ELSEVIER

Journal of Fluorine Chemistry 85 (1997) 129–133

JOURNAL OF FLUORINE CHEMISTRY

Trifluoromethylated $1,2\lambda^5\sigma^4$-oxaphospholanes via $\lambda^5\sigma^5$P tricyclic phosphoranes from 4,4,4-trifluoro-3-hydroxy-1-phenylbutane-1-one and dichlorophosphines. Molecular structure of a trapped phosphonite

Vitalij G. Ratner [a], Enno Lork [b], Kazimir I. Pashkevich [a], Gerd-Volker Röschenthaler [b,*]

[a] *Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, 20 S. Kovalevskoi, 620219 Ekaterinburg, Russia*

[b] *Institute of Inorganic and Physical Chemistry, University of Bremen, Leobener Strasse, 28334 Bremen, Germany*

Received 16 December 1996; accepted 16 March 1997

Abstract

Reacting 4,4,4-trifluoro-3-hydroxy-1-phenylbutane-1-one (**1**) with the dichlorophosphines $RPCl_2$ (**2a**, R = Me; **2b**, R = Ph) gave the phosphonites **3a** and **3b**, which, in the case of **3a**, was trapped using hexafluoroacetone to furnish the $1,3,2\lambda^5\sigma^5$-dioxaphospholane **4a**. In a concerted mechanism, compounds **3a** and **3b** rearranged forming the thermally unstable tricyclic diastereoisomeric phosphoranes **5a** and **5b**. After splitting off 1,1,1-trifluoro-4-phenyl-2-butene-4-one (**6**) the diastereoisomeric $1,2\lambda^5\sigma^4$-oxaphospholanes **7a** and **7b** were obtained. The molecular structure of **4a** (triclinic, $P\bar{1}$, $a = 1020.3(1)$ pm, $b = 1239.0(1)$ pm, $c = 1298.7(2)$ pm, $\alpha = 85.55(1)°$, $\beta = 70.10(1)°$, $\gamma = 79.85(1)°$) was determined. © 1997 Elsevier Science S.A.

Keywords: 1,1,1-Trifluoro-2-hydroxy-4-phenyl-butane-4-one; Methyl dichlorophosphine; Phenyl dichlorophosphine; $1,2\lambda^5\sigma^4$-Oxaphospholanes; Molecular structure

1. Introduction

Trifluoromethylated ketoenols, e.g. 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoro-2-hydroxy-2-pentene-4-one (tautomers of the corresponding pentane-2,4-diones) reacted with dichloro organylphosphines, $RPCl_2$ (R = Me, Et, *i*Pr, *t*Bu, CH_2SiMe_3, CH_2Ph, Ph, NEt_2), to give thermally stable tricyclic $\lambda^5\sigma^5$P phosphoranes in a highly concerted diastereospecific mechanism [1,2] (Scheme 1). In the case of 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one only one diastereoisomer was observed with two CF_3 groups in a *cisoid* arrangement.

Using 2-trifluoroacetylphenol, also having a $CF_3C(OH){=}CHC({=}O)$ fragment, similar phosphoranes with the same geometry for the CF_3 groups were obtained [3,4]. In none of the cases was the proposed intermediate, a phosphonite, isolated, trapped or even characterized at low temperatures. When methyl salicylate and phenylphosphonous dichloride were allowed to interact the respective phosphonite was stable at room temperature and could be converted by tetrachloro-*o*-benzoquinone to the expected $\lambda^5\sigma^5$P species [3]. To the best of our knowledge trifluoromethylated β-hydroxyketones with a $CF_3CH(OH)$–$CH_2C({=}O)$ grouping have never been investigated in their ability to form tricyclic phosphoranes with organylphosphonous dichlorides. Here we report the reactions of one β-hydroxyketone with methyl and phenylphosphonous dichlorides.

