

IMPROVED PREPARATIONS OF DIFLUOROPHOSPHORYL AND  
DIFLUOROTHIOPHOSPHORYL ISOCYANATES.  
ALCOHOL AND THIOL ADDITION REACTIONS  
WITH ISOCYANATES

STEPHEN R. O'NEILL AND JEAN'NE M. SHREEVE\*

*Department of Chemistry, University of Idaho, Moscow, Idaho 83843 (U.S.A.)*

(Received March 24, 1973)

---

SUMMARY

Methane thiol and ethane thiol add readily to trifluoromethyl thioisocyanate and difluorophosphoryl isocyanate in the presence of a solvent. These thiols, together with methanol and ethanol, form thiocarbamates and carbamates with difluorothiophosphoryl isocyanate. Both  $\text{OPF}_2\text{NCO}$  and  $\text{SPF}_2\text{NCO}$  have been prepared in 70-75% yields by the reaction of  $\text{OPF}_2\text{Cl}$  or  $\text{SPF}_2\text{Cl}$  with  $\text{AgNCO}$ .

---

INTRODUCTION

We report some recent studies on the addition of alcohols and thiols to fluorinated isocyanates, including difluorophosphoryl, difluorothiophosphoryl and trifluorothiomethyl isocyanates. The latter behaves as a typical isocyanate with many compounds that contain active hydrogen<sup>1,2</sup>, but exceptions do occur and phenol, thiophenol, ethane thiol and triphenylcarbinol are reported not to add<sup>3</sup>. However, it has now proved possible to add methane thiol and ethane thiol to the nitrogen-carbon double bond of  $\text{CF}_3\text{SNCO}$  provided that the reactions are carried out under absolutely anhydrous conditions in acetonitrile as a solvent.

Earlier Olah<sup>4</sup> synthesized  $\text{OPF}_2\text{NCO}$  and found that it reacted with alcohols and primary and secondary amines to give simple addition compounds with yields in excess of 90%. Other methods for the preparation of both  $\text{OPF}_2\text{NCO}$ <sup>5-7</sup> and  $\text{SPF}_2\text{NCO}$ <sup>8,9</sup> are available, but reactions of difluorophosphoryl chloride and difluorothiophosphoryl chloride with silver isocyanate to form the phosphorus(V) isocyanates are more convenient and give higher yields.

---

\* Alfred P. Sloan Foundation Fellow, 1970-72.

Addition of thiols to OPF<sub>2</sub>NCO and of thiols and alcohols to SPF<sub>2</sub>NCO in solution occur rapidly to give thiocarbamates and carbamates in high yield. These compounds are readily sublimable, colorless, crystalline solids which readily hydrolyze in moist air.

#### EXPERIMENTAL

##### *General methods*

A standard Pyrex vacuum system equipped with a Heise-Bourdon tube gauge was used in all reactions. Infrared spectra were recorded with either a Perkin-Elmer Model 621 or a Perkin-Elmer Model 457 spectrometer using Nujol mulls between potassium bromide discs. A Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV at 25° was used to record the mass spectra. Nuclear magnetic resonance spectra were obtained at 94.1 MHz (Varian HA-100) for <sup>19</sup>F nuclei and at 60 MHz (Varian A-60) for <sup>1</sup>H nuclei. For fluorine or hydrogen, trichlorofluoromethane or tetramethylsilane was used as the internal reference in 25% solutions. Solvents used were dimethylsulfoxide, acetonitrile or diethyl ether. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Melting points of the solid carbamates and thiocarbamates were determined by using a Thomas Hoover Uni-Melt capillary melting point apparatus. The solids were sealed in capillary tubes under an atmosphere of dry nitrogen.

##### *Reagents*

Silver isocyanate was prepared by the method described in the literature<sup>10</sup>. It was found necessary to prepare the fresh silver salt to avoid products attributable to the presence of hydrous silver oxide in the commercially available material. Difluorophosphoryl isocyanate was obtained in 70% yield by condensing difluorophosphoryl chloride<sup>11</sup> (10 mmol) on to silver isocyanate (1 g) at -195° and allowing it to react for 0.5 h at 25°. The pure OPF<sub>2</sub>NCO was collected in a trap at -78° and its infrared spectrum compared with the published values<sup>4,7</sup>. Difluorothiophosphoryl isocyanate was prepared in 75% yield by the rapid reaction of difluorothiophosphoryl chloride<sup>12</sup> (10 mmol) with a slurry of AgNCO (1 g) in acetonitrile. The infrared spectrum agreed with the literature values<sup>8</sup>, although our assignments differ (see below).

