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Reactions of Fluorinated Hydroxy and Epoxy Ketones with Tris(trimethylsilyl) Phosphite

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ABSTRACT: *Reacting the fluoroalkyl β-trimethylsiloxy ketones $R^FC(OSiMe_3)CH_2C(:O)R$ ($R^F = CF_3$, R = Ph, $R^F = C_6F_{13}$, R = Me) with tris(trimethylsilyl) phosphite gave a diastereomeric mixture of α,γ-hydroxy phosphonic acids and their derivatives. With a fluorinated β-epoxy ketone and tris(trimethylsilyl) phosphite, corresponding silyl esters and, after hydrolysis, an α-hydroxy-β-epoxy phosphonic acid were obtained as two diastereomers. The molecular structure of the latter compound (triclinic P $\bar{1}$ with a = 579.30(10), b = 1291.8(2), c = 1630.3(2) pm, α = 72.73(1)°, β = 87.97(1)°, γ = 86.33(1)°, Z = 4) was determined, exhibiting two independent molecules with (RRR) configuration and strong intra and intermolecular hydrogen bridges.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:632–637, 1999

INTRODUCTION

Silyl esters of phosphorous acid serve as versatile reagents in organic synthesis because of their high reactivity toward a variety of organic substrates [1], the largest being carbonyl compounds. Tris(trimethylsilyl) phosphite reacts under fairly mild conditions with ketones, which yields 1:1 adducts. The reaction is believed to proceed stepwise by nucleophilic attack of phosphorus at the carbonyl center followed by 1,4-migration of the silyl group, but a one-step concerted mechanism cannot be excluded. In addition to simple aldehydes and ketones, carbonyl compounds bearing other functional groups such as halogen, C=O, and C=C double bonds have also been studied. The objective of the present study was to investigate the interaction between tris(trimethylsilyl) phosphite and ketones that have a hydroxy group, $R^FC(OH)CH_2C(:O)R$, **1a** and **1b**(**1a**, $R^F = CF_3$, R = Ph; **b**, $R^F = C_6F_{13}$, R = Me), and an epoxide ring (**3**) as supplementary functional groups and fluoroalkyl substituents of different chain length that possibly influence the reaction pathway. There is only one article where tris(trimethylsilyl) phosphite deoxygenates simple epoxides at 130 to 150°C giving the respective alkenes [2].

RESULTS AND DISCUSSION

To obtain good yields in a straightforward clean reaction, it was advantageous to silylated the HO group of the hydroxy ketones, **1a** and **1b** (**a**, $R^F = CF_3$, R = Ph; **b**, $R^F = C_6F_{13}$, R = Me) prior to the interaction because tris(trimethylsilyl) phosphite also acts as a silylating agent. When Me_3SiCl/Et_3N, was used, only a poor yield of the silylated product

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Dedicated to Alfred Schmidpeter on the occasion of his 70th birthday.

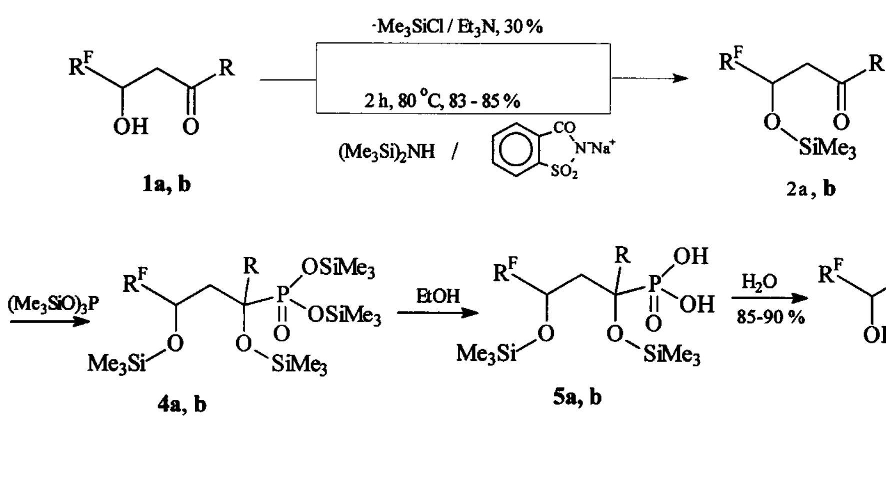
2a was formed, but in the case of hexamethyldisilazane with a catalytic amount of sodium saccharin [3], the silyl ethers **2a** and **2b** were formed in high yield irrespective of the fluoroalkyl chain length (Scheme 1).