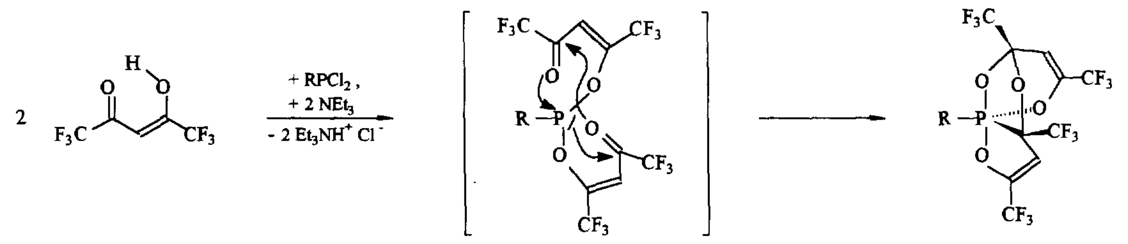
2. Results and discussion

The reaction of 1,1,1-trifluoro-2-hydroxy-4-phenylbutane-4-one (**1**) [6] with the phosphorous dichlorides $RPCl_2$ (**2a**, R = Me; **2b**, R = Ph) afforded unequivocally the phosphonites **3a** and **3b** at temperatures below 0 °C, which were characterized by their typical δ_P shift values (δ_P values of similar compounds, $RP[OCH(CF_3)_2]_2$, are 224 for R = Me [5]a and 191 for R = Ph [5]b), but not isolated. Compound **3a** could be trapped using hexafluoroacetone which added oxidatively at phosphorus to form the new $1,3,2\lambda^5\sigma^5$-dioxaphospholane **4a** when temperature is above 0 °C. The phosphonites **3a** and **3b** rearranged in a concerted mechanism beginning with the interaction of the phosphorus lone pair with one of the carbonyl moieties to probably give the unstable diastereoisomeric tricyclic phosphoranes **5a** and

---

[*] Corresponding author.

PII S0022-1139(97)00061-4



Scheme 1.

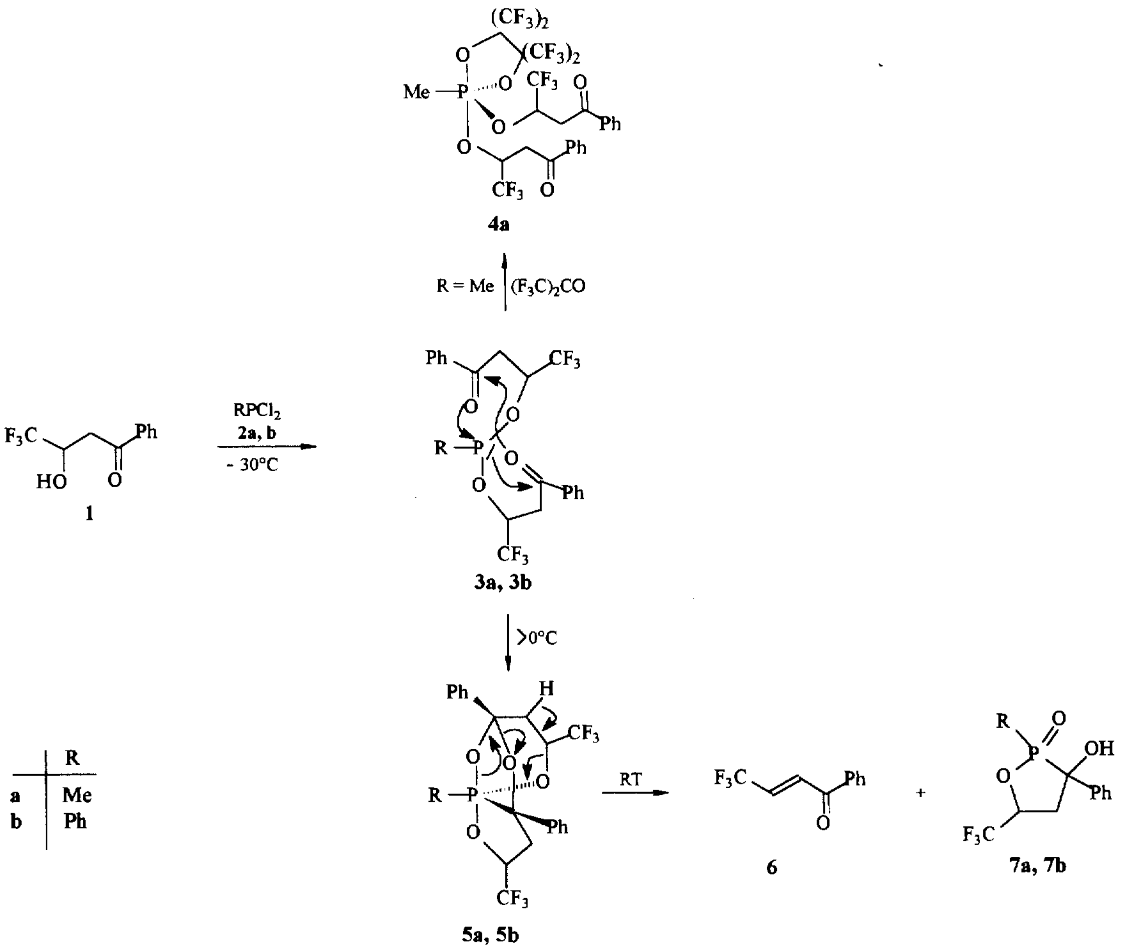
5b, which decomposed (monitored by ^{31}P NMR spectroscopy) shortly after their formation to give the unsaturated ketone **6** [6] (proved by comparison with an authentic sample) and the corresponding stereoisomeric oxaphospholanes **7a** and **7b** and other not yet identified phosphorus-containing compounds. The latter could have been formed by a rearrangement process found for the tricyclic system obtained from dibenzoylmethane and phenyl phosphorous dichloride [7]. These observations are in contrast to the properties of the tricyclic phosphoranes obtained from fluorinated 2-hydroxy-2-pentene-4-ones [1,2] which were found to be thermally stable at ambient temperatures. It is thermodynamically favorable to cleave a strained $\lambda^5\sigma^5$P tricyclic system into a monocyclic five-membered ring with a $\lambda^5\sigma^4$ phosphorus and an α,β-unsaturated carbonyl compound where the conjugation between C=C and C=O bonds decreases significantly the energy of the whole system. The phosphorous dichlorides **2a** or **2b** neither dehydrated β-hydroxyketone **1** to give the unsaturated ketone **6** nor reacted with **6** in a further interaction.