Trifluoromethylsulfenyl isocyanate was prepared by allowing CF<sub>3</sub>SCI (10 mmol, PCR, Inc.) to react with silver isocyanate (1 g) in acetonitrile. The product was isolated in 50% yield using a trap cooled to -78°. Purity was determined by comparison of infrared spectra<sup>13</sup>. Methane thiol (Matheson) and ethane thiol (Aldrich Chemical Co.) were used as received.

##### *General preparative procedure for fluorine-containing thiocarbamates and carbamates*

Essentially the same method was employed in the preparation of all of the new carbamates and thiocarbamates. Dry acetonitrile (1 ml), the appropriate thiol

or alcohol (6 mmol) and isocyanate (2 mmol) were condensed into a reaction vessel. While the trifluoromethylsulfenyl isocyanate–thiol reaction required about 0.5 h for complete reaction to occur, the  $\text{OPF}_2\text{NCO}$ –thiol,  $\text{SPF}_2\text{NCO}$ –thiol or  $\text{SPF}_2\text{NCO}$ –alcohol reactions were complete in 5 min or less after warming to 25°. The yields of the colorless thiocarbamates were quantitative and these compounds were pure when the excess thiol and solvent were distilled away. However, further purification by sublimation of the carbamates resulting from the  $\text{SPF}_2\text{NCO}$ –alcohol reactions was necessary to free them from unidentified contaminants (detected by  $^{19}\text{F}$  NMR spectroscopy). The resulting yields were reduced to about 90%.

Elemental analyses and melting point, infrared spectral and  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data are given in Tables 1–3.

## RESULTS AND DISCUSSION

All the new isocyanate derivatives are white crystalline solids which are readily hydrolyzed in moist air to the thiol or alcohol and are thermally stable at least to their melting points. The presence of a solvent is important; thus, in the absence of acetonitrile, trifluoromethylsulfenyl isocyanate required up to 6 h to react completely with methane thiol, whilst it did not react with ethanol thiol at all.

The mass spectra of these thiocarbamates and carbamates are typical<sup>14</sup>. With the exception of  $\text{SPF}_2\text{N}(\text{H})\text{C}(\text{O})\text{SCH}_3$ , molecule ions were not observed; base peaks were either  $\text{PF}_2^+$  or  $\text{CH}_3^+$ . No proton–fluorine or phosphorus–proton coupling was observed in the nuclear magnetic resonance spectra (Table 3). The chemical shifts and coupling constants observed are consistent with the proposed structures<sup>15</sup>.

Unfortunately, the C–H stretching activity in the infrared spectra is not clear due to similar Nujol frequencies that obscure or partially overlap with those due to the compounds. However, other stretching frequencies can be assigned as follows:  $\nu(\text{N–H})$ , between 3120 and 3240  $\text{cm}^{-1}$ ;  $\nu(\text{C=O})$ , between 1658 and 1733  $\text{cm}^{-1}$ ;  $\nu(\text{P=O})$ , at 1322 and 1330  $\text{cm}^{-1}$ ; asymmetric and symmetric  $\nu(\text{P–F})$ , between 870 and 965  $\text{cm}^{-1}$ ;  $\nu(\text{C–F})$ , between 1110 and 1175  $\text{cm}^{-1}$ ; and  $\nu(\text{C–N})$ , between 1077 and 1118  $\text{cm}^{-1}$ . The P–N and P=S bands are more difficult to assign. The P–N linkage is sensitive to mass changes and its position is easily shifted<sup>16</sup>. Phosphorus–nitrogen stretching vibrations are usually strong<sup>6</sup>, but sometimes medium, and occur reasonably within the range 680–847  $\text{cm}^{-1}$ . In  $\text{OPF}_2\text{NCO}$  and  $\text{SPF}_2\text{NCO}$ ,  $\nu(\text{P–N})$  is assigned at 763 (s) and 815 (vs),  $\text{cm}^{-1}$ . Bands at 777 and 805  $\text{cm}^{-1}$  in  $\text{OPF}_2\text{N}_3$  and  $\text{OPF}(\text{N}_3)_2$  are also assigned to  $\nu(\text{P–N})$ , whilst in  $\text{SPF}_2\text{N}_3$  and  $\text{SPF}(\text{N}_3)_2$  bands at 825  $\text{cm}^{-1}$  in both cases were similarly assigned. Bands in the range 842–862  $\text{cm}^{-1}$  in the thiocarbamates and in the range 775–782  $\text{cm}^{-1}$  in the carbamates were also assigned to  $\nu(\text{P–N})$ .

