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# 1,1,1,4,5,5,5-Heptafluoro-4-(trifluoromethyl)-2,3-pentanedione, a Potent Reagent for the Synthesis of Cyclic $\lambda^5\sigma^5$ Phosphoranes

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## ABSTRACT

*1,1,1,4,5,5,5-Heptafluoro-4-(trifluoromethyl)-2,3-pentanedione reacted with $\lambda^3\sigma^3$-phosphorus compounds, $PR^1R^2R^3$ ($R^1 = CF_3$, $R^2 = R^3 = Me$, iPr, $NEt_2$; $R^1 = NCO$, $R^2 = R^3 = OMe$, OEt, $R^2-R^3 = OCH_2CH_2O$, $OCMe_2CMe_2O$; $R^1 = OSiMe_3$, $R^2 = R^3 = OEt$; $R^1 = NEt_2$, $R^2 = R^3 = OCH_2CF_3$; $R^1 = R^2 = Et_2N$, $R^3 = OCH_2CF_3$, $OCH(CF_3)_2$, $OCH_2Ph$, $OC_6F_5$) to give new 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes. The first $\lambda^5\sigma^5$ phosphoranes with an OCN group bonded to phosphorus were obtained.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:109–113, 1998

## *INTRODUCTION*

Several examples of the oxidative addition of 1,1,1,4,4,4-hexafluoro-2,3-butanedione to phosphorus(III) derivatives, such as $(MeO)_3P$ [1], $PhOPR_2$ (R = Me, Et, *i*Pr [2]), $Me_2POCH(CF_3)_2$ [3], $Et_2NPF_2$ [4], and $Me_3SiN{=}PN(SiMe_3)_2$ [5], are known to furnish 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes. Less information is available for the reaction of 1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2,3-pentanedione [6], which has been reacted with phosphites $(RO)_3P$ (R = Et, Ph [7]), 1,3,2-benzoxazaphosphininones [7], 1,3,5,2-triazaphosphininane-diones [8], and 1,3,2-diazaphosphininanones [8]. However, a systematic study has not been carried out yet as to how substituents at phosphorus influence product formation and stability. Since hexafluoroacetone and phosphites $(RO)_2PNCO$ (R = Me, Et; R–R = $CH_2CH_2$, $CMe_2CMe_2$) are known to have undergone reactions to give 1,3,2$\lambda^5\sigma^4$-oxazaphospholenes [9,10] or bicyclic $\lambda^5\sigma^5$-phosphoranes [9,11], it was of interest to study and compare the corresponding properties of 1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2,3-pentanedione. The investigation undertaken now also includes descriptions of the reactions of a number of $\lambda^3\sigma^3$P derivatives containing $CF_3$, $Et_2N$, and RO moieties.

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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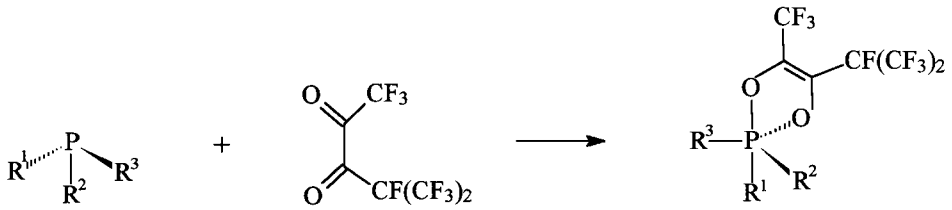
## *RESULTS AND DISCUSSION*

