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SYNTHESIS AND CHARACTERIZATION OF NEW BIS(PENTAFLUOROETHYL)PHOSPHINIC ACID AMIDES AND HYDRAZIDES. CRYSTAL STRUCTURE OF $(C_2F_5)_2P(O)NH_2$

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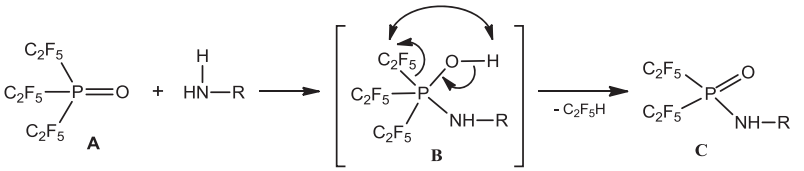
GRAPHICAL ABSTRACT



R = H, C_6H_5, $CH_3C_6H_4$, $C_6H_5CH_2$, *p*-$CH_3C_6H_4CH_2$, *p*-$CH_3OC_6H_4CH_2$, $C_6H_5CH_2CH_2$, C_4H_9, C_8H_{17}, $NHCH_3$, NHC_6H_5, $NHCH_2$[3,5-(*t*-C_4H_9)$_2$-C_6H_2-4-OH], $N(CH_3)_2$

Abstract *Previously unknown bis(pentafluoroethyl)phosphinyl amides and hydrazides have been prepared in good yields by the reaction of bis(pentafluoroethyl)phosphinyl chloride or tris(pentafluoroethyl)phosphine oxide with the corresponding primary amines or hydrazines. The crystal structure of* $(C_2F_5)_2P(O)NH_2$ *was determined. The compound* $(C_2F_5)_2P(O)NH$-$NHCH_2C_6H_2$-*3,5-(t-*C_4H_9*)-4-OH was oxidized with* PbO_2 *to the corresponding oxo-radical.*

Keywords Bis(pentafluoroethyl)phosphinic acid; amides; hydrazides; crystal structure

INTRODUCTION

Amides of di(alkyl)phosphinic acids or diamides of alkylphosphonic acids are well-known classes of phosphorus-nitrogen compounds.[1] Numerous phosphorus amides have been synthesized since the first organophosphorus compounds were prepared in the nineteenth century.[2] Some phosphorus amides are useful chemicals for practical applications,

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.

for instance phosphoric acid hexamethyl triamide is a well-known polar solvent. Cyclophosphamides are valuable anticancer drugs.[2]

Only a few fluorinated phosphinic acid amides are described in the literature. Their syntheses are based on interaction of phosphinic acid chloride with amines. For example, bis(perfluoroalkyl)phosphinic acid amides $(C_nF_{2n+2})_2P(O)NHR$ (R = H, CH_3, C_6H_5, 3-FC_6H_4, and 4-FC_6H_4) were prepared in moderate yields by the reaction of $(C_nF_{2n+1})_2P(O)Cl$ (n = 1, 3, and 4) with ammonia, methylamine, and aromatic amines.[3–5] Tris(perfluoroalkyl)phosphine oxides are also suitable starting materials for the synthesis of bis(perfluoroalkyl)phosphinic acid amides. Burg and Sarkis reported the quantitative reaction of tris(trifluoromethyl)phosphine oxide with dimethyl amine.[6] Later on, it was found that tris(nonafluorobutyl)phosphine oxide reacts with dimethyl amine resulting in the formation of a complex mixture of products.[7]

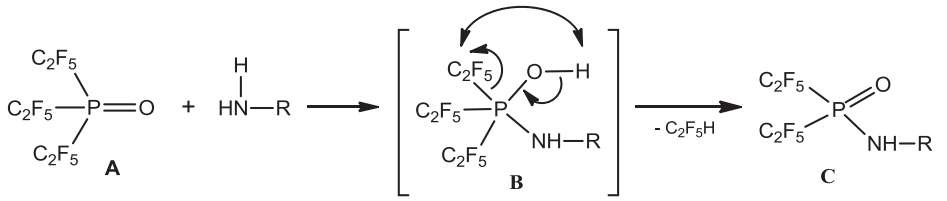
There are few reports on the preparation of phosphinic acid hydrazides, for example: $(CH_3)_2P(O)NHNHPh$ and $Ph_2P(O)NHNHPh$;[8] $(CH_3)_2P(O)NHNH_2$;[9] $(C_2H_5)_2P(O)NHNH(t\text{-}C_4H_9)$;[10] and $Ph_2P(O)NHNH_2$ and $Ph_2P(O)NHN(CH_3)_2$,[11] but no fluorinated phosphinyl hydrazides are described in the literature.

Recently Merck KGaA (Darmstadt, Germany) has applied for a patent claiming the preparation of bis(perfluoroalkyl)phosphinyl hydrazides.[12] Here, the syntheses and properties of previously unknown bis(perfluoroalkyl)phosphinyl amides and hydrazides are described.

RESULTS AND DISCUSSION

Synthesis of Bis(pentafluoroethyl)phosphinic Acid Amides

Tris(pentafluoroethyl)phosphine oxide **A** reacts with ammonia, primary aliphatic and aromatic amines yielding the corresponding bis(pentafluoroethyl)phosphinyl amides **C** (Scheme 1).



R = H, C_6H_5, $CH_3C_6H_4$, $C_6H_5CH_2$, *p*-$CH_3C_6H_4CH_2$, *p*-$CH_3OC_6H_4CH_2$, $C_6H_5CH_2CH_2$, C_4H_9, C_8H_{17},

Scheme 1 Preparation of bis(pentafluoroethyl)phosphinyl amides.

The strong electrophile, tris(pentafluoroethyl)phosphine oxide **A**, reacts with equimolar quantities of primary amines forming the intermediate complex **B**, which is not stable under the reaction conditions and is converted into the final product, bis(pentafluoroethyl)phosphinyl amide **C**. The reactions proceed at low temperature (−30 to 20°C).

The yields of bis(pentafluoroethyl)phosphinyl amides **C** generally range from good to excellent as it is shown in Table 1. A low yield is observed in the reaction with aniline **6c**. This can be attributed to the reduced nucleophilicity of aromatic amines.

