ELSEVIER

Journal of Fluorine Chemistry 85 (1997) 135–139

JOURNAL OF FLUORINE CHEMISTRY

Chemistry of phenylphosphonous acid fluoride: single crystal X-ray diffraction study of the acetone adduct $PhP(:O)(F)C(CH_3)_2OH$ [1]

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Received 18 December 1996; accepted 13 March 1997

Abstract

The reaction of phenyldifluorophosphine **1** with calcium hydroxide is an alternative route to form phenylphosphonous acid fluoride **2**. The reaction of **2** with methyl ketones, MeC(:O)R, leads to addition products of type PhP(:O)(F)C(Me)(R)OH.

A single crystal X-ray structure determination is described for the adduct $PhP(:O)(F)C(CH_3)_2OH$ **8** obtained from phenylphosphonous acid fluoride **2** and acetone; hydrogen bonds of the form O–H···O=P are observed. © 1997 Elsevier Science S.A.

Keywords: Phosphonous acid fluoride; Single crystal X-ray structure determination; Hydrogen bonding

1. Introduction

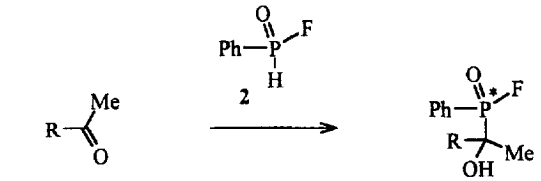
In contrast to fluorophosphoric acids, e.g. $(HO)_2P(:O)F$ and $(HO)P(:O)F_2$, phosphonous acid fluorides $HP(:O)(R)F$ have only been known for a few decades. The corresponding fluorophosphonous(III) acid (R=H) was obtained during the hydrolysis of PF_3 or by the reaction of an aqueous solution of phosphonous acid, $(HO)_2P(:O)H$, with HF by Blaser and Worms [1] in 1968. Small amounts of the same compound, $H_2P(:O)F$, were obtained in the reorganization reaction of $HP(:O)F_2$ by Centofanti and Parry [2]. In 1972, Ahrens and Falius reported the synthesis of organo-substituted (R=Me, Et, Ph) phosphonous acid fluorides [3] by treatment of organophosphonous acid dichlorides with aqueous HF (Eq. (1)).

$$RPCl_2 + HF + H_2O \longrightarrow HP(:O)(R)F + 2\,HCl \qquad (1)$$

In this paper an alternative synthesis of phenylphosphonous acid fluoride **2** is described that involves reaction of phenyldifluorophosphine **1** with calcium hydroxide (Eq. (2)).

$$\underset{\mathbf{1}}{2\,PhPF_2} + Ca(OH)_2 \longrightarrow \underset{\mathbf{2}}{2\,PhP(:O)FH} + CaF_2 \qquad (2)$$

Several reactions of carbonyl compounds with compounds containing P–H bonds are known [4–6]. The products of these reactions are alcohols with a newly formed P–C bond, regardless of the phosphorus-containing precursor compound. The addition of P–H compounds to carbonyl groups is known for σ^3-, σ^4- and σ^5-phosphorus compounds [7,8]. In the latter case the addition is sometimes found to be reversible upon heating [9]. We now report the addition of phenylphosphonous acid fluoride **2** to methyl ketones (Eq. (3)) and a single crystal X-ray diffraction determination of one of the adducts, **8**, formed from phenylphosphonous acid fluoride and acetone.



R	
Me	3
Et	4
Ph	5
tert-Bu	6
sec-Bu	7

R	
Me	8
Et	9
Ph	10
tert-Bu	11
sec-Bu	12

(3)

* = Chiral Centre of phosphorus

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[1] Dedicated to Professor Walter Siebert on the occasion of his 60th birthday.

PII S0022-1139(97)00062-6

2. Results and discussion

2.1. Formation of phenylphosphonous acid fluoride 2 in the reaction of phenyldifluorophosphine 1 with calcium hydroxide

The stability of P–F bonds in monofluorinated phosphorus compounds towards hydrolysis has often been noted, and the formation of phenylphosphonous acid fluoride PhP(:O)FH **2** via hydrolysis of $PhPF_2$ **1**, therefore, seemed possible. However, reaction of water with **2** will give rise to the formation of HF (Eq. (4)).

$$\underset{\mathbf{1}}{PhPF_2} + H_2O \longrightarrow \underset{\mathbf{2}}{PhP(:O)FH} + HF \qquad (4)$$

