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Oxidative fluorination of some organoantimony and organotellurium compounds by 2-hydroperfluoropropyl azide

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Abstract

Triphenylantimony and diphenyltellurium are readily oxidatively fluorinated by 2-hydroperfluoropropyl azide, $CF_3CHFCF_2N_3$, to form appropriate difluorides from moderate to high yields. \bigcirc 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Fluorinated compounds are of considerable interest in inorganic, organic, polymer, industrial and medicinal chemistry [1-6]. Particularly valuable are mild and selective fluorinating agents, and methods for the ready fluorination of organic and organoelement compounds [5-7]. The great majority of fluorinating agents are of nucleophilic character. The reagents which are capable of electrophilic fluorination include F2 itself [8-10], XeF2 [11-13], PhIF2 [14-16], acetyl hypofluorite, MeCOOF [17-20] and N- fluoroamines and amides [21-24]. Unfortunately, these reagents have various drawbacks and limitations such as hazardous handling (F₂, RCOOF), high cost and lack of selectivity (XeF2, N-F compounds) or weak fluorinating ability (PhIF₂), and finally, they are all usually prepared from F₂. Therefore, new electrophilic fluorinating agents that allow the ready introduction of fluorine under mild conditions into electron rich substrates are highly desirable and useful.

We have recently shown [25] that stable 2-hydroperfluoropropyl azide, $CF_3CHFCF_2N_3$ (1), readily fluorinates various organophosphorus (III) compounds, affording difluorophosphoranes in high yields and serving, hence, as an oxidative fluorinating agent.



To determine the scope and limitations of the fluorinating ability of the azide 1 we studied its reactions with some low-valent compounds of main groups V and VI elements, namely with Ph_3Sb , Ph_3Bi , Ph_2Te and Ph_2Te_2 .

1.1. Group V compounds

We have found that the reaction of the azide 1 with Ph_3Sb in methylene chloride leads to a high yield of Ph_3SbF_2 (2) over a wide temperature range (reaction (1)):

$$\begin{array}{c} Ph_{3}Sb+CF_{3}CHFCF_{2}N_{3} \xrightarrow{8S-160^{\circ}C, 3-6h} Ph_{3}SbF_{2} \\ + CF_{3}CHFCN+N_{2} \uparrow \end{array}$$
(1)

This reaction needs higher temperatures than the analogous reactions with organophosphorus compounds (see Table 1). Some decrease in the diffuoride 2 yield at 160°C is probably due to the thermal instability of the product.

The reaction of 1 with Ph₃Bi does not take place even on heating, probably due to a high oxidation potential of Bi(V) compounds [26] (reaction (2)):

$$Ph_{3}Bi \xrightarrow[150°C, 3h]{i} no reaction$$
(2)

1.2. Group VI compounds

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The reaction of Ph_2Te with the azide 1 proceeds at higher temperatures and also gives the desired product of oxidative

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Substrate	Temperature (°C)	Solvent	Reaction time (h)	Product	Yield (%)
Ph ₃ Sb	85	CH ₂ Cl ₂	5	2	60
	120	CH_2Cl_2	5	2	100
	160	CH_2Cl_2	3	2	83
	85	CH ₃ CN	6	2	59
Ph ₂ Te	120	CH_2Cl_2	5	3	6
	120 ^a	CH_2Cl_2	5	3	14
	170	CH_2Cl_2	3	3	32
	170 ^a	CH_2Cl_2	3	3	60
Ph ₂ Te ₂	160	CH ₂ Cl ₂	4	3	5 ^b
	140	CH ₃ CN	7.5	3	11 ^b

Table 1							
Fluorination	of	organoelement con	npounds	by	the	azide	1

^aHMPTA added.

^bDiphenyltellurium difluoride.

fluorination – difluoride Ph_2TeF_2 (**3**) in a moderate yield (reaction (3)). It was found useful to charge the reaction vessel (stainless steel bomb) with inert CO₂ at high pressure (45–50 atm) prior to heating in order to retain highly volatile azide **1** and CH₂Cl₂ in a liquid state at elevated temperatures. In contrast to Ph₃Sb, the reaction appeared to be sensitive to the presence of a dipolar aprotic solvent, e.g. hexamethylphosphortriamide (HMPTA). The addition of 0.4 ml of HMPTA to a reaction mixture increased the yield of **3** significantly (see Table 1). However, the addition of HMPTA to Ph₃Sb did not affect the yield of the product **2**.

$$Ph_{2}Te + CF_{3}CHFCF_{2}N_{3} \xrightarrow[p(CO)_{2}=45-50 \text{ atm}]{}^{12-170^{\circ}C, 3-5 \text{ h}} Ph_{2}TeF_{2}$$
(3)