Table 1 Products from the reaction of $(C_2F_5)_3P(O)$ with NH_2R and their melting points and yield

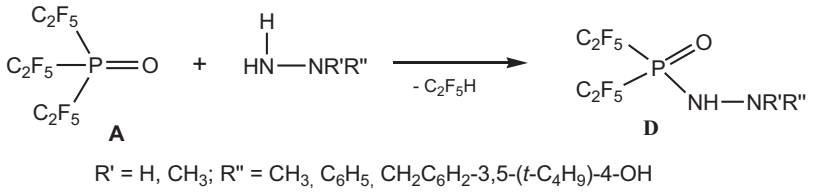
Product (C)	*R*	Mp (°C)	Yield (%)
1c	H	98	86
2c	$CH_2C_6H_5$	94	89
3c	$CH_2CH_2C_6H_5$	110	84
4c	$CH_2C_6H_4CH_3$	102	62
5c	$CH_2C_6H_4OCH_3$	90	72
6c	C_6H_5	141	13
7c	$C_6H_4CH_3$	150	76
8c	$CH_2CH_2CH_2CH_3$	210	75
9c	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	76	92

The hydrolytic stability of bis(pentafluoroethyl)phosphinyl amides depends on the substituent *R*. Amides **2c**–**9c** having longer alkyl chain attached to the nitrogen atom are more stable against hydrolysis in comparison to $(C_2F_5)_2P(O)NH_2$ **1c** which forms an ammonium salt by dissolving in wet solvents.

Details of the reaction's conditions and workup procedures are given in the experimental part.

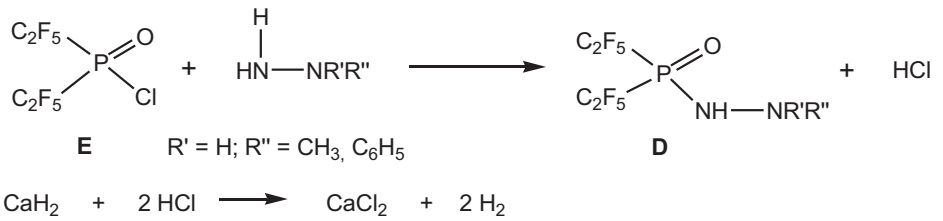
Synthesis of Bis(pentafluoroethyl)phosphinic Acid Hydrazides

Reaction of **A** with different hydrazines in dry acetonitrile at room temperature yields bis(pentafluoroethyl)phosphinic acid hydrazides **D** (Scheme 2).



Scheme 2 Synthesis of substituted phosphinyl hydrazides **D** from $(C_2F_5)_3P = O$.

Bis(pentafluoroethyl)phosphinic acid chlorides[13] **E** are more reactive towards hydrazines (Scheme 3). CaH_2 was used as scavenger for HCl to avoid the formation of $[NH_3NRR']Cl$ as a side product.

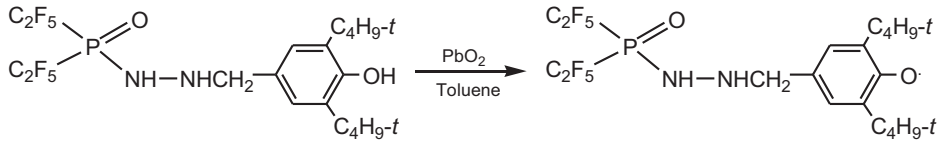


Scheme 3 Synthesis of substituted phosphinyl hydrazides **D** from $(C_2F_5)_2P(O)Cl$.

Table 2 Products from the reaction of $(C_2F_5)_3P(O)$ with NH_2NRR' and their melting points

Product (D)	*R*	*R'*	Mp (°C)	Yield, (%)
1d	H	CH_3	72	84
	H	CH_3	72	<75*
2d	H	C_6H_5	88	81
	H	C_6H_5	88	77*
3d	CH_3	CH_3	71	82
4d	H	$NHCH_2C_6H_2$-3,5-(*t*-C_4H_9)-4-OH	107	88

*Obtained from the reaction with $(C_2F_5)_2P(O)Cl$.



Scheme 4 Oxidation of bis(pentafluoroethyl)phosphinyl-*N*(3,5-di-*t*-butyl-4-hydroxy-benzyl)hydrazide to form a stable radical.

The yields of bis(pentafluoroethyl)phosphinyl hydrazides **D** obtained according to Scheme 3 are lower in comparison to those in the reaction of hydrazines with $(C_2F_5)_3P(O)$ due to the more difficult product isolation.

The bis(pentafluoroethyl)phosphinyl hydrazides (Table 2) are very moisture sensitive compounds. For this reason, all reactions with hydrazines were carried out using vacuum line techniques and glass flasks equipped with a glass valve with PTFE piston (Young, London). The manipulations with nonvolatile compounds were carried out in a glove box under argon. Volatile compounds were handled at the vacuum line. Traces of water in the reaction mixture or in the solvent (acetonitrile) caused hydrolysis of the products.

Bis(pentafluoroethyl)phosphinyl-*N*(3,5-di-*t*-butyl-4-hydroxy-benzyl)hydrazide **4d** can be oxidized with PbO_2 in toluene to a stable radical (Scheme 4).

The reaction mixture was stirred for 30 min at room temperature. The colorless solution changed to yellow indicating the formation of a radical species, which can be also followed in the UV-VIS spectrum (Figure 1). In a closed flask, the color remains unchanged for several weeks.

NMR Study

The ^1H, ^{19}F, ^{31}P NMR data for all synthesized compounds are given in the experimental part. The NMR spectra were measured in dry CD_3CN or CD_2Cl_2 solutions.

In the ^1H NMR spectrum of **1c** a broad singlet and in the spectra of amides **2c–9c** a broad doublet at about 5 ppm is assigned to the NH-proton.

The ^{19}F NMR spectra of the bis(pentafluoroethyl)phosphinyl amides **C** are more complex. Due to the presence of diastereotopic fluorine atoms in α-position, the C_2F_5 group in these spectra gives a singlet at −81 ppm and multiplets at −125 ppm with an integral intensity ratio of 3:2.