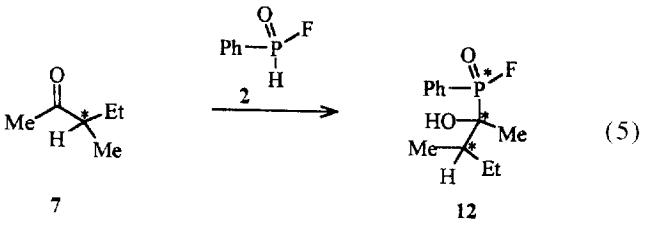
The addition of base instead of water should suppress the formation of HF, but bases such as sodium hydroxide could lead to complete hydrolysis and salt formation. A less reactive base is calcium hydroxide, which here reacts with HF to form poorly soluble calcium fluoride and water; thus its reaction with **1** gave **2** and calcium fluoride (Eq. (2)). Rapid addition of **1** to calcium hydroxide led to a short but violent and exothermic reaction, resulting in a high yield of **2**, whereas slow addition of calcium hydroxide to **1** and stirring for 12 h at room temperature gave poor yields of **2**. However, for large scale reactions the best results were obtained by preparing a suspension of 2 mol of calcium hydroxide and 1 mol of **1**, which was stirred and slowly warmed to 140 °C (for details of the work-up procedure, see Section 3).

2.2. Reaction of phenylphosphonous acid fluoride 2 with methylketones

The reaction of the methylketones **3–7** with **2** gave **8–12** (see Eq. (3)). In all these reactions, the ketones served as the solvents. Mixtures of **2** and the ketones **3–7** were refluxed for several hours and, in the case of higher boiling ketones, the reaction temperature was 100–110 °C. During further work-up, the products crystallised as colourless solids.

The resonances of the addition products **8–12** in the ^{31}P-NMR spectra were doublets at 50–60 ppm with $^1J(PF) = 1079–1092$ Hz, and in the ^{19}F-NMR spectra doublets at −83 to −97 ppm. Since **2** contains a prochiral phosphorus centre, and in view of the use of asymmetrically substituted ketones (**4–6**), the adducts **9–11** have two chiral centres, the phosphorus atom and the carbon atom adjacent to it. Therefore the ^{31}P- and ^{19}F-NMR spectra of **9** and **10** exhibit two doublets with different intensities for the diastereoisomers with $\Delta\delta(P) = 0.4$ (**9**) and 0.7 ppm (**10**), $\Delta\delta(F) = 0.9$ (**9**) and 2.6 ppm (**10**), and $\Delta^1J(PF) = 2–3$ Hz. However, the diastereoisomers could not be assigned. For **11** just one doublet could be observed in both the ^{31}P- and the ^{19}F-NMR spectra. This means that the electronic properties of the diastereoisomers are very similar at the phosphorus and the fluorine atoms, so that no differentiation is observable in the NMR spectra. The high symmetry of the tert. butyl group favours the spectroscopic similarity of the diastereoisomers.

With the chiral ketone **7** (the racemate was used) three chiral centres are present in the adduct **12** (Eq. (5)).



(5)

Therefore, the signals of four diastereoisomers are observed as doublets in the ^{31}P- and ^{19}F-NMR spectra; the signals of the diastereoisomers could not be assigned. However, the different intensities show that the diastereoisomers were not formed in equal quantities.

The methyl groups of **8** are diastereoisotopic and their resonances were observed as two doublets (δ 0.94, $^3J(HP) = 15.57$ Hz and δ 1.10, $^3J(HP) = 14.82$ Hz) in the ^1H NMR spectrum. The number of distinguishable ^1H NMR signal sets of the methyl groups of the adducts **9**, **11** and **12** equals the number of diastereoisomers; these resonances are doublets at 0.9–1.4 ppm with $^3J(HP) = 14–20$ Hz. For the adduct of phenylmethylketone **10**, the resonance of the methyl group is shifted 0.5 ppm downfield (δ 1.94 and 1.99), compared to the other adducts, probably because of anisotropy effects arising from the phenyl group.

In the ^1H-NMR spectrum of **12**, $^4J(HF)$ coupling could be observed (1.3–2.1 Hz).

2.2.1. X-ray crystal structure determination of 8

The structure of compound **8** is shown in Fig. 1. The P–O bond length of 1.4713(13) Å indicates a localised double bond, and the P–C7 bond (sp^3 carbon) is, as expected, longer than P–C1 (aromatic carbon); 1.834(2) Å, 1.785(2) Å. The P–F bond length is 1.5596(11) Å. The widest angles at phosphorus involve the sterically demanding P=O group. A search of the Cambridge Crystallographic Database revealed no other structure with the same substituents (two C, F, =O) at phosphorus for comparison.

