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TRIPHENYLBISMUTH DIFLUORIDE—A NOVEL REAGENT FOR THE OXIDATIVE FLUORINATION OF P(III), Se(II) AND Sb(III) COMPOUNDS

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Triphenylbismuth difluoride, Ph_3BiF_2 , is a mild source for the oxidative fluorination of organic compounds of P(III), Sb(III) and Se(II), bearing electron donating, non-bulky substituents.

Key words: Triphenylbismuth difluoride, oxidative fluorination, compounds of trivalent phosphorus, trivalent antimony, divalent selenium.

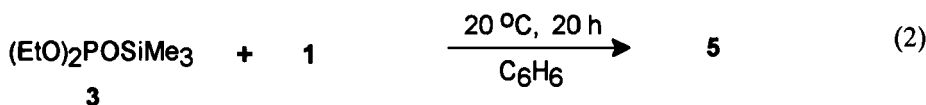
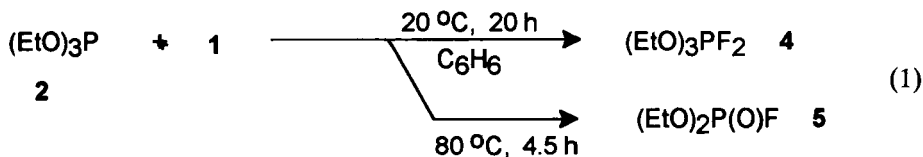
INTRODUCTION

Triphenylbismuth difluoride, Ph_3BiF_2 (1), while known for many years,¹ remains almost totally unexplored although the fluorination of tellurium(II) compounds by the difluoride 1 is known.² At the same time bismuth(V) compounds exhibit unusually strong oxidizing power. For instance, NaBiO_3 even converts $\text{Mn}(+2)$ into $\text{Mn}(+7)$.³ This work describes our study of the oxidative properties of the difluoride 1, in particular, towards organic compounds of phosphorus(III), antimony(III) and selenium(II) as part of our joint efforts concerning the investigation of 10-electron electrophilic reagents.⁴

RESULTS AND DISCUSSION

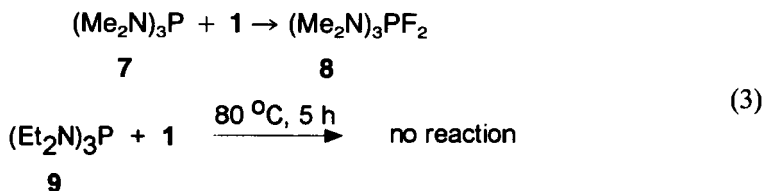
Fluorination of Organic Compounds of Trivalent Phosphorus

Difluoride 1 is a fluorinating agent for P(III) compounds. For instance, it reacts with triethylphosphite, 2, and diethyl(trimethylsilyl)phosphite, 3, affording either difluorophosphorane 4 or diethyl fluorophosphate, 5, depending on the reaction conditions (Equations 1 and 2).

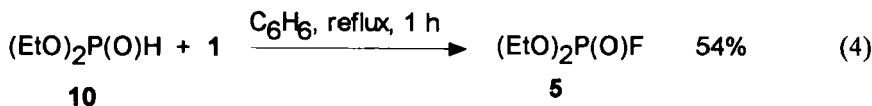


If a twofold excess of triethylphosphite, **2**, is used, a 1:1 mixture of **4** and $\text{EtP}(\text{O})(\text{OEt})_2$ is formed. The latter product is undoubtedly the result of an Arbuzov rearrangement of **2** under the action of one of electrophilic products.

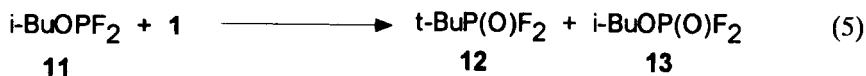
Tris-(trifluoroethyl) phosphite, $(\text{CF}_3\text{CH}_2\text{O})_3\text{P}$ (**6**), with more electron withdrawing groups, remains unchanged upon heating with the difluoride **1**. Surprisingly, electron rich *tris*-(dialkylamino) phosphines **7** and **9** do not exhibit a profound reactivity towards **1**. For instance, the hexamethyl derivative **7** after 20 h at 20°C gives about 30% of the difluoride **8** and 1 h reflux in benzene is necessary to increase the yield up to 63% (Equation 3). The hexaethyl derivative **9** does not react with **1** even at elevated temperatures.



