

An alternative route for the synthesis of tris(trifluoromethyl)bismuth, $\text{Bi}(\text{CF}_3)_3$

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Abstract

$\text{Bi}(\text{CF}_3)_3$ can be prepared easily in c. 70% yield from the metathesis reaction of $\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$ with BiCl_3 .

Introduction

In our recent investigations concerning the chemistry of organobismuth derivatives containing perfluoroalkyl groups, $\text{Bi}(\text{CF}_3)_3$ turned out to be a useful tool for the selective transfer of trifluoromethyl groups either to inorganic [1] or organic [2] derivatives. The preparative route for obtaining $\text{Bi}(\text{CF}_3)_3$ via the metathesis reactions of $\text{Cd}(\text{CF}_3)_2$ complexes with BiCl_3 or BiBr_3 [3] has the disadvantage that highly toxic cadmium derivatives are involved and have finally to be disposed of. In this paper we describe the synthesis of $\text{Bi}(\text{CF}_3)_3$ by an alternative route from BiCl_3 and $\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$.

Experimental

BiCl_3 was purchased from Riedel-de Haën, Seelze (Germany) and used as received. $\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$ was prepared from the reaction of elemental zinc with CBrF_3 [4]. ^{19}F NMR spectra were recorded on a Bruker AC 200 spectrometer at 188.3 MHz with CCl_3F as an external standard. All analytical data are in accordance with those reported in ref. 3.

In a dry nitrogen atmosphere, 25.3 g (85.5 mmol) $\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$ were suspended in 50 ml of carefully dried dichloromethane at ambient temperature. The reaction vessel was equipped with a bubble counter to allow the gaseous by-products (CHClF_2 , CHBrF_2) to leak. The suspension was cooled to 0 °C when 3.0 g (9.5 mmol) BiCl_3 was added to the cooled solution. The reaction temperature was raised to 30 °C.

The reaction may be monitored by ^{19}F NMR spectroscopy. After a reaction time of 14 d, unreacted

$\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$ could no longer be detected. Low intensity signals corresponding to $\text{Bi}(\text{CF}_3)_2\text{Cl}$ with traces of $\text{Zn}(\text{C}_2\text{F}_5)$ derivatives, CHClF_2 and CHBrF_2 could be detected in the ^{19}F NMR spectra. These compounds are by-products of parallel carbenoid reactions.

The red-brown reaction mixture was filtered via a glass frit and the solid residue washed several times with small portions of dichloromethane.

Using a small distillation apparatus equipped with a Vigreux column, CH_2Cl_2 and other readily volatile compounds were slowly distilled off at standard pressure (c. 1 drop s^{-1}) with the bath temperature not exceeding c. 75 °C. Under these conditions, $\text{Bi}(\text{CF}_3)_3$ and some acetonitrile [from $\text{ZnBr}(\text{CF}_3) \cdot 2\text{CH}_3\text{CN}$] as well as ZnCl_2 , ZnBr_2 and small amounts of $\text{Zn}(\text{C}_2\text{F}_5)$ compounds remained in the distillation residue. Using other conditions, $\text{Bi}(\text{CF}_3)_3$ was carried over.

This mixture was distilled for a second time under reduced pressure (2×10^{-3} hPa) with a bath temperature of 75 °C which was increased over a period of 1 h to a maximum of 90 °C. According to our experience, it is important to use an extremely short condensing tube to avoid poor yields. After distilling for an additional hour, $\text{Bi}(\text{CF}_3)_3$ and CH_3CN could be completely removed from the remaining zinc derivatives. The condensate contained only $\text{Bi}(\text{CF}_3)_3$ and CH_3CN , and was free from other impurities.

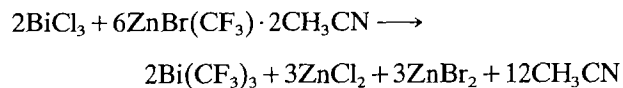
A further vacuum condensation with a bath temperature of 0 °C allowed separation of CH_3CN from $\text{Bi}(\text{CF}_3)_3$. The product obtained contained less than 5% acetonitrile; the yield was c. 70% (based on BiCl_3).

It is noteworthy that small amounts of CH_3CN stabilize $\text{Bi}(\text{CF}_3)_3$; absolutely pure $\text{Bi}(\text{CF}_3)_3$ decomposes within a few days even at temperatures below 0 °C, but traces of CH_3CN allow storage of $\text{Bi}(\text{CF}_3)_3$ for several weeks even at room temperature.

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Results and discussion

This preparative-scale route to $\text{Bi}(\text{CF}_3)_3$ provides an alternative to the previously described method [3] avoiding toxic cadmium reagents. According to the equation



the desired product can be obtained in *c.* 70% yield with the formation of ecologically less damaging zinc halides.

Traces of trifluoromethylbismuth halides, which may be present in the reaction mixture, dismutate on heating to give $\text{Bi}(\text{CF}_3)_3$ and BiCl_3 in a similar manner to mixed aryl(trifluoromethyl)bismuth derivatives [5].

The large amounts of gaseous by-products detected are the subject of on-going investigation.

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References

- 1 W. Tyrra and D. Naumann, *Can. J. Chem.*, **67** (1989) 1949.
- 2 S.V. Pasenok, N.V. Kirij, Yu. L. Yagupolskii, D. Naumann and W. Tyrra, *1st Ukrainian-German Symp. Fluorine Chem.*, Odessa (Ukraine), Aug. 31-Sept. 5, 1992, Abs. P14.
- 3 D. Naumann and W. Tyrra, *J. Organomet. Chem.*, **334** (1987) 323.
- 4 D. Naumann, W. Tyrra, B. Kock, W. Rudolph and B. Wilkes, *Eur. Pat.* 291 860; [*Chem. Abs.*, **110** (1989) P156515x]
- 5 S. Pasenok, D. Naumann and W. Tyrra, *J. Organomet. Chem.*, **417** (1991) C47.