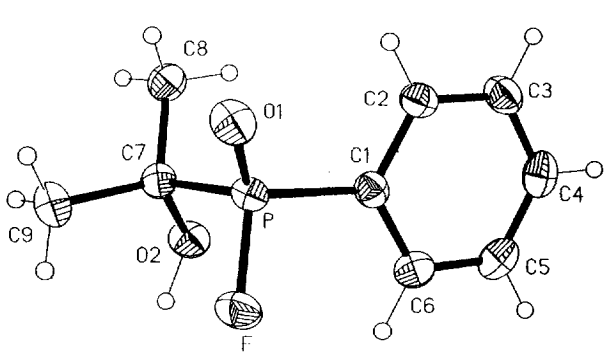


Fig. 1. The molecule of compound **8** in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

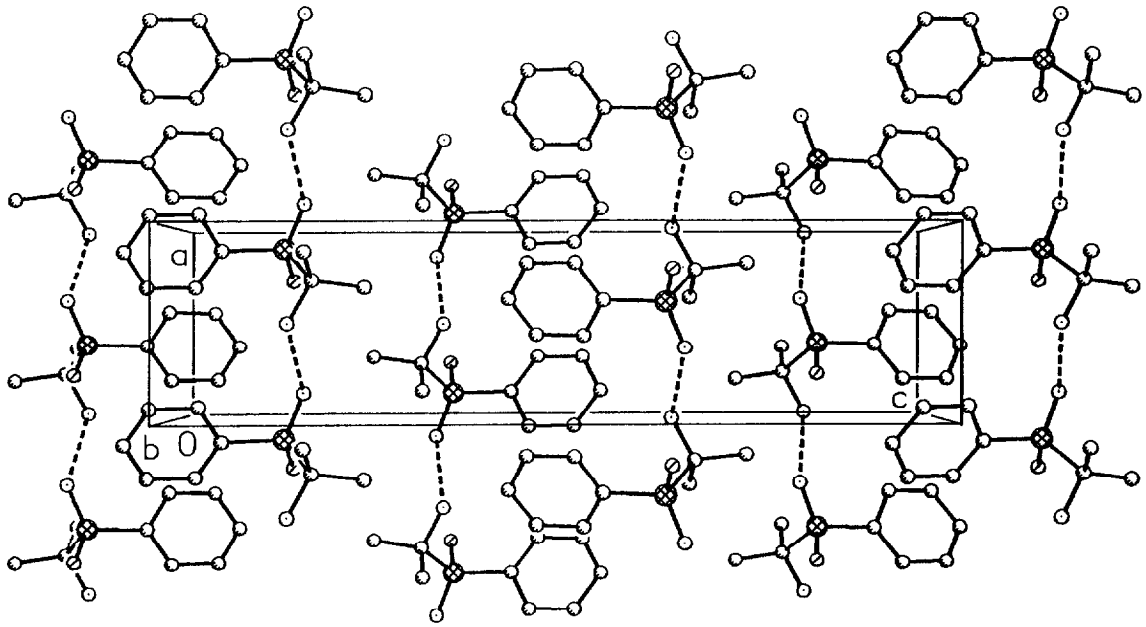


Fig. 2. Packing diagram of compound **8** (H atoms omitted for clarity). Hydrogen bonds are indicated by dashed lines.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **8**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	6103.8(7)	5852.7(5)	6420.4(2)	23.1(1)
F	7749.2(19)	7437.2(12)	6483.7(4)	34.4(2)
O(1)	3700(2)	6179.5(16)	6665.5(5)	32.1(3)
O(2)	9983(2)	3952.9(17)	6530.0(5)	32.1(3)
C(1)	6197(3)	5418.6(18)	5616.3(7)	24.1(3)
C(2)	4343(3)	4465(2)	5366.3(7)	29.0(4)
C(3)	4404(3)	4015(2)	4750.5(8)	34.5(4)
C(4)	6274(4)	4549(2)	4383.0(7)	35.7(4)
C(5)	8100(4)	5501(2)	4627.7(8)	35.4(4)
C(6)	8098(3)	5934(2)	5247.1(7)	29.9(3)
C(7)	7771(3)	4216(2)	6837.0(7)	24.1(3)
C(8)	6363(3)	2578(2)	6792.5(8)	30.9(3)
C(9)	8124(3)	4756(2)	7503.8(8)	33.8(4)

