

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

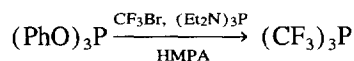
## 1. Introduction

Perfluoroalkylbromides and iodides are of considerable importance in organofluorine chemistry. They are versatile reagents for introducing fluorinated groups into organic molecules [1]. Trifluoromethyl derivatives of phosphorus [2] have been known since 1950. Tris(trifluoromethyl)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

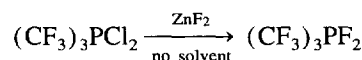
Monotrifluoromethylphosphanes were synthesized from the three component system [13]  $P(NEt_2)_3/PCl_3/CF_3Br$ .

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%.



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].



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 ( $^{19}\text{F}$ , internal standard  $\text{CCl}_3\text{F}$  and 32.44 MHz ( $^{31}\text{P}$ , external standard 85%  $\text{H}_3\text{PO}_4$ ), respectively.

#### 3.1. Tris(trifluoromethyl)phosphine

A 0.216 mol (32.2 g) sample of  $\text{CF}_3\text{Br}$  was condensed into a round-bottomed flask containing 0.048 mol (15.0 g) of  $(\text{PhO})_3\text{P}$  dissolved in 30 ml HMPA and kept at  $-60^\circ\text{C}$  for the whole reaction. During vigorous stirring 0.216 mol (53.4 g)  $(\text{Et}_3\text{N})_3\text{P}$  was added in 1 h. After reaching  $36^\circ\text{C}$  the mixture was stirred for 1 h and turned dark brown. All volatiles ( $\text{CF}_3\text{Br}$ ,  $\text{CF}_3\text{H}$  and  $(\text{CF}_3)_3\text{P}$ ) were pumped off in vacuo. Then a trap-to-trap condensation ( $-60^\circ\text{C}$  for  $(\text{CF}_3)_3\text{P}$ ,  $-196^\circ\text{C}$  for  $\text{CF}_3\text{H}$  and excess  $\text{CF}_3\text{Br}$ ) allowed the isolation of the colourless, spontaneously inflammable liquid  $(\text{CF}_3)_3\text{P}$  at  $-60^\circ\text{C}$  in 85% yield; b.p.  $17^\circ\text{C}$  (Ref. [3]  $17.3^\circ\text{C}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $-51.2$  (d,  $^2J_{\text{PF}} = 85.4$  Hz; Ref. [16] 50.8 ppm, 85.5 Hz);  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : 2.9 (dec, Ref. [16] 2.6 ppm).

#### 3.2. Difluorotris(trifluoromethyl)phosphorane

A 0.009 mol (2.65 g) sample of  $(\text{CF}_3)_3\text{PCl}_2$  was condensed into an evacuated glass vessel at  $-196^\circ\text{C}$ , equipped with a stirrer and filled with approximately 0.026 mol (2.69 g) of anhydrous  $\text{ZnF}_2$  (excess of  $\text{ZnF}_2$  is very important). After being warmed to  $25^\circ\text{C}$ , the mixture was stirred for 12 h.  $(\text{CF}_3)_3\text{PF}_2$  was removed under vacuum. The white solid remaining in the reaction vessel was a mixture of  $\text{ZnCl}_2$  and excess  $\text{ZnF}_2$ . Yield: 0.0084 mol (97.6%)  $(\text{CF}_3)_3\text{PF}_2$ ; b.p.  $19^\circ\text{C}$  (Ref. [11]  $20^\circ\text{C}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $-62.6$  (d,  $\text{CF}_3$ ),  $^2J_{\text{PF}} = 166$  Hz (Ref. [17] 167 Hz);  $\delta = -59.4$  (d, PF),

$^1J_{\text{PF}} = 992$  Hz (Ref. [18,19]  $-60.7$  ppm, 988 Hz);  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $-59.4$  (t, dec) (Ref. [18,19]  $-59.8$  ppm).

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