The phosphorus(III) compounds, $PR^1R^2R^3$, **1** ($R^1$ = $CF_3$, $R^2$ = $R^3$ = Me (**1a**) [12], *i*Pr (**1b**) [13], $NEt_2$ (**1c**) [14]; $R^1$ = NCO, $R^2$ = $R^3$ = OMe (**1d**), OEt (**1e**) [15], $R^2$–$R^3$ = $OCH_2CH_2O$ (**1f**), $OCMe_2CMe_2O$ (**1g**) [16]; $R^1$ = $OSiMe_3$, $R^2$ = $R^3$ = OEt (**1h**) [17]; $R^1$ = $NEt_2$, $R^2$ = $R^3$ = $OCH_2CF_3$ (**1i**) [18]; $R^1$ = $R^2$ = $Et_2N$, $R^3$ = $OCH_2CF_3$ (**1j**) [19], $OCH(CF_3)_2$ (**1k**) [20], $OCH_2Ph$ (**1l**) [21], $OC_6F_5$ (**1m**) [19]) were reacted with 1,1,1,4,5,5,5-heptafluoro-4-(trifluoromethyl)-2,3-pentanedione (**2**) to yield 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes **3a–m,** mainly colorless liquids but solids in the case of **3f, 3g,** and **3m** (Scheme 1). There was no interaction of the isocyanato group in **1d–g** with the diketone observed, unlike the corresponding reaction with hexafluoracetone [9–11] (Table 1).

The NMR data of the phosphoranes were consistent with the constitutions proposed. The $\delta_p$ values were in the expected range [22]. The $^{19}F$ resonances for the 4-trifluoromethyl-5-[1′,2′,2′,2′-tetrafluoro-1′-(trifluoromethyl) ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4) ring system were observed at $\delta$ = −62.1 ÷ −69.1 for the 4-$CF_3$ group, split into a doublet ($^5J_{FF}$, 27.9 ÷ 38.4 Hz) of septuplets ($^6J_{FF}$, 1.9 ÷ 1.6 Hz, not found in the case of **3a–c** and **3h**), $\delta$ = −75.9 ÷ −82.0 and −185.4 ÷ −190.8 for the 5-$(CF_3)_2CF$ moiety (doublet of quatruplets for the two $CF_3$ groups with $^3J_{FF}$, 5.6 ÷ 9.1 Hz, and a quatruplet of septuplets for the CF unit). The surprisingly large coupling $^5J_{FF}$, not observed in similar phosphoranes [7] and in the starting diketone, is probably due to the double bond formed that renders a rotation around the C–C impossible and accounts for a possible "through-space" interaction because of closer contacts between the $CF_3$ and the $(CF_3)_2CF$ substituents. The $(CF_3)_2CF$ resonance was shifted to high field compared to the $CF_3$ signal, opposite to the findings in the starting diketone [6]. The ground-state structure of the phosphoranes **3a–c** have the P–$CF_3$ group probably in the axial position of a trigonal bipyramid [23,24]. The OCN ligand in the spirophosphoranes **3f** and **3g** presumably occupies an equatorial position.

## *EXPERIMENTAL*

The appropriate precautions in handling moisture- and oxygen-sensitive compounds were observed throughout this work. Elemental analysis: Mikroanalytisches Laboratorium Beller, Göttingen. MS: MAT 8222 (EI, electron energy 70 eV). NMR: AC 80, operating at 80.13 MHz ($^1H$, internal standard TMS), 75.39 MHz ($^{19}F$, internal standard $CCl_3F$), and 32.44 MHz ($^{31}P$, external standard 85% $H_3PO_4$). Compounds **1a** [12], **1b** [13], **1c** [14], **1d** and **1e** [15], **1f** and **1g** [16], **1h** [17], **1i** [18], **1j** [19], **1k** [20], **1l** [21], **1m** [19], and **2** [6] were prepared according to literature procedures.