Table 2
Selected bond lengths (Å) and angles (°) for compound **8**

P–O(1)	1.4713(13)	P–F	1.5596(11)
P–C(1)	1.785(2)	P–C(7)	1.834(2)
O(2)–C(7)	1.424(2)	C(7)–C(8)	1.518(2)
C(7)–C(9)	1.526(2)		
O(1)–P–F	111.61(7)	O(1)–P–C(1)	114.60(8)
F–P–C(1)	102.90(7)	O(1)–P–C(7)	114.21(7)
F–P–C(7)	102.71(7)	C(1)–P–C(7)	109.59(7)
C(2)–C(1)–P	117.73(12)	C(6)–C(1)–P	122.11(12)
O(2)–C(7)–C(8)	107.34(14)	O(2)–C(7)–C(9)	112.00(13)
C(8)–C(7)–C(9)	111.45(14)	O(2)–C(7)–P	108.30(11)
C(8)–C(7)–P	107.69(11)	C(9)–C(7)–P	109.90(12)

The molecules are connected in chains parallel to the x axis by hydrogen bonds of the form O2–H2···O1($1+x,y,z$), with O···O 2.741(2), H···O 1.93 Å, O–H···O 163° (Fig. 2).

3. Experimental details

All experiments were carried out with exclusion of air and moisture; solvents were purified and dried according to the usual methods [10]. 'In vacuo' refers to a pressure of 0.1 mm Hg at 25 °C, unless otherwise stated.

NMR: Bruker AC 200 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz; ^{19}F, 188.3 MHz; ^{31}P, 81.0 MHz); reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C), and $CFCl_3$ ext. (^{19}F), 85% H_3PO_4 ext. (^{31}P); high-field shifts were given negative, low-field shifts positive signs.

MS: Finnigan MAT 8430; Elemental analyses: Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität Braunschweig.

Crystal structure analysis: Crystal data: $C_9H_{12}FO_2P$, space group $P2_12_12_1$, $a=5.602(2)$, $b=7.892(2)$, $c=21.778(4)$ Å, $V=962.9$ Å^3, $Z=4$, $T=-95$ °C, $\mu=0.27$ mm^{-1}. Data collection and reduction: Colourless tablet $0.6\times0.5\times0.2$ mm^3, $2\theta_{max}$ 55° (Mo Kα), Siemens R3 diffractometer, 5180 data, 2222 unique (R_{int} 0.025). Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°. Structure solution and refinement: Direct methods; refined anisotropically on F^2 (program SHELXL-93, G.M. Sheldrick, University of Göttingen). Hydrogen atoms: riding or rigid OH group. Absolute structure: Flack x parameter [11] −0.07(10). Final $wR(F^2)$ 0.078 for 121 parameters, $R(F)$ 0.028; max. $\Delta\rho=0.39$ e Å^{-3}, $S=1.09$. Final atomic coordinates are presented in Table 1, with selected molecular dimensions in Table 2.

Full details can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-

Leopoldshafen, Germany, quoting the literature citation and the reference number CSD 405997.

3.1. Reaction of phenyldifluorophosphine 1 with $Ca(OH)_2$: formation of PhP(:O)FH 2

Calcium hydroxide (42.60 g; 0.58 mol) was added with rapid stirring in portions within 1 min to $PhPF_2$ (84.15 g; 0.58 mol) at 0 °C (ice bath) in a 250 ml two-necked flask, fitted with a reflux condenser. After removing the ice bath, the reaction mixture was heated using a hot air gun until it started refluxing. The heat source was removed and the reaction mixture was allowed to reflux for 10 min. Subsequently, unreacted $PhPF_2$ was removed in vacuo at 20 °C. The residue was filtered and extracted with diethyl ether. All volatile compounds were removed in vacuo. A vacuum distillation gave 30.20 g (0.21 mol, 36.5% yield) of pure **2** (b.p. 100 °C, 2 mm Hg). ^{1}H NMR ($CDCl_3$): δ = 7.2 [m, aryl-H]; 7.33 ppm [dd, ^1J(HP) = 617.80 Hz, ^2J(HF) = 87.13 Hz, P(F)*H*]. ^{13}C NMR ($CDCl_3$): δ = 128.09 [dd, ^1J(CP) = 295.45 Hz, ^2J(CF) = 14.31 Hz, ipso-C_6H_5]; 127.97 [d, ^3J(CP) = 14.89 Hz, m-C_6H_5]; 129.43 [d, ^2J(CP) = 13.47 Hz, o-C_6H_5]; 133.30 ppm [d, ^4J(CP) = 2.88 Hz, p-C_6H_5]. ^{31}P NMR ($CDCl_3$): δ = 33.32 ppm [d, ^1J(PF) = 1009.96 Hz]. ^{19}F NMR ($CDCl_3$): δ = −74.23 ppm [d, ^1J(FP) = 1010.07 Hz].

