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ON THE EXCHANGE REACTION, $\geq C{=}S \longrightarrow \geq C{=}O$, USING HEXAFLUOROACETONE

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SUMMARY

The reaction of λ^3-phospha-diazetidin-thione, **1** with hexafluoroacetone (HFA) furnished not only the expected addition product, the λ^5P-perfluoropinacolyl phosphorane, **2**. In addition, HFA was observed to cause $\geq C{=}S \longrightarrow \geq C{=}O$ exchange in **2**, and exclusive formation of a urea derivative, **3**, was noted upon prolonged interaction of HFA with **2**. Likewise, N,N,N',N'-tetramethylthiourea, **4**, was found to be converted to N,N,N',N'-tetramethylurea, **5**, by HFA. The reactions were followed by ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P-n.m.r. spectroscopy.

INTRODUCTION

The oxidative addition of hexafluoroacetone (HFA) to P(III) compounds is a well known method of synthesis of perfluoropinacolyl phosphoranes, i.e. compounds with λ^5phosphorus [1]. We have extended this type of reaction to 1,3-diaza-2λ^3-phosphetidin-4-thione, **1** [2], and observed that, initially, the formation of the expected addition product of HFA to **1**, **2** predominates. Formation of a second perfluoropinacolyl phosphorane, **3**, was, however, also noted. Upon prolonged interaction of **1** and HFA, **3** was the sole reaction product. The reaction amounts to the exchange of the sulfur of the $\geq C{=}S$ group for oxygen, i.e. formation of the $\geq C{=}O$ group takes place. This type of conversion of a thiocarbonyl group into a carbonyl group by HFA has, to the best of our knowledge, not previously been observed (eq. (1)).

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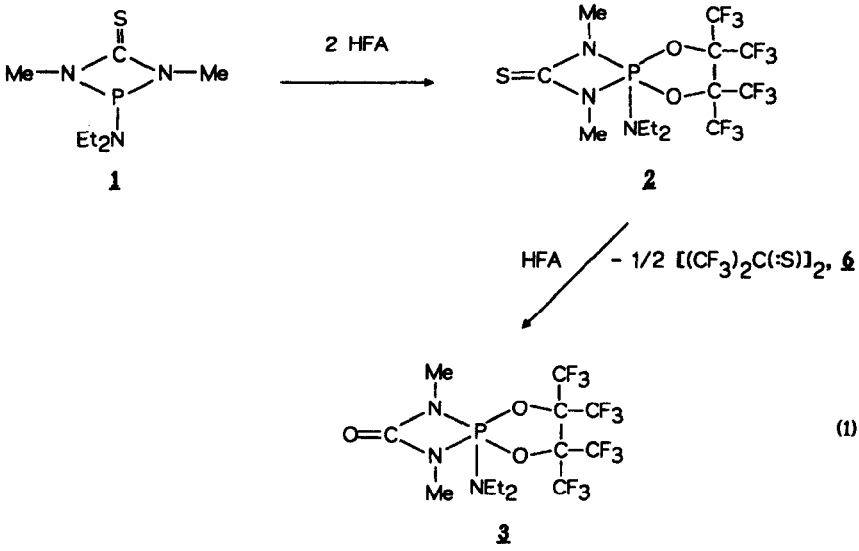
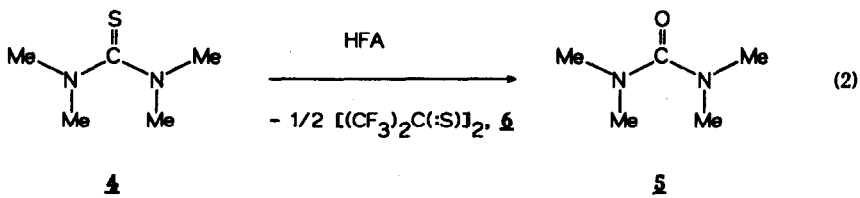


(1)

In a separate experiment, N,N,N',N'-tetramethylthiourea, **4** was quantitatively converted by HFA (molar ratio **4** : HFA = 1 : 1.6) to N,N,N',N'-tetramethylurea, **5** (eq. (2)) after 24 h at room temperature, and 24 h at 40° C. In this case, care was taken to isolate the other reaction product which was identified (δ(F) = -73.5, [3]) as the dimer of hexafluorothioacetone, $[(CF_3)_2C(:S)]_2$, **6**.