Despite C-2 in β-hydroxyketone **1** being a chiral centre only one sharp ^{31}P NMR signal is found in the expected region for phosphonites **3a** ($\delta_P = 206$) and **3b** ($\delta_P = 181$) with (*RR*/*SS*) and *RS* configuration. The same is true for the monocyclic phosphorane **4a**, where in addition one ^{19}F NMR signal ($\delta_F = -68.4$) at ambient temperature for the four dioxaphospholane CF_3 groups is indicating rapid pseudo-rotation on the NMR time scale. When the tricyclic ring is formed the configuration differences become evident. We assume that during the diastereospecific phosphorane formation the two phenyl groups will occupy strictly a *cisoid* position comparable to what was found for the interaction of phosphorous dichlorides and 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one (see Scheme 1 and Refs. [1,2]). The ground state structure should also be the same with an axial–equatorial–axial arrangement of the fused five-membered ring system [P–C_{eq}Ph] and the six-membered ring occupying an axial–equatorial position (Scheme 2). Taking this into account one can expect four NMR spectroscopically different isomers **A**–**D** of **5a** and **5b** (Scheme 3). Two of them in each case could be observed in the ^{31}P NMR spectrum (**5a**, $\delta_P = 2.1, 3.7$; **5b**, -15.5, -13.0), values similar to those recorded for the tricyclic phosphoranes obtained from 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one and methyl ($\delta_P = 12.0$ [8]) or phenyl ($\delta_P = -8.4$ [1]) phosphorous dichloride. Being unable to obtain pure compounds **5a** and **5b** we could isolate and characterize one isomer of oxaphospholane **7b**. After splitting off the unsaturated ketone **6**, only two isomers **E** and **F** (see Scheme 3) remain, which were observed in the ^{31}P NMR spectra (**7a**, $\delta_P = 66.4, 69.8$; **7b**, 54.7, 57.1).

