ELSEVIER

Journal of Fluorine Chemistry 76 (1996) 29–35

JOURNAL OF FLUORINE CHEMISTRY

The reaction of secondary phosphines and di-1-adamantylphosphine oxide with trifluoroacetic anhydride and hexafluoroacetone

Jens R. Goerlich, Volker Plack, Reinhard Schmutzler *

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

Received 16 January 1995; accepted 12 April 1995

Abstract

While the secondary phosphines $(1\text{-Ad})_2PH$ (**1**) (1-Ad = adamantyl) and Trt(Ph)PH (**2**) (Trt = triphenylmethyl) reacted readily with trifluoroacetic anhydride (TFAA) to give the trifluoroacetylphosphines **7** and **8**. $(1\text{-Ad})_2P(:O)H$ (**6**) could not be converted into the corresponding trifluoroacetylphosphine oxide **10** by treatment with TFAA. Compound **10** was observed by ^{19}F and ^{31}P NMR spectroscopy in the reaction of $(1\text{-Ad})_2PC(:O)CF_3$ (**7**) with $(H_2N)_2C(:O)\cdot H_2O_2$. Two pathways were observed for the reaction of **1** with excess hexafluoroacetone (HFA), starting from the primary HFA adduct $(1\text{-Ad})_2PC(CF_3)_2OH$ (**13**). Oxidation of **13** led to the tertiary phosphine oxide **14** which was also available from $(1\text{-Ad})_2P(:O)H$ (**6**) and HFA. Isomerization of **13** gave $(1\text{-Ad})_2POCH(CF_3)_2$ (**15**) whose oxidation with excess HFA furnished the phosphorane **16**. Hydrolysis of **16** led to the phosphinic ester **17**. As is known for Ph_2PH (**3**), $Ph(C_6F_5)PH$ (**4**) reacted with HFA to give the α-hydroxyphosphine **19**. No reaction was observed when Trt(Ph)PH (**2**) and $(C_6F_5)_2PH$ (**5**) were treated with HFA.

Keywords: Secondary phosphines; Di-1-adamantylphosphine oxide; Trifluoroacetylation; Hexafluoroacetone; NMR spectroscopy; IR spectroscopy

1. Introduction

In the course of our studies on the reactivity of the P–H bond in phosphines and phosphine oxides bearing sterically demanding substituents [1–8], it seemed of interest to investigate the behaviour of selected compounds of this type towards trifluoroacetic anhydride (TFAA) and hexafluoroacetone (HFA), both of which are known to be highly reactive representatives of these classes of compounds.

2. Reactions with trifluoroacetic anhydride (TFAA)

Trifluoroacetic anhydride is a common reagent for the introduction of the trifluoroacetyl moiety by substitution of P–H protons in phosphines [3,9–11] and phosphine oxides [11–14]. Despite the fact that a triphenylmethyl group bonded to phosphorus lowers the reactivity of the P–H bond [7], Trt(Ph)PH (**2**) was found to react readily with TFAA in the same fashion as $(1\text{-Ad})_2PH$ (**1**) [3] and several secondary phosphines [9–11], with formation of the trifluoroacetylphosphine **8** [Eq. (1)]. For comparison $Ph_2PC(:O)CF_3$ (**9**) [15,16] was synthesized in the same way.

$$R^1R^2PH \xrightarrow{TFAA} R^1R^2P{-}\overset{\overset{O}{\|}}{C}{-}CF_3 \qquad (1)$$

R^1	R^2	No.	R^1	R^2	No.
1-Ad	1-Ad	**1**	1-Ad	1-Ad	**7**
Trt	Ph	**2**	Trt	Ph	**8**
Ph	Ph	**3**	Ph	Ph	**9**

The investigation of **7–9** by ^{19}F and ^{31}P NMR spectroscopy led to the following results: the values of $\delta(F)$ and $^3J(PF)$ are all in the same range when a phenyl group is bonded to phosphorus, while $\delta(P)$ lies between 40 ppm and 45 ppm when a tertiary alkyl group is attached to phosphorus (Table 1).

The absorption band for the C=O group in the IR spectra of **7–9** was always observed in the vicinity of 1700 cm^{-1} (Table 1), as expected for trifluoroacetylphosphines [11,15,16].

The synthesis and properties of diaryl- and alkylaryl-trifluoroacetylphosphine oxides have been studied by Lindner et al. [11,12,17–20] and dimethyltrifluoroacetylphosphine oxide has been prepared by Well [13,14]. In the examples described, treatment of the parent secondary phosphine oxides with TFAA led to the desired products in good yield.

* Corresponding author.

