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An alternative route for the synthesis of tris(trifluoromethyl)bismuth, $Bi(CF_3)_3$

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Abstract

$Bi(CF_3)_3$ can be prepared easily in *c.* 70% yield from the metathesis reaction of $ZnBr(CF_3)\cdot 2CH_3CN$ with $BiCl_3$.

Introduction

In our recent investigations concerning the chemistry of organobismuth derivatives containing perfluoroalkyl groups, $Bi(CF_3)_3$ 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 $Bi(CF_3)_3$ via the metathesis reactions of $Cd(CF_3)_2$ 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 $Bi(CF_3)_3$ by an alternative route from $BiCl_3$ and $ZnBr(CF_3)\cdot 2CH_3CN$.

Experimental

$BiCl_3$ was purchased from Riedel-de Haën, Seelze (Germany) and used as received. $ZnBr(CF_3)\cdot 2CH_3CN$ 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) $ZnBr(CF_3)\cdot 2CH_3CN$ 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 $ZnBr(CF_3)\cdot 2CH_3CN$ could no longer be detected. Low intensity signals corresponding to $Bi(CF_3)_2Cl$ with traces of $Zn(C_2F_5)$ 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, $Bi(CF_3)_3$ and some acetonitrile [from $ZnBr(CF_3)\cdot 2CH_3CN$] as well as $ZnCl_2$, $ZnBr_2$ and small amounts of $Zn(C_2F_5)$ compounds remained in the distillation residue. Using other conditions, $Bi(CF_3)_3$ 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, $Bi(CF_3)_3$ and CH_3CN could be completely removed from the remaining zinc derivatives. The condensate contained only $Bi(CF_3)_3$ 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 $Bi(CF_3)_3$. 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 $Bi(CF_3)_3$; absolutely pure $Bi(CF_3)_3$ decomposes within a few days even at temperatures below 0 °C, but traces of CH_3CN allow storage of $Bi(CF_3)_3$ for several weeks even at room temperature.

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Results and discussion

This preparative-scale route to $Bi(CF_3)_3$ provides an alternative to the previously described method [3] avoiding toxic cadmium reagents. According to the equation

$$2BiCl_3 + 6ZnBr(CF_3)\cdot 2CH_3CN \longrightarrow 2Bi(CF_3)_3 + 3ZnCl_2 + 3ZnBr_2 + 12CH_3CN$$

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 $Bi(CF_3)_3$ 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.