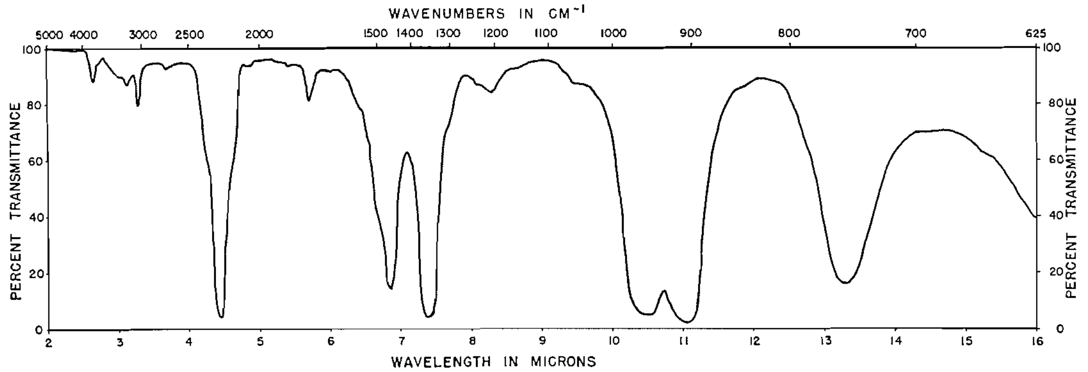
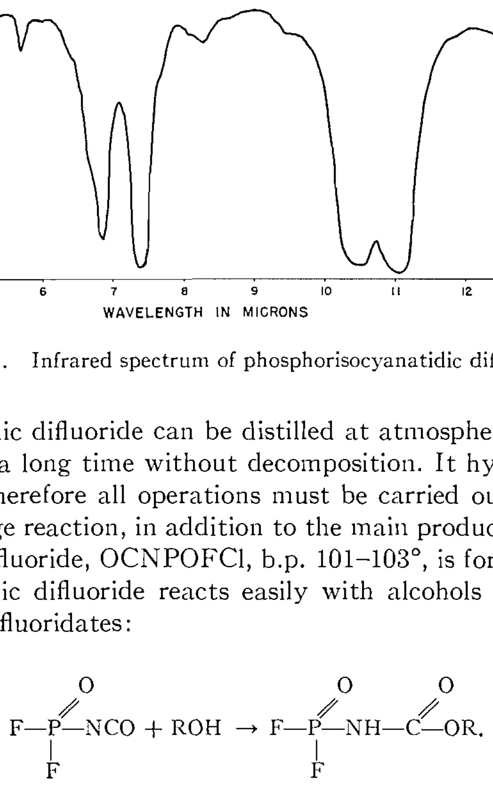


FIG. 1. Infrared spectrum of phosphorisocyanatidic difluoride.

Phosphorisocyanatidic difluoride can be distilled at atmospheric pressure and kept at room temperature for a long time without decomposition. It hydrolyzes, however, very rapidly with water. Therefore all operations must be carried out under dry conditions. In the halogen exchange reaction, in addition to the main product, about 10% phosphorisocyanatidic chloride fluoride, OCNPOFCl, b.p. 101–103°, is formed.

Phosphorisocyanatidic difluoride reacts easily with alcohols (phenol), yielding alkyl carbamatophosphorodifluoridates:



$$F-\underset{F}{\overset{O}{P}}-NCO + ROH \rightarrow F-\underset{F}{\overset{O}{P}}-NH-\overset{O}{C}-OR.$$

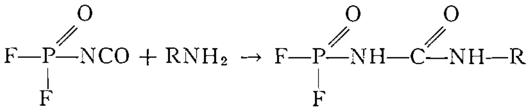
The carbamate derivatives are stable solid compounds and can be distilled under reduced pressure without decomposition. Table I lists the new carbamates that have been prepared. With an excess of alcohol the fluorides can be replaced by alkoxy groups only with difficulty. The use of sodium alcoholates is more advantageous.