When compounds **2a** and **2b** are allowed to react with $(Me_3SiO)_3P$ in equimolar ratio the phosphonates **4a** and **4b** are formed, (Scheme 1). In the case of **2a**, the process proceeds, even at room temperature, for 1 day (3 hours at 80°C); **2b** requires 8 hours at 80°C; **4a** and **4b** were not isolated but characterized by mass spectrometry and ^{31}P NMR spectroscopy. When distilled in vacuo, they decompose substantially into the starting materials found in similar cases [1]. In the mass spectra, the molecular ion has low abundance, but the fragments corresponding to the loss of one CH_3 group are well defined (*m/e* = 573 and 761, respectively). As each of these compounds possess two chiral centers, two pairs of diastereomers are possible. Two singlet signals in the ^{31}P NMR spectrum are observed in the expected region [4] for **4a** (δ = 5.19 and 6.10) and two for **4b** (δ = 7.4 and 7.6), the respective diastereomeric pairs in a 70:30 ratio, which reflects the directing influence of the preferred conformations at the chiral carbon in **2a** and **2b** in the course of the nucleophilic attack of phosphorus at the keto carbon. Hydrolysis of the products confirmed the proposed structure. At the first stage, aqueous ethanol (95%) was added, and the reaction was monitored by ^{31}P NMR spectroscopy. Obviously a two step hydrolysis takes place; the first at phosphorus, which yields two diastereomers of the phosphonic acids **5a** (δ_p = 12.3 and 12.7) and **5b** (δ_p = 16.2 and 16.6). These signals disappear upon addition of a few drops of water, and the second, slower process at the silyl ether leads finally to the α,γ-hydroxy phosphonic acids **6a**, δ_P = 20.1 (**6aA**) and 19.3 (**6aB**), an extremely hygroscopic solid, and **6b**, which is insoluble in water most probably due to the influence of the highly hydrophobic C_6F_{13} group. In both cases, surprisingly, the ratio between diastereomers is 70:30, only slightly altered after purification (Scheme 1).

When the epoxy ketone **3** and tris(trimethylsilyl) phosphite are mixed, a rapid but moderately exothermic reaction proceeds. Judging from the ^{31}P NMR spectrum of the reaction mixture, two isomers **7A** and **7B** were formed similar to the products of 1-benzoyl-2-trifluoromethyl aziridine and the silylated phosphite [5]. Distillation led to thermal decomposition, giving **1a, 3**, and 1,1,1-trifluoro-4-phenyl-but-2-ene-4-one [6]. The structure of **7** was confirmed by ^1H NMR spectroscopy. In the mass spectrum, the molecular ion (*m/e* = 514) is present, as well as a fragment (*m/e* = 499) due to the loss of one methyl group. When two equivalents of the phosphite were applied, no deoxygenation occurred, even at 80°C, which is consistent with a similar case [2]. After addition of ethanol to **7**, two new signals (δ_P = 8.3 and 9.0) are immediately formed with an overall intensity of 64% along with 28% of **7** and 9% of a compound with δ_P = 15.7. A few drops of water gave products with δ_P = 8.3 and 9.0 (**8A, B**, 36%) and two new signals with δ_P = 16.0 and 16.4 (**9A, B**, 59%). After 1 day, only the β-epoxy phosphonic acids 9A:9B = 58:42 were present in the ^{31}P NMR spectrum, isolated in 89% yield.

If the oxirane ring stays intact during the hydrolysis and/or an oxaphospholane is formed, preliminary conclusions can be made from the $^3J_{HH}$ value (1.60 Hz) for vicinal hydrogen nuclei, just as for the starting epoxy ketone **3**. Carbon-phosphorus coupling constant for C-4 atom is 8.67 Hz and differs from 11.7 to 12.3 Hz of a five-membered system [7].