The nature of *R* group in the amides **C** has moderate influence on the phosphorus chemical shifts (7–13 ppm). Figure 2 shows the proton-coupled and -decoupled ^{31}P NMR

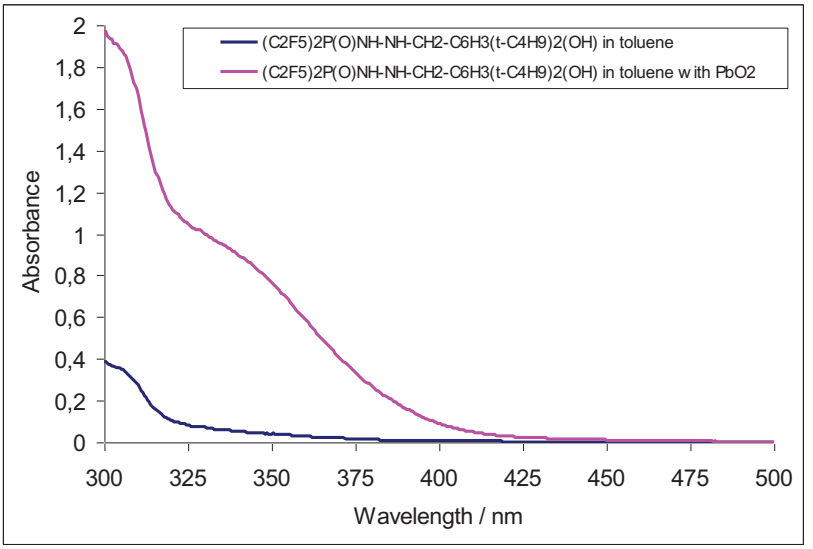


Figure 1 UV-VIS spectrum of bis(pentafluoroethyl)phosphinyl-*N*(3,5-di-*t*-butyl-4-hydroxy-benzyl)hydrazide and the corresponding oxo-radical.

spectrum of **2c**. The ^{31}P NMR spectrum showed overlapping triplet of triplet of doublet of triplet, due to the P,H spin-spin coupling ($^2J_{PH} = 20.3$ Hz and $^3J_{PH} = 11.6$ Hz). In the $^{31}P\{^1H\}$ NMR spectrum an overlapping triplet of triplets is observed due to the coupling with the four ^{19}F nuclei of the two CF_2 groups.

Bis(pentafluoroethyl)phosphinic acid hydrazides were also characterized by ^1H, ^{19}F, ^{31}P NMR spectroscopy. The ^{19}F NMR spectrum of the C_2F_5 group is complex as a consequence of nonequivalent fluorine atoms in the CF_2 groups. The experimental ^{19}F

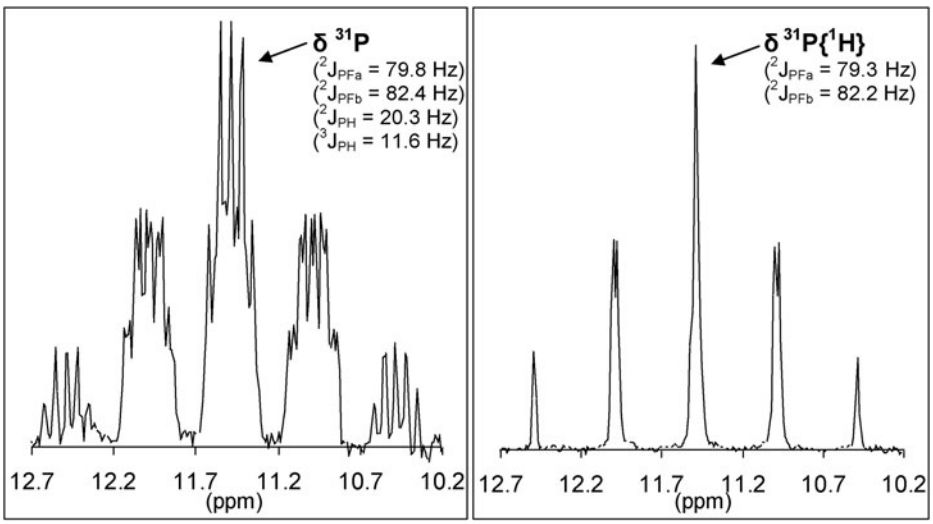


Figure 2 ^{31}P and $^{31}P\{^1H\}$ NMR spectra of $(C_2F_5)_2P(O)NHCH_2C_6H_5$ (**2c**) in acetonitrile-D_3.

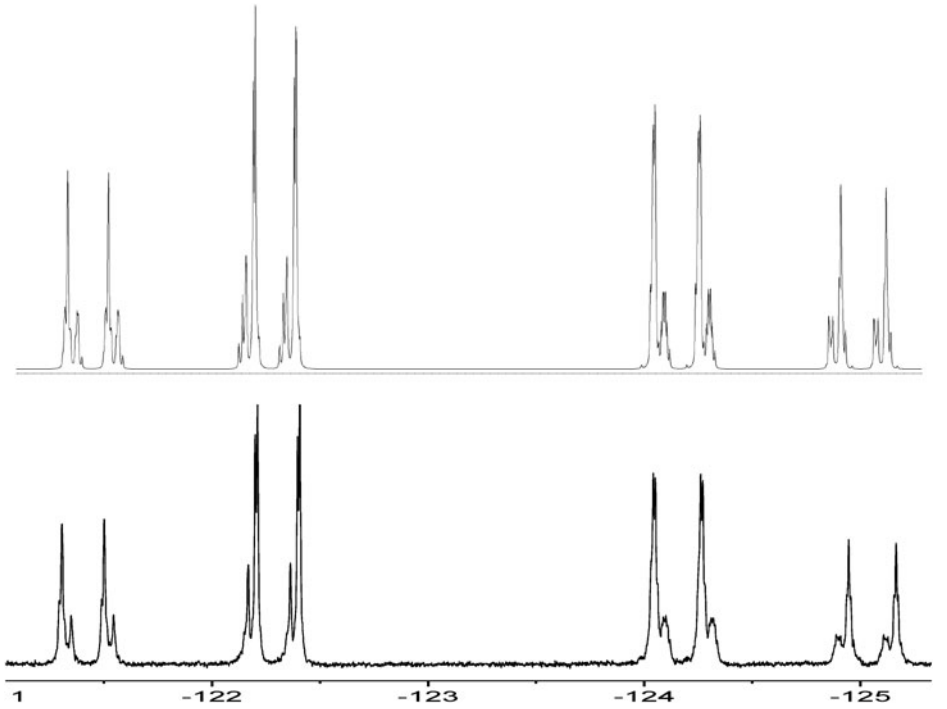


Figure 3 Simulated (top) and observed (bottom) ^{19}F NMR spectrum of $(C_2F_5)_2P(O)NHNHC_6H_5$ **2d**, resonances of the CF_2 groups; solvent: acetonitrile-D_3.

NMR parameters were used to simulate (**gNMR 4.1** program) the ^{19}F NMR spectrum of $(C_2F_5)_2P(O)NHNHC_6H_5$ **2d** as an AA'BB'X spin system. The observed and simulated AA' part of the spectrum is depicted in Figure 3. The ^{31}P NMR spectrum of **2d** shows an overlapping triplet of triplets of doublets of doublets (Figure 4) due to the P,H spin-spin-coupling ($^2J_{PH} = 44.2$ Hz and $^3J_{PH} = 4.0$ Hz).

