Preparation and Properties of Difluorophosphino Monothioacetate †

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When difluorophosphino monothioacetate is prepared by the exchange reaction of $PBrF_2$ with $CH_3COSSnBu_3$ (which contains an S–Sn bond) the isomer in which the difluorophosphino-group is bound to oxygen is formed first. When it is prepared from $PBrF_2$ and $CH_3CSOSiH_3$ (which contains an O–Si bond) the S-bonded isomer is formed. In each case equilibration then occurs to give *ca.* 80% O-bonded and 20% S-bonded at room temperature. Thermodynamic data are reported. The new ester has been isolated, and characterised by n.m.r., vibrational, and mass spectroscopy. Difluorophosphino monoselenoacetate has been prepared by analogous reactions, but it is unstable and has not been isolated.

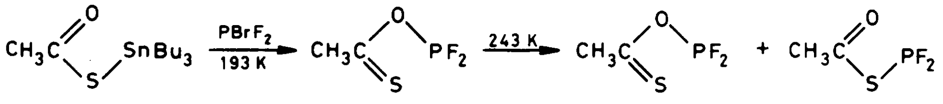
In recent years there has been considerable interest in the structures and bonding of silyl and germyl esters and thioesters. It has been shown spectroscopically [1] that in silyl and trimethylsilyl monothioacetates the silyl groups are bonded to oxygen, whereas the germyl and trimethylgermyl analogues are S-bonded. However, silyl monoselenoacetate exists at room temperature as a mixture of O-bonded and Se-bonded isomers, and the position of equilibrium and exchange rate have been studied by n.m.r. spectroscopy.[2]

The ease of intra- and inter-molecular exchange in these compounds may be related to their molecular structures. In silyl formate [3] and silyl acetate [4] in the gas phase there are short non-bonded Si $\cdots$ O contacts, about 280 pm, compared with 350 pm for the sum of van der Waals radii for silicon and oxygen. The short intramolecular contact in silyl acetate is retained in the solid phase,[4] but in the crystal there is also a short intermolecular Si $\cdots$ O contact, again about 280 pm. Similar behaviour is found for silyl monothioacetate, which has a short non-bonded Si $\cdots$ S interaction in the gas phase, and short inter- and intra-molecular contacts in the crystal.[5] In germyl monothioacetate, in which the germyl group is bound to sulphur, there is a short Ge $\cdots$ O contact in the gaseous phase: [6] the structure of the solid phase has not been determined.

In view of these similarities and contrasts in bonding, it is of interest to study other related esters. It has been shown that when bis(trimethylsilyl)acetamide (which has one silyl group N-bonded and one O-bonded) is treated with $PBrF_2$ the N-bonded trimethylsilyl group is first replaced by a difluorophosphino-group, then the O-bonded group is displaced, and finally an intramolecular rearrangement occurs, giving *N,N*-bis(difluorophosphino)acetamide.[7] We have therefore studied the preparation of difluorophosphino monothioacetate by methods leading to the formation of two different isomers, and describe here the preparation and interconversion of these two isomers and their spectroscopic properties.

Results and Discussion

When equimolar quantities of $PBrF_2$ and $CH_3COSSnBu_3$ were allowed to react in an n.m.r. tube at 193 K the ^{31}P n.m.r. spectrum showed a wide triplet ($^1J_{PF}$ 1 343 Hz) at 114.5 p.p.m., assigned on the basis of its n.m.r. parameters to O-bonded CH_3CSOPF_2. The spectrum did not change until the temperature reached 243 K, when a second triplet (δ 211.5 p.p m., $^1J_{PF}$ 1 269 Hz) appeared. The parameters of the new compound are consistent with it being S-bonded CH_3COSPF_2. The preparation has therefore involved an intermolecular exchange, followed by partial intramolecular exchange [equation (1)].


(1)

The tube was then left at 243 K to equilibrate, and the intensities of the triplets were integrated. Further integrals were recorded at temperatures from 253 to 308 K, by which temperature the ratio of O-bonded to S-bonded isomers had reached 4.3 : 1. There was no evidence for fast exchange at any time. The relative concentrations of the two species over the temperature range studied yielded $\Delta H^\circ = 5.1$ kJ mol^{-1} and $\Delta S^\circ = 4.6$ J K^{-1} mol^{-1} for the O-bonded $\rightleftharpoons$ S-bonded equilibrium.