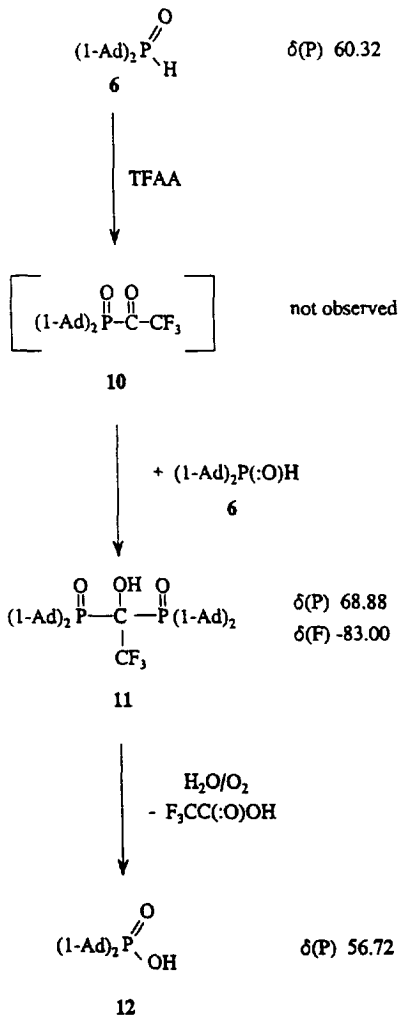
SSDI 0022-1139(95)03288-6

Table 1
^{19}F, ^{31}P NMR data and C=O absorptions in the IR spectra of the trifluoroacetylphosphines **7–9** and of $^{t}Bu(Ph)PC(:O)CF_3$

Compound	δ(P) (ppm)	δ(F) (ppm)	^3J(PF) (Hz)	ν(C=O) (cm^{-1})	Ref.
$(1\text{-Ad})_2PC(:O)CF_3$ (**7**)	44.84	−79.91	19.6	1697	[3]
$Trt(Ph)PC(:O)CF_3$ (**8**)	47.54	−73.43	16.5	1690	
$Ph_2PC(:O)CF_3$ (**9**)	20.01	−74.84	16.0	1702	[15,16]
$^{t}Bu(Ph)PC(:O)CF_3$	39.2	−73.5	15	1688	[11]

Even when employed in large excess, TFAA in its reaction with $(1\text{-Ad})_2P(:O)H$ (**6**) never yielded the expected trifluoroacetylphosphine oxide **10** (^{19}F and ^{31}P NMR evidence). $(1\text{-Ad})_2P(:O)C(:O)CF_3$ (**10**) functions as a highly reactive intermediate whose C=O bond readily adds a further molecule of **6**, giving the bis-phosphorylated alcohol **11**, which was identified by its ^1H, ^{19}F and ^{31}P NMR data (Scheme 1).

The reaction pathway observed is well known from several studies [11,12,17,21], but surprising in the case of the reaction of **10** with **6** because the latter is known to react only with highly activated carbonyl compounds like chloral



Scheme 1. The reaction of $(1\text{-Ad})_2P(:O)H$ (**6**) with trifluoroacetic anhydride (TFAA).

$Cl_3CC(:O)H$ [6]. Instead of the alcohol **11**, $(1\text{-Ad})_2P(:O)OH$ (**12**) [6] and $F_3CC(:O)OH$, resulting from the oxidative/hydrolytic cleavage of P–C bonds in **11**, were identified by NMR spectroscopy as the final products (**12**: ^{13}C, ^{31}P [6]; $F_3CC(:O)OH$: ^{19}F [22]). The formation of **12** under these reaction conditions is unexpected, because all attempts to synthesize **12** by oxidation of $(1\text{-Ad})_2P(:O)H$ (**6**) with hydrogen peroxide (as a 30% aqueous solution) were unsuccessful [2].

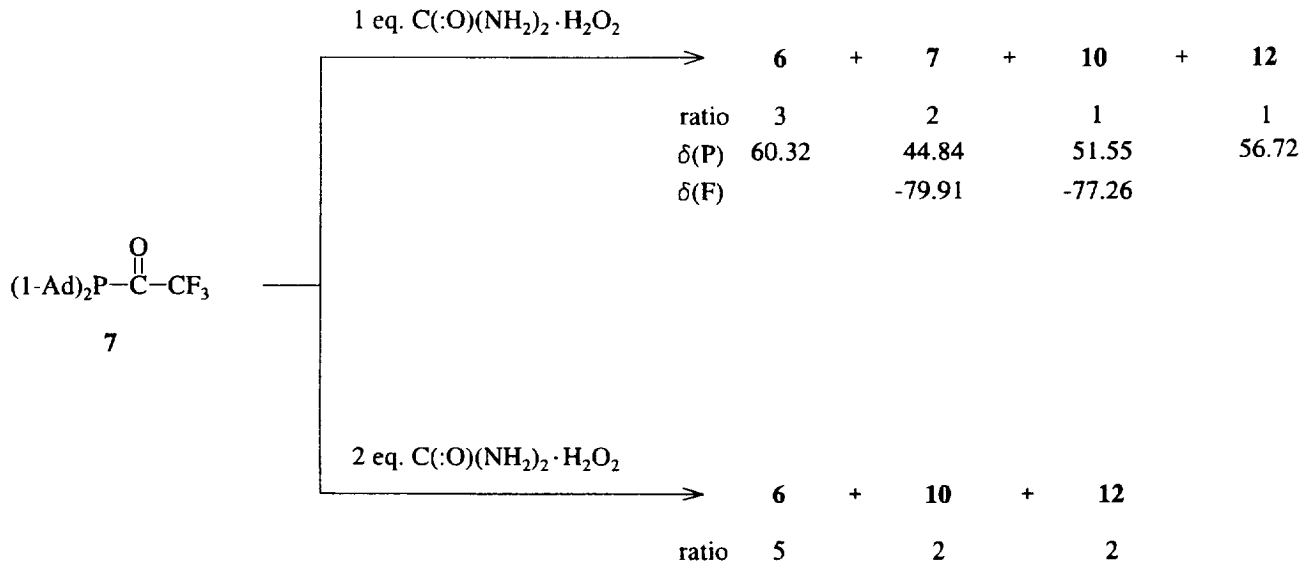
When a solution of **7** was treated with 1 equiv. of the urea/hydrogen peroxide 1:1 adduct (Scheme 2), the formation of a mixture of **6**, **7**, **10** and **12** was observed (^{19}F and ^{31}P NMR evidence). Instead of causing high selectivity, the bulky 1-adamantyl groups bonded to phosphorus seemed to destabilize the phosphine oxide **10**. The addition of another equivalent of the oxidizing agent led to a higher proportion of **10** in the reaction mixture, accompanied by **6** and **12**, the products of its hydrolysis and oxidation (Scheme 2). In the IR spectrum of this mixture, the most characteristic band is caused by the absorption of the C=O group of **10** at 1780 cm^{-1}. Compared to **7** with a λ^3-phosphorus atom, this means a shift of 83 cm^{-1} to higher wavenumbers. The same tendency was found for the C=O absorption of the pair $Ph_2PC(:O)CF_3/Ph_2P(:O)C(:O)CF_3$ [12,15,16,18].

