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Short communication

Nucleophilic activation of a nitrile group: Synthesis of trifluoromethyl substituted 4H-1,3,5-dioxazines

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ABSTRACT

The negatively charged carbon atom of phosphorus ylides is capable of increasing the nucleophilicity of the triple CN bond. The nitrile group activated in this way can add two equivalents of hexafluoroacetone with the formation of trifluoromethyl substituted 4H-1,2,3-dioxazines. Due to delocalization of the ylidic negative charge one of the C–C bonds acquires a double bond character, the consequence of which is the existence of E/Z-isomerism in these compounds.

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1. Introduction

Due to high energy of the triple C≡N bond (224 kcal/mol) the nitrile group is chemically rather stable. On the other hand, there are several examples of nitriles X-CN (where X = NR_2, SR, SeR, PR_2, Cl) which display the increased nucleophilicity and can add two equivalents of hexafluoroacetone (HFA) to the CN group with the formation of 4H-1,3,5-dioxazines (Scheme 1) [1].

As the cyanide anion itself $(CN)^-$ does not react with HFA in this way [2], one can conclude, that the conjugation of the electrons of the substituents with CN triple bond is the necessary condition for such reactions.

2. Results and discussion

We have found that the negatively charged carbon atom of phosphorus ylides is also capable of increasing the nucleophilicity of the triple CN bond. For example, CN group in ylides **3** easily adds two equivalents of HFA with the formation of appropriate 4H-1,2,3-dioxazines **4a–c** (Scheme 2). The reactions proceed almost quantitatively to give NMR spectroscopically rather pure products, which can also be isolated in crystalline form. The molecular structure of dioxazine **4a** containing dimethylamino groups at the phosphorus atom has been investigated by X-ray analysis (Fig. 1). A peculiarity of this molecule is the structure of the PCCN fragment, which is absolutely coplanar. Both carbon atoms in this fragment C7-C11 also have ideal flat geometry, and the bond length between them is only 1.396 Å. This value is abnormally short for a single C–C bond and it is comparable with the length of a double C=C bond. This testifies to the considerable level of conjugation between the p_n orbital of the ylidic carbon atom and the π-system of the C=N double bond as well as to the delocalization of the ylidic negative charge. Apparently the delocalization is promoted by the electronegative atoms and groups forming the six-member ring and stabilizing the zwitterionic structure (Scheme 3). Because of the double bond character of the C7–C11 bond, compound **4a** can be represented by E- and Z-isomers. According to the X-ray data the crystal lattice of this compound consists of only E-isomers. E- and Z-isomers are well distinguishable in the NMR spectra. Since all NMR data show the presence in the reaction solution of only one compound, one can conclude that the interaction of HFA with the nitrile group of ylide **3a** proceeds stereoselectively with the formation of E-isomer.

Unlike the abovementioned example the reactions of ylides **3b** and **3c** with HFA are not stereoselective and result in the formation of a mixture of E- and Z-isomers (Scheme 3). This is probably accounted for by lower degree of double bond character between the two carbon atoms in the PCCN chain and consequently by lower energetic barrier separating the isomers. The NMR data of E-isomers in compounds **4a–c** are similar which allows clear assignment. In solution there is a dynamic equilibrium between the isomers. For instance, the E/Z ratio in chloroform for **3b** and **3c** is 2:1 and 4:1, respectively. The position of the equilibrium depends also on the solvent used. It is interesting that

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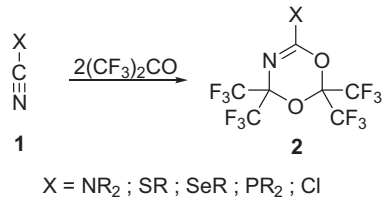
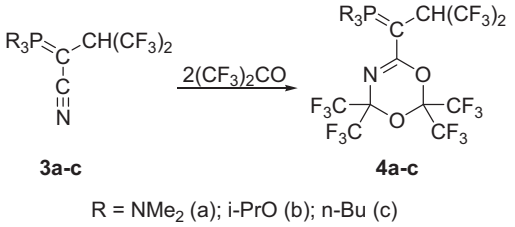


Scheme 1.



Scheme 2.

in the solid phase after crystallization only the E-isomer is present, which in 15–20 min after dissolution comes again to the equilibrium with Z-isomer.

