

Short Communication

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

Michaela Görg<sup>a</sup>, Gerd-Volker Röschenhaler<sup>a,\*</sup>, Alexander A. Kolomeitsev<sup>b,\*</sup>

<sup>a</sup> Institute of Inorganic and Physical Chemistry, University of Bremen, Leobener Straße, 28334 Bremen, Germany

<sup>b</sup> Institute of Organic Chemistry, Ukrainian Academy of Sciences, Murmanskaya 5, 252660 Kiev, Ukraine

Received 19 February 1996; accepted 17 March 1996

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

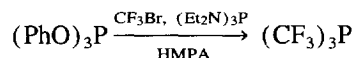
1. Introduction

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

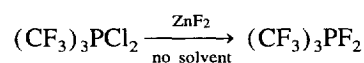
Monotrifluoromethylphosphanes were synthesized from the three component system [13]  $P(NEt_2)_3/PCl_3/CF_3Br$ .

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.

\* Corresponding authors.

### 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  $-60\text{ }^\circ\text{C}$  for the whole reaction. During vigorous stirring 0.216 mol (53.4 g)  $(\text{Et}_2\text{N})_3\text{P}$  was added in 1 h. After reaching  $36\text{ }^\circ\text{C}$  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 ( $-60\text{ }^\circ\text{C}$  for  $(\text{CF}_3)_3\text{P}$ ,  $-196\text{ }^\circ\text{C}$  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  $-60\text{ }^\circ\text{C}$  in 85% yield; b.p.  $17\text{ }^\circ\text{C}$  (Ref [3]  $17.3\text{ }^\circ\text{C}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $-51.2$  (d,  $^2J_{\text{PF}} = 85.4\text{ Hz}$ ; Ref. [16]  $50.8\text{ ppm}$ ,  $85.5\text{ Hz}$ );  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $2.9$  (dec, Ref. [16]  $2.6\text{ ppm}$ ).

#### 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  $-196\text{ }^\circ\text{C}$ , 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  $25\text{ }^\circ\text{C}$ , 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.  $19\text{ }^\circ\text{C}$  (Ref. [11]  $20\text{ }^\circ\text{C}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ :  $-62.6$  (d,  $\text{CF}_3$ ),  $^2J_{\text{PF}} = 166\text{ Hz}$  (Ref. [17]  $167\text{ Hz}$ );  $\delta = -59.4$  (d, PF),

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

### Acknowledgment

The authors thank Deutsche Forschungsgemeinschaft for financial support and Hoechst AG, Frankfurt, for generous gifts of valuable chemicals.

### References

- [1] C. Wakszeman and A. Lantz, in R.E. Banks, B.E. Smart and J.C. Tatlow (eds.), *Organofluorine Chemistry*, Plenum, 1994, pp. 177–194.
- [2] F.W. Bennett, G.R.A. Brandt, H.J. Emeleus and R.N. Haszeldine, *Nature*, **166** (1950) 223.
- [3] F.W. Bennett, H.J. Emeleus and R.N. Haszeldine, *J. Chem. Soc.*, (1953) 1565.
- [4] A.B. Burg, W. Mahler, A.J. Bilbo, C.P. Haber and D.L. Herring, *J. Am. Chem. Soc.*, **79** (1957) 247.
- [5] J. Apel, R. Bacher, J. Grobe and D.Z. Le Van, *Z. Anorg. Allg. Chem.*, **453** (1979) 39.
- [6] A.B. Burg, *Inorg. Chem.*, **25** (1986) 4751.
- [7] H.G. Ang, L.L. Koh, C.H. Koh, W.L. Kwik, W.K. Leong and W.Y. Leong, *J. Chem. Soc. Dalton Trans.*, (1993) 847.
- [8] K.A. Khokhryakov, E.I. Grigorov, N.S. Pamina and V.N. Yakovlev, *Koord. Khim.*, **13** (1987) 237.
- [9] A.B. Burg and J.E. Griffiths, *J. Am. Chem. Soc.*, **82** (1960) 3514.
- [10] A.B. Burg and A.J. Sarkis, *J. Am. Chem. Soc.*, **87** (1965) 238.
- [11] W. Mahler, *Inorg. Chem.*, **2** (1962) 230.
- [12] S.S. Chan and C.J. Willis, *Can. J. Chem.*, **46** (1968) 1237.
- [13] W. Volbach and I. Ruppert, *Tetrahedron Lett.*, **24** (1983) 5509.
- [14] W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Met. Org. Chem.*, **4** (1974) 149.
- [15] A.A. Kolomeitsev, F.U. Seifert and G.-V. Rösenthaller, *J. Fluorine Chem.*, **71** (1995) 47.
- [16] K. Packer, *J. Chem. Soc.*, (1963) 960.
- [17] R.G. Cavell, J.A. Gibson and K.I. The, *J. Am. Chem. Soc.*, **99** (1977) 7841.
- [18] E.L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.*, **2** (1963) 613.
- [19] J.F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **20** (1964) 1835.