Diastereoselective Synthesis and Molecular Structure of a Bicyclic and a Cage Phosphane

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A two-step formal insertion of 1,1,1,5,5,5-hexafluoro- (**2a**) and 1,1,1-trifluoropentane-2,4-dione (**2b**) into the P−H bonds of phosphane gave the primary α-hydroxyphosphanes **3** and **4**, precursors for the resulting secondary phosphanes, 6,9-dioxa-2-phosphabicyclo[3.3.1]nonane (**6a**) and 2,4,8-trioxa-6-phosphaadamantane (**7**), both formed diastereospecifically. The molecular structures of **6a** and **7** were established by single-crystal X-ray structure analysis which revealed two independent molecules for **6a** in the unit cell possessing a chair-boat conformation with a C−P−C angle of 95.4(2) °, and a characteristic heteroadamantane geometry for **7**, with the corresponding angle being smaller by 4.9 °.

Phosphane, PH_3, adds to activated ketones, e. g. 1,1,1,3,3,3-hexafluoro- and 1,1,1-trifluoropropanone, to furnish primary and secondary α-hydroxyphosphanes: $H_{3-n}P[C(CF_3)R(OH)]_n$ (n = 1, 2; R = CF_3, CH_3).[1][2][3][4] A similar reaction carried out with pentane-2,4-dione, in the presence of a strong acid, results in the formation of diastereomerically pure 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane.[5] 1,3,5-Triaza-7-phosphaadamantane and its reductive cleavage products, namely *N*-methyl-*P*-alkylbicyclo[3.3.1]nonanes, are already used as transition-metal ligands.[6][7] Fluorinated pentane-2,4-diones (e.g. the tautomers[8] of 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentane-2,4-dione) and phosphane could lead to bicyclic compounds or to phosphaadamantanes. Both diones proved to be versatile reactants for the synthesis of phosphorus-containing mono-, bi- and tricyclic phosphoranes.[9][10][11]

Results and Discussion

In an "insertion" reaction[1][2][3][4] without any auxiliary acid, phosphane (**1**), and the keto/enol tautomers **2a** and **2b** of 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoropentane-2,4-dione furnished the primary (*R,S*)-α-hydroxyphosphanes **3a** and **3b**, whose enol functions probably isomerized rendering the corresponding ketones **4a** and **4b** (Scheme 1). A similar tautomerism was observed in the reaction product with diethyl phosphite, where the keto group of compound **2a** "inserted" into the P−H function.[12][13] Further addition of **2a** and **2b** to **4a** and **4b** and isomerisation afforded the formation of the secondary bis(α-hydroxy-γ-oxo)phosphanes **5a** and **5b**, which, upon standing for 7 d at ambient temperature, or heating for a short time at 80 °C, produced colorless crystalline solids, surprisingly 1,3α,5,7β-Tetrakis(trifluoromethyl)-6,9-dioxa-2-phosphabicyclo[3.3.1]nonane-3β,7α-diol (**6a**) and 1,7-trifluoromethyl-3,5-methyl-2,4,8-trioxa-6-phophaadamantane (**7**) (Scheme 2), in good yields (82 % for **6a**, 73 % for **7**), exclusively *one* diastereomer in each case. The main mechanistic feature of these reactions is a consecutive diastereoselective hemiketal cyclization. The PH_2 group of (*RS*)-**4a** and (*RS*)-**4b** probably add to the keto functions of **2a** and **2b**, assuming an orientation of the internal chelates[14] by an additional attractive OH···π interaction[15] [see Scheme 2; pathways are depicted for (*S*)-**4**, exemplarily] to give (*RR*)- and (*SS*)-**5a** and -**5b** exclusively. The α-hydroxy group in *one* $C(OH)(CF_3)CH_2C(O)CF_3$ substituent of compound **5** could form a cyclic chair-configurated hemiketal (intermediate **A**, R = CF_3, route *I*, Scheme 2) with the γ-oxo group of the neighboring substituent. The new 6-hydroxy group in the proposed 1,3-oxaphosphirane ring by virtue of the anomeric effect[16] is located axially (like the already existing 4-hydroxy group), thus creating a new (*S*)-carbon center starting from the (*RR*) precursor and a new (*R*)-carbon center from the (*SS*) precursor. The *axially* oriented 6-hydroxy and not the possibly competing 4-hydroxy[17] group in its turn induced a further anomeric effect[16] controlled hemiketal cyclisation with the remaining keto function furnishing bicyclic compound **6a** in the (1*S*,3*S*,5*R*,7*R*) or the mirror image (1*R*,3*R*,5*S*,7*S*) configuration (see Scheme 2). The HO groups in **6a** are in an α,β-arrangement (chair-boat conformation of the two rings, see discussion of the X-ray structure determination), unable to split off water intramolecularly. An additional final (1*R*,3*S*,5*S*,7*R*) or (1*S*,3*R*,5*R*,7*S*)