The X-Ray single-crystal structure analysis of the



SCHEME 1

successfully separated **9A** confirms that the retention of the three-membered ring is probably due to the strong electron withdrawing influence of the CF_3 group because epoxide **3** is also resistant to hydrolysis [8]. Two independent molecules **9Aa** and **9Ab**, which have slightly different bond lengths and angles with an (*RRR*) configuration (three chiral centers), were found in the unit cell (Figure 1, Table 1) and show that the substituents are arranged in a distorted tetrahedral coordination at phosphorus with P–O double = bond distances of 150.9(2) (**a**) or P(2)–O(6) 149.0(3) pm (**b**) [9] and angles O(1)–P(1)–C(1) 109.60(15) (**a**) or O(6)–P(1)–C(11) 111.86(16)° (**b**). There is a fairly strong and remarkable asymmetry in intramolecular hydrogen bonding: (P1)O(1)···H–O(3) 256.9 pm, 83.6°; (C1)O(4)–H···O(5) 278.4 pm, 112.9°; (P2)O(7)–H···O(8)H 246.5, 87.7°; (C11)O(9)–H···O(10) 283.8 pm, 105.9°; and intermolecular hydrogen bonding: (P1)O(2)–H···O(6)(P2) 256.9 pm, 167.3°; (P1)O(3)–H···O(6)(P2) 257.2 pm, 146.9°; (P1)O(1)···H–O(7)(P2) 255.8 pm, 155.8°; (P1)O(1)···H–O(8)(P2) 258.6 pm, 157.8°.

EXPERIMENTAL

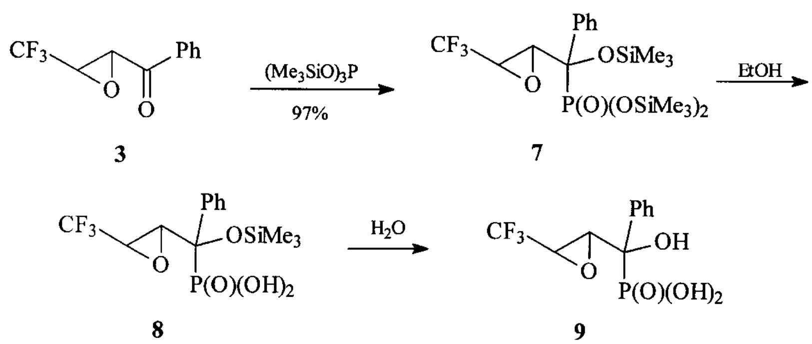
Mass spectra (EI, 70 eV) were performed on a Finnigan MAT 8222 spectrometer as well as FAB measurements glycerol matrix. NMR spectra were obtained on a Bruker AC 80 instrument operating at 75.39 MHz (^{19}F, internal standard CCl_3F), 32.44 MHz (^{31}P, external standard 85% H_3PO_4), and a Bruker DPX-200 spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C (internal standard TMS), 188.31 MHz for ^{19}F, and 81.01 MHz for ^{31}P. IR spectra were recorded on BioRad FT-IR FTS 7-80 Spectrometer in KBr pellets. All reactions and manipulations were conducted under an atmosphere of dry nitrogen. Compound **1a** was synthesized according to [10], and **1b** [2] and **3** were synthesized according to [11].

General Procedure for Silylation of Hydroxy Ketones 1a,b

To a mixture of 25 mmol of **1a** or **1b** and 0.26 g (1.25 mmol) of anhydrous saccharin sodium salt 2.42 g (15 mmol), hexamethyl disilazane were added. The mixture was stirred at 80°C for 2 hours and then distilled at low pressure.

4,4,4-Trifluoro-3-trimethylsiloxy-1-phenylbutan-1-one (2a)

Yield: 6.22 g, 85.6%. Colorless liquid, b.p. 88.5–90°C/0.01 mm. MS (19°C, *m/e*, %): 290 (M^+, <1), 275 (M^+-