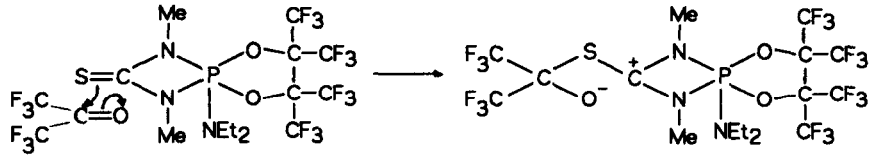


(2)

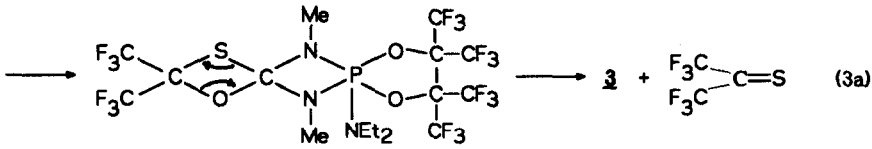
The conversion of the thiocarbonyl to the carbonyl group has been effected previously by a number of reagents, e.g. 3N NaOH/dichloromethane under phase transfer conditions [4], or by sodium nitrite in acidic solution [5]. The C=S bond of thiourea was not affected upon its reaction with HFA which produced 1,3,5-oxadiazine derivatives [6]. In the reaction of dithiooxamide with

HFA formation of 1,1,1,3,3,3-hexafluoro-2-propylamino-1-thiooxamide, $(CF_3)_2CHNHC(:S)C(:O)NH_2$, accompanied by elemental sulfur, has been reported [7]. The reaction of HFA with $P(:S)Cl_3$ leads to a formal twofold oxidative addition of HFA to sulfur [8]. A conversion, $\geq C{=}Se \longrightarrow \geq C{=}O$, has been observed during the interaction of HFA with triphenylphosphine selenide, producing tetrakis(trifluoromethyl)-1,3-diselenetane and triphenylphosphine oxide [9].

While the exact mechanism of this unusual reaction is not known, we suggest the following pathway for, e.g., the reaction of **2** with HFA to produce **3**, similar to [9] (eq. (3a/b)).



2



(3a)

(3b)

6

EXPERIMENTAL

All experiments were conducted with careful exclusion of air and moisture [10]. Solvents were dried by standard procedures [11]. NMR spectra were

recorded on the instruments BRUKER AC 200: ^{1}H (200.1 MHz; ext. TMS); ^{13}C (50.3 MHz; ext. TMS); ^{19}F (188.3 MHz; $CFCl_3$ ext.); ^{31}P (81.0 MHz; H_3PO_4 ext.). BRUKER AM 400: ^{1}H (400.1 MHz; ext. TMS); ^{13}C (100.6 MHz; ext. TMS). Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; dq, doublet of quartets. Mass spectra were recorded on the instrument FINNIGAN MAT 8430, IR spectra on the Beckman spectrometer IR 4260.
The synthesis of **1** is described elsewhere [2].