Vibrational Spectroscopy

The IR and Raman spectra of $(C_2F_5)_2P(O)NH_2$ **1c** are shown in Figure 5 and all band positions are listed in the experimental part. Two ν(N–H) stretching bands are expected for one NH_2 group, but 4 are observed (3344 w, 3222 m, 3087 m, 2888 w) because four molecules are linked *via* hydrogen bonds in the unit cell (see crystal structure below). Other fundamental vibrations in the region between 1400 and 1000 cm^{-1}, are attributed to the P=O stretching, NH_2 deformation and CF stretching modes. The strongest Raman band at 754 cm^{-1} is assigned to the symmetric CF_3 deformation. A more detailed description of modes is not possible, due to strong vibrational coupling. The spectra are just of "finger pint" value.

Crystal Structure of $(C_2F_5)_2P(O)NH_2$

The structural parameters for $(C_2F_5)_2P(O)NH_2$ and the values of angles/distances are given in the Supplementary Material. The asymmetric unit contains one independent formula unit (Figure 6).

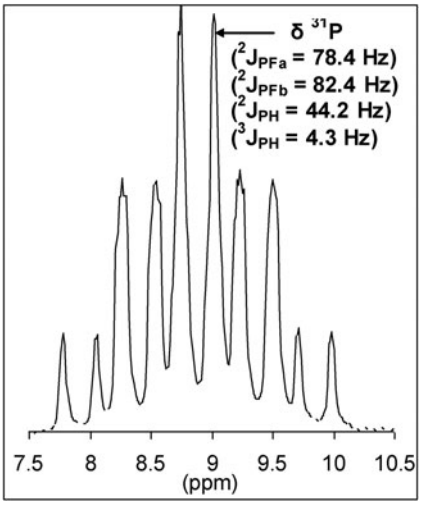


Figure 4 ^{31}P NMR spectrum of $(C_2F_5)_2P(O)NHNHC_6H_5$ **2d** in acetonitrile–D_3.

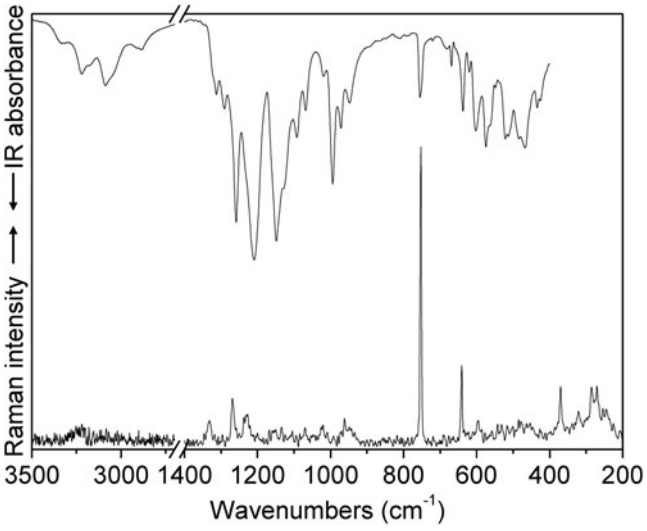


Figure 5 Infrared and Raman spectra of solid $(C_2F_5)_2P(O)NH_2$ recorded for the neat compound.

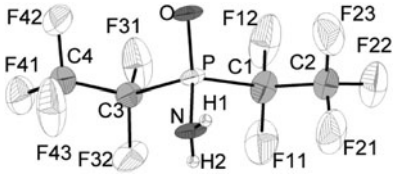


Figure 6 Molecular structure of the asymmetric unit of $(C_2F_5)_2P(O)NH_2$ in the unit cell. Thermal ellipsoids are drawn at the 50% probability level.

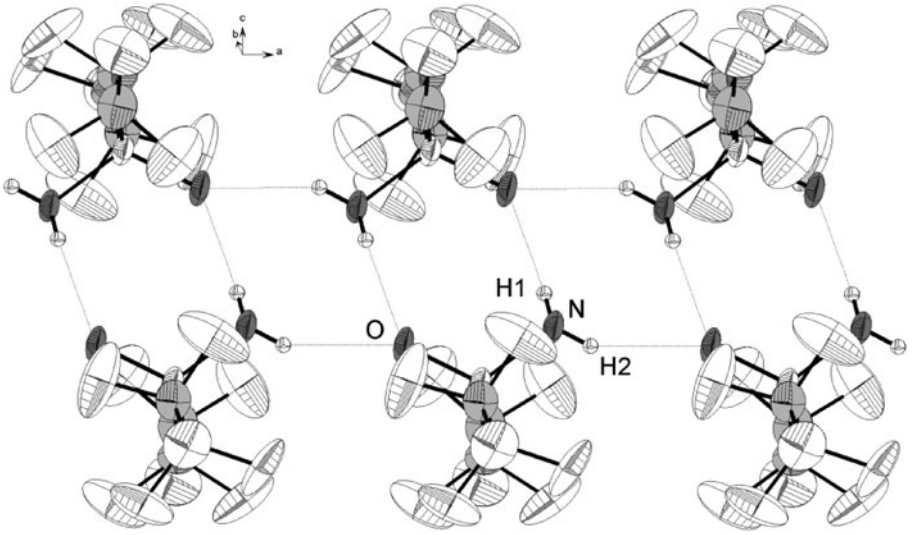


Figure 7 Network of hydrogen bonds in $(C_2F_5)_2P(O)NH_2$. Thermal ellipsoids are drawn at the 50% probability level.

The phosphorus atom is tetrahedrally coordinated. The interatomic distances of the C—F, C—C, C—P, P═O, P—N bonds and F—C—F, C—C—F, P—C—F, C—P—C, C—P—O, C—P—N, O—P—N angles observed for $(C_2F_5)_2P(O)NH_2$ are in the typical range as for example in $P(O)(NH_2)_3$,[14] $H[\{(C_2F_5)_2P(O)\}_2N]$,[15] and $POCl_3$.[16] The crystal structure is stabilized by intermolecular hydrogen bonds of the types N–H···O (H1···O 2.20(4), H2···O 2.30(5), N···O 2.907(4), 2.916(5), and N–H 0.72(4) Å, (Figure 7). These form a one-dimensional hydrogen bonds network along the *a*-axis.