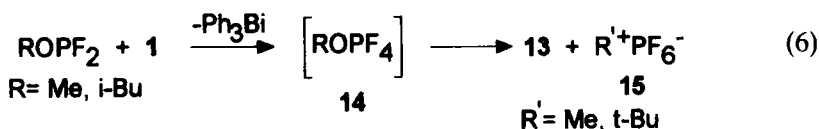
Diethyl phosphite, **10**, reacts with **1** upon heating, being smoothly converted into diethyl fluorophosphate **5** (Equation 4).⁵



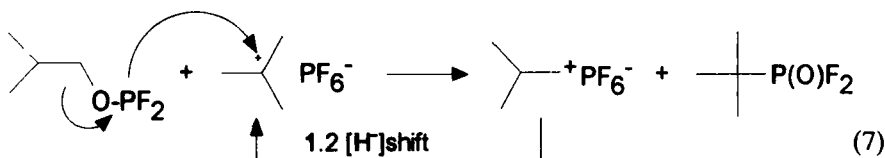
The reaction of the difluoride **1** with an equimolar amount of isobutyl difluorophosphite, **11**, is rather fast and proceeds without solvent. The major product is *tert*-butyl phosphonic difluoride, **12**, which appears after 20–30 min at ambient temperature along with the by-product, *iso*-butyl difluorophosphate, **13** (Equation 5).



The amount of the phosphonic difluoride **12** approximately corresponds to the amount of the difluoride **1**. The intermediate compound here is apparently tetrafluorophosphorane **14** which, in turn, gives a mixture of **13** and *tert*-butyl hexafluorophosphate **15** (Equation 6). The analogous reaction for the cases where R = CH₃, *i*-Bu is documented in the literature.^{6,7}



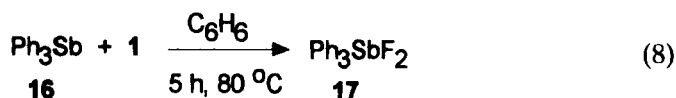
The cation **15** appears to be a true catalyst of the Arbuzov-like rearrangement and it can be recovered during the process. The following scheme for the *i*-Bu \Rightarrow *t*-Bu case illustrates these transformations (Equation 7).



The rearrangement **11** \Rightarrow **12** with other fluorinating reagents, such as XeF₂ and 2-hydroperfluoropropyl azide was described earlier.⁷

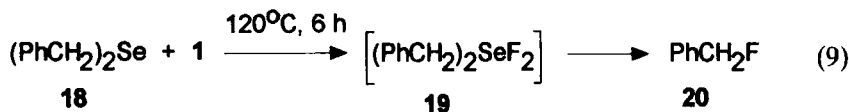
Fluorination of Organic Compounds of Sb(III) and Se(II)

Triphenyl antimony Ph₃Sb, **16**, is smoothly converted into the appropriate difluoride **17** upon heating with **1** in benzene (Equation 8).



The reaction is easily monitored by ¹⁹F NMR; it begins at ambient temperature but needs heating for completion.

Selenium(II) compounds are much less reactive and need strong heating for fluorination. Diphenyl selenide Ph₂Se does not react with **1** even at 140–150°C. We could not find dibenzylselenium difluoride in the reaction of dibenzyl selenide **18** with **1**. Instead, we found 29% of benzyl fluoride **20**, probably as a result of decomposition of the intermediate difluoride **19** (Equation 9).



Thus, triphenylbismuth difluoride, Ph₃BiF₂ (**1**), is a mild reagent for the oxidative fluorination of some derivatives of V and VI main groups elements exhibiting good selectivity in some cases.