3. Reactions with hexafluoroacetone (HFA)

Until now the reaction of secondary phosphines with HFA has been studied only for dimethylphosphine [23,24] and diphenylphosphine [23,25,26]. In both cases mixtures of products were obtained.

A mixture of products was also observed when $(1\text{-Ad})_2PH$ (**1**) was treated with a six-fold excess of HFA (Scheme 3). Attempts to separate the products formed were unsuccessful. Although it was never observed in the reaction mixture, it makes sense to assume that the initial step was the formation of tertiary phosphine **13** by nucleophilic attack of the phosphorus atom of **1** at the carbon atom of the carbonyl group, followed by the transfer of the P–H proton to the oxygen atom of the carbonyl group. Starting from **13** two reaction pathways were observed.

Oxidation of **13** led to the tertiary phosphine oxide **14** which was synthesized independently by the reaction of **6** with HFA (Scheme 3). As in the case of its dimethyl analogue, no P–F coupling was observed for **14** [13,14].

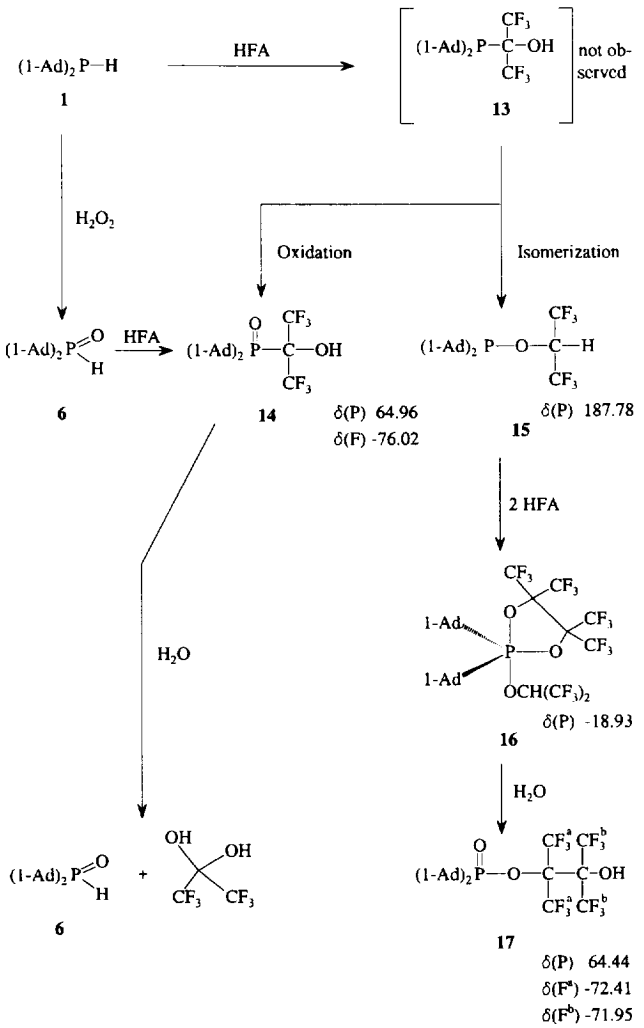


Scheme 2. The reaction of $(1\text{-Ad})_2PC(:O)CF_3$ (**7**) with $C(:O)(NH_2)_2\cdot H_2O_2$.

Although the 1-adamantyl and the methyl group are very different with regard to their steric requirements, the $\delta(P)$ value of **14** (64.96 ppm, Scheme 3) is very similar to that of the analogous dimethyl compound $Me_2P(:O)C(CF_3)_2OH$ ($\delta(P)$ 66.56 ppm [13,14]). The existence of the hydroxy group in **14** was proved by ^1H NMR and IR spectroscopy. The bathochromic shift of the O–H band and its broadening reveal the presence of hydrogen bonds in solutions of **14**, presumably with participation of the P=O group [27]. Phosphorus–carbon cleavage in **14** with formation of $(1\text{-Ad})_2P(:O)H$ (**6**) and $F_3CC(OH)_2CF_3$ or their P/O deuterated analogues was observed when solutions of **14** were treated with H_2O or D_2O, respectively (^{19}F and ^{31}P NMR evidence).