EXERIMENTAL

Analytical Procedures

All NMR spectra were recorded with a **Bruker Avance DRX-400 MHz** (^{1}H, 400.13 MHz; ^{19}F, 376.49 MHz; ^{31}P, 161.97 MHz) spectrometer. For simulation of the NMR spectra the program **gNMR 4.1** was used. The spectra were recorded at room temperature. The chemical shifts are given in parts per million (ppm) relative to external TMS (^{1}H), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P).

Elemental analyses were performed using a **HEKATECH EA 3000** (Wegberg, Germany) elemental analyzer and the **Callidus** software.

Infrared spectra were recorded at room temperature with a FTIR spectrometer **TENSOR 27** (Bruker, Karsruhe, Germany) equipped with an ATR_IR accessory (**HARRICK, MVP Star^{TM}**) with a diamond as the ATR crystal operating in the region 4000–400 cm^{-1}.

Raman spectra were recorded at room temperature with a **Bruker EQUINOX 55** FT Raman spectrometer using the 9394.8 cm^{-1} exciting line (500 mW) of an Nd: YAG laser. Solid samples were placed in melting point capillaries and used for recording spectra in the region 3000–50 cm^{-1} with a resolution of 2 cm^{-1}. For each spectrum, 32–500 scans were added.

The **Schmelzpunkt SMP 10 – STUART** apparatus was used for visual determinations of the melting point in glass capillaries (Ø 2 mm).

X-ray Crystal Structure Determination

(a) Crystal Growth and Crystal Mounting. Single crystals of $(C_2F_5)_2P(O)NH_2$ were obtained by recrystallization from a mixture of benzene and hexane (1:2). Suitable crystals were selected under the microscope and mounted.

(b) Collection and Reduction of X-Ray Data. Crystals were mounted on an Oxford Diffraction Gemini E Ultra diffractometer, equipped with a 2K × 2K EOS CCD area detector, a four-circle κ goniometer, an Oxford Instruments cryojet, and sealed-tube enhanced (Mo) and enhanced ultra (Cu) sources. For data collection, the Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) was used. The diffractometer was controlled by *CrysAlisPro* Graphical User Interface software.[17] The diffraction data collection strategy was optimized with respect to complete coverage and consisted of 10 ω scans with a width of 1°, respectively. The data collection was carried out at 150 K, in a 1024 × 1024 pixel mode using 2 × 2 pixel binning. Processing of the raw data, scaling of the diffraction data, and application of an empirical absorption correction was completed by using the *CrysAlisPro* program.[17]

(c) Solution and Refinement of the Structure. The solution of the structure was performed by direct methods, which located the positions of all atoms. The final refinement was obtained by introducing anisotropic thermal parameters and the recommended weightings for all atoms. All calculations were performed using the *WinGX v1.64.05* package program for structure determination, solution refinement, and molecular graphics.[18–21]

Crystallographic data for $(C_2F_5)_2P(O)NH_2$ (**1c**, CCDC 876561) were deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on www.ccdc.cam.ac.uk/data_request/cif Fax: (+44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

Synthesis of Amides and Hydrazides

Bis(pentafluoroethyl)phosphinyl Amide, $(C_2F_5)_2P(O)NH_2$ (1c). 35.9 g (0.089 mol) of $(C_2F_5)_3PO$ was placed in a 250 mL round bottom flask, equipped with a cooler condenser (dry ice/ethanol), magnetic stirring bar, gas dispersion tube and a thermometer. Excess of ammonia gas was bubbled through $(C_2F_5)_3PO$ for about 20 min. The reaction mixture was kept at temperatures between −35 and −30°C using an ethanol bath. The reaction end was visually estimated when the resulting white product was formed. To complete the reaction, the mixture was kept at −30°C for 10 min and then all volatile products were removed in vacuum (10^{-3} mbar). 23.1 g of a white solid was obtained. Yield 86%; mp: 98°C. ^{1}H NMR (CD_3CN): $\delta = 5.29$ (br s, NH_2). ^{19}F NMR (CD_3CN): $\delta = -81.1$ (s, 6F, CF_3), −124.9 (m, 2F, CF_a), −127.7 (m, 2F, CF_b), $^2J_{PFa} = 78.3$ Hz, $^2J_{PFb} = 83.6$ Hz, $^2J_{FaFb} = 338.6$ Hz. ^{31}P NMR (CD_3CN): $\delta = 12.9$ (quint of m, $^2J_{PF} = 81.2$ Hz). IR (cm^{-1}): 3344 (w); 3222 (m); 3087 (m); 2884 (w); 1313 (m); 1290 (m); 1259 (vs); 1209 (vs); 1149 (vs); 1127 (s); 1092 (s); 1068 (m); 1020 (w); 994 (s); 971 (m); 948 (m); 756 (m); 751 (m); 689 (vw); 669(m); 637 (m); 619 (w); 602(s); 575 (s); 563 (m); 548 (m); 521 (s); 513 (s); 489(s); 468 (s); 434 (m); 426 (m). Raman (cm^{-1}): 1333(10); 1292 (4); 1266 (15); 1231 (10); 1140 (5);1071(4); 1020 (5); 952 (5); 754 (100); 641 (26); 596 (10); 545 (5); 471 (6); 370 (16); 327 (10); 284 (10); and 151 (30).

Bis(pentafluoroethyl)phosphinyl N–(benzyl)amide, $(C_2F_5)_2P(O)NHCH_2C_6H_5$ (2c). A 10 mL flask, equipped with a magnetic stirring bar, septum and drying tube filled with Sicapent®, was charged under nitrogen with $(C_2F_5)_3PO$ (3.22 g, 7.9 mmol). The benzyl amine (0.85 g, 7.9 mmol) was slowly added under good stirring at 0°C. The reaction is exothermic and was let to warm up at room temperature to liberate C_2F_5H. The flask was connected to the membrane vacuum for 5 min to remove not reacted $(C_2F_5)_3PO$. The resultant solid was solved in benzene and transferred to a separator funnel and washed three times with water. The solvent was distilled off under reduced pressure (< 0.05 mbar). After drying under vacuum, 2.76 g of white solid material was obtained. Yield: 89%; mp: 94°C. ^{1}H NMR (CD_3CN): δ = 7.39–7.29 (m, 5H, CH); 5.68 (br d, $^2J_{PH}$ = 20.3 Hz, 1H, NH), 4.31 (dd, $^2J_{PH}$ = 11.6 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2). ^{19}F NMR (CD_3CN): δ = −81.0 (m, 6F, CF_3), −124.5 (dd of m, 2F, CF_a), −126.6 (dd of m, 2F, CF_b), $^2J_{PFa}$ = 79.2 Hz, $^2J_{PFb}$ = 86.0 Hz, $^2J_{FaFb}$ = 317.7 Hz. ^{31}P NMR (CD_3CN): δ = 12.6 (ttdt, $^2J_{PH}$ = 17.9 Hz, $^3J_{PH}$ = 10.6 Hz, $^2J_{PFa}$ = 79.8 Hz, $^2J_{PFb}$ = 82.4 Hz. For $C_{11}H_8NF_{10}OP$ Calcd: C 33.78; H 2.06; N 3.58; Found C 33.92; H 2.03; N 4.14%.