Analogously to the examples described earlier, dioxazines **4a–c** slowly eliminate one equivalent of HFA even in solution [1a]. This process accelerates in the presence of water. We have studied the hydrolysis of dioxazines **4b** and **4c**. In both cases the process is slow and includes the successive formation of acylimines **5b–c** and amides **6b–c** during several days at 25 °C. The intermediate compounds **5b–c** cannot be isolated under these reaction conditions, but they are detectable in the ^{31}P NMR and in the mass spectra. For example, **5c** in the reaction mixture showed M+1 signal at 558.2 (APCI). Unlike iso-propoxy compound **6b** which is stable, the butyl-substituted derivative **6c** is capable of further hydrolyses with the cleavage of the PC bond to give tributylphosphine oxide **7** and amidoalcohol **8**. As the rates of all these stages are approximately equal, the reaction mixture before completion

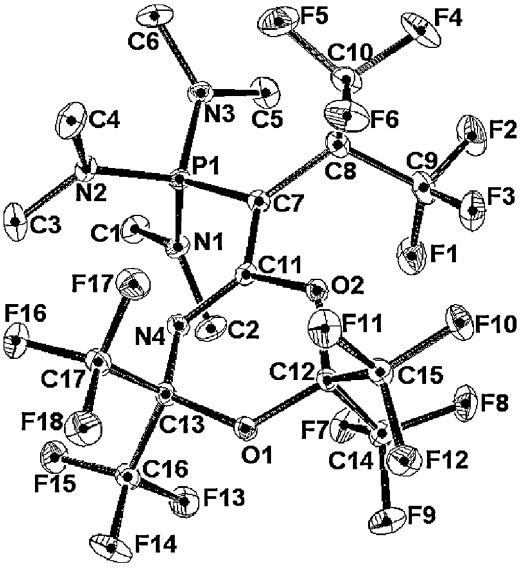
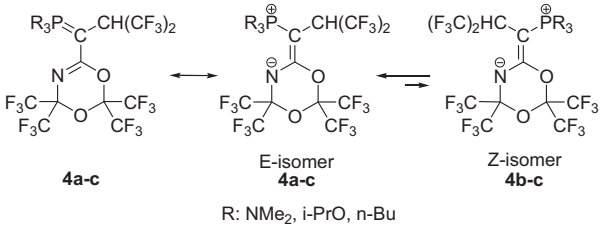
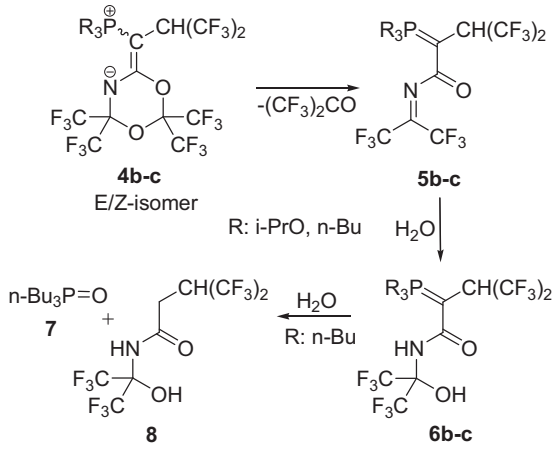


Fig. 1. Ortep drawing of **4a** (ellipsoids are drawn at the 30% probability level, bonds to H atoms are missed for clarity). Selected bond lengths [Å] and angles [°]: C7–C11 1.397, C7–P1 1.747, C11–N4 1.295, C7–C8 1.512, C11–O2 1.399, C12–O2 1.392, C12–O1 1.398; C8–C7–P1 118.8, C11–C7–P1 117.0, C11–C7–C8 124.1, C7–C11–O2 113.6, N4–C11–C7 125.4, N4–C13–O1 117.9, O2–C12–O1 115.8, O2–C11–C7–C8 0.56, N4–C11–C7–P1 0.82.



Scheme 3.



Scheme 4.

of the hydrolysis contains a mixture of these intermediate compounds in different proportions (Scheme 4).

3. Conclusions

The negatively charged carbon atom of phosphorus ylides activates the nucleophilicity of the adjacent nitrile group. Such nitriles can add two equivalents of hexafluoroacetone to the CN triple bond to give trifluoromethyl substituted 4H-1,3,5-dioxazines. Because of delocalization of the negative charge one formally single C–C bond acquires a double bond character and such compounds can exist as E- and Z-isomers. Depending on the substituents at phosphorus atom this reaction can go stereoselectively with the formation of only one isomer.

