

P-Bis(trifluoromethyl) Ylides: Synthesis and Reactions

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ABSTRACT: Bis(trifluoromethyl)phosphines $RP(CF_3)_2$ ($R = Me, NEt_2$) were methylated by $MeOSO_2CF_3$, yielding the respective phosphonium salts $[RP(CF_3)_2Me]^+$ and $CF_3SO_3^-$. Deprotonation using $MeN=P(NEt_2)_3$ led to the phosphorus ylides $RP(CF_3)_2=CH_2$, stable in solution at ambient temperature, which could be converted into $1,2\lambda^5\sigma^5$ -oxaphosphetanes by adding hexafluoroacetone. © 2002 Wiley Periodicals, Inc. *Heteroatom Chem* 13:650–653, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10061

INTRODUCTION

Phosphorus ylides are versatile reactants in organic chemistry, e.g. in the synthesis of naturally occurring compounds [1]. There are only a few ylides containing fluorine or perfluoroalkyl groups in the alkylidene moiety [2] and not many *P*-halogeno derivatives [3]. Recently, we synthesized the first *P*-trifluoromethyl ylides, having one CF_3 group

bonded to phosphorus [4]. Because the phosphines $RP(CF_3)_2$ ($R = Me, NEt_2$) are easily accessible by using “Ruppert’s reagent” [5] $[CF_3Br/P(NEt_2)_3]$, methylation followed by deprotonation should yield the desired ylides.

RESULTS AND DISCUSSION

The Ruppert-system $CF_3Br/(Et_2N)_3P$ [5] proved to be a useful system to synthesize the bis(trifluoromethyl)phosphines **2a–c** as oxygen-sensitive liquids (**2a** being pyrophoric) from the respective dichlorophosphines **1a–c** (Scheme 1) in good yields. Compounds **2a** and **2c** have already been obtained by other methods [6,7].

While **2b** and **2c** could be obtained in dichloromethane, in the case of **2a** ($R = Me$), triglyme had to be used as a solvent because of its higher boiling point, necessary to isolate **2a** (bp 30°C). Methylation was possible only using methyl triflate at 100°C without a solvent to give the first bis-trifluoromethyl phosphonium salts **3a** and **3c**, moisture sensitive compounds, in good yields. In the case of **2b**, decomposition was observed during this procedure. Compounds **3a** and **3c** decomposed rapidly in diethyl ether and THF. The phosphonium triflates **3a** and **3c** could be deprotonated using as a neutral base a weak nucleophile *N*-methyliminotris(diethylamino) phosphine imide **4** [$pK_s = 28$] [8], yielding the desired ylides **5a** and **5c** (Scheme 2) which were stable in solution at room temperature, whereas $CF_3Me_2P=CH_2$ decomposed at

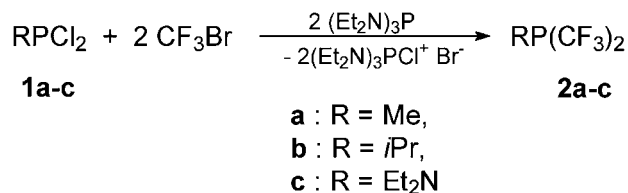
Presented in part at the *XIII Int Conf on Phosphorus Chemistry*, Jerusalem, Israel, July 16–21, 1995; A. A. Kolomeitsev, M. Goerg, U. Dieckbreder, E. Lork, G.-V. Rösenthaller, *Phosphorus, Sulfur Silicon Relat Elem* **109**, 1996, 597–600.

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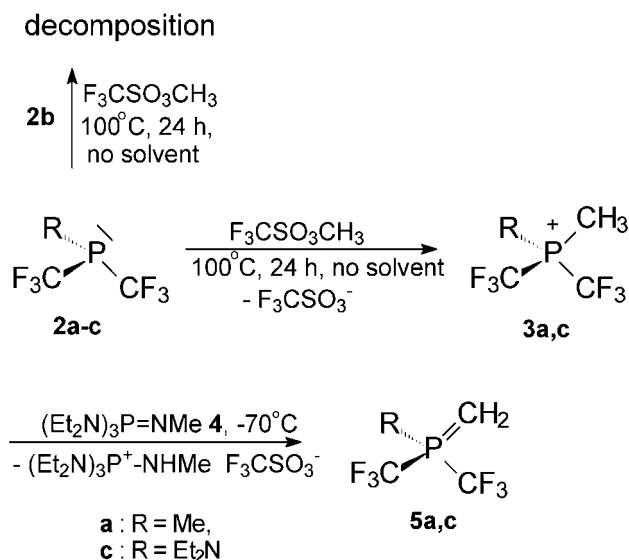