The second pathway consists in the rearrangement of **13** to the isomeric phosphinate **15** which proceeded readily under the reaction conditions [28]. The $\delta(P)$ value for **15** (187.78 ppm) is typical of a compound of this type [29]; for its diphenyl analogue, a $\delta(P)$ value of 142 ppm was reported [26,30]. The ability of HFA to oxidize P(III) compounds with formation of phosphoranes is well documented [23]. In most cases, phosphorus in the resulting phosphoranes is part of a five-membered ring system, consisting of the P atom and a perfluoropinacolyl unit [23,31,32]. The latter is known to stabilize λ^5 P compounds with unusual substituents such as OH, SH and N_3 at the phosphorus atom [33–35]. As is known for $(^tBu)_2POCH(CF_3)_2$ [28], **15** was completely oxidized within 3 days by excess HFA to give the 1,3,2λ^5-dioxaphospholane **16**. Its $\delta(P)$ value (-18.93 ppm) is typical of a phosphorane [36] and, compared to its t-butyl analogue, is slightly shifted to lower field ($R = {}^tBu$: $\delta(P) -21.0$ ppm [28]). In contrast to this, less bulky alkyl groups at the phosphorus-atom in $R_2POCH(CF_3)_2$, e.g. methyl, cause the formation of 1,2λ^5-oxaphosphetanes [28,36,37].

The phosphorane **16** was readily hydrolyzed by traces of water to give the phosphinic ester **17** (Scheme 3). Thus the



Scheme 3. The reaction of $(1\text{-Ad})_2PH$ (**1**) and $(1\text{-Ad})_2P(:O)H$ (**6**) with hexafluoroacetone (HFA).

formation of a mixture of **6**, **14** and **17** was observed after 3 days. The phosphinic ester **16** is stable towards water; the treatment of the mixture of **6**, **14** and **17** with water led only to the decomposition of **14** as described above (Scheme 3).

Although the steric hindrance at the phosphorus atom of Trt(Ph)PH (**2**) is less than in $(1\text{-Ad})_2$PH (**1**), no reaction between **2** and HFA took place [Eq. (2)]. This might be a consequence of the electronic influence of the triphenylmethyl group, which often remarkably lowers the reactivity of the P–H bond [7,8].

$$R^1R^2PH \xrightarrow{HFA} R^1R^2P\text{–}C(CF_3)_2\text{–}OH \qquad (2)$$

R^1	R^2	No.	R^1	R^2	No.
Trt	Ph	**2**	Trt	Ph	no reaction
Ph	Ph	**3**	Ph	Ph	**18**
Ph	C_6F_5	**4**	Ph	C_6F_5	**19**
C_6F_5	C_6F_5	**5**	C_6F_5	C_6F_5	no reaction

The strong electron-withdrawing effect of perfluoroalkyl and aryl substituents, caused by the high electronegativity of fluorine, influences the reactivity of compounds bearing perfluoralkyl or perfluoraryl groups compared to their alkyl and aryl analogues, often in a dramatic way [38]. This electronic effect is taken advantage of in the kinetic stabilization of compounds which are thermodynamically unstable, e.g. diphosphenes [39].

Completing investigations on the behaviour of HFA towards Ph_2PH (**3**) [25,26], it seemed of interest to study the effect of the successive substitution of phenyl for pentafluorophenyl groups in the secondary phosphine. As reported for Ph_2PH (**3**) [25,26], $Ph(C_6F_5)PH$ (**4**) reacted readily with HFA to give the tertiary phosphine **19** [Eq. (2)]. In contrast to this, no reaction occurred when $(C_6F_5)_2PH$ (**5**) was treated with excess HFA. This may be interpreted as a consequence of the decreased nucleophilicity of the phosphorus atom in **5**, caused by the $-I$ effect of the two pentafluorophenyl groups. This observation is supported by the fact that **19** is unstable even at -18 °C in the absence of excess HFA. While **18** is permanently stable under these conditions, **19** decomposes within days with formation of the parent phosphine **4**, HFA and several other phosphorus-containing products which could not be identified. Thus a decreased electron density at the phosphorus atom of the secondary phosphines **3–5** leads to decreased stability and a tendency to form the corresponding HFA adducts of the type mentioned above.

The asymmetry of the phosphorus atom in **19** causes the magnetic inequivalence of the fluorine atoms of the two trifluoromethyl groups in **19**. As a consequence of this, the ^{19}F and ^{31}P NMR spectra of **19** are of higher order (spin system: $AX_3X'_3$; A = P and X, X' = F). The coupling constants $J(AX)$ and $J(XX')$ were determined by computer simulation

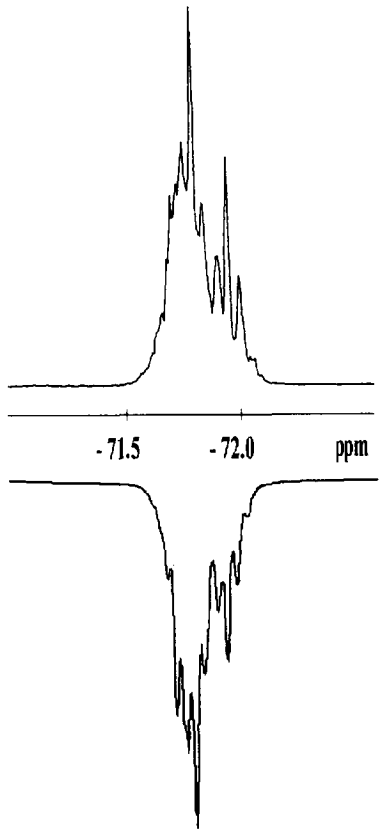


Fig. 1. Experimental (above) and simulated (below) $^{19}F\{^1H\}$ NMR spectrum of **19** (CF_3 groups).

of the ^{19}F NMR spectrum of **19** [40]. The experimental and the simulated ^{19}F NMR spectrum are presented in Fig. 1 [$^3J(AX) = 15.9$ Hz, $^3J(AX') = 23.8$ Hz, $^4J(XX') = 8.1$ Hz].