SCHEME 2

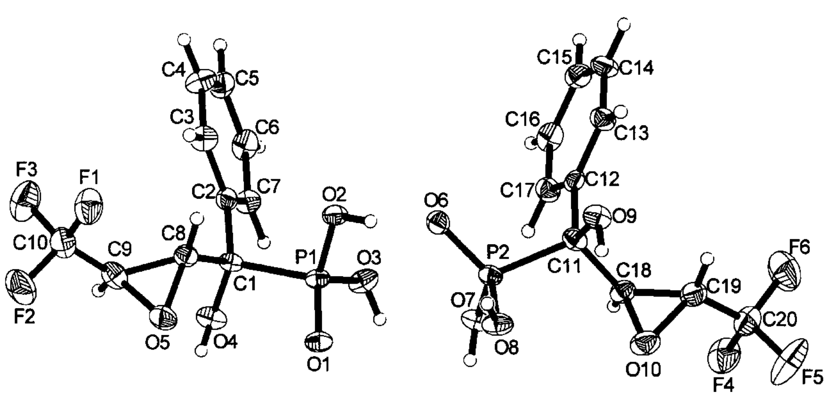


FIGURE 1 Molecular structure of **9A** (two independent molecules **9Aa** and **9Ab**, thermal elipsoids with 50% probability).

TABLE 1 Selected Bond Angles (°) of Compounds **9Aa** and **9Ab**

Bond Length (pm)	**9Aa**		**9Aa**
P(1)–O(1)	150.9(2)	P(2)–O(6)	149.0(3)
P(1)–O(2)	154.2(2)	P(2)–O(7)	154.4(3)
P(1)–C(1)	183.4(4)	P(2)–C(11)	183.5(4)
C(1)–O(4)	142.9(4)	C(11)–O(9)	142.1(4)
C(1)–C(8)	151.9(5)	C(11)–C(18)	152.0(5)
C(8)–O(5)	143.7(4)	C(18)–O(10)	143.6(4)
C(8)–C(9)	146.4(5)	C(18)–C(19)	146.2(5)
C(9)–C(10)	148.0(6)	C(19)–C(20)	148.1(6)
Bond Angles (°)			
O(1)–P(1)–O(3)	114.77(15)	O(6)–P(2)–O(7)	111.96(15)
O(1)–P(1)–O(2)	112.52(15)	O(6)–P(2)–O(8)	114.74(15)
O(2)–P(1)–O(3)	108.39(15)	O(7)–P(2)–O(8)	105.62(15)
O(1)–P(1)–C(1)	109.60(15)	O(6)–P(2)–C(11)	111.86(16)
O(3)–P(1)–C(1)	108.01(16)	O(7)–P(2)–C(11)	106.55(17)
O(2)–P(1)–C(1)	102.80(16)	O(8)–P(2)–C(11)	105.49(16)
C(8)–O(5)–C(9)	61.1(2)	C(18)–O(10)–C(19)	61.2(2)

CH_3, 100), 181 (10), 105 ($PhCO^+$, 47), 77 (Ph^+, 17). ^1H NMR ($CDCl_3$): δ = 0.20 (s, $OSiMe_3$), 3.12 (dd, $C\underline{H}_AH_B$, J_{HH} = 16.73, J_{HH} = 2.34 Hz), 3.56 (dd, CH_AH_B, J_{HH} = 16.73, J_{HH} = 9.32 Hz), 4.84 (m, CF_3CH), 7.49 ÷ 8.03 (m, C_6H_5). ^{19}F NMR ($CDCl_3$: δ = −79.53 (d, $^3J_{HF}$ = 6.65 Hz). Anal. calcd for $C_{13}H_{17}F_3O_2Si$ (290.35): C, 53.78; H, 5.90; F, 19.63. Found: C, 54.06; H, 5.88; F, 20.30.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-4-trimethylsiloxydecan-2-one (2b)

Yield: 9.93 g, 83.0%. Colorless liquid, b.p. 45–47 °C/0.01 mm. MS (36°C, *m/e*, %): 478(M^+, 4), 463(M^+-CH_3, 38), 430(41), 115(25), 77(27), 73(Me_3Si^+, 63), 43(100). ^1H NMR ($CDCl_3$): δ = 0.18 (s, $OSiMe_3$), 2.26 (s, CH_3), 2.78 (dd, $C\underline{H}_AH_B$), 2.94 (dd, $CH_A\underline{H}_B$), 4.87 (m, R^FCH). Anal. calcd for $C_{13}H_{15}F_{13}O_2Si$ (478.32): C, 32.64; H, 3.16; F, 51.63. Found: C, 32.15; H, 3.32; F, 50.40.