**1a - m** **2** **3a - m**

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **a** | $CF_3$ | Me | Me |
| **b** | $CF_3$ | *i*Pr | *i*Pr |
| **c** | $CF_3$ | $Et_2N$ | $Et_2N$ |
| **d** | MeO | MeO | OCN |
| **e** | EtO | EtO | OCN |
| **f** | $OCH_2CH_2O$ | | OCN |
| **g** | $OCMe_2CMe_2O$ | | OCN |

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **h** | EtO | EtO | $Me_3SiO$ |
| **i** | $CF_3CH_2O$ | $CF_3CH_2O$ | $Et_2N$ |
| **j** | $CF_3CH_2O$ | $Et_2N$ | $Et_2N$ |
| **k** | $(CF_3)_2CHO$ | $Et_2N$ | $Et_2N$ |
| **l** | $PhCH_2O$ | $Et_2N$ | $Et_2N$ |
| **m** | $C_6F_5O$ | $Et_2N$ | $Et_2N$ |

**SCHEME 1**

**TABLE 1** $^1H$, $^{19}F$, and $^{31}P$ NMR Data[a] of the Phosphoranes **3a–3m** (*J* is given in Hz)

| *Compound* | *δF $CF_3$ ($^5J_{FF}$, $^6J_{FF}$)* | *δF $C(CF_3)_2$ ($^3J_{FF}$)* | *CF* | *δp* |
|---|---|---|---|---|
| **3a**[b] | −64.2 (31.6, -) | −76.8 (7.1) | −186.8 | −18.8 |
| **3b**[c] | −69.1 (27.9, -) | −75.9 (7.1) | −186.1 | −9.1 |
| **3c**[d] | −64.1 (31.4, -) | −76.2 (7.1) | −185.4 | −27.2 |
| **3d**[e] | −67.2 (30.3, 1.6) | −79.7 (9.2) | −190.0 | −53.5 |
| **3e**[f] | −67.8 (30.3, 1.6) | −77.5 (9.1) | −190.8 | −51.2 |
| **3f**[g] | −67.2 (30.3, 1.4) | −79.7 (7.0) | −190.3 | −32.6 |
| **3g**[h] | −67.9 (30.9, 1.5) | −80.1 (6.8) | −190.3 | −38.6 |
| **3h**[i] | −64.5 (38.4, -) | −79.5 (7.4) | −187.0 | −7.0 |
| **3i**[j] | −68.5 (31.2, 1.5) | −80.2 (7.8) | −189.0 | −47.8 |
| **3j**[k] | −67.5 (3.1, 1.6) | −79.0 (7.6) | −189.5 | −38.2 |
| **3k**[l] | −67.5 (30.6, 1.4) | −77.0 (7.7) | −189.0 | −37.2 |
| **3l**[m] | −62.5 (36.2, 1.6) | −77.5 (5.5) | −187.0 | −3.2 |
| **3m**[n] | −68.5 (30.9, 1.3) | −82.0 (5.6) | −189.5 | −38.2 |