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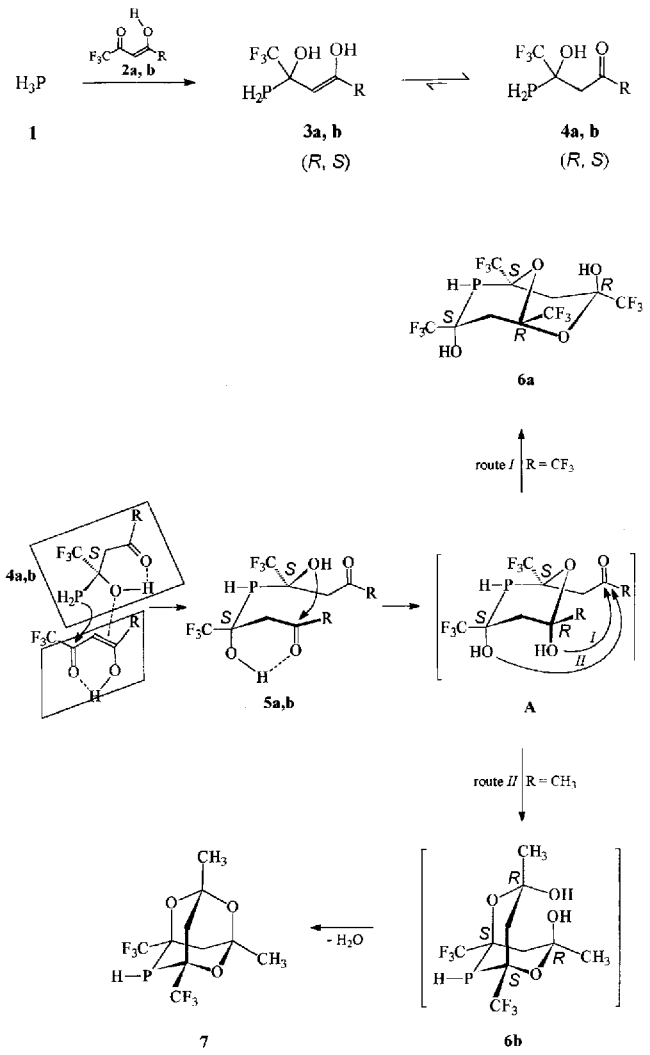

geometry of **6a** could not be found excluding the (*RS*) or (*SR*) configuration in the precursor phosphane **4a**.

Intermediate **A** (R = CH_3, route *II*, Scheme 2) led to the bicyclic phosphane **6b** having (*RRSS*) or (*SSRR*) configuration by allowing the axial α-hydroxy group in 4-position to interact with the free keto function. In this case, the 4-OH group is more acidic than the 6-OH moiety due to the presence of a CF_3 substituent at C-4 and thus is preferred in the hemiketal formation. The two new HO groups, because of the double chair conformation of the two rings in close vicinity to one another, enable a condensation reaction to give phosphaadamantane **7** and water. From (*RS*)- or (*SR*)-**4b** and **2b** and from their resulting (*RSS*) or (*SRR*) intermediates the second cyclisation with the respective α-hydroxy moiety (4-OH) is not possible for steric reasons.

The primary phosphane precursors **3** and **4** were not separated successfully, since upon distillation, only **6a** or **7** and phosphane were obtained, indicating the thermal instability of the primary phosphanes.