4,4,4-Trifluoro-1,3-bis(trimethylsiloxy)-1-phenylbutane bis(trimethylsilyl)phosphonic acid (4aA *and* 4aB)

1.45 g (5 mmol) **2a** and 1.49 g (5 mmol) $(Me_3SiO)_3P$ were heated to 80°C for 3 hours to give **4a**. ^{31}P NMR: δ_P = 6.10 (s, 25%, **4aB**), and 5.19 (s, 75%, **4aA**). MS (*m/e*, %): 573 (M^+ − CH_3), 483 (M^+ − PhCO) and other fragments.

9,9,9,8,8,7,7,6,6,5,5,4,4-Tridecafluoro-1,3-bis(trimethylsiloxy)-1-methylnonane bis(trimethyl-silyl)phosphonic Acid (4bA *and* 4bB)

Similarly to the procedure mentioned, 1.91 g (4 mmol) **2b** and 1.19 g (4 mmol) $(Me_3SiO)_3P$ were reacted at 80°C for 8 hours to give **4b** quantitatively. ^{31}P NMR: δ = 7.6 (s, 9%, **4bA**) and 7.4 (s, 91%, **4bB**). MS (66°C, *m/e*, %): 777 (M^+ + 1), 761 (M^+-CH_3), 705, 689, 73 (Me_3Si^+) and other fragments.

4,4,4-Trifluoro-1,3-bis(trimethylsiloxy)-1-phenylbutane Phosphonic Acid (5a) *and 4,4,4-Trifluoro-1,3-dihydroxy-1-phenylbutane Phosphonic Acid* (6a)

Ethanol (95%, 2 mL) and 1 mL of water was added to 3.12 g (0.53 mmol) **4a** and ^{31}P NMR spectra recorded: δ_P = 20.1 (s, **6aA**) and 19.3 (s, **6aB**) (ca. 25%); 12.7 (s, **5aB**) and 12.3 (s, **5aA**) (ca. 70%). 40 minutes after water addition: δ_P = 20.1 (s, **6aA**, 70%) and 19.3 (s, **6aB**, 30%). Then the mixture was evaporated in vacuo, dissolved in water (10 mL), and filtrated. The filtrate was dried in vacuo, giving **6a** as very hygroscopic solid. Yield: 1.36 g, 85%. MS (148°C, *m/e*, %): 282 (M^+ − H_2O, 17), 281 (M^+-F, 1), 264 (M^+-$2H_2O$, 22), 242 (11), 219 (15), 201 (55), 195 (33), 184 (30), 164 (48), 133 (13), 115 (36), 105 ($PhCO^+$, 94), 103 (24), 99 (42), 77 (Ph^+, 68), 51 (17) and other fragments. ^1H NMR (D_2O): δ = 2.53 + 2.45 (m, CH_2), 4.29 (m, CF_3CH), 7.33 ÷ 7.57 (m, C_6H_5). ^{13}C NMR (D_2O): δ = 35.32 (m, C-2 **6aB**), 36.74 (d, C-2 **6A**, $^2J_{CP}$ = 4.90 Hz), 66.09 (qd, C-3 **6aA**, $^2J_{CP}$ = 31.08, $^3J_{CP}$ = 11.68 Hz), 67.29 (qd, C-3 **6B**, $^2J_{CF}$ = 30.99, $^3J_{CP}$ = 14.22 Hz), 74.68 (d, C-1 **6aA**, $^1J_{CP}$ = 158.61 Hz), 76.04 (d, C-1 **6aB**, $^1J_{CP}$ = 163.38 Hz), 125.09 (q, C-4 **6aB**, $^1J_{CF}$ = 275.56 Hz), 125.51 (q, C-4 **6aA**, $^1J_{CF}$ = 281.35 Hz), 126.30 ÷ 139.26 (m, C_6H_5 **6aA** + **6aB**). ^{19}F NMR (D_2O): δ = −81.09 (d, **6aA**, $^3J_{HF}$ = 7.32 Hz, 80%), −81.29(d, **6aB**, $^3J_{HF}$ = 7.14 Hz, 20%). ^{31}P NMR (D_2O): δ = 21.19 (s, **6aA**, 80%), 21.99 (s, **6aB**, 20%). Precision mass determination for *m/z* = 300: 300.031264 (found), 300.03745 (calcd) (for $C_{10}H_{12}F_3O_5P$).