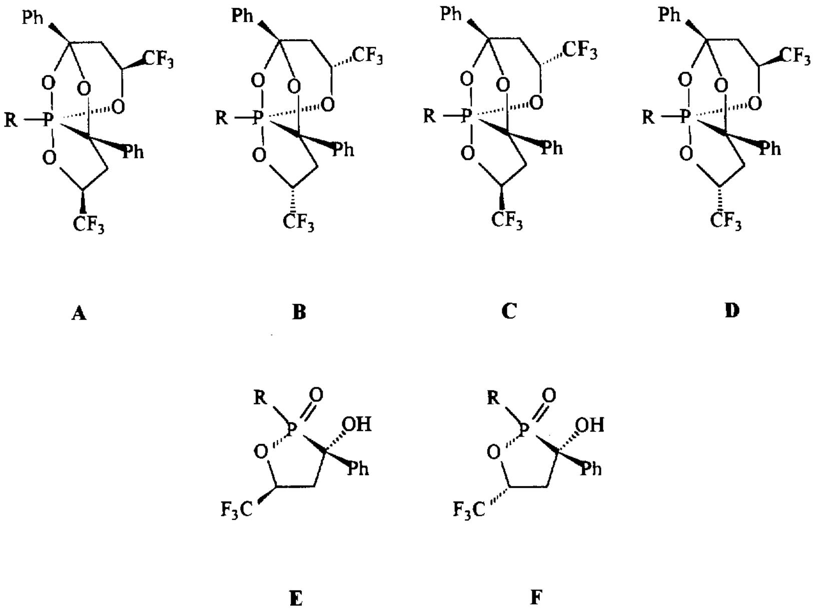
Although the mass spectrum of **4a** does not have a molecular ion, all other fragments give enough evidence to support the structure proposed. Precision mass determination for two fragments with 793 (M^+–F) and 743 (M^+–CF_3) proves unambiguously that they are derived from the loss of fluorine atom and a CF_3 group, respectively, from the molecular ion. The X-ray structure investigation of **4a** revealed a slightly distorted trigonal bipyramid at phosphorus (bond angles: O(1)–P(1)–O(5), 174.66(7); O(2)–P(1)–O(3), 118.71(7); O(3)–P(1)–O(5), 93.93(7); O(2)–P(1)–C(27), 124.57(9); O(3)–P(1)–C(27), 116.29(9)°) with 11.1% deviation along the Berry pseudorotation coordinate (O(3) as a pivot) [9] (see Table 1 and Fig. 1). The bond lengths P(1)–O(2) = 165.4(1), P(1)–O(3) = 158.9(1) pm for equatorial located endo- and exocyclic oxygen differ markedly, the corresponding values for the axial substituents are P(1)–O(1) = 174.8(1) and P(1)–O(5) = 165.2(1) pm. The corresponding bond lengths and angles in the axial and equatorial and axial PhC(=O)CH_2CH(CF_3)O ligands agree to within 2 pm. The five-membered ring appeared in a ^{3}E envelope conformation (Puckering parameters $Q = 30.9$ pm, $\Phi = 77.6°$ [10]); the phosphorus atom P(1) is out of plane [O(3), O(5), C(27)] by 73.32 pm. The carbon atoms C(15) and C(16) seemed to be disordered (Fig. 1).

3. Experimental details

The appropriate precautions for handling moisture- and oxygen-sensitive compounds were taken. Mass spectra (EI, 70 eV) were carried out on a Finnigan MAT 8222 spectrometer. NMR spectra were obtained on a Bruker AC 80 instrument operating at 80.13 MHz (^{1}H, internal standard TMS), 75.39 MHz (^{19}F, internal standard CCl_3F), 32.44 MHz (^{31}P, external standard 85% H_3PO_4) and on a WH-360 Bruker spectrometer operating at 360.00 MHz (^{1}H), 90.54 MHz (^{13}C) and 145.72 MHz (^{31}P). As solvent was used, for low temperature measurements toluene(d_8)/diethyl ether (1:1, v/v). IR spectra of KBr pellets were recorded on a BioRad FTIR FTS 7-80 spectrometer. The X-ray structure study of compound **4a** was performed on a Siemens P4-diffractometer at 173(2) K using graphite-monochromated Mo Kα radiation



Scheme 2.



Scheme 3.