The X-ray diffraction investigation showed two symmetry-independent molecules, **A** [absolute configuration (1*S*,3*S*,5*R*,7*R*)] and its mirror image **B** [absolute configuration (1*R*,3*R*,5*S*,7*S*)] in the unit cell of the heterobicyclononane **6a** (see Figure 1 and Table 1); **B** exhibiting minor but not significant differences. Therefore, only the molecular structure of **6aA** will be discussed. The bicyclic system consists of two six-membered rings, one [P(1),C(1a),C(2a) C(3a),O(1a),C(4a)] in a chair conformation (puckering parameters[18] Q = 60.1 pm, θ = 173.0 °, Φ = 108.2 °) with P(1)−H(1a)[19] and C(1a)−O(3a) in the axial, C(1a)−C(9a)F_3, C(3a)C10a)F_3, and C(4a)−C(8a)F_3 in the equatorial position; the other ring [O(1a),C(3a),O(2a),C(6a), C(5a),C(4a)] was found to be in a boat conformation (puckering parameters Q = 69.2 pm, θ = 91.3 °, Φ = 179.9 °) with C(6a)−O(4a) and C(6a)−C(7a) located equatorially. The two hydroxy groups are in an *endo*/*exo* position, unavailable for intramolecular water abstraction to give a heteroadamantane system. A double chair geometry is usually found in heterobicyclo[3.3.1]nonanes, e. g. *N*-methyl-*P*-alkylbicyclo[3.3.1]nonanes.[7] The conformation observed in **6a** is obviously due to steric and electrostatic repulsions of the rather bulky *endo* substituents at C(1) or C(6).[20] In addition, the chair/boat conformation is stabilized by the O(1a)···H(41)−O(4a) hydrogen bond [O(1a)···O(4a) 288.9 pm]. Finally, if the reaction path from **5a** to **6a** is simulated in a model, the C(6a)CF_3 group is forced into an *endo* position. The bond lengths and angles in the two rings, e.g. P(1)−C(1a) 189.6(4), P(1)−C(4a) 189.1(4) pm and C(1a)−P(1)−C(4a) 95.3(2) °, are similar to those found elsewhere.[7]

Figure 1. Molecular structure of compound **6aA** (only one of the two symmetry-independent molecules; thermal elipsoids with 50 % probability)

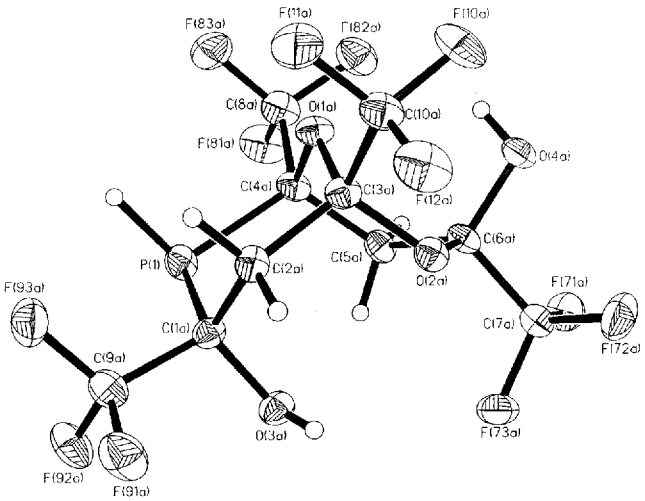

Table 1. Selected bond lengths [pm] and angles [°] of compound **6aA**

P(1)−C(1a)	189.5(4)	P(1)−C(4a)	189.2(4)
O(1a)−C(3a)	139.7(4)	O(1a)−C(4a)	144.6(4)
O(2a)−C(3a)	142.6(4)	O(4a)−C(6a)	139.8(4)
C(1a)−C(2a)	153.6(5)	C(3a)−C(10a)	155.3(5)
C(7a)−F(71a)	133.4(4)		
C(1a)−P(1)−C(4a)	95.4(2)	C(3a)−O(2a)−C(6a)	116.3(3)
C(3a)−O(1a)−C(4a)	113.4(3)	P(1)−C(1a)−O(3a)	105.2(2)
P(1)−C(1a)−C(2a)	113.9(2)	O(3a)−C(1a)−C(2a)	113.2(3)
C(1a)−C(2a)−C(3a)	114.6(3)	O(2a)−C(3a)−C(2a)	110.4(3)
P(1)−C(4a)−O(1a)	112.8(2)	O(1a)−C(4a)−C(8a)	101.3(3)