The reaction of Ph_2Te_2 with 1 does not produce the expected PhTeF₃, 4, but gives diffuoride 3, probably as a result of the thermal decomposition of the starting ditelluride (reaction (4)):

$$Ph_{2}Te_{2} \xrightarrow{140-160 \ ^{\circ}C} 1 \xrightarrow{1} PhTeF_{3}$$

$$Ph_{2}Te_{2} \xrightarrow{140-160 \ ^{\circ}C} 1 \xrightarrow{1} PhTeF_{3}$$

$$Ph_{2}TeF_{2} + [Te] \downarrow$$

$$3$$

$$(4)$$

The mechanism of the fluorination reaction is undoubtedly similar to that described for P(III) compounds [25] (Scheme 1), and includes a Staudinger-like reaction – steps (a) and (b), and sigmatropic fluorine transfer with the formation of a stable nitrile and strong Element-F bonds (c).

$$\begin{array}{c} Ph_{3}Sb: + N_{3}\text{-}CF_{2}CHFCF_{3} & \xrightarrow{a} [Ph_{3}Sb=N-N=N-CF_{2}CHFCF_{3}] & \longrightarrow \\ \\ \hline \\ \hline \\ -N_{2} & \end{array} \begin{array}{c} Ph_{3}Sb & \xrightarrow{e} Ph_{3}SbF_{2} + NC-CHFCF_{3} \\ \hline \\ F & CHFCF_{3} \end{array} \end{array} \begin{array}{c} c & Ph_{3}SbF_{2} + NC-CHFCF_{3} \end{array}$$



Thus, 2-hydroperfluoropropyl azide, 1, can be regarded, to some extent, as a synth of the following mixture:

 $CF_3CHFCF_2N_3 \Rightarrow [F_2] + N_2 + CF_3CHFCN$

2. Experimental

¹⁹ F NMR spectra were recorded on a Bruker CXP-200 spectrometer. Chemical shifts are reported in δ-units down-field from external CF₃COOH. Melting points are uncorrected. Ph₃Sb, Ph₂Te₂ and Ph₃Bi were commercial reagents, Ph₂Te [27] and 2-hydroperfluoropropyl azide, **1**, [25] were synthesized according to literature procedures. Ph₃SbF₂ and Ph₂TeF₂ for ¹⁹ F NMR spectra were synthesized from XeF₂ and Ph₃Sb [28] and Ph₂Te, respectively. When products were not isolated, their yields were determined by ¹⁹ F NMR (an exact amount of *m*-fluorotoluene was added to a reaction mixture and the signals were integrated).

2.1. Triphenylantimony difluoride, 2

350 mg (1 mmol) of Ph₃Sb, 580 mg (3 mmol) of azide **1** and 3 ml of dry methylene chloride were mixed in a Teflon vessel, sealed in a 100 ml stainless steel bomb and the bomb was heated at 120°C for 5 h. The bomb was cooled, the reaction mixture was evaporated. Three hundred and ninty mg (1 mmol, 100%) of Ph₃SbF₂ (**2**) was obtained, mp 118–119°C. After recrystallization from CH₂Cl₂: hexane mp 121°C. ¹⁹ F NMR (δ , ppm): -74.8 s. Lit. data: mp 121–122°C [28].

2.2. Diphenyltellurium difluoride, 3

280 mg (1 mmol) of Ph₂Te, 580 mg (3 mmol) of the azide 1, 3 ml of dry methylene chloride and 0.4 ml of HMPTA were mixed in a Teflon vessel and sealed in a 100 ml stainless steel bomb. The bomb was charged with CO₂ (45–50 atm), closed and then was heated at 170° C for 3 h. The bomb was cooled, the reaction mixture was evaporated. Two hundred μ l of 1 M solution of *m*-fluorotoluene in chloroform was added to the residue, and then the ¹⁹ F NMR spectrum was recorded. The yield of **3** was of 60% according to the integral intensity of the signals. ¹⁹ F NMR (δ , ppm): -49.5, *J*(Te–F)=568 Hz. After recrystallization from methylene chloride/hexane, mp 152°C. Lit. data: mp 153°C [29].

The authentic sample of **3** was also prepared by the reaction of equimolar amounts (1 mmol) of Ph_2Te and XeF_2 in dry CH_2Cl_2 (8 ml) at ambient temperature and had the same mp and ¹⁹ F NMR spectrum.

2.3. Fluorination of Ph_2Te_2

110 mg (0.27 mmol) of Ph_2Te_2 , 310 mg (1.6 mmol) of azide **1**, 0.4 ml of HMPTA and 2 ml of dry methylene chloride were mixed in a Teflon vessel, sealed in a 100 ml stainless steel bomb and the bomb was heated at 140°C for 7.5 h. The bomb was cooled, the reaction mixture was evaporated. ¹⁹ F NMR spectrum revealed the presence of 11% of difluoride **3**.

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