4. Experimental

All operations were performed under nitrogen in a dry box. Solvents were dried and purified according to common procedures. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with Varian Gemini 400 MHz, Bruker Avance 400 and JEOL FX-90Q spectrometers. The δ ^{1}H and δ ^{13}C chemical shifts are referenced to tetramethylsilane (TMS), the δ ^{31}P values were measured relative to 85% aqueous H_3PO_4 and the δ ^{19}F chemical shifts are given relative to CCl_3F.

4.1. Ylides 3a–c: common procedure

A solution of $(CF_3)_2C{=}C(H)CN$ (1.05 equiv.) in hexane (1 mL) was added to a solution of the corresponding phosphorus compound [$(Me_2N)_3P$, $(i\text{-}PrO)_3P$, $(n\text{-}Bu)_3P$] (0.5 mmol) in hexane (1 mL) at room temperature. The reaction completed in 20 min for **3a**, **c** and in ca. 1 week (^{31}P NMR control) for **3b**. The products crystallized from the reaction mixture during 2 days at −16 °C.

4.1.1. 4,4,4-Trifluoro-3-(trifluoromethyl)-2-[tris(dimethylamino)phosphoranylidene]-butanenitrile (3a)

White solid (148.5 mg, 84.3%), mp 184–186 °C. 1H NMR (400 MHz, $CDCl_3$): δ 2.7 (1H, m, $CH(CF_3)_2$), 2.7 (18H, d, J = 9.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 11.0 (1C, dm, J = 232 Hz, P=*C*), 37.3 (6C, d, J = 4 Hz, CH_3), 46.4 (1C, dsept, J = 30 Hz, J = 15 Hz, $CH(CF_3)_2$), 123.8 (2C, q, J = 284 Hz, CF_3), 124.9 (1C, d, J = 14 Hz, CN); ^{19}F NMR (84 MHz, $CDCl_3$): δ 67.4 (6F, d, J = 9 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 64.1 (1P, s); APCI-MS m/z: 353.1 $[M+H]^+$.

4.1.2. 4,4,4-Trifluoro-3-(trifluoromethyl)-2-(triisopropoxyphosphoranylidene)butanenitrile (3b)

White needless (196.7 mg, 99%), mp 44–46 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.4 (18H, d, J = 6.3 Hz, CH_3), 3.1 (1H, dsept, J = 15.6 Hz, J = 8.3 Hz, $CH(CF_3)_2$), 4.8 (1H, oct, J = 6.34 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 9.2 (1C, dm, J = 270 Hz, P=*C*), 23.3 (6C, d, J = 5 Hz, CH_3), 46.5 (1C, dsept, J = 30 Hz, J = 11 Hz, $CH(CF_3)_2$), 75.5 (3C, d, J = 6 Hz, CH), 122.0 (1C, d, J = 18 Hz, CN), 123.5 (2C, q, J = 282 Hz, CF_3); ^{19}F NMR (84 MHz, $CDCl_3$): δ −67.8 (6F, d, J = 8 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 46.7 (1P, s); ESI-MS m/z: 398.2 $[M+H]^+$.

4.1.3. 4,4,4-Trifluoro-2-(tributylphosphoranylidene)-3-(trifluoromethyl)butanenitrile (3c)

White needless (160.5 mg, 82%), mp 94–96 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.9 (9H, t, J = 6.8 Hz, CH_3), 1.4–1.6 (12H, m, $(CH_2)_2$), 1.8–1.9 (6H, m, CH_2), 2.9 (1H, dsept, J = 15.6 Hz, J = 6.2 Hz, $CH(CF_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 0.3 (1C, dm, J = 135 Hz, P=*C*), 13.2 (3C, s, CH_3), 22.0 (3C, d, J = 55 Hz, P–C), 23.1 (3C, d, J = 3 Hz, CH_2), 23.7 (3C, d, J = 15 Hz, CH_2), 46.6 (1C, dsept, J = 29 Hz, J = 11 Hz, $CH(CF_3)_2$), 123.6 (2C, q, J = 286 Hz, CF_3), 125.0 (1C, d, J = 13 Hz, CN); ^{19}F NMR (84 MHz, $CDCl_3$): δ −67.4 (6F, d, J = 7 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 30.5 (1P, s); APCI-MS m/z: 392.3 $[M+H]^+$.