The single-crystal X-ray study of **7** (see Figure 2 and Table 2) showed the structure to consist of two equivalent phosphaadamantane molecules in the unit cell. The CF_3 groups were found in α-positions to the phosphorus atom. The bond lengths P(1)–C(1) and P(1)–C(4) of 188.5(2) and 188.7(2) pm are similar to those observed for **6a** and 1,3,5-triaza-7-phosphaadamantane, whereas the angle C(1)–P(1)–C(4) [89.41(7) °] is significantly smaller than the corresponding parameter of **6a**; the C–C distances in the six-membered rings are comparable with those obtained here. The conformational analysis of the four six-membered rings proved the expected chair geometry. A minor deviation of the phosphorus-containing ring [P(1),C(1),C(2),C(3),O(1),C(4)] was observed leading to the puckering parameters[17] Q = 70.9 pm, θ = 170.0 °, Φ = 198.8 °.

Figure 2. Molecular structure of compound 7 (thermal elipsoids with 50 % probability)

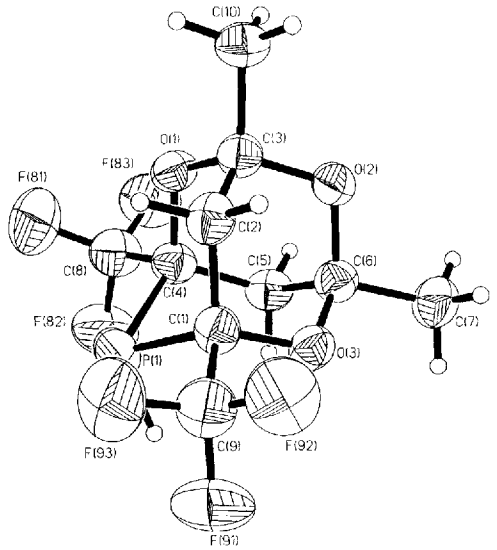

Table 2. Selected bond lengths [pm] and angles [°] of compound **7**

P(1)–C(1)	188.6(2)	P(1)–C(4)	188.7(2)
C(1)–C(2)	152.6(2)	C(1)–O(3)	142.8(2)
C(1)–C(9)	151.9(2)	C(8)–F(81)	132.6(3)
C(1)–P(1)–C(4)	89.5(1)	P(1)–C(1)–C(2)	108.3(1)
P(1)–C(1)–O(3)	112.7(1)	C(2)–C(1)–O(3)	110.0(2)
C(2)–C(1)–C(9)	111.8(1)	O(3)–C(1)–C(9)	105.2(1)
C(1)–C(2)–C(3)	108.8(1)	O(1)–C(3)–O(2)	110.6(1)
C(2)–C(3)–C(10)	114.5(1)	C(3)–O(1)–C(4)	114.7(1)
P(1)–C(4)–O(1)	109.5(1)	P(1)–C(4)–C(5)	111.6(1)
O(1)–C(4)–C(8)	103.9(1)	C(4)–C(5)–C(6)	108.9(1)

NMR spectroscopy was essential for monitoring the reaction pathway and supporting the proposed mechanism. For **1** and **2a** after 2 d at room temperature, the α-hydroxyphosphanes **3a**/**4a** and the secondary phosphane **5a** could be identified as intermediate products by their ^{31}P-NMR shift and $^1J_{PH}/^3J_{PF}$ values[21] [**3a**/**4a**:[22] δ = −115.3 (tdq), −118.5 (ttq); **5a**: −76.6 (dm)]. Within the limits of error one tautomer of **5a** was present exclusively. For the bicyclononane **6a**, the main product, one would expect a doublet of quadruplets of quadruplets of triplets of triplets. We observed a doublet of deceptively simple multiplets (11 lines) at δ_P = −72.8[20] ($^1J_{PH}$ = 207.4, $^3J_{PF}$ = 15.2, $^3J_{PF}$ = 13.2, $^3J_{PH}$ = 10.5 Hz). The two resonances at δ_F = −83.5 ($^3J_{PF}$ = 15.7, $^4J_{FH}$ = 1.1 Hz) and δ_F = −85.7 ($^3J_{PF}$ = 12.9, $^4J_{HF}$ = 1.3 Hz) in the ^{19}F-NMR spectrum were assigned to the CF_3 groups in vicinity of phosphorus, the two signals for the other two CF_3 groups were overlapping to give *one* resonance at δ_F = −90.1.