TABLE I

Carbamatophosphorodifluoridates, $RO-\overset{O}{\overset{\|}{C}}-NH-POF_2$

R	% yield	B.p., °C/mm Hg	M.p., °C	% N Calc.	% N Found	% P Calc.	% P Found
Methyl	90	95/5	51–52	8.80	8.74	19.44	19.31
Ethyl	94	91–92/3	35–36	8.09	7.97	17.91	17.80
Isopropyl	93	101–102/6	54–55	7.48	7.52	16.57	16.42
Phenyl	94	—	80–83	6.33	6.28	14.01	14.14

Primary and secondary amines react with phosphorocyanatidic difluoride to give substituted alkyl (aryl) ureidophosphorodifluoridates:



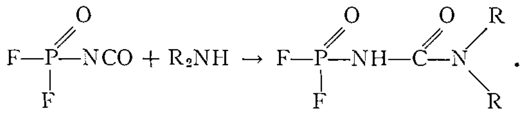
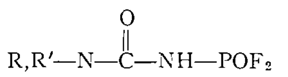


Table II summarizes data of the prepared ureidophosphorodifluoridates.

TABLE II

Ureidophosphorodifluoridates, 

$R,R'-N-\overset{\overset{O}{\|}}{C}-NH-POF_2$

R	R′	% yield	M.p., °C	% N Calc.	% N Found	% P Calc.	% P Found
C_2H_5	H	91	66–67	16.28	16.16	18.00	17.85
C_2H_5	C_2H_5	90	Visc. oil	14.00	13.95	15.48	15.52
C_6H_5	H	94.4	111–112	12.73	12.64	14.08	14.15
$C_6H_5CH_3$	CH_3	92	87	11.96	11.87	13.23	13.30

EXPERIMENTAL

Preparation of Phosphorisocyanatidic Dichloride (2)

One mole of PCl_5 and 1 mole of ethylcarbamate were placed in a 1-liter round-bottomed flask equipped with a reflux condenser and drying tube, and kept at 10° by means of external cooling. In a few minutes HCl formation begins. The temperature of the bath was kept 10° for 45 minutes, then it was carefully raised at a rate of 1°/6 minutes up to 50°, then by 1°/2 minutes up to 80° (5.5 hours total reaction time). The by-product HCl and ethyl chloride escaped through the reflux condenser. Fractionation of the residual liquid product gave 140 g of pure $POCl_2NCO$ (87.5%), b.p. 64–60° at 50 mm. CCl_2NO_2P: found: P 19.5, Cl 44.3, N 8.6; Calc.: P 19.4, Cl 44.37, N 8.75%.

Preparation of Phosphorisocyanatidic Difluoride

Phosphorisocyanatidic dichloride (160 g, 1 mole) was placed into a two-necked flask equipped with powder feeder and condenser. SbF_3 (150 g) was added in 6–10 portions to the chloride. The reaction is exothermic and the product distills out as it forms. After the addition of the SbF_3 the flask was heated to remove all the remaining product. Liquid product (130 g) was obtained, which after fractionation through a 300-mm Widmer column gave two fractions: POF_2NCO: b.p. 68–68.5°; 115 g (90% yield); n_D^{25} 1.3381; d_{25} 1.5899 (CF_2NO_2P (127): calc.: N 11.0, P 24.4, F 29.9; found: N 10.80, P 23.9, F 29.7%) and POFClPNCO: b.p. 101–103°; 10 g; n_D^{25} 1.4024 (calc. N 9.76, P 21.0, Cl 24.7; found: N 9.78, P 21.4, Cl 24.6%).

Reaction of Phosphorisocyanatidic Difluoride with Alcohols

POF_2NCO (0.25 mole) was dissolved in 50 ml of CH_2Cl_2 and into the stirred solution 0.25 mole of alcohol in 20 ml of CH_2Cl_2 was added dropwise at 0°. The reaction is completed in a few minutes. Methylene chloride was pumped off and the residual liquid product fractionated under reduced pressure.

The reaction with phenol was carried out in essentially the same manner, but due to decomposition the product could not be distilled and was purified by recrystallization from chloroform or benzene.

Reaction of Phosphorisocyanatidic Difluoride with Amines

POF_2NCO (0.25 mole) was dissolved in 50 ml of CH_2Cl_2 and into the stirred solution 0.25 mole of amine in 20 ml of CH_2Cl_2 was added dropwise, while the temperature of the mixture was kept around 0°. The reaction is completed in a few minutes. The methylene chlorided was removed by distillation and finally by pumping the product in vacuum. Attempted distillation of the products, even under pressure, resulted in decomposition. The products, which are essentially pure after removal of the solvent, and any possible volatile starting materials were recrystallized from chloroform or CCl_4.

ACKNOWLEDGMENTS

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