Table 1
The main geometrical parameters of **4a**

Bond lengths (pm)			
P(1)–O(1)	174.8(1)	C(1)–C(2)	156.7(3)
P(1)–O(2)	165.4(1)	C(1)–C(4)	159.9(3)
P(1)–O(3)	158.9(1)	C(2)–F(1)	131.8(3)
P(1)–O(5)	165.2(1)	C(7)–C(8)	151.5(3)
P(1)–C(27)	179.6(2)	C(7)–C(9)	152.0(3)
O(1)–C(1)	137.3(2)	C(9)–C(10)	152.0(3)
O(2)–C(4)	141.1(2)	C(11)–C(16)	138.1(3)
O(3)–C(7)	144.4(2)		
Bond angles (°)			
O(1)–P(1)–O(2)	86.59(6)	O(2)–C(4)–C(1)	103.1(1)
O(1)–P(1)–O(3)	87.75(7)	C(7)–O(3)–P(1)	130.3(1)
O(1)–P(1)–O(5)	174.66(7)	C(7)–O(3)–P(1)	130.3(1)
O(2)–P(1)–O(3)	118.71(7)	C(8)–C(7)–C(9)	110.4(2)
O(2)–P(1)–O(5)	88.16(7)	O(4)–C(10)–C(11)	120.7(2)
O(3)–P(1)–O(5)	93.93(7)	C(4)–O(2)–P(1)	119.9(1)
O(1)–P(1)–C(27)	89.15(9)	O(3)–C(7)–C(8)	106.0(2)
O(2)–P(1)–C(27)	124.57(9)	C(10)–C(9)–C(7)	112.4(2)
O(3)–P(1)–C(27)	116.29(9)	C(11)–C(10)–C(9)	118.8(2)
O(5)–P(1)–C(27)	94.63(9)	C(17)–O(5)–P(1)	125.6(1)
C(1)–O(1)–P(1)	117.2(1)	O(5)–C(17)–C(18)	106.3(2)
O(1)–C(1)–C(4)	102.3(1)		

($\lambda = 71.073$ pm). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL PLUS (VMS) program package.

*3.1. General procedure for the interaction of hydroxyketones **1** with the dichlorophosphines **2a** and **2b***

To a solution of 2.20 g (10 mmol) **1** and 11 mmol Et_3N in 50 ml diethyl ether were added 5 mmol **2a** (0.6 g) or **2b** (0.9 g) at −50 °C. The mixture was stirred overnight without external cooling. After filtration and washing the precipitated $Et_3N \cdot HCl$ using diethyl ether, the filtrate was concentrated at ambient temperature under reduced pressure and analyzed by NMR spectroscopy.

*3.2. 1,1,1-trifluoro-2-hydroxy-4-phenyl-butane-4-one (**1**) and methyl phosphorous dichloride (**2a**)*

^{31}P-NMR: At −30 °C $\delta = 206$ (**3a**); after 1 h at 0 °C no changes; after 0.5 h at r.t. $\delta = 2.1$, 3.7 (**5a**, 6%); 65.9, 68.0 (**7a**, 15%); 206 (79%); after 1 h at r.t. $\delta = 2.1$, 3.7 (16%), 66.2, 69.1 (42%), 206.1 (42%); after 1.5 h at r.t. $\delta = 2.1$, 3.7 (21%); 16.3 (m, 9%), 66.3, 69.6 (60: 40, 58%), 206.0 (10%); after 2.0 h at r.t. $\delta = 2.1$, 3.7 (65: 35, 19%), 16.2 (m, 14%), 66.4, 69.8 (54: 46, 63%), 206.0 (4%).

*3.3. 4,4,5,5-Tetrakis(trifluoromethyl)-2,2-bis(4',4',4'-trifluoro-1'-oxo-1'-phenylbutyl-3'-oxy)-2-methyl-1,3,2λ^5s^5-dioxaphospholane (**4a**)*

Compounds **1**, **2a** and Et_3N (see General procedure) in diethylether were allowed to react for 2 h at −25 °C, 2.5 g (15 mmol) hexafluoroacetone were added and the mixture allowed to warm up slowly to r.t. After filtration the colorless solution was evaporated under reduced pressure to give a very viscous liquid which began to crystallize after 1 d. Recrystallization from CCl_4 gave 1.1 g **4a** as colorless cubes (yield 27%, m.p. 110–111 °C). MS (128 °C): (m/e, %): 812 (M^+, 0), 793 (M^+–F, 1), 743 (M^+–CF_3, 5), 627 (2), 595 (M^+–$CF_3CH(OH)CH_2C(O)Ph$, 64), 489 (2), 395