Bis(pentafluoroethyl)phosphinyl N–(2–phenylethyl)amide, $(C_2F_5)_2P(O)NHCH_2CH_2C_6H_5$ (3c). Under an inert atmosphere of nitrogen 2.29 g (17.7 mmol) of 2–phenylethyl amine was added slowly to $(C_2F_5)_3PO$ (7.15 g, 17.7 mmol) at 0°C with good stirring. During this time, the reaction mixture turned into a white solid. Then the same procedure was followed as that described above. 6.12 g of white solid was obtained. Yield: 84%; mp: 110°C. ^{1}H NMR (CD_3CN): δ = 7.34–7.26 (m, 5H, CH), 5.26 (br d, $^2J_{PH}$ = 20.3 Hz, 1H, NH); 3.37 (m, 2H, CH_2), 2.84 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2). ^{19}F NMR (CD_3CN): δ = −81.1 (m, 6F, CF_3), −124.6 (m, 2F, CF_a), −126.6 (m, 2F, CF_b), $^2J_{PFa}$ = 76.6 Hz; $^2J_{PFb}$ = 84.7 Hz, $^2J_{FaFb}$ = 319.9 Hz. ^{31}P NMR (CD_3CN): δ = 11.2 (quint of m, $^2J_{PF}$ = 82.5 Hz).

Bis(pentafluoroethyl)phosphinyl N–(4–methylbenzyl)amide, $(C_2F_5)_2P(O)NHCH_2C_6H_4CH_3$ (4c). 4-$CH_3C_6H_4CH_2NH_2$ (0.68 g, 5.96 mmol) was added carefully by means of syringe to $(C_2F_5)_3P(O)$ (2 g, 5.96 mmol) and the resulting homogeneous solution was stirred for 4 h at room temperature. The white precipitate formed was filtered off and washed with water. Then the same procedure was followed as that described above. Yield: 62%; mp: 102°C. ^{1}H-NMR (CD_3CN): δ = 7.25–7.35 (m, 4H, CH), 5.66 (br d, $^2J_{PH}$ = 19.8 Hz, 1H, NH), 4.25 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 10.6 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3). ^{19}F NMR (CD_3CN): δ = −81.1 (m, 6F, CF_3), −124.5 (m, 2F, CF_a), −126.6 (m, 2F, CF_b); $^2J_{PFa}$ = 78.0 Hz, $^2J_{PFb}$ = 83.7 Hz, $^2J_{FaFb}$ = 318.4 Hz. ^{31}P NMR (CD_3CN): δ = 12.7 (quint of m, $^2J_{PF}$ = 81.2 Hz). For $C_{12}H_{10}NF_{10}OP$: Calcd: C 35.57; H 2.49; N 3.46; Found: C 35.84; H 2.56; N 3.43%.

Bis(pentafluoroethyl)phosphinyl N–(4–methoxybenzyl)amide, $(C_2F_5)_2P(O)NHCH_2C_6H_4OCH_3$ (5c). 4-CH_3O-$C_6H_4CH_2NH_2$ (2.4 g, 5.96 mmol) was added carefully by means of a syringe to $(C_2F_5)_3P(O)$ (0.68 g, 5.96 mmol) cooled in a two-necked flask equipped with a standard assembly *via* an ice/water-bath. The reaction was very violent and a solid white product was formed. The resulting solid was filtered off, was dissolved in benzene, the mixture was transferred to a separator funnel and washed three times with water. The solvent was distilled off and remaining product was dried under vacuum (< 0.05 mbar). 1.8 g of a white solid material was obtained. Yield: 72%; mp: 90°C. ^{1}H-NMR (CD_3CN): δ = 7.23 (m, 2H, CH), 6.90 (m, 2H, CH), 5.61 (br d, $^2J_{PH}$ = 20.7 Hz, 1H, NH), 4.24 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 10.4 Hz, 2H, CH_2), 3.76 (s, 3H, CH_3). ^{19}F NMR (CD_3CN): δ = −81.1 (m, 6F, CF_3), −124.6 (m, 2F, CF_a), −126.6 (m, 2F, CF_b), $^2J_{PFa}$ =

78.7 Hz, $^2J_{PFb}$ = 79.7 Hz, $^2J_{FaFb}$ = 320.4 Hz. ^{31}P NMR (CD_3CN): δ = 12.5 (quint of m, $^2J_{PF}$ = 81.0 Hz). For $C_{12}H_{10}NF_{10}O_2P$: Calcd: C 34.22; H 2.39; N 3.33; Found: C 34.46; H 2.11; N 3.67%.

Bis(pentafluoroethyl)phosphinyl N–phenylamide, $(C_2F_5)_2P(O)NHC_6H_5$ (6c). The method was essentially the same as that outlined (described) above. $C_6H_5NH_2$ (0.23 g, 2.48 mmol) was added carefully *via* syringe to $(C_2F_5)_3P(O)$ (1 g, 2.48 mmol), the resulting homogeneous solution was stirred for 23 h at room temperature when a white precipitate was formed. Filtration, washing with water and drying in vacuum ($<10^{-2}$ mbar) gave 0.12 g of **6c**. Yield: 13%; mp: 141°C. ^{1}H-NMR (CD_3CN): δ = 7.5 (br d, $^2J_{PH}$ = 17.8 Hz, 1H, NH), 7.38–7.20 (m, 5H, CH). ^{19}F NMR (CD_3CN): δ = −81.0 (m, 6F, CF_3), −123.6 (m, 2F, CF_a), −126.3 (m, 2F, CF_b), $^2J_{PFa}$ = 77.8 Hz, $^2J_{PFb}$ = 85.4 Hz, $^2J_{FaFb}$ = 337.9 Hz. ^{31}P NMR (CD_3CN): δ = 8.6 (tt, $^2J_{PFa}$ = 79.8 Hz, $^2J_{PFb}$ = 82.4 Hz).