In contrast, reaction between $PBrF_2$ and $CH_3CSOSiH_3$ (in which the silicon is bound to oxygen) at 193 K gave a product having a triplet resonance (δ = 209.9 p.p.m., $^1J_{PF}$ 1 269 Hz) in the ^{31}P n.m.r. spectrum, assigned to the S-bonded difluorophosphino monothioacetate. On warming to 228 K, a second triplet, assigned to the O-bonded species (δ = 114.9 p.p.m., $^1J_{PF}$ 1 342 Hz) appeared. On further warming the exchange of the PF_2 site continued until the final equilibrium position was the same as for the sample prepared from $CH_3COSSnBu_3$. On prolonged standing at room temperature some decomposition, giving PF_3 and $O(PF_2)_2$, was observed. Thus the preparation by this route has again involved an intermolecular exchange, followed by partial intramolecular rearrangement [equation (2)].

In both reactions, the incoming PF_2 group has added to the vacant atom, whether it is O or S, and rearrangement to give the thermodynamically stable mixture of isomers has only occurred later. This suggests that the reaction involves a six-membered ring intermediate [equation (3)].

The preparation of difluorophosphino monoselenoacetate from silyl monoselenoacetate was then studied. The latter compound exists as a mixture of O- and Se-bonded isomers, and these rapidly interconvert on the n.m.r. time-scale at 300 K, but slowly at 223 K.[2] On treatment of the silyl ester with $PBrF_2$ at 193 K the ^{31}P n.m.r. spectrum showed that a single

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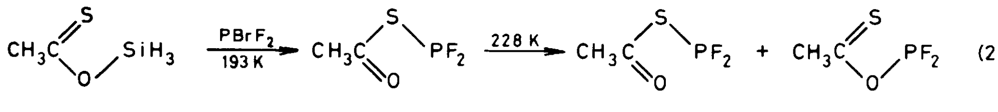
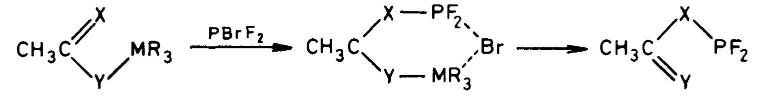
† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

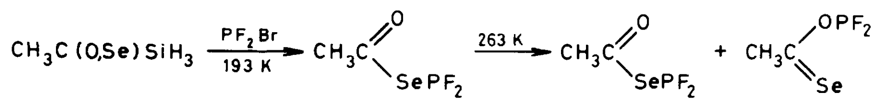


(2)



(3)

product with a triplet resonance pattern was formed. Satellites due to ^{77}Se were not observed because the quality of the spectra was not high. The parameters (δ = 244 p.p.m., $^1J_{PF}$ 1 265 Hz) are consistent with the product being Se-bonded $CH_3COSePF_2$. On warming to 263 K a second species (δ = 112.2 p.p.m., $^1J_{PF}$ 1 344 Hz) appeared, and this was assigned to the O-bonded isomer. There was never more than about 10% of this isomer, and on further warming it decomposed, giving PF_3, $O(PF_2)_2$, and PF_2HSe. The reactions can therefore be represented by equation (4).



(4)

Thus, comparing the silyl and difluorophosphino esters, we find that the phosphorus compounds have higher proportions of the S- or Se-bonded isomers than their silicon counterparts, and that intramolecular exchange is much slower in the phosphorus compounds. The equilibrium positions of course depend on a fine balance of bond energies, while the exchange rates probably depend on the ease of formation of transition states involving five-co-ordinate silicon or four-co-ordinate phosphorus.

N.M.R. Parameters.—The ^{31}P chemical shifts and ^{31}P–^{19}F coupling constants for the esters are very close to those reported for other compounds having difluorophosphino-groups bound to oxygen, sulphur, or selenium.[8] The assignments are also supported by ^{19}F, ^{1}H, and ^{13}C n.m.r. data. At room temperature the ^{19}F n.m.r. spectrum of difluorophosphino monothioacetate showed two doublets, one about five times as intense as the other. Under high-resolution conditions each line was further split into a quartet. The more intense doublet (δ −78.2 p.p.m., $^1J_{PF}$ 1 269.1 Hz) was assigned to CH_3COSPF_2, and the other (δ −58.3 p.p.m., $^1J_{PF}$ 1 343 Hz) was assigned to CH_3CSOPF_2. Again, these parameters are very similar to those in related PF_2S and PF_2O compounds. Similarly, the ^{1}H spectrum of an equilibrium mixture showed two groups of resonances, and each group was a doublet ($^4J_{HP}$) of triplets ($^5J_{HF}$). In the ^{13}C spectrum the resonances of the methyl group carbons of the two isomers could be assigned, but only one other signal was observed, a doublet at 219.0 p.p.m. Presumably the second resonance of the less-abundant isomer was too weak to be observed under the conditions used. All the n.m.r. parameters are listed in Table 1.