[a]High field shifts from TMS, $CCl_3F$, and 85% $H_3PO_4$ were given negative signs.
[b]$\delta_H$ = 1.34 ($CH_3$, d, $^2J_{PH}$ = 12.3); $\delta_F$ = −77.9 ($CF_3$–P, d, 3F, $^2J_{PF}$ = 51.8).
[c]$\delta_H$ = 1.10 ($CH_3$, dd, 12H, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 21.1), 2.10–2.50 (CH, m, 2H); $\delta_F$ = −66.0 ($CF_3$–P, d, 3F, $^2J_{PF}$ = 68.1).
[d]$\delta_H$ = 0.83 ($CH_3$, t, 12H, $^3J_{HH}$ = 7.0), 2.84 ($CH_2$, dq, 8H, $^3J_{PH}$ = 11.3); $\delta_F$ = −60.2 ($CF_3$–P, d, 3F, $^2J_{PF}$ = 72.4).
[e]$\delta_H$ = 3.90 ($CH_3$, d, $^3J_{PH}$ = 16.1)
[f]$\delta_H$ = 1.30 ($CH_3$, t, 6H, $^3{}_{HH}$ = 7.0), 4.20 ($CH_2$, dq, 4H, $^3J_{PH}$ = 15.1).
[g]$\delta_H$ = 4.00–4.20 ($CH_2$, m, 4H).
[h]$\delta_H$ = 0.12 ($CH_3$).
[i]$\delta_H$ = 0.30 ($CH_3$, s, 9H), 0.72 ($CH_3$, t, 6H, $^3J_{HH}$ = 7.0), 3.57 ($CH_2$, dq, 4H, $^3J_{PH}$ = 12.9).
[j]$\delta_H$ = 0.90 ($CH_3$, t, 6H, $^3J_{HH}$ = 7.0), 2.90 ($CH_2$, q, 4H), 3.70 ($CH_2CF_3$, q, 4H, $^3J_{FH}$ = 8.4); $\delta_F$ = −80.1 ($CF_3CH_2$, t, 6F, $^4J_{PF}$ = 5.9).
[k]$\delta_H$ = 1.00 ($CH_3$, t, 12H, $^3J_{HH}$ = 6.2), 2.80 ($CH_2$, g, 8H), 3.90 ($CH_2CF_3$, q, 2H, $^3J_{FH}$ = 8.7); $\delta_F$ = −80.0 ($CF_3CH_2$, t, 3F, $^4J_{PF}$ = 6.0).
[l]$\delta_H$ = 0.90 ($CH_3$, t, 12H, $^3J_{HH}$ = 6.9), 2.90 ($CH_2$, q, 8H), 4.40 (CH, sep, 1H, $^3J_{FH}$ = 6.2); $\delta_F$ = −80.1 ($CF_3$, d, 6F, $^4J_{PF}$ = 9.2).
[m]$\delta_H$ = 1.10 ($CH_3$, t, 12H, $^3J_{HH}$ = 6.6), 3.10 ($CH_2$, q, 8H), 4.70 ($CH_2Ph$, 2H, $^3J_{PH}$ = 7.6), 6.8–7.7 (Ph, m, 5H).
[n]$\delta_H$ = 1.0 ($CH_3$, t, 12H, $^3J_{HH}$ = 6.7), 3.00 ($CH_2$, q, 8H); $\delta_F$ = −159.1 ÷ −160.2 ($C_6F_5$, o-F, m, 2F), −169.0 ÷ −170.6 ($C_6F_5$, p-F, m, 1F), −171.0 ÷ −172.0 ($C_6F_5$, m-F, m, 2F).

**TABLE 2** Experimental Details for the Preparation of Compounds **3a–3m**

| *Compound* | *Reactants [g (mmol)]* | *Yield [g (%)]* |
|---|---|---|
| **3a**[a] | **1a:** 1.3 (10), **2:** 2.9 (10) | 3.6 (87) |
| **3b**[a] | **1b:** 1.9 (10), **2:** 2.9 (10) | 3.9 (82) |
| **3c**[a] | **1c:** 2.4 (10), **2:** 2.9 (10) | 5.0 (94) |
| **3d** | **1d:** 0.3 (2.4), **2:** 0.7 (2.4) | 1.0 (100) |
| **3e** | **1e:** 0.6 (3.5), **2:** 1.0 (3.5) | 1.1 (70) |
| **3f**[b] | **1f:** 0.3 (2.4), **2:** 0.7 (56) | 1.0 (100) |
| **3g**[c] | **1g:** 0.7 (3.5), **2:** 1.0 (35) | 1.7 (100) |
| **3h**[d] | **1f:** 1.8 (10), **2:** 2.9 (10) | 4.7 (100) |
| **3i**[e] | **1i:** 0.7 (2.4), **2:** 0.7 (2.4) | 1.4 (100) |
| **3j**[f] | **1j:** 0.7 (2.4), **2:** 0.7 (2.4) | 1.4 (100) |
| **3k**[g] | **1k:** 0.8 (2.4), **2:** 0.7 (2.4) | 1.5 (100) |
| **3l**[h] | **1l:** 0.7 (2.4), **2:** 0.7 (2.4) | 1.4 (100) |
| **3m**[i] | **1m:** 0.9 (2.4), **2:** 0.7 (2.4) | 1.6 (100) |

[a]Decomposition upon distillation.
[b]Mp 35°C.
[c]Mp 38°C.
[d]Bp 63 − 64°C/0.01 Torr.
[e]Bp 35°C/0.001 Torr.
[f]Bp 33°C/0.001 Torr.
[g]Bp 35°C/0.001 Torr.
[h]Bp 32°C/0.001 Torr.
[i]Mp 42°C.