TABLE 1  
ELEMENTAL ANALYSES AND MELTING POINTS

Compound	M.p. (°C)	Found (%)				Calculated (%)			
		F	P	S	H	F	P	S	H
OPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	64-65	21.60	17.54	18.51	13.61	21.60	17.67	18.29	13.68
OPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	69-70	20.00	16.35	17.09	19.08	19.76	16.12	16.64	18.72
SPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	60-61	19.70	16.08	33.42	12.62	19.87	16.21	33.47	12.56
SPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	62-63	18.60	15.15	31.42	16.98	18.43	15.04	31.04	17.46
SPF <sub>2</sub> N(H)C(O)OCH <sub>3</sub>	50-51	—	17.55	18.52	13.72	—	17.70	18.27	13.70
SPF <sub>2</sub> N(H)C(O)OCH <sub>2</sub> CH <sub>3</sub>	56-57	—	15.84	17.48	19.10	—	16.40	16.93	19.04
CF <sub>3</sub> SN(H)C(O)SCH <sub>3</sub>	32-33	—	—	33.01	—	—	—	33.50	—
CF <sub>3</sub> SN(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	34-35	—	—	30.09	—	—	—	31.22	—

TABLE 2  
INFRARED SPECTRA

OPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	3120 (m), *2920, *2860, 1710 (s), *1460, *1368, 1322 (m), 1109 (s), 965 (s), (br), 870 (m), 842 (m), *720, 648 (m).
OPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	3130 (m), 2920, 2860, 1700 (m), 1460, 1368, 1330 (m), 1112 (s), 955 (s), (br), 870 (mw), 842 (m), 645 (m).
SPF <sub>2</sub> NCO	2300 (vs), 1430 (s), 950 (vs), 930 (s), 815 (vs), 750 (vw), 600 (m), 420 (m).
SPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	3165 (m), 2920, 2860, 1660 (s), 1460, 1368, 1107 (m), 936 (m), 910, 888 (s), 860 (m), 713, 677 (m).
SPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	3175 (m), 2920, 2860, 1658 (s), 1460, 1368, 1104 (s), 938 (s), 910, 897 (s), 862 (m), 682 (m).
SPF <sub>2</sub> N(H)C(O)OCH <sub>3</sub>	3240 (s), 2920, 2860, 1722 (s), 1460, 1368, 1260 (ms), 1097 (m), 963, 935 (s), 898, 782 (m), 740 (m), 692, 655 (m).
SPF <sub>2</sub> N(H)C(O)OCH <sub>2</sub> CH <sub>3</sub>	3220 (w), 2920, 2860, 1733 (s), 1460, 1368, 1305 (s), 1225 (w), 1077 (w), 1005, 955 (ms), 905 (s), 857 (ms), 775 (w), 720, 687 (m).
CF <sub>3</sub> SN(H)C(O)SCH <sub>3</sub>	3230 (m), 2920, 2860, 1665 (s), 1460, 1368, 1300 (w), 1215 (w), 1175 (s), 1150 (s), 1118 (s).
CF <sub>3</sub> SN(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	3210 (s), 2920, 2860, 1675 (s), 1460, 1368, 1210 (w), 1170 (s), 1140 (s), 1110 (s).

\* C-H modes in these regions obscured due to Nujol bands.