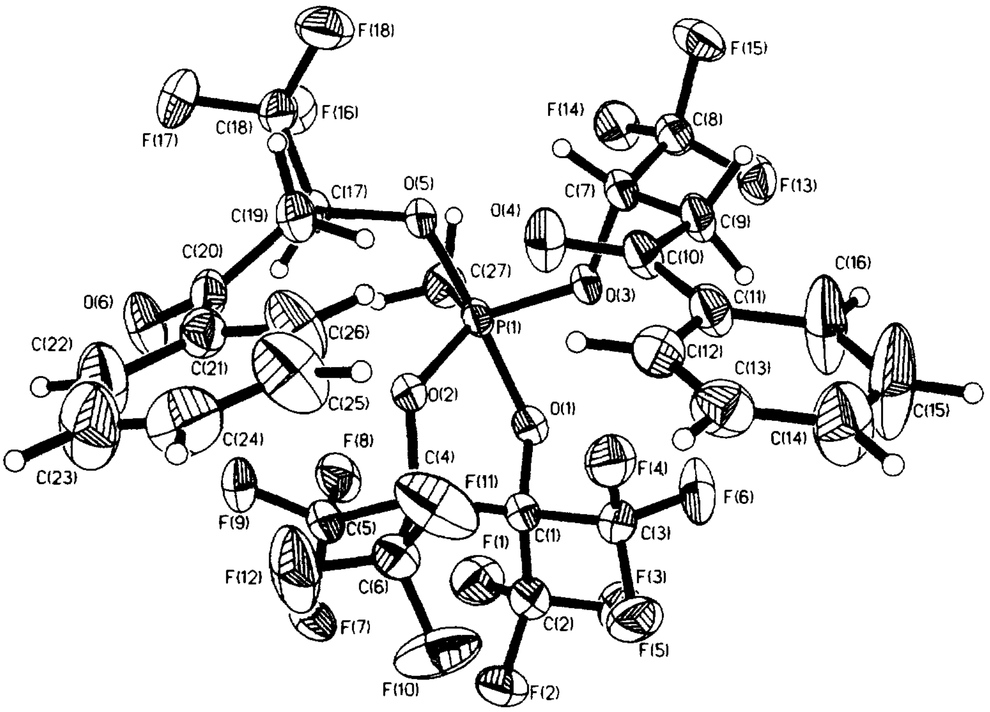


Fig. 1. Molecular structure of **4a** (thermal ellipsoids with 50% probability).

(6), 201 ($CF_3CH{=}CHC(OH)Ph^+$, 55), 105 ($PhCO^+$, 100), 77 (Ph^+, 14) and other fragments. Precision mass determination for $m/z=793$: 793.06320 (found), 793.06476 (calcd) (for $C_{27}H_{19}F_{17}O_6P$) (2.0 ppm, 1.6 mmu), $m/z=743$: 743.06820 (found), 793.06799 (calcd) (for $C_{26}H_{19}F_{15}O_6P$) (−0.3 ppm, −0.2 mmu). ^{1}H-NMR: $\delta=1.97$ (3 H, d, CH_3, $^2J_{HP}=17.63$ Hz), 3.65 (4 H, m, CH_2), 5.70 (2 H, m, CF_3CH), 7.59–7.94 (10 H, m, C_6H_5); ^{19}F: −68.4 (12 F), −78.2 (6 F, d, $^3J_{HF}=4.0$ Hz); ^{31}P: $\delta=-22.1$ (q, $^2J_{PH}=17.5$ Hz).

3.4. *Crystal structure analysis of **4a*** [1]

$C_{27}H_{19}F_{18}O_6P$ single crystal $0.5\times0.3\times0.3$ mm^3, triclinic $P\bar{1}$, $a=1020.3(1)$, $b=1239.0(1)$, $c=1298.7(2)$ pm, $\alpha=85.55(1)$, $\beta=70.10(1)$, $\gamma=79.85(1)°$, $Z=2$, $D=1.776$ Mg m^{-3} ($M_r=812.39$; cell volume, 1.5193(3) nm^3); absorption coefficient, 0.244 mm^{-1}; difference electron density, 347 and −615 e nm^{-3}; Θ-range, 2.50 to 27.53°; reflections collected, 8275; independent reflections, 6974 ($R_{int}=0.0504$); goodness of fit at F^2, 0.916; final R values [$I>2\sigma(I)$], $R_1=0.0440$, $wR_2=0.1091$; R value (all reflections) $R_1=0.0651$, $wR_2=0.1162$.

3.5. *1,1,1-trifluoro-2-hydroxy-4-phenyl-butane-4-one (**1**) and phenyl phosphonous dichloride (**2b**)*

^{31}P-NMR: −30 °C $\delta=181$ (**3b**); after 1 h at −30 °C no changes; after 1 h at r.t. $\delta=-15.5$, −13.0 (**5b**, 72: 28, 15%); 54.7, 57.1 (**7b**, 34: 66, 64%); after 16 h at r.t. $\delta=-15.5$, −13.0 (37: 63, 7%), 54.8, 57.2 (36: 64, 93%). ^{19}F-NMR: $\delta=-65.42$ (**6**, d, $^3J_{HF}=5.80$ Hz, 35%), −78.00, −78.47 (d, **7b**, 36%), −79.54, −80.06 (d, **5b**, 29%).