4.2. Dioxazines 4a–c: common procedure

Hexafluoroacetone (2.5 equiv.) was condensed in a solution of ylide (0.2 mmol) in $CDCl_3$ (2 mL) in a small autoclave (10 mL). The reaction mixture was heated at 50 °C for 2 h and then left at room temperature for 4 days. As the reaction goes almost quantitatively, $CDCl_3$ was used as a solvent to record the NMR spectra of the reaction solutions. In the case of R = NMe_2 the formation of only E-isomer was observed in the reaction solution. Compounds **4a, 4c** crystallized from the reaction mixture in 3 days at −16 °C. Compound **4b** crystallized from hexane at −16 °C during 3 days. In all cases the solvent could slowly evaporate from the crystallization flask through a needle to provide the slow concentration of the solution during crystallization. In crystalline form the compounds exist as E-isomers.

4.2.1. (E)-2,2,4,4-Tetrakis(trifluoromethyl)-6-{3,3,3-trifluoro-2-(trifluoromethyl)-1-[tris(dimethylamino)phosphoranylidene]-propyl}-4H-1,3,5-dioxazine (4a)

Yellow crystals (63.4 mg, 46.3%), mp 99–101 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.7 (18H, d, J = 9.3 Hz, CH_3), 3.2 (1H, dsept, J = 20.5 Hz, J = 8.8 Hz, $CH(CF_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 37.2 (6 C, d, J = 5 Hz, CH_3), 44.0 (1 C, d, J = 200 Hz, P=*C*), 48.2 (1C, dsept, J = 31 Hz, J = 14 Hz, $CH(CF_3)_2$), 83.8 (1C, m, $C(CF_3)_2$), 90.7 (1C, m, $C(CF_3)_2$), 118.8 (2C, q, J = 290 Hz, CF_3), 120.1 (2C, q, J = 289 Hz, CF_3), 123.8 (2C, q, J = 282 Hz, CF_3), 157.8 (1C, d, J = 25 Hz, C=N); ^{19}F NMR (84 MHz, $CDCl_3$): δ −80.8 (6F, s, CF_3), −79.9 (6F, s, CF_3), −63.9 (6F, br s, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 64.8 (1P, s).

4.2.2. (E)-2,2,4,4-Tetrakis(trifluoromethyl)-6-[3,3,3-trifluoro-2-(trifluoromethyl)-1-(triisopropoxyphosphoranylidene)propyl]-4H-1,3,5-dioxazine (4b)

Colorless crystals (59.1 mg, 40.5%), mp 48–50 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.4 (18H, d, J = 6.4 Hz, CH_3), 3.9 (1H, dsept, J = 20.0 Hz, J = 9.3 Hz, $CH(CF_3)_2$), 4.9 (1H, oct, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 23.2 (6C, d, J = 5 Hz, CH_3), 43.3 (1C, dm, J = 237 Hz, P=*C*), 48.2 (1C, dsept, J = 32 Hz, J = 11 Hz, $CH(CF_3)_2$), 76.1 (3C, d, J = 8 Hz, P–C), 83.4 (1C, m, $C(CF_3)_2$), 91.5 (1C, m, $C(CF_3)_2$), 118.7 (2C, q, J = 290 Hz, CF_3), 120.5 (2C, q, J = 290 Hz, CF_3), 123.3 (2C, q, J = 282 Hz, CF_3), 159.6 (1C, d, J = 18 Hz, C=N); ^{19}F NMR (84 MHz, $CDCl_3$): δ −83.2 (6F, br s, CF_3), −82.5 (6F, br s, CF_3), −67.4 (6F, br s, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): 41.2 (1P, s).