TABLE 3  
<sup>1</sup>H AND <sup>19</sup>F NMR SPECTRA\*

Compound	<sup>1</sup> H spectra			<sup>19</sup> F spectra	
	δ(CH <sub>3</sub> )	δ(CH <sub>2</sub> )	J(H-H)	φ*	J(P-F)
OPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	2.36s			75.0	1080
OPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	1.26t	2.95q	7	72.5	1031
SPF <sub>2</sub> N(H)C(O)SCH <sub>3</sub>	3.32s			44.7	1118
SPF <sub>2</sub> N(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	1.26t	2.92q	7	44.7	1128
SPF <sub>2</sub> N(H)C(O)OCH <sub>3</sub>	3.26s			45.4	1068
SPF <sub>2</sub> N(H)C(O)OCH <sub>2</sub> CH <sub>3</sub>	2.76t	3.70q	7	46.9	1119
CF <sub>3</sub> SN(H)C(O)SCH <sub>3</sub>	2.33s			50.7	
CF <sub>3</sub> SN(H)C(O)SCH <sub>2</sub> CH <sub>3</sub>	1.25t	2.90q	7	51.0	

\* Chemical shifts, δ, and φ\* values in ppm; coupling constants in Hz.

The stretching mode of P=S, although sometimes strong but generally of variable intensity and sometimes absent, most likely appears between 600–760 cm<sup>-1</sup>. As fluorine atoms progressively replace chlorine in SPCl<sub>3</sub>, ν(P=S) decreases from 770 to 753 to 738 to 695 cm<sup>-1</sup> (in the gas phase)<sup>17</sup>. Except for a moderate band in SPF<sub>3</sub>, the bands are intense. Whilst we assign the band at 750 (vw) cm<sup>-1</sup> in

SPF<sub>2</sub>NCO to  $\nu(\text{P}=\text{S})$ , others<sup>8</sup> assign  $\nu(\text{P}=\text{S})$  to 815 cm<sup>-1</sup> which we attribute to  $\nu(\text{P}-\text{N})$ . The latter has also been assigned to  $\nu(\text{P}-\text{F})$ <sup>9</sup>. In the compounds SPF<sub>2</sub>N(H)C(O)SR and SPF<sub>2</sub>N(H)C(O)OR,  $\nu(\text{P}=\text{S})$  modes are found in the range 677–692 cm<sup>-1</sup>.

#### ACKNOWLEDGEMENTS

Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Dr. R. A. De Marco for the mass spectra and Dr. D. T. Sauer for the nuclear magnetic resonance spectra.

#### REFERENCES

- 1 A. HAAS, *Chem. Ber.*, **97** (1964) 2189.
- 2 A. HAAS AND P. SCHOTT, *Chem. Ber.*, **99** (1966) 3103.
- 3 A. HAAS in E. A. V. EBSWORTH, A. G. MADDOCK AND A. G. SHARPE (Eds.), *New Pathways in Inorganic Chemistry*, Cambridge University Press, Cambridge, 1968, Chapter 5.
- 4 S. J. KUHN AND G. A. OLAH, *Canad. J. Chem.*, **40** (1962) 1951.
- 5 H. W. ROESKY, *Chem. Ber.*, **100** (1967) 2142.
- 6 H. W. ROESKY, *Chem. Ber.*, **100** (1967) 2147.
- 7 O. GLEMSE, U. BIERMANN AND M. FILD, *Chem. Ber.*, **100** (1967) 1082.
- 8 H. W. ROESKY, *J. Inorg. Nuclear Chem.*, **32** (1970) 1845.
- 9 C. B. COLBURN, W. E. HILL AND D. W. A. SHARP, *J. Chem. Soc. (A)*, (1970) 222.
- 10 R. E. NEVILLE AND J. J. MCGEE, *Inorg. Synth.*, **8** (1966) 23.
- 11 H. W. ROESKY, *Chem. Ber.*, **101** (1968) 636.
- 12 S. R. O'NEILL AND J. M. SHREEVE, *Inorg. Chem.*, **11** (1972) 1629.
- 13 H. J. EMELÉUS AND A. HAAS, *J. Chem. Soc.*, (1963) 1272.
- 14 H. BUDZIKIEWICZ, C. DJERASSI AND D. H. WILLIAMS, *Mass Spectrometry of Organic Compounds*, Holden-Day, Inc., San Francisco, 1967.
- 15 R. SCHMUTZLER, *Adv. Fluorine Chem.*, **5** (1965) 254.
- 16 L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1968.
- 17 J. R. DURIG AND J. W. CLARK, *J. Chem. Phys.*, **46** (1967) 3057.