3.6. *5-Trifluoromethyl-3-hydroxy-2-oxo-2,3-diphenyl-1,2λ^5s^5-oxaphospholane (**7b**)*

Compound **7b** was filtered together with the precipitate of $Et_3N\cdot HCl$. The precipitate was washed with small amounts of water several times and dried. Another portion of **7b** was recovered from the sample recrystallizing from carbon tetrachloride. Yield 0.7 g (41%), m.p. 203–204 °C. MS (169 °C): (m/z, %): 342 (M^+, 100), 302 (M^+–2HF, 77), 261 (M^+–81,5), 201 ($CF_3CH{=}CHC(OH)Ph^+$, 100), 164 (15), 159 (60), 142 ($PhP(OH)_2^+$, 40), 133 (10), 105 ($PhCO^+$,30), 77 (Ph^+, 15) and other fragments. IR (cm^{-1}): 3234 (ν_{OH}), 3066, 2986, 1593 ($\nu_{C=C}$), 1495, 1439, 1397, 1339, 1295, 1282–1146 (ν_{CF}), 1103, 1068, 1033, 958, 839, 803, 760, 732, 694. ^{1}H-NMR ($CDCl_3$): $\delta=2.32$ (1 H, dd, OH), 2.73 (1 H, ddd, H-4′), 2.98 (1 H, ddd, H-4″), 5.04 (1 H, m, H-5), 7.33–7.89 (10 H, m, Ph); ^{13}C-NMR (acetone-d_6): $\delta=37.71$ (d, C-4, $^2J_{PC}=9.76$ Hz), 74.89 (qd, C-5, $^2J_{FC}=33.77$ Hz, $^2J_{POC}=2.44$ Hz), 77.38 (d, C-3, $^1J_{PC}=101.93$ Hz), 124.21 (qd, CF_3, $^1J_{FC}=279.40$, $^3J_{POC}=4.27$ Hz). ^{19}F-NMR ($CDCl_3$): $\delta=-78.5$ (d, $^3J_{HF}=5.50$ Hz). ^{31}P-NMR (acetone-d_6): $\delta=54.9$. Analysis: Found: C, 56.06; H, 4.10; F, 16.70; P, 9.00. Calc.: C, 56.15; H, 4.12; F, 16.65; P, 9.05.

Acknowledgements

V.G.R. is grateful to the Deutsche Forschungsgemeinschaft for generous financial support. We are grateful to I. Erxleben and Dr. P. Schulze, Institute of Organic Chemistry, University of Bremen, for carrying out high-resolution mass spectrometry measurements and Dr. W. Offermann for helpful discussions.

References

[1] G. Bekiaris, G.-V. Röschenthaler, Z. Naturforsch. 45b (1990) 1460.
[2] G. Bekiaris, R.-D. Hund, F.U. Seifert, G.-V. Röschenthaler, Phosphorus, Sulfur, Silicon 93–94 (1994) 289.
[3] S.D. Harper, A.J. Arduengo, J. Am. Chem. Soc. 104 (1982) 2497.
[4] R.D. Hund, G.-V. Röschenthaler, Phosphorus, Sulfur, Silicon 66 (1992) 301; R.D. Hund, U. Behrens, G.-V. Röschenthaler, Phosphorus, Sulfur, Silicon 69 (1992) 119.
[5] (a) G.-V. Röschenthaler, Z. Naturforsch. 33b (1978) 131; (b) D. Dakternieks, G.-V. Röschenthaler, R. Schmutzler, Z. Naturforsch. 33b (1978) 501.
[6] R.R. Latypov, V.D. Belogay, K.I. Pashkevich, Izv Nauk. SSSR Ser. Khim. 35 (1986) 108.
[7] W.V. Dahlhoff, K.M. Taba, R. Mynott, Z. Naturforsch. 44b (1989) 41.
[8] G. Bekiaris, G.-V. Röschenthaler, Chem. Ber., submitted for publication.
[9] R.R. Holmes, Progr. Inorg. Chem. 32 (1984) 119.
[10] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.

---

[1] Further details of the crystal structure investigation are available from the Fachin-formationsdienst Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD No. 406692.