9,9,9,8,8,7,7,6,6,5,5,4,4-Tridecafluoro-1,3-dihydroxy-1-methylnonanephosphonic acid (6b)

Ethanol (95%, 2 mL) was added into an NMR tube, and the ^{31}P NMR spectrum was recorded. After 1 minute: δ = 7.0 (s, 8%), 8.3 (s, 3%), 16.2 (s) and 16.6 (s, 69%), 23.5 (s, 17%). After 10 minutes: δ = 8.3 (s, 6%), 16.5 (s) and 17.0 (s, 45%), 23.9 (s) and 24.1 (s, 45%). After 40 minutes: δ = 17.0 (4%), 23.4 (s, 26%), 23.9 (s, 56%). The mixture was evaporated to dryness, and a solid residue was washed repeatedly by cold water, dried, washed by $CHCl_3$, and then finally dried, giving **6b** as a white powder. Yield: 1.76 g, 90%. m.p. 144–146°C. MS (152°C, *m/e*, %): 471 (M^+ − OH, 40), 389 (M^+ − $P(O)(OH)_2$, 11), 191 (12), 103 (9), 99 (100). MS FAB: positive *m/e* = 489, negative *m/e* = 487. [1]H NMR (acetone-d_6): δ = 1.60 (d, CH_3 for **6bA**, $^3J_{PH}$ = 15.41 Hz), 1.62 (d, CH_3 for **6bB**, $^3J_{PH}$ = 14.65 Hz), 2.13 ÷ 2.62 (m, CH_2 for **6bA, 6bB**), 4.81 (m, R^FCH for **6bA, 6bB**), 7.11 (4(OH) for **6bA, 6bB**). [31]P NMR (acetone-d_6): δ = 27.72 (s, **6bB**, 38%), 28.24 (s, **6bA**, 62%). Anal. calcd for $C_{10}H_{10}F_{13}O_5P$ (488.14): C, 24.61; H, 2.06; F, 50.60; P, 6.35. Found: C, 24.37; H, 2.13; F, 50.30; P, 6.31.

2,3-Epoxy-4,4,4-trifluoro-1-phenyl-1-trimethylsiloxy-butane bis(trimethylsilyl) phosphonate (**7**)

Ketone **3** (1.08 g, 5 mmol), 1.49 g (5 mmol) of $(Me_3SiO)_3P$, and 1 mL of C_6D_6 were placed into a [31]P NMR tube at room temperature. Moderate heating took place. The reaction was monitored by NMR spectroscopy. After 5 minutes: δ = 0.78 (s, **7A**, 58%), 1.45 (s, **7B**, 42%). [In one experiment, the reaction mixture was vacuum distilled at this stage. The main fraction, boiling in the range of 45 to 60 °C/0.01 mm, [19]F NMR: δ = −65.44 (dd, 1,1,1-trifluoro-4-phenyl-but-2-ene-4-one), −73.6, −74.04 (d, **3**), −79.53 (d, **1a**)]. Evaporation in vacuo gave a colorless, slightly viscous liquid, **7A, B**. Yield 0.75 g, 97%. MS (36°C, *m/e*, %): 514(M^+, 4), 499 (M^+ − CH_3, 15), 299 (37), 298 (72), 289 (M^+ − $P(O)(OSiMe_3)_2$, 28), 225 ($P(O)(OSiMe_3)_2^+$, 10), 211 (29), 147 (100), 146 (46), 131 (13), 105 ($PhCO^+$, 61), 73 (Me_3Si^+, 73). [1]H NMR ($CDCl_3$): −0.04 ÷ 0.35 (m, Me_3SiO), 3.45 ÷ 4.11 (m, CHCH), 7.33 ÷ 7.88 (m, C_6H_5).

Compound **3** (0.32 g (1.5 mmol), 0.90 g (3.0 mmol) of $(Me_3SiO)_3P$ and 2 ml of C_6D_6 were mixed in an [31]P NMR tube at room temperature. Moderate heating took place. [31]P NMR: δ = 114.0 [s, $(Me_3SiO)_3P$, 40%], 1.0 (s, **7A**) and 1.7 (s, **7B**, 60%). After 1 day: δ = 1.0 and 1.7 (60%), 114.0 (40%). At this stage, the tube was heated at 80°C for 3.5 hours with no changes in the [31]P NMR spectrum.