For $C_{10}H_6NF_{10}OP$: Calcd: C 31.85; H 1.60; N 3.71; Found: C 32.35; H 1.72; N 3.98%.

Bis(pentafluoroethyl)phosphinyl N–(4–methylphenyl)amide, $(C_2F_5)_2P(O)NHC_6H_4CH_3$ (7c). A solution of *p*-methylphenylamine (0.29 g, 2.73 mmol) in 10 mL benzene was added to $(C_2F_5)_3P(O)$ (1.1 g, 2.73 mmol) and the resultant mixture was stirred at room temperature for 12 h to form a white precipitate. The solid product was filtered off and washed with water. $(C_2F_5)_2P(O)NHC_6H_4CH_3$, **7c**, was obtained in 76% isolated yield; mp: 150°C. ^{1}H-NMR (CD_2Cl_2): δ = 7.15 (m, 4H, CH), 5.92 (br d, $^2J_{PH}$ = 17.3 Hz, 1H, NH), 2.31 (s, 3H, CH_3). ^{19}F NMR (CD_2Cl_2): δ = −80.4 (m, 6F, CF_3), −122.7 (m, 2F, CF_a), −125.6 (m, 2F, CF_b), $^2J_{PFa}$ = 76.2 Hz, $^2J_{PFb}$ = 93.9 Hz, $^2J_{FaFb}$ = 318.3 Hz. ^{31}P NMR (CD_2Cl_2): δ = 7.8 (tt, $^2J_{PFa}$ = 79.5 Hz, $^2J_{PFb}$ = 86.1 Hz). For $C_{11}H_{10}NF_{10}OP$: Calcd: C 33.78; H 2.06; N 3.58; Found: C 33.94; H 1.85; N 3.69%.

Bis(pentafluoroethyl)phosphinyl N–(n–butyl)amide, $(C_2F_5)_2P(O)NHC_4H_9$ (8c). *n*-$C_4H_9NH_2$ (0.18 g, 2.48 mmol) was added drop-wise by means of a syringe, carefully, to $(C_2F_5)_3P(O)$ (1 g, 2.48 mmol), cooled in a two-necked flask equipped with a standard assembly *via* an ice/water-bath. The reaction was very violent. The resulting mixture was stirred at room temperature for 1 h when a solid white product was formed. The solid was dissolved in benzene and the mixture was transferred to a separator funnel and washed with water. The solvent was distilled off under reduced pressure yielding 0.66 g (75%) of a white compound (**8c**); mp: 210°C. ^{1}H-NMR (CD_3CN): δ = 5.15 (br d, $^2J_{PH}$ = 16.7 Hz, 1H, NH); 3.13 m (CH_2); 1.52 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 0.89 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3). ^{19}F NMR (CD_3CN): δ = −81.2 (m, 6F, CF_3), −124.8 (m, 2F, CF_a), −126.8 (m, 2F, CF_b), $^2J_{PFa}$ = 79.7 Hz, $^2J_{PFb}$ = 82.3 Hz, $^2J_{FaFb}$ = 321.8 Hz. ^{31}P NMR (CD_3CN): δ = 12.5 (quint of m, $^2J_{PF}$ = 80.5 Hz. For $C_8H_{10}NF_{10}OP$: Calcd: C 26.91; H 2.82; N 3.92; Found: C 26.79; H 2.81; N 3.91%.

Bis(pentafluoroethyl)phosphinyl N–(2–ethylhexyl)amide, $(C_2F_5)_2P(O)NHCH_2CH(C_2H_5)(CH_2)_3CH_3$ (9c). The same procedure as described above was applied. 2–Ethylhexyl amine (2.19 g, 16.9 mmol) was added slowly to $(C_2F_5)_3PO$ (6.8 g, 16.9 mmol) at 0°C with good stirring. The product **9c** was obtained as a white solid (glue) (6.45 g). Yield: 92%; mp: 76°C. ^{1}H NMR (CD_3CN): δ = 5.08 (br d, $^2J_{PH}$ = 19.8 Hz, 1H, NH), 3.05 (td, $^3J_{PH}$ = 9.6 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, CH), 1.35 (m, 10H, CH_2), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 0.85 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3). ^{19}F NMR (CD_3CN): δ = −81.1 (m, 6F, CF_3), −124.6 (m, 2F, CF_a), −126.5 (m, 2F, CF_b), $^2J_{PFa}$ = 78.3 Hz, $^2J_{PFb}$ = 82.7 Hz, $^2J_{FaFb}$ = 322 Hz. ^{31}P NMR (CD_3CN): δ = 11.2 (dtt, $^2J_{PH}$ = 20.4 Hz, $^3J_{PH}$ = 9.8 Hz, $^2J_{PF}$ = 80.6 Hz).

Bis(pentafluoroethyl)phosphinyl N–(methyl)hydrazide, $(C_2F_5)_2P(O)NHNHCH_3$ (1d). A dry 25 mL flask, equipped with a glass valve with PTFE piston (Young), was charged in a vacuum line with 0.10 g (2.1 mmol) of methylhydrazine, 1 mL of dry acetonitrile, and 1.3 g (3.2 mmol) of $(C_2F_5)_3PO$. The reaction mixture was left stirring at room temperature for 16 h and then all volatile products were removed under vacuum (10^{-3} mbar). 0.58 g of a white solid product was obtained. Compound **1d** was handled in a dry–box for NMR and melting point measuring. Yield: 84%; mp: 72°C. ^{1}H NMR (CD_3CN): $\delta = 6.75$ (br d, $^2J_{PH} = 39.2$ Hz, 1H NH), 4.12 (br s, 1H, NH), 2.57 (s, 3H, CH_3). ^{19}F NMR (CD_3CN): $\delta = -81.4$ (m, 6F, CF_3), -122.4 (m, 2F, CF_a), -124.6 (m, 2F, CF_b), $^2J_{PFa} = 70.1$ Hz, $^2J_{PFb} = 82.0$ Hz, $^2J_{FaFb} = 321.8$ Hz. ^{31}P NMR (CD_3CN): $\delta = 8.9$ (quint of d, $^2J_{PF} = 76.8$ Hz, $^2J_{PH} = 40.9$ Hz). For $C_5H_5N_2F_{10}OP$: Calcd: C 18.19; H 1.53; N 8.49; Found: C 17.93; H 1.94; N 9.28%.