For the reaction of phosphane and **2b** only one signal [δ = −117.5, tq, $^1J_{PH}$ = 200.0, $^3J_{PF}$ = 4.3 Hz) in the ^{31}P-NMR spectrum was found due to the primary α-hydroxyphosphane[22], whose four resonances in the ^{1}H-NMR spectrum [δ = 2.26 (CH_3), 3.10 (CH_2), 3.28 (PH_2), 5.17 (OH)] showed the presence of isomer **4b**. The chiral center at the α-carbon atom did not cause magnetic inequivalence for the methylene group hydrogen nuclei. The proposed intermediates **5b** and **6b** could not be observed. For the phosphaadamantane **7** a doublet of quadruplets of quadruplets was found in the ^{31}P-NMR spectrum (δ_P = −74.6[21], $^1J_{PH}$ = 206.3, $^3J_{PF}$ = 15.3, $^3J_{PF}$ = 16.0 Hz). The assignment for the CF_3 groups was difficult because of the similar chemical environment.

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Experimental Section

The appropriate precautions for handling moisture- and oxygen-sensitive compounds were observed throughout this work. – Analyses: Mikroanalytisches Laboratorium Beller, Göttingen. – MS: Varian-MAT CH 7A spectrometer at 70 eV (EI). – NMR: Bruker AC 80 instrument at 80.13 MHz (^{1}H, standard TMS), 75.39 MHz (^{19}F, standard CCl_3F), and 32.44 MHz (^{31}P, standard 85% H_3PO_4). High-field shifts from TMS, CCl_3F, and 85 % H_3PO_4 were given negative signs. – The single-crystal X-ray structure determination was performed at 153 K with a Siemens P4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXSTL PLUS (VMS) program package.

(1S,3S,5R,7R)- and (1R,3R,5S,7S)-1,3α,5,7β-Tetrakis(trifluoromethyl)-6,9-dioxa-2-phosphabicyclo[3.3.1]nonane-3β,7α-diol (**6a**), *(RS)-[4,4,4-Trifluoro-1-hydroxy-3-oxo-1-(trifluoromethyl)-butyl]phosphane* (**4a**) *and (RR,SS)-Bis[4,4,4-trifluoro-1-hydroxy-3-oxo-1-(trifluoromethyl)butyl]phosphane* (**5a**): Into a heavy-walled glass tube, equipped with a Teflon® stopcock, was placed 30.0 g (143 mmol) of **2a** and 2.7 g (80 mmol) of **1**. This mixture was kept for 2 d at ambient temperature. After removal of the volatiles in vacuo, a viscous liquid remained containing compounds (*RS*)-**3a**, (*RS*)-**4a**, (*RR,SS*)-**5a** and (*RRSS,SSRR*)-**6a** in a 1:1:2:10 ratio [(*RS*)-**3a**/(*RS*)-**4a**: ^{31}P NMR ($CDCl_3$): δ = −115.3 (ttq, $^1J_{PH}$ = 206.5, $^3J_{PH}$ = 8.5, $^3J_{PF}$ = 5.2 Hz), −118.5 (tdq, $^1J_{PH}$ = 204.2, $^3J_{PH}$ = 10.5 Hz, $^3J_{PF}$ = 4.1 Hz). **5a**: ^{31}P NMR ($CDCl_3$): −76.6 (dm, $^1J_{PH}$ = 211.0, $^3J_{PH}$ = 10.5, $^3J_{PF}$ = 10.1 Hz)]. Crystalline colorless (*RRSS,SSRR*)-**6a** slowly precipitated. After 5 d at ambient temperature and successive removal of phosphane, 29.0 g (82 %) of compound **6a** (m. p. 76 °C, subl. 40 °C/0.001 Torr) remained. Heating of the starting materials, 3.0 g of **2a** and 0.3 g of **1**, for 2.5 h