3.2. General procedure for the reaction of PhP(:O)FH 2 with the ketones 3–7: formation of the adducts 8–12

A mixture of the ketone and **2** was heated for the time indicated below in a Schlenk tube, fitted with a reflux condenser. After removing the unreacted ketone under reduced pressure, the residue was recrystallised from diethyl ether/hexane at −30 °C. The solid formed was filtered, washed twice with cold diethyl ether (5 ml) and dried in vacuo.

(**A**), (**B**), (**C**) and (**D**) are the diastereoisomers for **8–12** observed in the NMR spectra and distinguished by different intensities.

3.2.1. Phenyl-2-(2-hydroxypropyl)-phosphinic acid fluoride 8

PhP(:O)FH **2**, 1.8 g (12.5 mmol); acetone **3**, 2.6 g (44.8 mmol); reaction time, 3 h reflux; adduct **8**, 2.2 g (10.9 mmol, 87.2%); m.p. 72–73 °C. Anal.: Found: C, 53.44; H, 6.07; P, 15.70%. $C_9H_{12}O_2PF$ (202.17) requires: C, 53.47; H, 5.98; P, 15.32%. ^{1}H-NMR ($CDCl_3$) δ: 0.94 [d, ^3J(HP) = 15.57 Hz, PC(OH)–C*H*$_3$ (B)]; 1.10 [d, ^3J(HP) = 14.82 Hz, PC(OH)–C*H*$_3$ (A)]; 7.2 [m, Aryl-*H*]; 7.5 ppm [s, C–O*H*]. ^{13}C-NMR ($CDCl_3$) δ: 23.90 [d, ^2J(CP) = 8.21 Hz, PC(OH)–*C*H$_3$]; 70.22 [dd, ^1J(CP) = 115.17 Hz, ^2J(CF) = 18.67 Hz, P(F)*C*(OH)]; 124.56 [dd, ^1J(CP) = 121.44 Hz, ^2J(CF) = 17.42 Hz, ipso-C_6H_5]; 128.40 [d, ^3J(CP) = 12.71 Hz, m-C_6H_5]; 132.71 [dd, ^2J(CP) = 10.12 Hz, ^3J(CF) = 2.23 Hz, o-C_6H_5]; 133.47 ppm [d, ^4J(CP) = 2.30 Hz, p-C_6H_5]. ^{31}P-NMR ($CDCl_3$) δ: 54.60 ppm [d, ^1J(PF) = 1079.54 Hz]. ^{19}F-NMR ($CDCl_3$) δ: −96.10 ppm [d, ^1J(FP) = 1079.55 Hz]. MS (70 eV) *m/z* (%): 202 (8) $[M]^+$; 187 (3) $[M–CH_3]^+$; 144 (100) $[PhPOFH]^+$; 78 (68) $[C_6H_6]^+$; 77 (40) $[C_6H_5]^+$; 59 (78) $[CH_3C(OH)CH_3]^+$.