Reaction of 2-diethylamino-1,3-dimethyl-1,3-diaza-2λ^{3}-phosphetidin-4-thione, **1** with HFA: Synthesis of 2-diethylamino-1,3-dimethyl-5,8-dioxa-6,6,7,7-tetrakis(trifluoromethyl)-1,3-diaza-4λ^{5}-phosphaspiro[3.4]octane-2-thione, **2**

The reaction was conducted in a 150 ml heavy-wall glass tube, fitted with a TEFLON®stopcock. At -196 °C 3.75 g (18.3 mmol) of **1** [2] and 11 g (66.3 mmol) of HFA were condensed into the tube. The reaction mixture was magnetically stirred at -10 °C for 24 h. Subsequently, excess HFA was removed in vacuo (0.1 mm). According to the ^{31}P NMR spectrum the reaction was not yet complete, at this stage. The formation of **3**, resulting from $\geq C{=}S \longrightarrow \geq C{=}O$ exchange, together with **2**, was observed (integration ratio **1** : **2** : **3** = 3 : 3 : 1). The reaction mixture was pumped to dryness (0.1 mm), and the residue was dissolved in 10 ml of acetonitrile. The product, **2** crystallized at -20 °C over 12 h, and was subsequently twice recrystallized.

Yield of **2**, 3.8 g (39%); mp. 55 °C.

Found: C, 29.26; H, 3.16; F, 42.5%; $C_{13}H_{16}F_{12}N_3O_2PS$ (537.30) requires C, 29.06; H, 3.00; F, 42.43%]. E.I.-M.S. (20 °C): 537 ([M]$^+$, 20%); 518 ([M-F]$^+$, 6%); 468 ([M-CF_3]$^+$, 4%); 434 ([M-N,N'-dimethylthiourea-H]$^+$, 100%); 197 ([$POC(CF_3)_2$]$^+$, 22%).

^{1}H NMR (400.1 MHz) in $CDCl_3$: δ 1.11 (t), $^{3}J(HH)$ 7.12 [$N(CH_2\underline{C}H_3)_2$]; δ 3.61 (d), $^{3}J(HP)$ 13.04 [$P(NC\underline{H}_3)$]; δ 3.15 (dq), $^{3}J(HP)$ 8.38, $^{3}J(HH)$ 7.12 [$N(C\underline{H}_2CH_3)_2$].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.67 (s), [$N(CH_2\underline{C}H_3)_2$]; δ 30.32 (d), $^2J(CP)$ 3.38 [$P(N\underline{C}H_3)$]; δ 44.49 (d), $^2J(CP)$ 5.40 [$N(\underline{C}H_2CH_3)_2$]; δ 120.3 (q), $^1J(CF)$ 290; δ 187,9 (d), $^2J(CP)$ 3.31 [$\underline{C}$=S]. ^{19}F NMR (188.3 MHz, in $CDCl_3$): δ -67.80 (septet), $^{4,5}J(FF)$ 8.3; δ -69.13 (septet), $^{4,5}J(FF)$ 8.3 [12]; $^{31}P\{^1H\}$-NMR (81.0 MHz in $CDCl_3$): δ -32.11 (s).

Reaction of 2-diethylamino-1,3-dimethyl-1,3-diaza-2λ^3-phosphetidin-4-thione, **1** with HFA: Preparation of 2-diethylamino-1,3-dimethyl-5,8-dioxa-6,6,7,7-tetrakis-(trifluoromethyl)-1,3-diaza-4λ^5-phosphaspiro[3.4]octane-2-one, **3**

Compound **1** (3.1 g; 15.1 mmol) was placed into a 150 ml heavy-wall glass tube, fitted with a TEFLON® stopcock. After condensation of 10.5 g (63.2 mmol) of HFA at -196 °C the temperature was increased to 25 °C, and the reaction mixture was stirred magnetically for 24 h. According to a ^{31}P NMR spectrum recorded at this stage all of **1** had been consumed, and compounds **2** and **3** were present in a ca. 1 : 1 ratio. The ratio, **2** : **3** changed to 1 : 4 after a stirring period of 48 h (60 °C), and was increased to 1 : 7 after another 24 h (80 °C). After the mixture had been stirred for a further period of 4 d (65 °C) the ^{31}P NMR spectrum revealed that only **3** was present. The product left after excess HFA had been pumped off was dissolved in acetonitrile (10 ml). **3** crystallized upon standing of the acetonitrile solution at -20 °C (12 h).

Yield of **3**, 2.3 g (29%); mp. 60 - 63 °C.