The location of the O–H absorption band in the IR spectrum of **19** (3035 cm^{-1}) suggests strong hydrogen bonding in solutions of **19** [27]. Presumably, as a consequence of the strong electron-withdrawing effect of the pentafluorophenyl group in **19**, these interactions are stronger in the case of **19** than for **18** [ν(O–H) 3160 cm^{-1}].

4. Experimental details

The following compounds were synthesized according to the literature procedures indicated: $(1\text{-Ad})_2$PH (**1**) [2], Trt(Ph)PH (**2**) [8], Ph_2PH (**3**) [41], $(1\text{-Ad})_2P(:O)H$ (**6**) [2], $(1\text{-Ad})_2PC(:O)CF_3$ (**7**) [3], $Ph(C_6F_5)PX$ (X = Cl, Br) [42] and $(C_6F_5)_2PX$ (X = Cl, Br) [42]. All other compounds were obtained commercially. For preparative and NMR spectroscopic details, see Ref. [3].

4.1. Phenyl(pentafluorophenyl)phosphine (4)

To a solution consisting of 2 g of $Ph(C_6F_5)PX$ (X = Cl, Br) in 60 ml of Et_2O were added 0.25 g (6.6 mmol) of $LiAlH_4$

at −14 °C. After stirring for 1 h at room temperature, 80 ml of 0.1 M hydrochloric acid were added, the layers separated and the organic layer evaporated at 0 °C in vacuo (0.1 mmHg) to leave **4** as a colourless liquid. The purity of **4** was shown by NMR-spectroscopy (^1H, ^{19}F, ^{31}P). Yield: 1.34 g. ^1H NMR ($CDCl_3$) δ: 5.47 [d, 1 H, $^1J(PH) = 229.5$ Hz, P*H*]; 7.03–7.98 [m, 5H, C_6H_5] ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −161.0 [m, *m*-F]; −152.5 [m, *p*-F]; −129.9 [m, *o*-F] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −89.01 [s] ppm.

4.2. Bis(pentafluorophenyl)phosphine (5)

To a solution consisting of 8.7 g of $(C_6F_5)_2PX$ (X = Cl, Br) in 25 ml of Et_2O at −14 °C were added 1.01 g (26.6 mmol) of $LiAlH_4$ over a period of 30 min. After stirring for 1 h at room temperature, the reaction mixture was treated with 100 ml of 0.1 M hydrochloric acid, the layers separated and the organic layer evaporated to give 5.51 g of **5** as a colourless solid; mp. 41 °C. ^1H NMR ($CDCl_3$) δ: 5.53 [m, P*H*] ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −160.2 [m, *m*-F]; −149.8 [m, *p*-F]; −128.8 [m, *o*-F] ppm. ^{31}P NMR ($CDCl_3$) δ: −139.13 [d, $^1J(PH) = 217.5$ Hz] ppm.

4.3. Reaction of 2, 3 and 6 with trifluoroacetic anhydride. General procedure

A solution of the phosphorus compound, in the solvent indicated, was cooled to −196 °C. Then trifluoroacetic anhydride was added via a syringe, the reaction mixture warmed to room temperature and stirred for the time given below. After that, volatile components of the reaction mixture were removed in vacuo (0.1 mmHg). Further work-up was as described below.

4.3.1. Triphenylmethyl(phenyl)trifluoroacetylphosphine (8)

Trt(Ph)PH (**2**), 0.92 g (2.1 mmol); TFAA, 0.6 g (2.9 mmol); toluene, 10 ml; reaction time, 1.5 h. Recrystallization from n-hexane furnished 0.65 g (69.0%) of **8** as an amorphous, pale yellow solid. M.p. 105 °C. Analysis: Found: C, 71.96; H, 4.51%. $C_{27}H_{20}F_3OP$ (448.42) requires: C, 72.32; H, 4.50%. ^1H NMR ($CDCl_3$) δ: 6.88–7.46 [m, 20H, C_6H_5] ppm. MS (70 eV) *m/z* (%): 351 (<1) $[M-C(:O)CF_3]^+$; 243 (100) $[Ph_3C]^+$; 165 (62) $[C_{13}H_9]^+$ (fluorenyl).

4.3.2. Diphenyl(trifluoroacetyl)phosphine (9)

Ph_2PH (**3**), 0.42 g (2.3 mmol); TFAA, 1.02 g (4.9 mmol); CH_2Cl_2, 5 ml; reaction time, 1 h. No further work-up, checked by ^{19}F and ^{31}P NMR spectroscopy. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −74.84 [d, $^3J(PF) = 16.0$ Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 20.01 [quart, $^3J(PF) = 15.9$ Hz] ppm.