SCHEME 1

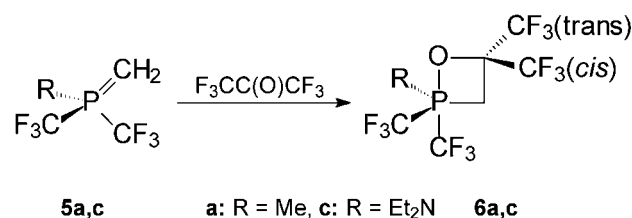
temperatures as low as -50°C . It was of advantage to obtain the nonvolatile amidophosphonium salt, $[(\text{Et}_2\text{N})_3\text{PNHMe}]^+\text{CF}_3\text{SO}_3^-$, which could easily be separated (Scheme 2).

The reaction of the bis(trifluoromethyl) ylides **5a** and **5c** with hexafluoroacetone furnished the 2,2,4,4-tetrakis(trifluoromethyl)-1,2 $\lambda^5\sigma^5$ -oxaphosphetanes, **6a** and **6c**, as colourless, moisture-sensitive liquids (Scheme 3).

The structure of the compounds **2–6** was confirmed by their NMR spectra (see Table 1). The ylides **5a** and **5c** were characterized at -70°C . In the ^{19}F NMR spectra for the *P*-CF₃ groups at 308 K, broad doublets were observed, while sharp singlets were recorded for the *C*-CF₃ groups. Because of *Berry*-pseudorotation, which was fast on the NMR time scale, axial and equatorial CF₃ substituents at phosphorus could not be distinguished. Cooling a solution of phosphetane **6c** (R = Et₂N) in toluene-*d*₈ slowed down the ligand permutation process, resulting in the magnetic inequivalence of the *P*-CF₃ groups and, also of the *C*-CF₃ groups (*cis* and *trans* with respect to the equatorial *P*-CF₃) below the coalescence temperature of 273 K. At 213 K, a doublet of quartets for the axial *P*-CF₃ was observed



SCHEME 2



SCHEME 3

($\delta = -62.6$, $^2J_{\text{FP}} = 52.4$, $^4J_{\text{FF}} = 13.9$ Hz), a doublet of quartets for the equatorial *P*-CF₃ group ($\delta = -67.0$, $^2J_{\text{FP}} = 123.0$, $^4J_{\text{FF}} = 13.9$ Hz) split further by “through-space” coupling ($J_{\text{F}\cdots\text{F}} = 7.0$ Hz) between *C*-CF₃(*cis*) and *P*-CF₃(equatorial). The smaller absolute value of $^2J_{\text{FP}} = 52.4$, compared to $^2J_{\text{FP}} = 123.0$ Hz, is typical of an axially bonded CF₃ moiety [4,9]. In a similar oxaphosphetane, F $\cdots$ F “through-space” coupling *C*-CF₃(*cis*) $\cdots$ *P*-CF₃(equatorial) was found ($J_{\text{F}\cdots\text{F}} = 4.7$ Hz) [9].

TABLE 1 NMR Data of **2a–c**, **3a**, **3c**, **5a**, **5c**, **6a**, and **6c** at 308 K (*J* in Hz)

Compound	δ_{H} (<i>P</i> -CH) ^a ($^2J_{\text{HP}}$)	δ_{F} (<i>P</i> -CF ₃) ^a	δ_{F} (<i>C</i> -CF ₃) ^a	δ_{P} ^a ($^2J_{\text{FP}}$)
2a	0.95 (4.4)	-62.2		-5.0 (75.7)
2b^b	2.47 (6.8)	-53.1		13.9 (65.2)
2c^c		-59.8		41.7 (86.6)
3a^d	2.95 (16.8)	-54.7		59.8 (108.8)
3c^e	3.08 (13.8)	-61.9		47.7 (113.4)
5a^f		-67.0		17.8 (79.3)
5c^f		-71.9		32.2 (87.5)
6a	1.25, 3.45 ^g (15.5), (17.1)	-66.9	-78.5	-60.7 (80.5)
6c^{h,i}	3.03 ^g (16.0)	-64.0	-77.0	-51.5 (88.0)

^aHigh-field shifts from TMS, CCl₃F, and 85% H₃PO₄ were given negative signs.

^{b1}H: $\delta = 1.19$ (6 H, Me₂CH, dd, $^3J_{\text{HH}} = 6.9$, $^3J_{\text{HP}} = 16.2$).