3.2.2. Phenyl-2-(2-hydroxybutyl)-phosphinic acid fluoride 9

PhP(:O)FH **2**, 2.59 g (17.99 mmol); ethylmethylketone **4**, 2.58 g (35.80 mmol); reaction time, 3 h at 75 °C; adduct **9**, 3.13 g (14.50 mmol, 80.6%); m.p. 82 °C. Anal.: Found: C, 55.83; H, 6.64; P, 14.71%. $C_{10}H_{14}O_2PF$ (216.19) requires: C, 55.56; H, 6.53; P, 14.33%. ^{1}H-NMR ($CDCl_3$) δ: 0.87 [t, ^3J(HH) = 7.37 Hz, C(OH)–CH_2–C*H*$_3$ (A)]; 0.93 [t, ^3J(HH) = 7.30 Hz, C(OH)–CH_2–C*H*$_3$ (B)]; 1.28 [d, ^3J(HP) = 18.64 Hz, PC(OH)–C*H*$_3$ (A)]; 1.36 [d, ^3J(HP) = 15.93 Hz, PC(OH)–C*H*$_3$ (B)]; 1.7 [m, C(OH)–C*H*$_2$–CH_3]; 5.04 [s, C–O*H*]; 7.5 ppm [m, Aryl-*H*]. ^{13}C-NMR ($CDCl_3$) δ: 6.00 [d, ^3J(CP) = 8.68 Hz, PC(OH)–CH_2–*C*H$_3$]; 19.48 [d, ^2J(CP) = 23.98 Hz, PC(OH)–*C*H$_3$ (A)]; 19.61 [d, ^2J(CP) = 28.59 Hz, PC(OH)–*C*H$_3$ (B)]; 28.24 [d, ^2J(CP) = 11.93 Hz, PC(OH)–*C*H$_2$–CH_3 (A)]; 28.40 [d, ^2J(CP) = 16.21 Hz, PC(OH)–*C*H$_2$–CH_3 (B)]; 72.24 [dd, ^1J(CP) = 115.08 Hz, ^2J(CF) = 17.38 Hz, P(F)*C*(OH) (A)]; 72.43 [dd, ^1J(CP) = 114.96 Hz, ^2J(CF) = 17.13 Hz, P(F)*C*(OH) (B)]; 124.59 [dd, ^1J(CP) = 120.84 Hz, ^2J(CF) = 17.62 Hz, ipso-C_6H_5 (A)]; 124.62 [dd, ^1J(CP) = 120.45 Hz, ^2J(CF) = 17.88 Hz, ipso-C_6H_5 (B)]; 127.91 [d, ^3J(CP) = 12.61 Hz, m-C_6H_5]; 132.44 [dd, ^2J(CP) = 10.05 Hz, ^3J(CF) = 2.20 Hz, o-C_6H_5]; 132.99 ppm [s, p-C_6H_5]. ^{31}P-NMR ($CDCl_3$) δ: 54.63 [d, ^1J(PF) = 1079.03 Hz (B)]; 55.29 ppm [d, ^1J(PF) = 1081.06 Hz (A)]. ^{19}F-NMR ($CDCl_3$) δ: −94.69 [d, ^1J(FP) = 1081.05 Hz (A)]; −93.83 ppm [d, ^1J(FP) = 1078.90 Hz (B)]. MS (70 eV) *m/z* (%): 216 (3) $[M]^+$; 201 (3) $[M–CH_3]^+$; 187 (7) $[M–C_2H_5]^+$; 161 (35) $[PhPF(OH)_2]^+$; 144 (100) $[PhPOFH]^+$; 78 (36) $[C_6H_6]^+$; 73 (91) $[CH_3CH_2C(OH)CH_3]^+$; 55 (21) $[C_4H_7]^+$; 43 (13) $[CH_3C=O]^+$.

3.2.3. Phenyl-1-(1-hydroxy-1-phenylethyl)-phosphinic acid fluoride 10

PhP(:O)FH **2**, 2.0 g (14.2 mmol); methylphenylketone **5**, 3.5 g (29.0 mmol); reaction time, 1 h at 105 °C; adduct **10**, 3.3 g (12.5 mmol, 88.0%); m.p. 129 °C. Anal.: Found: C, 63.46; H, 5.35; P, 11.42%. $C_{14}H_{14}O_2PF$ (264.24) requires: C, 63.64; H, 5.34; P, 11.72%. ^{1}H-NMR ($CDCl_3$) δ: 1.94 [d, ^3J(HP) = 14.93 Hz, PC(OH)–C*H*$_3$ (A)]; 1.99 [d, ^3J(HP) = 15.03 Hz, PC(OH)–C*H*$_3$ (B)]; 4.54 [s, C–O*H*]; 7.4 ppm [m, Aryl-*H*]. ^{13}C-NMR ($CDCl_3$) δ: 24.00 [d, ^2J(CP) = 21.77 Hz, PC(OH)–*C*H$_3$ (A)]; 24.09 [d, ^2J(CP) = 20.90 Hz, PC(OH)–*C*H$_3$ (B)]; 74.55 [dd, ^1J(CP) = 112.62 Hz, ^2J(CF) = 26.93 Hz, P(F)*C*(OH) (A)]; 74.92 [dd, ^1J(CP) = 113.13 Hz, ^2J(CF) = 26.39 Hz, P(F)*C*(OH) (B)]; 124.05 [dd, ^1J(CP) = 125.69 Hz, ^2J(CF) = 16.75 Hz, ipso-C_6H_5 (A,B)]; other observed aromatic ^{13}C resonances could not be clearly assigned. ^{31}P NMR ($CDCl_3$) δ: 49.78 [d, ^1J(PF) = 1091.38 Hz (B)]; 50.14 ppm

[d, ^1J(PF) = 1088.40 Hz (A)]. ^{19}F-NMR ($CDCl_3$) δ: −95.34 [d, ^1J(FP) = 1088.30 Hz (A)]; −92.77 ppm [d, ^1J(FP) = 1091.42 Hz (B)]. MS (70 eV) *m/z* (%): 264 (0.3) $[M]^+$; 222 (0.9) $[M-C_2H_2O]^+$; 221 (1.2) $[M-C_2H_3O]^+$; 144 (1.0) $[PhPOFH]^+$; 120 (38) $[C_6H_5C(O)CH_3]^+$; 105 (100) $[C_6H_5C(O)]^+$; 77 (68) $[C_6H_5]^+$; 43 (10) $[CH_3C=O]^+$.