Found: C, 29.5; H, 3.0; F, 41.5; N, 8.3%; $C_{13}H_{16}F_{12}N_3O_3P$ (521.23) requires C, 29.95; H, 3.09; F, 43.74; N, 8.06%]. E.I.-M.S. (20 °C): 521 ([M]$^+$, 4%); 502 ([M-F]$^+$, 5%); 452 ([M-CF_3]$^+$, 7%); 449 ([M-$N(C_2H_5)_2$]$^+$, 7%); 197 ([$POC(CF_3)_2$]$^+$, 8%); 70 ([CH_3NCNCH_3]$^+$, 100%); 57 ([CH_3NCO]$^+$, 37%).
IR (in toluene solution, compensated): ν(CO) 1785.

^1H NMR (400.1 MHz, $CDCl_3$): δ 1.15 (t), $^3J(HH)$ 7.1 ([$N(CH_2C\underline{H}_3)_2$]; δ 2.81 (d) $^3J(HP)$ 13.18 [$P(NC\underline{H}_3)$]; δ 3.18 (dq), $^3J(HP)$ 8.39, $^3J(HH)$ 7.1 [$N(C\underline{H}_2CH_3)_2$]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.83 (s), [$N(CH_2\underline{C}H_3)_2$]; δ 27.62 (d), $^2J(CP)$

4.32 [P(N$\underline{C}H_3$)]; δ 44.58 (d), ^{2}J(CP) 5.55 [N($\underline{C}H_2CH_3$)$_2$]; δ 120.41 (q), ^{1}J(CF) 294; δ 156.69 (d), ^{2}J(CP) 16.3 [$\underline{C}$=O]. ^{19}F NMR (188.3 MHz, $CDCl_3$): δ -67.91 (septet), ^{4,5}J(FF) 8.4; δ -69.21 (septet), ^{4,5}J(FF) 8.4 [12]; ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ -39.48 (s).

Reaction of N,N,N',N'-tetramethylthiourea, **4** with HFA: Formation of N,N,N',N'-tetramethylurea, **5** and of hexafluorothioacetone dimer, **6**

The reaction was conducted in a 150 ml heavy-wall glass tube, fitted with a TEFLON® stopcock. HFA (11.1 g; 66.9 mmol) was condensed onto a solution of **4** (5.5 g; 41.6 mmol) in 30 ml actonitrile at liquid nitrogen temperature, and the mixture was subsequently allowed to reach room temperature (30 min). Within another 30 min it assumed a yellow colour. After the reaction mixture had been stirred magnetically for 24 h at room temperature the presence of **4** and **5** in a ratio of 2.5 : 1 was observed by ^{1}H and ^{13}C NMR spectroscopy. Only **5** was observed after another 24 h (40 °C) stirring period. Volatile products were then allowed to evaporate at atmospheric pressure, and the residue was distilled. First, the dimer of hexafluorothioacetone, **6**, of bp. ca. 40 °C (4.0 g; 53%) was obtained, followed by 3.5 g (72%) of **5** of bp. 64 °C (10 mm).

5: ^{1}H (200.1 MHz, $CDCl_3$): δ 2.67 (s). ^{13}C (50.3 MHz, $CDCl_3$): δ 37.9 (s) [N($\underline{C}H_3$)$_2$]; δ 164.9 (s) [$\underline{C}$O] (Lit. [13] δ 165.7).

6: E.I.-M.S. (20 °C): 364 ([M]$^+$, 12%); 345 ([M-F]$^+$, 14%); 295 ([M-CF_3]$^+$, 76%); 182 ([$F_3CC(S)CF_3$]$^+$, 4%); 163 [($F_3CC(S)CF_3$-F]$^+$, 30%); 113 ([F_3CCS]$^+$, 100%). ^{13}C (100.6 MHz, $CDCl_3$): δ 122.65 (q), ^{1}J(CF) 284 [$\underline{C}F_3$]. ^{19}F (188.3 MHz, $CDCl_3$): δ -73.51 (s) (Lit. [3] -75.4).

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