^{c1}H: $\delta = 0.88$ (6 H, MeCH₂, t, $^3J_{\text{HH}} = 7.1$), 2.95 (4 H, CH₃CH₂, dq, $^3J_{\text{HP}} = 10.7$).

^{d19}F: $\delta = -74.8$ (s, F₃CSO₃⁻).

^{e1}H: $\delta = 1.27$ (6 H, CH₃CH₂, t, $^3J_{\text{HH}} = 7.1$), 3.48 (4 H, CH₃CH₂, dq, $^3J_{\text{HP}} = 12.8$); ¹⁹F: $\delta = -74.2$ (s, F₃CSO₃⁻).

^f1H: Not observed because of overlapping signals of (Et₂N)₃PNMe.

^gPCH₂.

^{h1}H: $\delta = 0.77$ (6 H, CH₃CH₂, t, $^3J_{\text{HH}} = 6.9$), 3.03 (4 H, CH₃CH₂, dq, $^3J_{\text{HP}} = 13.9$).

ⁱ¹⁹F at 213 K: -62.6 (*P*-CF₃ (ax), $^2J_{\text{FP}} = 52.4$, $^4J_{\text{FF}} = 13.9$), -67.0 (*P*-CF₃ (eq), $^2J_{\text{FP}} = 123.0$, $J_{\text{F}\cdots\text{F}} = 7.0$), -77.6 (*C*-CF₃ (*cis*), qq, $^4J_{\text{FF}} = 7.8$, $J_{\text{F}\cdots\text{F}} = 7.0$), -77.0 (*C*-CF₃ (*trans*), $^4J_{\text{FF}} = 7.8$).

TABLE 2 Experimental Details for the Synthesis of Compounds **2a–c**

	1 (g) ^a	CF ₃ Br (g) ^a	(Et ₂ N) ₃ P (g) ^a	Solvent (ml)	Yield (g) ^b	bp (°C) ^c
2a ^d	1a 11.1 (95)	34.3 (230)	46.9 (190)	Triglyme 150	8.3 (47)	30 (1013)
2b	1b 11.6 (80)	30.0 (200)	39.5 (160)	CH ₂ Cl ₂ 120	4.2 (25)	85 (1013)
2c	1c 8.7 (50)	22.4 (150)	24.7 (100)	CH ₂ Cl ₂ 150	7.7 (64)	59 (100)

^aValues in parentheses are in millimoles.^bValues in parentheses are the percent values.^cValues in parentheses are in millibars.^dSee Ref. [6].

EXPERIMENTAL

Mass-spectra (EI, 70 eV) were recorded on a Finnigan MAT 8222 spectrometer. NMR spectra were obtained on a Bruker AC 80 instrument operating at 75.39 MHz (¹⁹F, internal standard CCl₃F) and 32.44 MHz (³¹P, external standard 85% H₃PO₄). All reactions and manipulations were conducted under an atmosphere of dry nitrogen.

General Procedure for the Synthesis of Compounds **2a–c**

In the respective solvent, bromotrifluoromethane and the dichlorophosphine (**1a–c**) were cooled to –60 to –80°C. Hexaethylphosphorus triamide was added, and the reaction mixture was allowed to warm to ambient temperature. All volatiles were pumped off in vacuo (10^{–3} mbar) and the residue distilled. (See Table 2 for data of **2a–c**.)

Isopropylbis(trifluoromethyl)phosphine (2b). Anal calcd for C₅H₇F₆P (212.07): C, 28.30; H, 3.33; F, 53.76; P, 14.61. Found: C, 28.13; H, 3.18; F, 53.10; P, 14.36.

Diethylaminobis(trifluoromethyl)phosphine (2c) [7]. MS: *m/e* (%) = 241 (M⁺, 8), 226 (M⁺ – CH₃, 5), 172 (M⁺ – CF₃, 22), 122 (Et₂NPF⁺, 100), 94 (Et(H)NPF⁺, 7), 69 (CF₃⁺, 18), 29 (C₂H₅⁺, 45), and other fragments.

General Procedure for the Synthesis of Compounds **3a–c**

Compounds **2a–c** and one equivalent, methyltrifluoromethanesulfonate were heated in a glass ampoule at 100°C for 16 h. The remaining solid was recrystallized in dichloromethane at –50°C and dried in vacuo (10^{–3} mbar). (See Table 3 for data of **3a–c**.)

Dimethylbis(trifluoromethyl)phosphonium triflate (3a). Anal calcd for C₅H₆F₉O₃PS (348.12): C, 17.24; H, 1.74; F, 49.14; P, 8.90. Found: C, 17.72; H, 1.89; F, 48.90; P, 8.57.

