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Short Communication

Facile syntheses of tris(trifluoromethyl)phosphine and difluorotris(trifluoromethyl)phosphorane

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Abstract

Tris(trifluoromethyl)phosphine is easily available in high yield using the three component system $P(NEt)_2)_3/CF_3Br/(PhO)_3P$ in HMPA. Addition of chlorine and fluorination with zinc difluoride yield difluorotris(trifluoromethyl)phosphorane.

Keywords: Tris(trifluoromethyl)phosphine; Hexaethylphosphorus triamide; Bromotrifluoromethane; Triphenylphosphite; Zinc difluoride; Difluorotris(trifluoromethyl)-phosphorane

1. Introduction

Perfluoroalkylbromides and iodides are of considerable importance in organofluorine chemistry. They are versatile reagents for introducing fluorinated groups into organic molecules [1]. Trifluoromethyl derivates of phosphorus [2] have been known since 1950. Tris(fluoromethyl)phosphine [3] was synthesized in a mixture with mono- and bis(trifluoromethyl)iodophosphines in yields approaching 54% by reacting red phosphorus with trifluoroiodomethane under pressure at 260 °C (48 h). A yield of 49% was found [4] at 200 °C (48 h). There are several disadvantages inherent to this method limiting the availability for an extensive study of the coordinating properties in transition metal chemistry: the high cost of trifluoroiodomethane and that the reaction has to be carried out under pressure at temperatures above 200 °C. The tertiary phosphine was coordinated to chromium, molybdenum, tungsten [5], iron [6], osmium [7], carbonyls and platinum(II) [8], respectively. Chlorine [9] and dinitrogen tetroxide [10] oxidized forming either $(CF_3)_3PCl_2$ or $(CF_3)_3PO$. Fluorination [11] using SF_4 furnished the phosphorane $(CF_3)_3PF_2$ which is a potent difluorocarbene source and could be converted into the phosphate anion [12] $[(CF_3)_3PF_3]^-$.

2. Results and discussion

Monotrifluoromethylphosphanes were synthesized from the three component system [13] $P(NEt_2)_3/PCl_3/CF_3Br$. Taking into account the 80% yield [14] preparation of trimethylphosphine from MeMgI and $P(OPh)_3$, we studied the reaction of $P(NEt_2)_3/P(OPh)_3/CF_3Br$ in HMPA as a solvent, which allowed easy separation of the volatile products. $P(CF_3)_3$ is formed well below room temperature in preparative yields up to 85%.

$$(PhO)_3P \xrightarrow[\text{HMPA}]{CF_3Br,\ (Et_2N)_3P} (CF_3)_3P$$

The advantages of this synthesis are the high selectivity of the trifluoro-methylation giving tertiary phosphine, the less expensive starting material CF_3Br and much lower reaction temperature. Furthermore no autoclave is required.

Addition of chlorine afforded the dichlorophosphorane [3,9] $(CF_3)_3PCl_2$ which was fluorinated using anhydrous ZnF_2 to furnish $(CF_3)_3PF_2$ in yields up to 95%. These straightforward results for the replacement of chlorine by fluorine proved ZnF_2 a useful, inexpensive non-oxidizing fluorinating reagent [15].

$$(CF_3)_3PCl_2 \xrightarrow[\text{no solvent}]{ZnF_2} (CF_3)_3PF_2$$

We have developed facile routes to tris(trifluoromethyl)phosphine and tris(trifluoromethyl)difluorophosphorane, which are thus available on larger scale; e.g. for transition metal chemistry and the study of difluorocarbene reactions, respectively.

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3. Experimental details

The appropriate precautions for handling moisture-sensitive and oxygen-sensitive compounds were observed throughout this work. NMR spectra were obtained on a Bruker AC 80 instrument operating at 75.39 MHz (^{19}F, internal standard CCl_3F and 32.44 MHz (^{31}P, external standard 85% H_3PO_4), respectively.

3.1. *Tris(trifluoromethyl)phosphine*

A 0.216 mol (32.2 g) sample of CF_3Br was condensed into a round-bottomed flask containing 0.048 mol (15.0 g) of $(PhO)_3P$ dissolved in 30 ml HMPA and kept at −60 °C for the whole reaction. During vigorous stirring 0.216 mol (53.4 g) $(Et_2N)_3P$ was added in 1 h. After reaching 36 °C the mixture was stirred for 1 h and turned dark brown. All volatiles (CF_3Br, CF_3H and $(CF_3)_3P$) were pumped off in vacuo. Then a trap-to-trap condensation (−60 °C for $(CF_3)_3P$, −196 °C for CF_3H and excess CF_3Br) allowed the isolation of the colourless, spontaneously inflammable liquid $(CF_3)_3P$ at −60 °C in 85% yield; b.p. 17 °C (Ref [3] 17.3 °C). ^{19}F NMR (C_6D_6) δ: −51.2 (d, $^2J_{PF} = 85.4$ Hz; Ref. [16] 50.8 ppm, 85.5 Hz); ^{31}P NMR (C_6D_6) δ: 2.9 (dec, Ref. [16] 2.6 ppm).

3.2. *Difluorotris(trifluoromethyl)phosphorane*

A 0.009 mol (2.65 g) sample of $(CF_3)_3PCl_2$ was condensed into an evacuated glass vessel at −196 °C, equipped with a stirrer and filled with approximately 0.026 mol (2.69 g) of anhydrous ZnF_2 (excess of ZnF_2 is very important). After being warmed to 25 °C, the mixture was stirred for 12 h. $(CF_3)_3PF_2$ was removed under vacuum. The white solid remaining in the reaction vessel was a mixture of $ZnCl_2$ and excess ZnF_2. Yield: 0.0084 mol (97.6%) $(CF_3)_3PF_2$; b.p. 19 °C (Ref. [11] 20 °C). ^{19}F NMR (C_6D_6) δ: −62.6 (d, CF_3), $^2J_{PF} = 166$ Hz (Ref. [17] 167 Hz); $\delta = -59.4$ (d, PF), $^1J_{PF} = 992$ Hz (Ref. [18,19] −60.7 ppm, 988 Hz); ^{31}P NMR (C_6D_6) δ: −59.4 (t, dec) (Ref. [18,19] −59.8 ppm).

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