at 80°C gave 2.9 g of **6a**. – MS (20°C); *m/z* (%): 450 (3) [M – H_2O]$^+$, 335 (5) [M – H_2O – CF_3CO]$^+$, 242 (32) [M – $CF_3C(O)CH_2C(O)CF_3$]$^+$, 161 (48) [$CF_3C(O)CH_2CF_2^+$], 139 (72) [$CF_3C(O)CHC(O)H^+$], 97 (46) [CF_3CO^+], 69 (100) [CF_3^+], and other fragments. – ^{1}H NMR ($CDCl_3$): δ = 2.30–2.70 (m, 2 H, ABX system), 2.85–3.45 (m, 2 H, ABX system), 3.05 (s, 1 H, OH), 3.98 (dqq, 1 H, PH, $^1J_{PH}$ = 207.4, $^4J_{PH}$ = 1.3, $^4J_{FH}$ = 1.1 Hz). – ^{19}F NMR ($CDCl_3$): δ = –83.5 (dd, 3 F, CF_3, $^3J_{PF}$ = 15.7, $^4J_{FH}$ = 1.1 Hz), –85.7 (dd, 3 F, CF_3, $^3J_{PF}$ = 12.9, $^4J_{FH}$ = 1.3 Hz), –90.1 (s, 6 F, CF_3). – ^{31}P NMR ($CDCl_3$): δ = –72.8 (dqq"quint", $^1J_{PH}$ = 207.4, $^3J_{PF}$ = 15.2, $^3J_{PF}$ = 13.2, $^3J_{PH}$ = 10.5 Hz). – $C_{10}H_7F_{12}O_4P$ (450.12): calcd. C 26.68, H 1.57, F 50.65, P 6.88; found C 26.56, H 1.71, F 50.40, P 7.08. – The data collection for the X-ray structural study of compound (*SSRR*)-**6aA** and (*RRSS*)-**6aB**[23] (single crystal 0.3 × 0.5 × 0.65 mm, monoclinic $P2_1/c$ with *a* = 1217.3(2), *b* = 1009.0(2), *c* = 2439.8(4) pm, β = 96.03(2) °, *Z* = 8, *D*(calcd.) = 2.007 Mg/m^3, cell volume 2.9801(9) nm^3, absorption coefficient 0.343 mm^{-1}, difference electron density 519 and –561 e nm^{-3}) was carried out in a θ-range 1.68–27.06 °, reflections collected 7057, independent reflections 6527 (R_{int} = 0.0518), goodness of fit on F^2 1.069; final *R* values [$I > 2\sigma(I)$], *R*1 = 0.0561, *wR*2 = 0.1301; *R* value (all reflections) *R*1 = 0.0921, *wR*2 = 0.1585.