Diethylaminomethylbis(trifluoromethyl)phosphonium triflate (3c). Anal calcd for C₈H₁₃F₉NO₃PS (405.21): C, 23.70; H, 3.23; F, 42.22, P, 7.65. Found: C, 24.02; H, 3.38; F, 41.30; P, 7.42.

General Procedure for the Synthesis of Compounds **5a** and **5c**

To compounds **3a** (0.18 g, 0.52 mmol) and **3c** (0.28 g, 0.69 mmol) one equivalent of (Et₂N)₃PNMe **4** (0.15 g, 0.52 mmol in the case of **3a**; 0.20 g, 0.69 mmol in the case of **3c**) in 3 ml toluene-d₈ was added at –80°C. The reaction mixture was allowed to warm, first to –50°C, then to ambient temperature, and was NMR-spectroscopically characterized. There was no change in the NMR parameters for 2 days. *Methyl-bis(trifluoromethyl)methylene phosphorane (5a)* and *diethylamino-bis(trifluoromethyl)methylene phosphorane (5c)*, according to the NMR evidence, were quantitatively formed.

General Procedure for the Synthesis of Compounds **6a** and **6c**

To a solution of **3a** (2.61 g, 7.5 mmol) and **3c** (3.49 g, 8.4 mmol) one equivalent of (Et₂N)₃PNMe **4** (1.93 g,

TABLE 3 Experimental Details for the Synthesis of Compounds **3a** and **3c**

	2 (g) ^a	Yield (g) ^b	mp (°C)
3a	2a 3.68 (20)	6.9 (99)	131
3b ^c	2b 4.24 (20)	100 (12)	
3c	2c 8.44 (35)	12.5 (89)	53

^aValues in parentheses are in millimoles.^bValues in parentheses are the percent values.^cNonseparable mixture of decomposition products.

7.0 mmol in the case of **3a**; 2.21 g, 8.0 mmol in the case of **3c**) in 10 ml THF was added at -80°C and stirred for 1 h. The reaction mixture was cooled to -196°C , evacuated and 1.5 equivalents of hexafluoroacetone (2.57 g, 15.5 mmol in the case of **3a**; 2.94 g, 17.7 mmol in the case of **3c**) added. Within 12 h the reaction mixture was allowed to warm to ambient temperature and the volatiles were pumped off in vacuo. The residue was extracted with 5 ml of pentane, which was pumped off in vacuo to yield pure products.

2-Methyl-2,2,4,4-tetrakis(trifluoromethyl)-1,2 $\lambda^5\sigma^5$ -oxaphosphetane (6a). mp -15°C . MS: *m/e* (%): 345 ($\text{M}^+ - \text{F}$, 13); 295 ($\text{M}^+ - \text{CF}_3$, 85); 245 ($\text{M}^+ - \text{CF}_3 - \text{CF}_2$, 100); and other fragments. Anal calcd for $\text{C}_7\text{H}_5\text{F}_{12}\text{OP}$ (364.07): C, 23.90; H, 1.38; F, 62.62, P, 8.51. Found: C, 24.02; H, 1.40; F, 61.80; P, 8.42.

2-Diethylamino-2,2,4,4-tetrakis(trifluoromethyl)-1,2 $\lambda^5\sigma^5$ -oxaphosphetane (6c). mp -5°C . MS: *m/e* (%): 402 ($\text{M}^+ - \text{F}$, 8); 352 ($\text{M}^+ - \text{CF}_3$, 42); 257 [$\text{Et}_2\text{N}(\text{CF}_3)_2\text{PO}^+$, 19]; 242 [$\text{Et}_2\text{N}(\text{CF}_3)_2\text{PH}^+$, 100]; 214 [$\text{EtHN}(\text{CF}_3)_2\text{PH}^+$, 83]; 164 [$\text{F}_3\text{CC}(\text{CH}_2)\text{CF}_3^+$, 41]; 145 [$\text{H}_2\text{CC}(\text{CF}_3)\text{CF}_2^+$, 33]; 95 [$\text{H}_2\text{CCCF}_3^+$, 34]; 69 (CF_3^+ , 36); and other fragments. Anal calcd for $\text{C}_{10}\text{H}_{12}\text{F}_{12}\text{NOP}$ (421, 16): C, 28.50; H, 2.87; F, 54.15, P, 7.36. Found: C, 28.84; H, 3.02; F, 54.50; P, 7.39.

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