## *General Method for the Synthesis of Phosphoranes* **3a–3m** (*see Table 2*)

A stoichiometric amount of each phosphorus derivative **1** was added dropwise to a solution of compound **2** in 10 mL of diethyl ether at −10°C, stirred for 1 hour and then allowed to react at ambient temperature for 2 hours. The volatile materials were removed in vacuo. Each remaining colorless liquid or solid was analytically pure, unless indicated otherwise.

*2,2-Dimethyl-2,4-bis(trifluoromethyl)-5-[1′,2′,2′,2′-tetrafluoro-1′-(trifluoromethyl)ethyl]-1,3,2λ⁵σ⁵-dioxaphospholene-(4)* (**3a**). MS (50 °C): *m/z*(%): 424 ($M^+$, 30), 405 ($M^+ - F$, 35), 355 ($M^+ - CF_3$, 90), 305 ($M^+ - C_2F_5$, 12), 286 ($M^+ - 2\ CF_3$, 10), 130 ($Me_2PCF_3^+$, 100), 69 ($CF_3^+$, 18), and other fragments. Precision mass determination for *m/z* = 424 ($C_9H_6F_{13}O_2P$): 423.98967 (found), 423.98978 (calcd).

*2,2-Bis(1′-methylethyl)-2,4-bis(trifluoromethyl)-5-[1′,2′,2′,2′-tetrafluoro-1′-(trifluoromethyl)ethyl]-1,3,2λ⁵σ⁵-dioxaphospholene-(4)* (**3b**). MS (50°C): *m/z*(%): 480 ($M^+$, 7), 461 ($M^+ - F$, 10), 411 ($M^+ - CF_3$, 25), 369 ($M^+ - CF_3 - C_3H_6$, 5), 186 ($iPr_2PCF_3^+$, 8), 69 ($CF_3^+$, 12), 43 ($C_3H_7^+$, 100), and other fragments. Precision mass determination for *m/z* = 480 ($C_{13}H_{14}F_{13}O_2P$): 480.05145 (found), 480.05240 (calcd).

*2,2-Bis(diethylamino)-2,4-bis(trifluoromethyl)-5-[1′,2′,2′,2′-tetrafluoro-1′-(trifluoromethyl)ethyl]-1,3,2λ⁵σ⁵-dioxaphospholene-(4)* (**3c**). MS (50 °C): *m/z*(%): 538 ($M^+$, <1), 519 ($M^+ - F$, 16), 469 ($M^+ - CF_3$, 29), 466 ($M^+ - Et_2N$, 63), 416 ($M^+ - Et_2N - CF_2$, 50), 398 ($M^+ - CF_3 - C_4H_8N$, 41), 69 ($CF_3^+$, 100), and other fragments. Precision mass determination for *m/z* = 519 ($C_{15}H_{20}F_{12}N_2O_2P$): 519.10706 (found), 519.10714 (calcd); for *m/z* = 469 ($C_{14}H_{20}F_{10}N_2O_2P$): 469.11026 (found), 469.10980 (calcd).

*2,2-Dimethoxy-2-isocyanato-4-trifluoromethyl-5-[1′,2′,2′,2′-tetrafluoro-1′-(trifluoromethyl)ethyl]-1,3,2λ⁵σ⁵-dioxaphospholene-(4)* (**3d**). MS (26 °C): *m/z*(%): 429 ($M^+$, 1), 207 ($M^+ - C_3F_6 - NCO - HF$, 20), 107 ($C_3F_3O^+$, $(MeO)_2PO^+$, 100), 69 ($CF_3^+$, 4), and

other fragments. Anal. calcd for $C_9H_6F_{10}NO_5P$ (429.11): C, 25.19; H, 1.41; F, 44.27; P, 7.22. Found: C, 25.12; H, 1.57; F, 44.40; P, 7.17.