Table 1. N.m.r. parameters for difluorophosphino monothioacetate;[a] n.o. = not observed

	CH_3COSPF_2	CH_3CSOPF_2
$\delta(^{31}P)$/p.p.m.[b]	212.9	115.6
$\delta(^{19}F)$/p.p.m.[c]	−78.2	−58.3
$\delta(^1H)$/p.p.m.[d]	2.51	2.65
$\delta(^{13}C)$/p.p.m.[d]	34.0	35.3
	219.0	n.o.
$^1J(^{31}P^{19}F)$/Hz	1 269.1	1 343
$^4J(^{31}P^1H)$/Hz	2.2	2.1
$^5J(^{19}F^1H)$/Hz	1.0	0.7

[a] In CCl_2D_2 at room temperature. [b] To high frequency of 85% H_3PO_4. [c] To high frequency of CCl_3F. [d] To high frequency of $SiMe_4$.

Vibrational Spectra.—The explanation of the mode of formation of difluorophosphino monothioacetate is supported by vibrational spectra. The i.r. spectrum of a gaseous sample freshly prepared according to equation (1) showed only a very weak carbonyl stretching band, which rapidly increased in intensity over 30—40 min at room temperature. It was not

Table 2. Vibrational spectrum (cm^{-1}) of difluorophosphino monothioacetate; w = weak, m = medium, s = strong, v = very, br = broad, and sh = shoulder

I.r. (gas)[a]	I.r. (solid)[b]	Raman (liquid)[a]	Assignment
3 036vw			ν_{asym}(C–H)
2 982vw		2 940m	ν_{sym}(C–H)
1 747s	1 745m	1 720w,br	ν(C=O)
	1 680s		
1 442w	1 427m	1 435w	$\delta_{asym}(CH_3)$
1 377m	1 364m	1 375m	
	1 314w		$\delta_{sym}(CH_3)$
1 271s	1 256s	1 265vs	ν(C–O)
1 207s	1 213s	1 210w	ν(C=S)
1 131s	1 143s	1 140w	$\rho(CH_3)$
1 004s	997s	1 005m	
977s	951s		ν(C–C)
925w	908w		$\rho(CH_3)$
869vs	849vs,br	860s,br	ν_{asym}(P–F)
848vs			ν_{sym}(P–F)
815s	810vs	810m	
784w	749w	745vw	
692m	693m	702vvs	ν(P–O)
620m	638m	635vs	ν(C–S)
513w	519w		
	511w	510s	
480w			
461m	$\left.\begin{array}{l}466\\457\end{array}\right\}$m	460s	$\delta(PF_2)$
		455 (sh), m	
	430m		
	395w	400w	
370m	380w	360w	$\omega(PF_2)$
	355m	315m	
		270w	

[a] Equilibrium mixture of isomers at room temperature. [b] Sample obtained by condensing an equilibrated room-temperature gaseous mixture onto a window held at 77 K.

Table 3. Mass spectrum of difluorophosphino monothioacetate

	Relative abundance		
m/*e*	70 eV	16 eV	Assignment
144 *	18	49	$[CH_3COSPF_2]^+$
106	3		$[CH_3COSP]^+$
104	7		$[CHCOSP]^+$
102	14		$[PF_2HS]^+$
101	3		$[PF_2S]^+$
92	71	54	$[POCSH]^+$
91	71	2	$[POCS]^+$
88	26		$[PF_3]^+$
86	28		$[PF_2HO]^+$
85	14		$[PF_2O]^+$
76	14	3	$[CH_3COS]^+$
69	100	5	$[PF_2]^+$
67	11		$[PFHO]^+$
66	13		$[PFO]^+$
63	8		$[PS]^+$
59	44	49	$[CH_3CS]^+$
50	28	4	$[PF]^+$
44	17	4	$[PF_3]^{2+}$
43	100	100	$[CH_3CO]^+$
42	27		$[CH_2CO]^+$
41	4		$[CHCO]^+$
32	16		$[S]^+$
31	17		$[P]^+$

* Exact mass 143.961310 (error <2 p.p.m. for $C_2H_3F_2OPS$).

possible to obtain a satisfactory spectrum of either isomer in a pure state, so the frequencies given in Table 2 relate to equilibrium mixtures at room temperature: in the case of the solid, this was obtained by condensing a gaseous sample onto a pre-cooled window.