4.2.3. (Z)-2,2,4,4-Tetrakis(trifluoromethyl)-6-[3,3,3-trifluoro-2-(trifluoromethyl)-1-(triisopropoxyphosphoranylidene)propyl]-4H-1,3,5-dioxazine (4b)

^1H NMR (400 MHz, $CDCl_3$): δ 1.4 (18H, d, J = 6.4 Hz, CH_3), 4.4 (1H, dsept, J = 29.3 Hz, J = 9.3 Hz, $CH(CF_3)_2$), 4.8 (1H, oct, J = 6.4 Hz, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 23.0 (6C, d, J = 5 Hz, CH_3), 44.3 (1C, dm, J = 233 Hz, P=*C*), 46.8 (1C, dsept, J = 31 Hz, J = 8 Hz, $CH(CF_3)_2$), 84.3 (1C, m, $C(CF_3)_2$), 90.9 (1C, m, $C(CF_3)_2$), 118.8 (2C, q, J = 290 Hz, CF_3), 120.6 (2C, q, J = 290 Hz, CF_3), 123.4 (2C, q, J = 282 Hz, CF_3), 159.3 (1C, d, J = 18 Hz, C=N); ^{19}F NMR (84 MHz, $CDCl_3$): δ −83.4 (6F, br s, CF_3), −82.1 (6F, br s, CF_3), −66.7 (6F, d, J = 9 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): 39.0 (1P, s).

4.2.4. (E)-2,2,4,4-Tetrakis(trifluoromethyl)-6-[3,3,3-trifluoro-1-(tributylphosphoranylidene)-2-(trifluoromethyl)propyl]-4H-1,3,5-dioxazine (4c)

Colorless crystals (67 mg, 46.3%), mp 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.9 (9H, t, J = 6.8 Hz, CH_3), 1.4–1.5 (12H, m, $(CH_2)_2$), 2.0–2.1 (6H, m, P–CH_2), 2.86 (1H, dsept, J = 16.1 Hz, J = 8.3 Hz, $CH(CF_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 13.1 (3C, s, CH_3), 19.7 (3C, d, J = 56 Hz, P–C), 23.3 (3C, d, J = 4 Hz, CH_2), 23.6 (3C, d, J = 15 Hz, CH_2), 34.0 (1C, d, J = 120 Hz, P=*C*), 47.9 (1C, dsept, J = 31 Hz, J = 10 Hz, $CH(CF_3)_2$), 83.8 (1C, m, $C(CF_3)_2$), 91.1 (1C, m, $C(CF_3)_2$), 118.9 (2C, q, J = 290 Hz, CF_3), 120.2 (2C, q, J = 290 Hz, CF_3), 123.2 (2C, q, J = 282 Hz, CF_3), 158.1 (1C, d, J = 20 Hz, C=N); ^{19}F NMR (84 MHz, $CDCl_3$): δ −80.7 (6F, br s, CF_3), −80.5 (6F, br s, CF_3), −64.3 (6F, br d, J = 8 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 28.9 (1P, s).

4.2.5. (Z)-2,2,4,4-Tetrakis(trifluoromethyl)-6-[3,3,3-trifluoro-1-(tributylphosphoranylidene)-2-(trifluoromethyl)propyl]-4H-1,3,5-dioxazine (4c)

^1H NMR (400 MHz, $CDCl_3$): δ 0.9 (9H, t, J = 7.2 Hz, CH_3), 1.3–1.5 (12H, m, $(CH_2)_2$), 2.1–2.2 (6H, m, P–CH_2), 4.6 (1H, dsept, J = 23.5 Hz, J = 9.8 Hz, $CH(CF_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 13.3 (3C, s, CH_3), 19.5 (3C, d, J = 55 Hz, P–CH_2), 23.5 (3C, d, J = 4 Hz, CH_2), 23.9 (3C, d, J = 14 Hz, CH_2), 36.2 (1C, d, J = 114 Hz, P=*C*), 46.4 (1C, dsept, J = 31 Hz, J = 6 Hz, $CH(CF_3)_2$), 84.4 (1C, m, $C(CF_3)_2$), 90.4 (1C, m, $C(CF_3)_2$), 118.9 (2C, q, J = 290 Hz, CF_3), 120.2 (2C, q, J = 290 Hz, CF_3), 123.2 (2C, q, J = 282 Hz, CF_3), 157.8 (1C, d, J = 18 Hz, C=N); ^{19}F NMR (84 MHz, $CDCl_3$): δ −80.9 (6F, br s, CF_3), −80.3 (6F, br s, CF_3), −64.0 (6F, d, J = 10 Hz, $CH(CF_3)_2$); $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 26.9 (1P, s).