4.3.3. Reaction of 6 with TFAA

$(1\text{-Ad})_2P(:O)H$ (**6**), 1.67 g (5.2 mmol); TFAA, 3.06 g (14.7 mmol); CH_2Cl_2, 20 ml; reaction time, 2 h. After removal of volatile compounds, ^1H, ^{19}F and ^{31}P NMR spectra revealed the remaining colourless solid to consist of a mixture of 1,1-bis(di-1-adamantylphosphoryl)-2,2,2-trifluoroethanol (**11**) and di-1-adamantylphosphinic acid (**12**) [6]. All attempts to separate the mixture by recrystallization resulted in the formation of di-1-adamantyl-phosphinic acid (**12**) as the only phosphorus-containing compound (evidence: ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry [6]). Trifluoroacetic acid was identified in the reaction mixture by its δ(F) value of −78.5 ppm [22].

Compound **11**: $C_{42}H_{61}F_3O_3P_2$ (732.88): ^1H NMR ($CDCl_3$, mixture of **11** and **12**) δ: 1.76–2.10 [m, $C_{10}H_{15}$]; 2.72 [s (br), CO*H* (**11**)]; 7.54 [s (br), O*H* (**12**)] ppm.

Compound **12**: $C_{20}H_{31}O_2P$ (334.44): ^1H NMR ($CDCl_3$) δ: 1.67–1.98 [m, 30H, $C_{10}H_{15}$]; 7.48 [s (br), 1H, P(:O)OH] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 27.65 [d, $^3J(PC) = 10.1$ Hz, C^3 (1-Ad)]; 36.24 [s, C^2(1-Ad)]; 36.76 [s, C^4(1-Ad)]; 39.31 [d, $^1J(PC) = 86.5$ Hz, C^1(1-Ad)] ppm. MS (70 eV) *m/z* (%): 335 (5) $[M+H]^+$; 334 (13) $[M]^+$; 135 (100) $[C_{10}H_{15}]^+$.

4.4. Reaction of 7 with the urea–hydrogen peroxide (1:1) adduct; formation of di-1-adamantyltrifluoroacetylphosphine oxide (10)

To a solution of 0.34 g (0.9 mmol) of **7** in 20 ml of Et_2O was added at −14 °C 1 equiv. of $C(:O)(NH_2)_2 \cdot H_2O_2$ (0.085 g, 0.9 mmol) and a second equivalent after 30 min. Ten minutes after each addition, the reaction mixture was investigated by ^{31}P NMR spectroscopy. After 10 min: mixture of **6**, **7**, **10** and **12** (3:2:1:1). After 40 min: mixture of **6**, **10** and **12** (5:2:2). After 45 min, the mixture was filtered and volatile components were evaporated in vacuo (0.1 mmHg). The remaining oily residue was investigated by ^{19}F, ^{31}P NMR and IR spectroscopy $(1\text{-Ad})_2P(:O)H$ (**6**) and $(1\text{-Ad})_2P(:O)OH$ (**12**) were identified from their δ(P) values [2,6].

Compound **10**: $C_{22}H_{30}F_3O_2P$ (414.45): IR (CCl_4, mixture of **6**, **10** and **12**) ν (cm^{-1}): 2795 [vs, (O–H)]; 2303 [w, (P–H), **6**]; 1780 [m (C=O]; 1360–1165 [vs, (C–F)/(P=O)].

4.5. Reaction of 1–6 with hexafluoroacetone (HFA). General procedure

A solution of the phosphorus compound, in the solvent indicated, was cooled to −196 °C and HFA was condensed on the reaction mixture via a vacuum line. After warming to room temperature, the reaction mixture was stirred for the period of time given below. Then volatile components were removed in vacuo (0.1 mmHg). Further work-up is described below. The reaction mixtures of **2**/HFA and **5**/HFA were not worked-up further after ^{31}P NMR spectroscopy had indicated that no reaction had taken place.

4.5.1. Reaction of di-1-adamantylphosphine (1) with HFA; formation of a mixture of di-1-adamantylphosphine oxide (6), di-1-adamantyl-2-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-phosphine oxide (14) and di-1-adamantylphosphinic acid 3,3,3-trifluoro-2-hydroxy-1,1,2-tris(trifluoromethyl)propyl-ester (17)

$(1\text{-Ad})_2PH$ (**1**), 1.43 g (4.7 mmol); HFA, 4.91 g (29.6 mmol); toluene 30 ml. After 16 h stirring at room temperature, ^{31}P NMR spectroscopy revealed that a mixture of **14**, **15**, **16** and **17** (10:8:1:5) was present. After 3 d stirring at room temperature, the mixture was evaporated in vacuo (0.1 mmHg) to give 1.89 g of a colourless solid which was investigated by ^1H, ^{19}F and ^{31}P NMR and IR spectroscopy and by mass spectrometry. The formation of a mixture of **6**, **14** and **17** (2:2:1) was observed. When a solution of 50 mg of this mixture in CH_2Cl_2 was stirred with excess water, quantitative hydrolysis of **14** with formation of **6** and hexafluoroacetone hydrate, $F_3CC(OH)_2CF_3$, took place, while **17** was unchanged (^{19}F, ^{31}P NMR evidence, see below).