2,3-Epoxy-4,4,4-trifluoro-1-hydroxy-1-phenylbutanephosphonic acid (**9**)

Ethanol (95%, 2 mL) was added to an NMR tube with the reaction mixture. After 5 minutes: δ_P = 0.1 (s) and 0.8 (s, 28%), 8.3 (s, **8A**) and 9.0 (s, **8B**, 64%), 15.7 (s, 9%). Then a few drops of water were added. [31]P NMR: δ = 0.5 (s, 5%), 8.3 (s) and 9.0 (s, 36%), 16.0 (s, **9B**) and 16.4 (s, **9A**, 59%). Next day: δ = 16.5 (s, **9B**) and 17.0 (s, **9A**). The reaction mixture was evaporated to dryness, giving **9A,B** as a white powder. Yield: 1.33 g, 89%. [31]P NMR (D_2O): δ = 16.95 (s, **9B**, 42%), 18.20 (s, **9A**, 58%). When the mixture of **9A,B** was boiled in $CHCl_3$ and then filtered, 0.50 g of a white precipitate was collected (**9A**). Yield: 34%. m.p. 234–236°C. MS (125°C, *m/e*, %): 298 (M^+, 1), 280 (M^+-H_2O, 8), 199 (M^+ − H_2O − $P(O)(OH)_2$, 11), 171 (M^+ − H_2O − CF_3CHCO, 26), 151 (13), 131 (12), 105 ($PhCO^+$, 10), 81 (13), 69 (CF_3^+, 20) and other fragments. MS FAB: positive *m/e* = 299, negative *m/e* = 297. [1]H NMR ($CDCl_3$ + DMSO-d_6): δ = 3.48 (m, CF_3CH, $^3J_{HF}$ = 5.08 Hz), 4.06 (d, CHOH, $^3J_{HH}$ = 1.60 Hz), 6.96 (4(OH)), 7.25 ÷ 7.63 (m, 5H, C_6H_5). [19]F NMR ($CDCl_3$ + DMSO-d_6): δ = −73.52 (d, $^3J_{HF}$ = 2.99 Hz); (D_2O): δ = −71.09 (d, $^3J_{HF}$ = 3.87 Hz). [13]C NMR (D_2O): δ = 49.66 (qd, C-5, $^2J_{CF}$ = 40.94, $^2J_{COP}$ = 8.67 Hz), 58.19 (dq, C-4, $^2J_{CP}$ = 4.52, $^3J_{CF}$ = 2.26 Hz), 72.37 (d, C-3, $^1J_{CP}$ = 157.86 Hz), 122.88 (q, CF_3, $^1J_{CF}$ = 274.91 Hz), 126.03 ÷ 137.24 (m, C_6H_5). [31]P NMR ($CDCl_3$ + DMSO-d_6): δ = 24.16 (d, J = 1.49). Anal. calcd for $C_{10}H_{10}F_3O_5P$ (298.15): C, 40.28; H, 3.38; F, 19.12; P, 10.39. Found: C, 40.12; H, 3.50; F, 19.40; P, 8.90.

The X-ray structural study of compound **9A** (single crystal crystallized from an acetone-$CHCl_3$ mixture, 0.50 × 0.30 × 0.20 mm^3, triclinic P $\bar{1}$ with a = 579.30(10), b = 1291.8(2), c = 1630.3(2) pm, α = 72.73(1)°, β = 87.97(1)°, γ = 86.33(1)°, Z = 4, D = 1.704 Mg/m^3, absorption coefficient 0.292 mm^{-1}, difference electron density 0.323 and −0.429 e·Å^{-3}, extinction coefficient 0.0099(17)) was performed at 173(2) K on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 71.073 pm), θ-range 2.52–25.00°, reflections measured 5061, unique reflections 3689 (R_{int} = 0.0499). The structure was solved by direct methods and refined by full-matrix least squares at F^2 using SHELXTL PLUS (VMS); goodness of fit at F^2 1.001; final R values [I > 2σ(I)], R1 = 0.0498, wR2 = 0.1066; R value (all reflections) R1 = 0.0850, wR2 = 0.1221.

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