4.3. 4,4,4-Trifluoro-N-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]-3-(trifluoromethyl)-2-(triisopropoxyphosphoran-ylidene)butanamide (6b)

To dioxazine **4b** (E/Z = 2:1) (30 mg, 0.041 mmol) in $CDCl_3$ (0.5 mL) water (0.3 mL) was added. The reaction was conducted at 25 °C in a NMR tube to monitor the hydrolysis. After completion of

the reaction (ca. 24 h) water (1 mL) was additionally added and then separated from the mixture to remove the hexafluoroacetone hydrate. The solvent was evaporated in vacuo to give a light-yellow solid (20 mg, 83.9%); mp 63–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.3 (18H, d, J = 5.9 Hz, CH_3), 3.8 (1H, dsept, J = 22.0 Hz, J = 9.8 Hz, $CH(CF_3)_2$), 4.8 (1H, dsept, J = 8.3 Hz, J = 5.9 Hz, $CH(CH_3)_2$), 5.8 (1H, br s, NH), 11.3 (1H, br s, OH); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 23.3 (6C, d, J = 5 Hz, CH_3), 44.9 (1C, dm, J = 239 Hz, P=*C*), 46.9 (1C, dsept, J = 30 Hz, J = 12 Hz, $CH(CF_3)_2$), 79.0 (3C, d, J = 7 Hz, CH), 84.3 (1C, sept, J = 32 Hz, $C(CF_3)_2$), 121.4 (2C, q, J = 289 Hz, CF_3), 123.8 (2C, q, J = 285 Hz, CF_3), 173.6 (1C, d, J = 17 Hz, C=O); ^{19}F NMR (84 MHz, $CDCl_3$): δ −83.1 (6F, s, CF_3), −64.7 (6F, d, J = 10 Hz, $CH(CF_3)_2$); ^{31}P{^{1}H} NMR (36.2 MHz, $CDCl_3$): 43.0 (1P, s); ESI-MS m/z = 582.0 $[M+H]^+$.

4.4. Hydrolysis of **4c**

To dioxazine **4c** (E/Z = 4:1) (30 mg, 0.041 mmol) in $CDCl_3$ (0.5 mL) water (0.3 mL) was added. The reaction was conducted at 25 °C in a NMR tube to monitor the hydrolysis. After completion of the reaction (ca. 10 d) water (1 mL) was additionally added and then separated from the mixture to remove the hexafluoroacetone hydrate. The NMR and mass-spectroscopic study of the reaction mixture revealed tris(n-butylphosphine)oxide **7** and compound **8**.

4.4.1. 4,4,4-Trifluoro-N-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]-3-(trifluoromethyl)butanamide (8)

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.7 (2H, d, J = 5.9 Hz, CH_2), 3.9 (1H, m, $CH(CF_3)_2$), 5.9 (1H, br, NH), 10.1 (1H, br, OH); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 29.2 (1C, s, CH_2), 44.2 (1C, sept, J = 29 Hz, $CH(CF_3)_2$), 90.4 (1C, sept, J = 33 Hz, $C(CF_3)_2$), 123.0 (2C, q, J = 279 Hz, CF_3), 123.1 (2C, q, J = 279 Hz, CF_3), 174.1 (1C, s, CO); ^{19}F NMR (84 MHz, $CDCl_3$): δ −83.0 (6F, s, CF_3), −68.2 (6F, d, J = 9 Hz, $CH(CF_3)_2$); ESI-MS m/z: 374.0 $[M-H]^-$.

4.5. Crystal data for **4a**

Data were collected on Bruker Smart Apex II Enraf-Nonius CAD4 difractometer. C17H19F18N4O2P, M = 684.33, monoclinic, a = 10.6750(5), b = 16.2543(7), c = 15.3661(7) Å, β = 107.899(2)°, V = 2537.2(2) Å^3, T = 296(2) K, space group P 2(1)/c; Z = 4, μ(Mo-Kα) = 0.266 mm^{-1}, λ = 0.71073 Å, 27184 reflections measured, 5310 unique (R_{int} = 0.0570). Final R indices R_1 = 0.0432, w$R(F^2)$ = 0.0875 (for 3782 reflections with $I/\sigma(I) > 2.0$). The structure was solved by direct methods and refined by full-matrix least-squares on F2 using the SHELX-97-program system [3]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-820011. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033; deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/conts/retrieving.html.

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