*2,2-Diethoxy-2-isocyanato-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3e**). MS (26°C): *m/z*(%): 457 ($M^+$, 6), 359 ($M^+ - NCO - 2\ C_2H_4$, 40), 208 ($M^+ - NCO - 2\ C_2H_4 - C_3F_6 - H$, 58), 152 ($C_5F_4O^+$, 60), 124 ($C_4F_4^+$, 100), 69 ($CF_3^+$, 31), and other fragments. Anal. calcd for $C_{11}H_{10}F_{10}NO_5P$ (457.16): C, 28.90; H, 2.20; F, 41.56; P, 6.78. Found: C, 29.01; H, 2.15; F, 41.85; P, 6.80.

*2-Isocyanato-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-spiro-[1',3',2'$\lambda^5\sigma^5$-dioxaphospholane-2,2'-[1,3,2$\lambda^5\sigma^5$]-dioxaphospholen-(4)]* (**3f**). MS (55 °C): *m/z*(%): 427 ($M^+$, 80), 408 ($M^+$, − F, 40), 385 ($M^+ - NCO$, 25), 367 ($M^+ - C_2H_4O_2$, 10), 358 ($M^+ - CF_3$, 100), 133 ($OCNPOCH_2CH_2O^+$, 40), 91 ($POCH_2CH_2O^+$, 39), 69 ($CF_3^+$, 20), 43 ($C_2H_3O^+$, 40), and other fragments. Anal. calcd for $C_9H_4F_{10}NO_5P$ (427.09): C, 25.31; H, 0.94; F, 44.48; P, 7.25. Found: C, 25.10; H, 0.98; F, 44.60; P, 7.24.

*2-Isocyanato-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-4',4',5',5'-tetramethyl-spiro-[1',3',2'$\lambda^5\sigma^5$-dioxaphospholane-2,2'-[1,3,2$\lambda^5\sigma^5$]-dioxaphospholene-(4)]* (**3g**). MS (55°C): *m/z*(%): 483 ($M^+$, 6), 468 ($M^+ - CH_3$, 3), 425 ($M^+ - C_3H_6O$, 6), 367 ($M^+ - C_2(CH_3)_4O_2$, 30), 83 ($C_6H_{11}^+$, 100), 57 ($C_3H_5O^+$, 20), and other fragments. Anal. calcd for $C_{13}H_{12}F_{10}NO_5P$ (483.20): C, 33.31; H, 2.50; F, 39.32; P, 6.41. Found: C, 33.39; H, 2.77; F, 39.50; P, 6.25.

*2,2-Diethoxy-2-trimethylsiloxy-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3h**). MS (200°C): *m/z*(%): 505 ($M^+$ + H, 10), 461 ($M^+ - C_2H_3O$, 18), 433 ($M^+ - C_3H_7Si$, 38), 405 ($M^+ + H - CF_2CF_2$, 67), 377 ($M^+ + H - CF_2CF_2 - C_2H_4$, 79), 307 ($M^+ + H - C_3F_7 - C_2H_5$, 58), 197 ($C_4F_7O^+$, 63), 109 ($C_3F_3O^+$, 100), 81 ($C_2F_3^+$, 61), 73 ($Me_3Si^+$, 18), 69 ($CF_3^+$, 16), and other fragments. Anal. calcd for $C_{13}H_{19}F_{10}O_5PSi$ (504.33): C, 30.96; H, 3.80; F, 37.67; P, 6.14. Found: C, 29.82; H, 3.68; F, 37.20; P, 6.17.