Compound **14**, $C_{23}H_{31}F_6O_2P$ (484.46), and compound **17**, $C_{26}H_{31}F_{12}O_3P$ (650.48): After 16 h stirring at room temperature, the $\delta(P)$ values given in Scheme 3 (solvent toluene) were obtained. After 3 d stirring at room temperature, the $\delta(P)$ and $\delta(F)$ values listed in Scheme 3 (solvent $CDCl_3$) were observed. ^1H NMR ($CDCl_3$) δ: 1.74–2.03 [m, $C_{10}H_{15}$], 4.25 [sept. $^4J(FH) = 6.4$ Hz, $C(CF_3)_2OH$, (**17**)]; 5.57 [d, $^1J(PH) = 430.0$ Hz, $P(:O)H$, (**6**)]; 7.89 [s (br), $C(CF_3)_2OH$, (**14**)] ppm. IR (CH_2Cl_2) ν (cm^{-1}): 2920 [s, br, (O–H)]; 2300 [w, (P–H) (**6**)]; 1310–1220 [s, (C–F)/(P=O)]. MS (70 eV) *m/z* (%): 634 (<1) [M−O, (**17**)]$^+$; 484 (3) [M, (**14**)]$^+$; 318 (1) [M, (**6**)]$^+$; 317 (1) $[(C_{10}H_{15})_2PO]^+$; 135 (100) $[C_{10}H_{15}]^+$; 97 (11) $[CF_3CO]^+$; 69 (9) $[CF_3]^+$.

4.5.2. Di-1-adamantyl-2-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)phosphine oxide (14)

$(1\text{-Ad})_2P(:O)H$ (**6**), 1.14 g (3.6 mmol); HFA, 2.99 g (18 mmol); toluene 20 ml; reaction time, 3 d. After removal of the volatile components of the reaction mixture in vacuo (0.1 mmHg), **14** was recrystallized from Et_2O. Yield, 0.94 g (53.9%); m.p. 108 °C (dec.).

Compound **14**: $C_{23}H_{31}F_6O_2P$ (484.46): Analysis: Found: C, 56.33; H, 6.43%. $C_{23}H_{31}F_6O_2P$ requires: C, 57.02; H, 6.43%. ^1H NMR ($CDCl_3$) δ: 1.77–2.05 [m, 30H, $C_{10}H_{15}$]; 7.86 [s, (br), 1H, OH] ppm. IR (CH_2Cl_2) ν (cm^{-1}): 2940 [s, br, (O–H)]; 1300–1230 [s, (C–F)/(P=O)]. MS (70 eV) *m/z* (%): 484 (<1) [M]$^+$; 318 (<1) [M−HFA]$^+$; 147 (38) $[C_3F_5O]^+$; 135 (9) $[C_{10}H_{15}]^+$; 97 (42) $[CF_3CO]^+$; 69 (100) $[CF_3]^+$; 51 (41) $[CHF_2]^+$.

4.5.3. Reaction of 14 with water

A mixture of 0.3 g (0.4 mmol) of **14** and 1 ml of H_2O in 10 ml of CH_2Cl_2 was stirred for 3 d at room temperature and subsequently investigated by ^{19}F and ^{31}P NMR spectroscopy which indicated the formation of $(1\text{-Ad})_2P(:O)H$ (**6**) and $F_3CC(OH)_2CF_3$ ($\delta(F) = -83.14$ ppm; lit. value [43]: −82.63 ppm). The use of D_2O instead of H_2O led to $(1\text{-Ad})_2P(:O)D$ and $F_3CC(OD_2)CF_3$. $(1\text{-Ad})_2P(:O)D$: $\delta(P) = 60.54$ [t, $^1J(PD) = 66.1$ Hz] ppm.

4.6. Diphenyl-2-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-phosphine (18) [25,26]

Ph_2PH (**3**), 4.8 g (25.8 mmol); HFA, 6.0 g (36.1 mmol); toluene 10 ml; reaction time, 16 h. After removal of the volatile components, a colourless oil remained which was investigated by ^1H, ^{19}F, ^{31}P NMR and IR spectroscopy.

Compound **18**: $C_{15}H_{11}F_6OP$ (352.22): ^1H NMR ($CDCl_3$) δ: 4.90 [sept, 1H, $^4J(FH) = 5.2$ Hz, COH]; 7.34–7.62 [m, 10H, $(C_6H_5)_2P$] ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −70.26 [d, $^3J(PF) = 17.7$ Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 5.68 [sept, $^3J(PF) = 17.7$ Hz] ppm. IR (CCl_4) ν (cm^{-1}): 3160 [s, br, (O–H)].

4.7. Phenyl(pentafluorophenyl)-2(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)phosphine (19)

$Ph(C_6F_5)PH$ (**4**), 6.70 g (24.3 mmol); HFA, 4.03 g (24.3 mmol); toluene, 10 ml; reaction time, 16 h. Attempts to purify **19** by recrystallization from n-hexane led to its decomposition with the formation of **4**, HFA and further unidentified phosphorus-containing products (^{19}F, ^{31}P NMR evidence).

Compound **19**: $C_{15}H_6F_{11}OP$ (442.17): ^1H NMR ($CDCl_3$) δ: 3.92 [s (br), 1H, COH]; 7.19–7.81 [m, 5H, C_6H_5] ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −159.6 [m, *m*-F]; −146.4 [m, *p*-F]; −124.3 [m, *o*-F]; −71.8 [m, CF_3] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −16.5 [m] ppm. IR (CH_2Cl_2) ν (cm^{-1}): 3035 [s, br, (O–H].

Acknowledgments

We are grateful to BASF AG, Bayer AG and Hoechst AG, for generous supplies of chemicals used in this research and to Fonds der Chemischen Industrie for financial assistance. Prof. G.-V. Röschenthaler is thanked for helpful discussions.