3,5-Methyl-1,7-trifluoromethyl-2,4,8-trioxa-6-phophaadamantane (**7**) *and (RS)-[1-Hydroxy-3-oxo-1-(trifluoromethyl)butyl]phosphane* (**4b**): Into a heavy-walled glass tube, equipped with a Teflon® stopcock, was placed 22.7 g (150 mmol) of **2b** and 6.8 g (200 mmol) of **1**. The mixture was heated for 30 min at 80°C. After removal of all volatiles in vacuo, a liquid, compounds **4b** and **7** (1:5) [**4b**: ^{1}H NMR: δ = 2.26 (s, 3 H, CH_3), 3.10 (m, 2 H, CH_2), 3.28 (d, 2 H, PH_2, $^1J_{HP}$ = 200.0 Hz), 5.17 (s, 1 H, OH). – ^{19}F NMR: δ = –83.90 (d, $^3J_{FP}$ = 4.3 Hz). – ^{31}P NMR: δ = –117.5 (tq)] and a solid, compound **7**, remained. Heating of the liquid again under the conditions mentioned above gave rise to the formation of **1** and **7**. The yield of compound **7** (m. p. 67–69°C, subl. 45°C/0.001 Torr) was 17.4 g (73 %). – MS (20°C); *m/z* (%): 324 (53) [M$^+$], 281 (38) [M – CH_3CO]$^+$, 69 (42) [CF_3^+], 43 (100) [CH_3CO^+] and other fragments. – ^{1}H NMR ($CDCl_3$): δ = 1.51 (s, 6 H, CH_3), 1.90–2.50 (m, 4 H, ABX system), 3.45 (d, 1 H, PH, $^1J_{PH}$ = 206.3 Hz). – ^{19}F NMR ($CDCl_3$): δ = –86.2 (d, 3 F, CF_3, $^3J_{PF}$ = 15.3 Hz), –87.0 (d, 3 F, CF_3, $^3J_{PF}$ = 16.0 Hz). – ^{31}P NMR ($CDCl_3$): δ = –74.6 (dqq, $^1J_{PH}$ = 206.3, $^3J_{PF}$ = 15.3, $^3J_{PF}$ = 16.0 Hz). – $C_{10}H_{11}F_6O_3P$ (324.16): calcd. C 37.05, H 3.42, F 35.16, P 9.56; found C 37.14, H 3.48, F 35.20, P 9.64. – The data collection for the X-ray structural study of compound **7**[23] (single crystal 0.6 × 0.3 × 0.5 mm, triclinic $P\bar{1}$ with *a* = 809.1(2), *b* = 881.2(2), *c* = 984.7(2) pm, α = 85.62(2), β = 84.66(2), γ = 68.59(2) °, *Z* = 2, *D*(calcd.) = 1.656 Mg/m^3, cell volume 0.6501(3) nm^3, absorption coefficient 0.289 mm^{-1}, difference electron density 305 and –230 e nm^{-3}) was carried out in a &thetas; range 2.71–27.56 °, reflections collected 6220, independent reflections 3017 (R_{int} = 0.0185), goodness of fit on F^2 1.035; final *R* values [$I > 2\sigma(I)$], *R*1 = 0.0362, *wR*2 = 0.0892; *R* value (all reflections) *R*1 = 0.0484, *wR*2 = 0.0965.

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[13] E.g.: 1,1,1-Trifluoro-2-hydroxypentan-4-one shows no significant tautomerism, c.f.: A. Forni, I. Moretti, F. Prati, G. Torre, *Tetrahedron* **1994**, *50*, 11995–12000.

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[15] O. Casher, D. O'Hagan, C. A. Rosenkranz, H. S. Rzepa, N. A. Zaidi, *J. Chem. Soc., Chem. Commun.* **1993**, 1337–1340.

[16] F. A. Carey, R. J. Sundberg, *Organische Chemie*, VCH, **1995**, pp.140–146; A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer, Berlin, **1983**.

[17] The phosphadamantane chair-chair precursor (analogue of **6b**) was not obtained, since the hydrogen bond of the 4-OH group (with CF_3, CH_2, and PH substituents) is probably less pronounced than in the case of the 6-OH group (with CF_3, CH_2, and oxygen substituents) directing the hemiketal formation as described above; c.f. hydrogen-bonding properties of CF_3CH_2OH: A. D. Sherry, K. F. Purcell, *J. Phys.Chem.* **1970**, *74*, 3535–3543; I. A. Koppel, V. A. Eiber, U. H. Mölder, *Org. React.* **1984**, *21*, 40–58. The formation of water is unfavorable, too, and not observed under the reaction conditions applied, because of the strong C–O(H) bond at the trifluoromethylated carbon atoms present.

[18] J. B. Hendrickson, *J. Am. Chem. Soc.* **1967**, *89*, 7036–7043.

[19] Phosphorinane has an axial P–H bond in a chair conformation in solution, cf.: J. B. Lambert, W. L. Oliver, *Tetrahedron* **1971**, *27*, 4245.

[20] P. D. Cradwick, G. A. Sim, *J. Chem. Soc. B*, **1971**, 2218–2221.

[21] The δ_P ($^1J_{PH}$) values are in the expected region (of the expected order); see: S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spekroskopie von Nichtmetallen:* ^{31}P-NMR-Spekroskopie, Thieme, Stuttgart, **1993**, p. 6, p. 126.

[22] Possibly the (*Z*) isomer was formed. A signal at δ_P = –120.4 (tdq, $^1J_{PH}$ = 209.0, $^3J_{PH}$ = 17.6 Hz, $^3J_{PF}$ = 3.5 Hz) can be attributed to the (*E*) isomer.

[23] Further details of the crystal structure investigations are available from the Fachinformationsdienst Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406880 (**6a**) and -406881 (**7**).

[97048]