*2-Diethylamino-2,2-bis(2',2',2'-trifluoroethoxy)-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3i**). MS (150°C): *m/z*(%): 595 ($M^+$, 8), 526 ($M^+ - CF_3$, 14), 523 ($M^+ - Et_2N$, 100), 496 ($M^+ - OCH_2CF_3$, 80), 397 ($M^+ - 2\ OCH_2CF_3$, 32), 325 ($M^+ - 2\ OCH_2CF_3 - Et_2N$, 30), 99 ($CF_3CH_2O^+$, 8), 72 ($Et_2N^+$, 12), 69 ($CF_3^+$, 50), and other fragments. Anal. calcd for $C_{14}H_{14}F_{16}NO_4P$ (595.22): C, 28.25; H, 2.37; F, 51.07; P, 5.20. Found: C, 28.25; H, 2.44; F, 51.00; P, 5.17.

*2,2-Bis(diethylamino)-2-(2',2',2'-trifluoroethoxy)-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3j**). MS (150°C): *m/z*(%): 568 ($M^+$, 14), 499 ($M^+ - CF_3$, 10), 496 ($M^+ - Et_2N$, 100), 469 ($M^+ - OCH_2CF_3$, 22), 422 ($M^+ - 2\ Et_2N$, 24), 323 ($M^+ - OCH_2CF_3 - 2\ Et_2N$, 8), 99 ($CF_3CH_2O^+$, 12), 72 ($Et_2N^+$, 14), 69 ($CF_3^+$, 60), and other fragments. Anal. calcd for $C_{16}H_{22}F_{13}N_2O_3P$ (568.32): C, 33.82; H, 3.90; F, 43.46; P, 5.45. Found: C, 33.95; H, 3.95; F, 43.80; P, 5.54.

*2,2-Bis(diethylamino)-2-[1'-(trifluoromethyl)-2',2',2'-trifluoroethoxy]-4-trifluoro-methyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3k**). MS (150°C): *m/z*(%): 636 ($M^+$, 8), 567 ($M^+ - CF_3$, 20), 565 ($M^+ - Et_2N$, 100), 493 ($M^+ - 2\ Et_2N$, 20), 469 ($M^+ - OCH(CF_3)_2$, 95), 325 ($M^+ - OCH(CF_3)_2 - 2\ Et_2N$, 24), 72 ($Et_2N^+$, 24), 69 ($CF_3^+$, 40), and other fragments. Anal. calcd for $C_{17}H_{21}F_{16}N_2O_3P$ (636.31): C, 32.09; H, 3.33; F, 44.77; P, 4.87. Found: C, 32.99; H, 3.45; F, 45.70; P, 4.86.

*2,2-Bis(diethylamino)-2-(phenylmethoxy)-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3l**). MS (120°C): *m/z*(%): 576 ($M^+$, 5), 504 ($M^+ - Et_2N$, 100), 469 ($M^+ - OCH_2Ph$, 48), 422 ($M^+ - 2\ Et_2N$, 12), 314 ($M^+ - OCH_2Ph - 2\ Et_2N$, 10), 107 ($PhCH_2O^+$, 12), 77 ($Ph^+$, 12), 72 ($Et_2N^+$, 12), and other fragments. Anal. calcd for $C_{21}H_{27}F_{10}N_2O_3P$ (576.41): C, 43.76; H, 4.72; F, 32.96; P, 5.37. Found: C, 44.58; H, 4.94; F, 31.20; P, 5.51.

*2,2-Bis(diethylamino)-2-(pentafluorophenyloxy)-4-trifluoromethyl-5-[1',2',2',2'-tetrafluoro-1'-(trifluoromethyl)ethyl]-1,3,2$\lambda^5\sigma^5$-dioxaphospholene-(4)* (**3m**). MS (150°C): *m/z*(%): 652 ($M^+$, 2), 580 ($M^+ - Et_2N$, 100), 469 ($M^+ - OC_6F_5$, 35), 508 ($M^+ - 2\ Et_2N$, 12), 183 ($F_5C_6O^+$, 10), 167 ($F_5C_6^+$, 8), 72 ($Et_2N^+$, 15), and other fragments. Anal. calcd for $C_{20}H_{20}F_{15}N_2O_3P$ (652.34): C, 36.82; H, 3.09; F, 43.69; P, 4.75. Found: C, 37.58; H, 3.25; F, 42.20; P, 5.08.