Assignment of vibrational bands was done by comparison with frequencies reported for related difluorophosphino-compounds, thioacids, and thioesters. In addition to characteristic bands of methyl and difluorophosphino-groups, there are bands which can be assigned to skeletal vibrations of the two isomers, although all assignments must be tentative. In the i.r. spectra there are two strong bands between 1 200 and 1 300 cm^{-1}, which appear in the Raman spectrum as one strong band at 1 265 cm^{-1} and a weak one at 1 210 cm^{-1}. By comparison with silyl monothioacetate, in which the silicon is O-bonded,[1] the C–O stretch is assigned to the strong Raman band and the C=S stretch to the weaker one. The band at 620 cm^{-1} in the i.r. spectrum of the gas (635 cm^{-1} and very strong in the Raman spectrum of the liquid) is assigned to the C–S stretching mode. The equivalent mode occurs at 626 cm^{-1} for thioacetic acid, and is also very strong in the Raman spectrum, and at 625 and 637 cm^{-1} for germyl and trimethylgermyl monothioacetates.[1] Finally, the P–O stretch is assigned to the band at 692 cm^{-1}: the equivalent band in CH_3COOPF_2 (also very strong in the Raman spectrum) is at 770 cm^{-1}.[9] Assignments below 600 cm^{-1} cannot be conclusive, although bands at 461 and 370 cm^{-1} are characteristic of deformation modes of PF_2 groups. In the solid phase both isomers are clearly still present, but there are additional splittings, which probably arise from crystal effects.

The instability of difluorophosphino monoselenoacetate precluded the possibility of obtaining reliable vibrational spectra. The gas-phase i.r. spectrum included bands at 1 810, 1 210, 908, 780, and 550 cm^{-1}.

Mass Spectrum.—Details of the mass spectrum of an equilibrium mixture of the isomers of difluorophosphino monothioacetate are given in Table 3. The ions formed are consistent with both isomers being present, as species containing PF_2O and PF_2S are both prominent, as are $[CH_3CO]^+$ and $[CH_3CS]^+$. It is dangerous to argue from ion abundances to proportions of isomers, but it is noteworthy that ions containing phosphorus and oxygen are invariably more abundant than their phosphorus–sulphur analogues. Thus all the spectroscopic evidence is consistent with the proposal that two isomers exist in equilibrium at room temperature and that the O-bonded form is the more abundant.

Experimental

All preparations were carried out using a Pyrex glass vacuum line fitted with greaseless taps. I.r. spectra (4 000—200 cm^{-1}) were obtained using a Perkin-Elmer 457 spectrometer and CsI windows, and Raman spectra using a Cary 83 spectrometer with argon-ion (488-nm) laser excitation. N.m.r. spectra were recorded using Bruker WH360 (^1H, ^{13}C, and ^{31}P), Varian XL100 (^{19}F), and JEOL FX60 (^{31}P) spectrometers. Mass spectra were obtained using an AEI MS902 spectrometer.

Preparation of Difluorophosphino Monothioacetate.—Tributyltin monothioacetate was first prepared by treating $O(SnBu_3)_2$ (10 mmol) with CH_3COSH (20 mmol) in toluene (40 cm^3) for 1 min. The water thus produced and the solvent were removed with a hot water-bath and rotary evaporator. The compound was dried by pumping the involatile yellow liquid for 2—3 h. Equimolar portions of $CH_3COSSnBu_3$ and $PBrF_2$ were then mixed and allowed to react at room temperature for 1 min. The volatile products were removed and fractionated *in vacuo*. Difluorophosphino monothioacetate was volatile at 238 K, but retained at 209 K. The yield was typically 60%.

Alternatively, equimolar portions of $CH_3CSOSiH_3$ and $PBrF_2$ were condensed together into an n.m.r. tube containing a deuteriated solvent. On warming to 193 K the formation of difluorophosphino monothioacetate could be observed by ^{31}P or ^{19}F n.m.r. spectroscopy.

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