Bis(pentafluoroethyl)phosphinyl N–(phenyl)hydrazide, $(C_2F_5)_2P(O)NHNHC_6H_5$ (2d). Method A: A dry 25 mL flask, equipped with a glass valve with PTFE piston (Young), was charged in a vacuum line with 0.47 g (4.3 mmol) of phenylhydrazine, 1 mL of dry acetonitrile, and 1.9 g (4.7 mmol) of $(C_2F_5)_3P(O)$. After 1 h stirring at room temperature a homogeneous solution was formed. To complete the reaction, the mixture was left stirring at room temperature for 20 h and then all volatile products were removed under vacuum (10^{-3} mbar). The resulting slightly yellow solid material (1.37 g) was purified by sublimation in high vacuum at 82°C. Yield: 81%; mp: 88 °C. ^{1}H NMR (CD_3CN)**:** $\delta = 7.46$ (br d, $^2J_{PH} = 44.2$ Hz, 1H, NH), 7.24–7.31 (m, 2H, arom-H), 7.00–6.92 (m, 3H, arom-H), 6.47 (d, $^3J_{PH} = 4.0$ Hz, 1H, NH). ^{19}F NMR (CD_3CN): $\delta = -81.2$ (m, 6F, CF_3), -121.9 (m, 2F, CF_a), -124.6 (m, 2F, CF_b), $^2J_{PFa} = 73.9$ Hz, $^2J_{PFb} = 82.8$ Hz, $^2J_{FaFb} = 338.2$ Hz. ^{31}P NMR (CD_3CN): $\delta = 8.9$ (ddtt, $^2J_{PH} = 44.2$ Hz, $^3J_{PH} = 4.3$ Hz, $^2J_{PFa} = 78.4$ Hz, $^2J_{PFb} = 82.4$ Hz). For $C_{10}H_7N_2F_{10}OP$: Calcd: C 30.63; H 1.80; N 7.14; Found: C 30.76; H 2.13; N 7.47%.

Method B: A dry 25 mL flask, equipped with a glass valve with PTFE piston (Young), was charged with 0.15 g of CaH_2, 0.34 g (3.1 mmol) of phenylhydrazine and 1 mL of dry acetonitrile. At a vacuum line 1.5 g (4.6 mmol) of $(C_2F_5)_2P(O)Cl$ were condensed to the reaction mixture. After warming up to room temperature, the reaction mixture was left stirring for 20 h, filtered and washed with dry acetonitrile. Subsequently all volatile materials were removed under vacuum (10^{-3} mbar). The resulting yellow crystalline solid product (0.94 g) was handled only in a dry–box. Yield: 77%; mp: 88°C.

Bis(pentafluoroethyl)phosphinyl N,N–di(methyl)hydrazide, $(C_2F_5)_2P(O)NHN(CH_3)_2$ (3d). A dry 25 mL flask, equipped with a glass valve with PTFE piston (Young), was charged at a vacuum line with 0.23 g (3.8 mmol) of 1,1–dimethylhydrazine, 1 mL of dry acetonitrile and 1.78 g (4.4 mmol) of $(C_2F_5)_3P(O)$. The exothermic reaction started at room temperature and the reaction mixture became homogeneous. The reaction mixture was left stirring at room temperature for 15 h and then all volatile materials were removed under vacuum (10^{-3} mbar). The white solid product (1.45 g) was handled only in a dry–box. Yield: 82%; mp: 71°C. ^{1}H NMR (CD_3CN): $\delta = 6.90$ (br d, $^2J_{PH} = 41.6$ Hz, 1H, NH), 2.90 (s, 6H, CH_3). ^{19}F NMR (CD_3CN): $\delta = -81.2$ (m, 6F, CF_3), -121.4 (m, 2F, CF_a), -124.9 (m 2F, CF_b), $^2J_{PFa} = 71.7$ Hz, $^2J_{PFb} = 82.4$ Hz, $^2J_{FaFb} = 337.2$ Hz. ^{31}P NMR (CD_3CN): $\delta = 6.5$ (dtt, $^2J_{PH} = 41.4$ Hz, $^2J_{PFa} = 75.5$ Hz, $^2J_{PFb} = 81.3$ Hz). For $C_6H_7N_2F_{10}OP$: Calcd: C 20.94; H 2.05; N 8.14; Found: C 21.25; H 2.58; N 8.87%.

Bis(pentafluoroethyl)phosphinyl N–[3,5–di(t–butyl)–4–hydroxybenzyl]-hydrazi-de, $(C_2F_5)_2P(O)NHNHCH_2[3,5–(t–C_4H_9)_2–C_6H_2–4–OH]$ (4d)

A dry 25 mL flask, equipped with a glass valve with PTFE piston (Young), was charged with 0.80 g (3.2 mmol) of 3,5–di(*t*–butyl)–4–hydroxyphenyl hydrazine and then at a vacuum line with 1 mL of dry acetonitrile and 1.5 g (3.7 mmol) of $(C_2F_5)_3P(O)$ at 0°C. After stirring for 30 min at room temperature a homogeneous solution is formed. To complete the reaction, the mixture was left stirring at room temperature for 21 h and then all volatile products were removed under vacuum (10^{-3} mbar). The white solid product (1.5 g) was handled only in a dry–box. Yield: 88%; mp: 106–108°C. ^{1}H NMR (CD_3CN): $\delta = 7.09$ (s, 2H, CH), 6.69 (br d, $^2J_{PH} = 39.6$ Hz, 1H NH), 5.41 (s, 1H, NH), 4.38 (br s, 1H, OH), 3.82 (s, 2H, CH_2), 1.38 (br s, 3H, CH_3). ^{19}F NMR (CD_3CN): $\delta = -81.2$ (m, 6F, CF_3), −121.9 (m, 2F, CF_a), −124.3 (m, 2F, CF_b), $^2J_{PFa} = 73.6$ Hz, $^2J_{PFb} = 88.2$ Hz, $^2J_{FaFb} = 320.4$ Hz. ^{31}P NMR (CD_3CN): $\delta = 9.2$ (quint of d, $^2J_{PF} = 76.0$ Hz, $^2J_{PH} = 39.3$ Hz). For $C_{18}H_{23}N_2F_{10}O_2P$: Calcd: C 41.55; H 4.46; N 5.38; Found: C 38.99; H 4.45; N 6.34%.

CONCLUSION

The reactions of bis(pentafluoroethyl)phosphinyl chloride or tris(pentafluoroethyl)-phosphine oxide with primary amines or hydrazines result in the formation of the corresponding bis(pentafluoroethyl)phosphinyl amides or hydrazides in good yields.

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