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## *REFERENCES*

[1] F. Ramirez, J. F. Marecek, I. Ugi, D. Marquarding, *Phosphorus, 3,* 1973, 91.

[2] S. Trippett, J. I. Dickstein, *Tetrahedron Lett.,* 1973, 2203.
[3] D. Dakternieks, G.-V. Röschenthaler, K. Sauerbrey, R. Schmutzler, *Chem. Ber., 112,* 1979, 2380.
[4] H.-B. Eikmeier, K. C. Hodges, O. Stelzer, R. Schmutzler, *Chem. Ber., 111,* 1978, 2077.
[5] G.-V. Röschenthaler, K. Sauerbrey, R. Schmutzler, *Chem. Ber., 111,* 1978, 3105.
[6] M. A. Kurikin, L. S. German, Yu. N. Studnev, A. V. Fokin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1980, 1679.
[7] A. A. Kadyrov, I. Neda, T. Kaukorat, R. Sonnenburg, A. Fischer, P. G. Jones, R. Schmutzler, *Chem. Ber., 129,* 1996, 725.
[8] A. A. Kadyrov, I. Neda, T. Kaukorat, A. Fischer, P. G. Jones, R. Schmutzler, *J. Fluorine Chem., 72,* 1995, 29.
[9] F. U. Seifert, G.-V. Röschenthaler, unpublished results.
[10] I. V. Konovalova, L. A. Burnaeva, N. K. Novikova, O. S. Kedrova, A. N. Pudovik, *Zh. Obshch. Khim., 51,* 1981, 995.
[11] E. Duff, S. Trippett, P. J. Whittle, *J. Chem. Soc. Perkin. Trans. I,* 1973, 972.
[12] I. G. Maslennikov, A. N. Lavrentiev, N. V. Khovanskaya, V. B. Lebedev, E. G. Sochilin, *Zh. Obshch. Khim., 49,* 1979, 1498.
[13] U. Dieckbreder, A. A. Kolomeitsev, E. Lork, G.-V. Röschenthaler, *Heteroatom Chem., 7,* 1996, 281.
[14] W. Volbach, I. Ruppert, *Tetrahedron Lett., 24,* 1983, 5509.
[15] I. V. Konovalova, R. D. Gareev, L. A. Burnaeva, N. K. Novikova, T. A. Faskhutdinova, A. N. Pudovik, *Zh. Obshch. Khim., 50,* 1980, 1451.
[16] Zh. Ivanova, E. A. Stukalo, G. J. Derkach, *Zh. Obshch. Khim., 39,* 1969, 551.
[17] M. Sekine, K. Okimoto, K. Yamada, T. Hata, *J. Org. Chem., 46,* 1981, 2097.
[18] H. Suzuki, S. Katayama, F. Okada, Jpn. Kokai Tokyo Koho JP 04,210,695 [92,210,695].
[19] M. Görg, G.-V. Röschenthaler, *Phosphorus Sulfur Silicon,* in press.
[20] R. Francke, R. Di Giacomo, D. Dakternieks, G.-V. Röschenthaler, *Z. Anorg. Allg. Chem., 519,* 1984, 141.
[21] A. A. Kolomeitsev, K. Yu. Chabanenko, Yu. L. Yagupol'skij, G.-V. Röschenthaler, *Synthesis,* 1994, 145.
[22] S. Berger, S. Braun, H.-O. Kalinowski: *NMR-Spektroskopie von Nichtmetallen: $^{31}$P-NMR-Spektroskopie,* Thieme, Stuttgart, 48 pp. (1993).
[23] A. N. Chernega, A. A. Kolomeitsev, Yu. L. Yagupolskij, A. Gentzsch, R.-D. Hund, G.-V. Röschenthaler, *J. Fluorine Chem., 60,* 1993, 263.
[24] A. A. Kolomeitsev, Yu. L. Yagupolskij, A. Gentzsch, E. Lork, G.-V. Röschenthaler, *Phosphorus Sulfur Silicon, 92,* 1994, 179.