3.2.4. Phenyl-2-(2-hydroxy-3,3-dimethylbutyl)-phosphinic acid fluoride **11**

PhP(:O)FH **2**, 2.69 g (18.67 mmol); tert.-butylmethylketone **6**, 3.72 g (37.20 mmol); reaction time, 3 h at 110 °C; adduct **11**, 4.13 g (16.91 mmol, 90.4%); m.p. 119 °C. Anal.: Found: C, 59.17; H, 7.58; P, 12.73%. $C_{12}H_{18}O_2PF$ (244.25) requires: C, 59.01; H, 7.43; P, 12.68%. ^{1}H-NMR (CD_3OD) δ: 1.18 [s, C(OH)–C(CH_3)$_3$ (A)]; 1.19 [s, C(OH)–C(CH_3)$_3$ (B)]; 1.21 [d, ^3J(HP) = 19.84 Hz, PC(OH)–CH_3 (A)]; 1.22 [d, ^3J(HP) = 19.80 Hz, PC(OH)–CH_3 (A)]; 4.89 [s, C–O*H*]; 7.7 ppm [m, Aryl-*H*]. ^{13}C-NMR (CD_3OD) δ: 20.11 [d, ^2J(CP) = 10.87 Hz, PC(OH)–CH_3 (A)]; 20.15 [d, ^2J(CP) = 10.85 Hz, PC(OH)–CH_3 (B)]; 26.49 [d, ^3J(CP) = 4.25 Hz, PC(OH)–C(CH_3)$_3$ (A)]; 26.52 [d, ^3J(CP) = 3.90 Hz, PC(OH)–C(CH_3)$_3$ (B)]; 39.50 [d, ^2J(CP) = 5.48 Hz, PC(OH)–$C(CH_3)_3$ (A)]; 39.55 [d, ^2J(CP) = 5.35 Hz, PC(OH)–$C(CH_3)_3$ (B)]; 78.66 [dd, ^1J(CP) = 112.58 Hz, ^2J(CF) = 14.93 Hz, P(F)C(OH) (A,B)]; 128.27 [dd, ^1J(CP) = 122.87 Hz, ^2J(CF) = 19.16 Hz, ipso-C_6H_5 (A,B)]; 129.49 [d, ^3J(CP) = 12.51 Hz, m-C_6H_5]; 134.17 [dd, ^2J(CP) = 9.48 Hz, ^3J(CF) = 2.16 Hz, o-C_6H_5]; 134.56 ppm [d, ^4J(CP) = 2.62 Hz, p-C_6H_5]. ^{31}P-NMR (CD_3OD) δ: 57.76 ppm [d, ^1J(PF) = 1090.87 Hz (A,B)]. ^{19}F-NMR (CD_3OD) δ: −83.56 ppm [d, ^1J(FP) = 1090.57 Hz (A,B)]. MS (70 eV) *m/z* (%): 244 (0.7) $[M]^+$; 229 (3.9) $[M-CH_3]^+$; 188 (50) $[M-C_4H_8]^+$; 144 (68) $[PhPOFH]^+$; 101 (100) $[(CH_3)_3C(OH)CH_3]^+$; 83 (30) $[C_6H_{11}]^+$; 78 (44) $[C_6H_6]^+$; 43 (28) $[CH_3C=O]^+$.