EXPERIMENTAL

^{19}F and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer using CF_3COOH and 85% H_3PO_4 as external references respectively. The chemical shifts are reported in ppm, with negative values being upfield from the standard. The starting **1** was prepared either from triphenylbismuth and XeF_2 or from Ph_3BiCl_2 and KF according to Reference 1 and had the m.p. 160°C and ^{19}F NMR (δF): -83 ppm. Lit: ^{19}F NMR (δF): -81 ppm.^{8a} M.p. $158.5\text{--}159^\circ\text{C}$.^{1,8b}

Fluorination of triethylphosphite, 2. A solution of 0.140 g (2.92×10^{-4} mol) of **1** and 0.048 g (2.92×10^{-4} mol) of **2** in 0.7 mL of dry benzene was kept in argon atmosphere at rt during 20 h. Then 0.0536 g (2.94×10^{-4} mol) of triethyl phosphate were added as internal standard for NMR integration. ^{31}P NMR spectrum showed (besides starting **2**) the presence of 36% of difluorophosphorane **4**. δP : -74.4 , $J_{\text{P-F}} = 728$ Hz. Lit⁹: δP : -74.8 , $J_{\text{P-F}} = 723$ Hz. The reaction mixture was heated at 80°C during 4.5 h and analyzed. ^{31}P NMR spectrum showed the absence of **2** and **4** and the presence of 54% of diethyl fluorophosphate, **5**. δP : -8.1 , $J_{\text{P-F}} = 975$ Hz. Lit¹⁰: δP : -9.2 , $J_{\text{P-F}} = 963$ Hz.

When a twofold excess of **2** was used, the reaction mixture after heating contained 37% of **5** and 46% of EtP(O)(OEt)_2 (δP : 33.7 , Lit¹¹: δP : 32.8).

Fluorination of diethyl(trimethylsilyl)phosphite, 3. A solution of 0.113 g (2.36×10^{-4} mol) of **1** and 0.049 g (2.35×10^{-4} mol) of silyl phosphite **3** in 0.6 mL of dry benzene were kept at rt in argon atmosphere during 20 h. The reaction mixture contained (according to ^{31}P NMR spectrum, triethylphosphate as internal standard) 34% of diethyl fluorophosphate, **5**.

Fluorination of hexamethyltri amino phosphine, 7. A solution of equimolar amounts (2.36×10^{-4} mol) of **1** and hexamethyltri amino phosphine, **7**, in 0.7 mL of dry benzene were kept at rt in argon atmosphere during 20 h. The reaction mixture contained (according to ^{31}P NMR spectrum, triethylphosphate as internal standard) 33% of difluorophosphorane **8**. δP : -64.4 , $J_{\text{P-F}} = 700$ Hz. Lit¹²: δP : -65.7 , $J_{\text{P-F}} = 700$ Hz. After 1 h of heating at 80°C the amount of **8** in the reaction mixture increased up to 63%.

The reaction of 1 with diethyl phosphite, 10. A solution of equimolar amounts (3.88×10^{-4} mol) of **1** and diethyl phosphite, **10**, in 0.8 mL of dry benzene were kept at 80°C in argon atmosphere during 1 h. The content of **5** in the reaction mixture was 54%.

Fluorination of triphenyl antimony, 16. A solution of 0.284 g (5.94×10^{-4} mol) of **1** and 0.215 g (6.09×10^{-4} mol) of Ph_3Sb , **16**, in 2 mL of dry benzene was kept at rt during 5 h. The ratio **1**:**17** was 3:2. After 1 h reflux the ratio was 3:4 and after 5 h reflux $-1:10$. ^{19}F NMR for **17** (δF): -75 ppm. The ^{19}F NMR spectrum of **17** is identical with that for a sample, prepared by independent procedure¹³ from Ph_3Sb and XeF_2 .

Fluorination of dibenzyl selenide, 18. 57 mg (1.19×10^{-4} mol) of **1** and 81 mg (3.1×10^{-4} mol) of **18** were heated at 120°C in a sealed glass tube during 6 h. The yield of benzyl fluoride **20** (30%) was determined by ^{19}F NMR (δF : -127.8 , t, $J_{\text{F-H}} = 48$ Hz, C_6F_6 as internal standard for integration) and by gas chromatography. The ^{19}F NMR spectrum and retention times on two different columns (SE-30 and XE-60) of **20** coincide with those of a sample, prepared by an independent procedure¹⁴ from PhCH_2Cl and KF.

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