References

[1] J.R. Goerlich, A. Fischer, P.G. Jones and R. Schmutzler, *Polyhedron, 12* (1993) 2279.
[2] J.R. Goerlich and R. Schmutzler, *Phosphorus, Sulfur, and Silicon, 81* (1993) 141.
[3] J.R. Goerlich, C. Müller and R. Schmutzler, *Phosphorus, Sulfur, and Silicon, 85* (1993) 193.
[4] J.R. Goerlich and R. Schmutzler, *Phosphorus, Sulfur, and Silicon, 88* (1994) 241.
[5] J.R. Goerlich and R. Schmutzler, *Z. Anorg. Allg. Chem., 620* (1994) 898.
[6] J.R. Goerlich and R. Schmutzler, *Z. Naturforsch., 49b* (1994) 801.
[7] V. Plack, *Diplomarbeit*, Technische Universität Braunschweig, 1993.
[8] V. Plack, unpublished results.

[9] G. Elsner, in M. Regitz (ed.), *Houben-Weyl, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1982, Vol. E2, p. 106ff.
[10] E. Lindner and G. Frey, *Z. Naturforsch., 35b* (1980) 1150.
[11] E. Lindner and G. Frey, *Chem. Ber., 113* (1980) 2769.
[12] G. Frey, H. Lesiecki, E. Lindner and G. Vordermeyer, *Chem. Ber., 112* (1979) 763.
[13] M. Well, *Ph.D. Thesis*, Technische Universität Braunschweig, 1992.
[14] M. Well and R. Schmutzler, *Phosphorus, Sulfur, Silicon, 72* (1992) 171.
[15] E. Lindner and H. Kranz, *Z. Naturforsch., 22b* (1967) 675.
[16] E. Lindner and H. Kranz, *Chem. Ber., 101* (1968) 3438.
[17] E. Lindner, H.-D. Ebert and H. Lesiecki, *Angew. Chem., 88* (1976) 25; *Angew. Chem., Int. Ed. Engl., 15* (1976) 41.
[18] E. Lindner, H.-D. Ebert, H. Lesiecki and G. Vordermaier, *Angew. Chem., 89* (1977) 276; *Angew. Chem., Int. Ed. Engl., 16* (1977) 269.
[19] E. Lindner and H. Lesiecki, *Chem. Ber., 112* (1979) 773.
[20] E. Lindner and G. Vordermaier, *Chem. Ber., 112* (1979) 1456.
[21] R.S. Davidson, R.A. Sheldon and S. Trippett, *J. Chem. Soc. C,* (1968) 1700.
[22] S. Berger, S. Braun and H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Georg Thieme Verlag, Stuttgart 1994, Vol. 4, p. 2.
[23] M. Witt, K.S. Dhathathreyan and H.W. Roesky, *Adv. Inorg. Chem. Radiochem., 30* (1986) 223.
[24] G.V. Röschenthaler, *Z. Naturforsch., 33b* (1978) 311.
[25] A.F. Janzen and O.C. Vaidya, *Can. J. Chem., 51* (1973) 1136.
[26] E. Evangelidou-Tsolis, F. Ramirez, J.F. Pilot and C.P. Smith, *Phosphorus, 4* (1974) 109.
[27] J. Weidlein, U. Müller and K. Dehnicke, *Schwingungsspektroskopie*, Georg Thieme Verlag, Stuttgart 1982, p. 42ff.
[28] D. Dakternieks, G.-V. Röschenthaler, K. Sauerbrey and R. Schmutzler, *Chem. Ber., 112* (1979) 2380.
[29] S. Berger, S. Braun and H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Georg Thieme Verlag, Stuttgart, 1993, Vol. 3, p. 44ff.
[30] D.B. Denney, D.Z. Denney, J.-P. Hammond, L.T. Ling and Y.P. Wang, *J. Org. Chem., 48* (1983) 2159.
[31] F. Ramirez, C.P. Smith, A.S. Gulati and A.V. Patwardhan, *Tetrahedron Lett.,* (1966) 2151.
[32] G.V. Röschenthaler, J.A. Gibson and R. Schmutzler, *J. Chem. Soc., Dalton Trans.* (1975) 918.
[33] G.V. Röschenthaler and W. Storzer, *Angew. Chem., 94* (1982) 212; *Angew. Chem., Int. Ed. Engl. 21* (1982) 208.
[34] G.V. Röschenthaler, R. Bohlen and D. Schomburg, *Z. Naturforsch., 40b* (1985) 1589.
[35] M. Volkholz, O. Stelzer and R. Schmutzler, *Chem. Ber., 111* (1978) 890.
[36] Ref. [29], p. 49.
[37] G.-V. Röschenthaler, *Z. Naturforsch., 33b* (1978) 131.
[38] B.E. Smart, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Functional Groups: The Chemistry of Halides, Pseudo-halides and Azides, Supplement D*, John Wiley, Chichester, 1983, p. 603ff.
[39] M. Witt and H.W. Roesky, *Prog. Inorg. Chem., 40* (1992) 353.
[40] Program: PANIC (Bruker).
[41] V.D. Bianco and S. Doronzo, *Inorg. Synth., 16* (1976) 161.
[42] M. Fild, O. Glemser and I. Hollenberg, *Z. Naturforsch., 21b* (1966) 920.
[43] J.R. Goerlich, A. Fischer, P.G. Jones and R. Schmutzler, *J. Fluorine Chem., 72* (1995) 69.