3.2.5. Phenyl-2-(2-hydroxy-3-methylpentyl)-phosphinic acid fluoride **12**

PhP(:O)FH **2**, 4.7 g (32.7 mmol); sec.-butylmethylketone **7**, 4.8 g (48.0 mmol); reaction time, 3 h at 80 °C; adduct **12**, 3.4 g (14.1 mmol, 43.1%); m.p. 83 °C. Anal.: Found: C, 58.30; H, 7.43; P, 13.68%. $C_{12}H_{18}O_2PF$ (244.25) requires: C, 59.01; H, 7.43; P, 12.68%. ^{1}H-NMR ($CDCl_3$) δ: 0.9 [m, C(OH)–CH(CH_3)CH_2CH_3 (A,B,C,D)]; 1.28 [dd, ^3J(HP) = 17.46 Hz, ^4J(HF) = 1.77 Hz, PC(OH)–CH_3 (A)]; 1.29 [dd, ^3J(HP) = 17.44 Hz, ^4J(HF) = 2.12 Hz, PC(OH)–CH_3 (B)]; 1.31 [d, ^3J(HP) = 16.11 Hz, PC(OH)–CH_3 (C)]; 1.33 [d, ^3J(HP) = 15.79 Hz, PC(OH)–CH_3 (D)]; 1.8 [m, C(OH)–CH_2 (A,B,C,D)]; 5.42 [s, C–O*H*]; 7.6 ppm [m, Aryl-*H*]. ^{13}C-NMR ($CDCl_3$) δ: 12.01 [s, H_3C–CH_2–CH (A)]; 12.10 [s, H_3C–CH_2–CH (B)]; 12.28 [s, H_3C–CH_2–CH (C,D)]; 16.35 [d, ^3J(CP) = 5.63 Hz, C(OH)–CH–CH_3 (A)]; 16.60 [d, ^3J(CP) = 5.48 Hz, PC(OH)–CH–CH_3 (B)]; 17.55 [d, ^3J(CP) = 8.07 Hz, PC(OH)–CH–CH_3 (C)]; 17.94 [d, ^3J(CP) = 8.77 Hz, PC(OH)–CH–CH_3 (D)]; 21.85 [d, ^2J(CP) = 10.23 Hz, PC(OH)–CH_3 (A)]; 22.55 [d, ^2J(CP) = 8.23 Hz, PC(OH)–CH_3 (B)]; 23.97 [s, H_3C–CH_2–CH (A)]; 24.30 [s, H_3C–CH_2–CH (B)]; 39.87 [d, ^2J(CP) = 8.17 Hz, PC(OH)–CH–CH_3 (A)]; 40.12 [d, ^2J(CP) = 9.82 Hz, PC(OH)–CH–CH_3 (B)]; 40.42 [d, ^2J(CP) = 6.00 Hz, PC(OH)–CH–CH_3 (C)]; 40.71 [d, ^2J(CP) = 6.69 Hz, PC(OH)–CH–CH_3 (D)]; 76 [m, C(OH) (A,B,C,D) (not resolved)]; 126 [m, ipso-C_6H_5 (A,B,C,D) (not resolved)]; 128.32 [d, ^3J(CP) = 12.54 Hz, m-C_6H_5 (A)]; 128.36 [d, ^3J(CP) = 12.79 Hz, m-C_6H_5 (B)]; 132.73 [d, ^2J(CP) = 7.99 Hz, o-C_6H_5 (A)]; 132.90 [d, ^2J(CP) = 8.86 Hz, o-C_6H_5 (B)]; 133.25 ppm [s, p-C_6H_5]. ^{31}P-NMR ($CDCl_3$) δ: 54.01 [d, ^1J(PF) = 1081.75 Hz (B)]; 54.54 [d, ^1J(PF) = 1079.52 Hz (A)]; 55.51 [d, ^1J(PF) = 1086.16 Hz (D)]; 55.87 ppm [d, ^1J(PF) = 1086.06 Hz (C)]. ^{19}F-NMR ($CDCl_3$) δ: −90.80 [d, ^1J(FP) = 1086.01 Hz (D)]; −90.05 [d, ^1J(FP) = 1085.96 Hz (C)]; −87.71 [d, ^1J(FP) = 1079.66 Hz (A)]; −87.68 ppm [d, ^1J(FP) = 1081.87 Hz (B)]. MS (70 eV) *m/z* (%): 244 (0.7) $[M]^+$; 188 (11) $[M-C_4H_8]^+$; 161 (20) $[PhPF(OH_2)]^+$; 144 (49) $[PhPOFH]^+$; 101 (100) $[CH_3CH_2CH(CH_3)C(OH)CH_3]^+$; 78 (25) $[C_6H_6]^+$; 77 (20) $[C_6H_5]^+$; 59 (16) $[C_3H_7O]^+$; 57 (19) $[C_4H_9]^+$; 43 (32) $[CH_3C=O]^+$.

Acknowledgements

This research was supported by generous supplies of chemicals from BASF AG, BAYER AG, DEGUSSA AG and HOECHST AG. The continuing support of the Fonds der Chemischen Industrie is gratefully acknowledged.

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