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A practical, cheap and environmentally friendly preparation of bismuth(III) trifluoromethanesulfonate

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Abstract—A method for large scale preparation of $Bi(OTf)_3$ from Bi_2O_3 in a weakly hydrated form after freeze-drying. © 2002 Elsevier Science Ltd. All rights reserved.

Bismuth derivatives are attracting the attention of an increasing number of organic chemists.[1] Over the past few years, bismuth(III) triflate, $Bi(OTf)_3$ (**1**) ($Tf = SO_2CF_3$), has been reported as a new and efficient catalyst for organic synthesis,[2] which exhibits, in numerous cases, a stronger activity than other known metal triflates, in particular those of transition elements. However, procedures previously reported for the preparation of this compound suffer from serious drawbacks and cannot be easily transposed to a large scale: requirement of an excess of an expensive triflic reagent (TfOH and/or Tf_2O) and/or drastic experimental conditions.[3] An attractive route was the protiodemetallation of a triarylbismuth using a *stoichiometric* amount of TfOH.[2a,4] Nevertheless, it requires the use of a solvent and, from the solely commercially available and rather expensive triphenylbismuth, the by-product is the carcinogenic benzene. Most metal triflates, especially rare earth ones, have been prepared in boiling water via the direct reaction of triflic acid (in stoichiometric amount) on the corresponding metal oxide.[5] This method, which would involve the cheap bismuth(III) oxide as starting material, would become efficient for the preparation of **1** by the use of only a stoichiometric amount of TfOH. This result is reported here.[6]

In the first place, we tried the procedure reported for the preparation of rare earth triflates,[5] starting from Bi_2O_3. Unfortunately, this process led to the formation of a water-soluble bismuth salt (the expected product **1**) and a white insoluble solid (**2**), even when extremely pure starting materials were used. An X-ray diffraction powder analysis revealed that **2** was bismuth(III) oxide sulfate hydroxide (cannonite)[7] formed in about 20% yield. Incidentally, we also found that **2**, when exposed to air, is spontaneously transformed to an oxo-carbonated bismuth salt, $(BiO)_4(OH)_2CO_3$, (determined by Raman analysis).[8] Since **1** is soluble in some organic solvents (ketones, alcohols…), we decided to try the combination of these solvents with water. After numerous experiments, we found that a mixture of ethanol and water (75:25) completely avoids the formation of **2**, giving **1** in high yield (Eq. (1)). Surprisingly, when the reaction was carried out in pure ethanol, no reaction took place.

$$\mathrm{Bi_2O_3} + 6\ \mathrm{TfOH} \xrightarrow[65\ ^\circ\mathrm{C}\ ;\ 3\ \mathrm{h}]{\mathrm{EtOH\ /\ H_2O\ (75{:}25)}} 2\ \underset{\mathbf{1}}{\mathrm{Bi(OTf)_3}} + 3\ \mathrm{H_2O} \qquad (1)$$

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$$x\,\mathrm{Bi}^{3+} + y\,\mathrm{H_2O} \rightleftharpoons \underset{\mathbf{3}}{[\mathrm{Bi}_x(\mathrm{OH})_y]^{(3x-y)+}} + y\,\mathrm{H}^+ \qquad (2)$$

Evaporation of the solvents under reduced pressure led to a white paste, freely soluble in water. Since our previous study has shown that **1** is a thermo-sensitive compound,[9,10] complete removal of water has been carried out by freeze-drying. Under these conditions, a white powder was isolated. Its analysis by IR and NMR spectrometries gave data similar to those previously obtained for **1**.[3,4] Exposure of the lyophilizate to air gave the enneahydrate of **1**,[3c] and the latter, heated at 45°C, led to the formation of pure tetrahydrate (proved by XRD).[10] Finally, benzoylation of toluene catalyzed by **1** (10 mol%),[2c] prepared according to both methods, from $\mathrm{BiPh_3}$[4] and $\mathrm{Bi_2O_3}$ (this work), gave similar results.

Bi(III) salts are known to hydrolyze in water, leading to polynuclear cations (Eq. (2)).[11]

The $\mathrm{p}K_\mathrm{h}$ ($-\log K_{xy}$) varies with the Bi-condensation of these cations, which is dependent on the corresponding anion, on the concentration and on the pH of the solution ($x=1$, $y=1$, $\mathrm{p}K_\mathrm{h}=1.09$).[11] Other cationic forms, such as $[\mathrm{Bi_6O}_n(\mathrm{OH})_{12-2n}]^{6+}$, have also been identified from acidic solutions of Bi(III) perchlorate[12] and nitrate.[13] When **1** was dissolved in water, we observed that the solution is strongly acidic.[14] Consequently, the equilibrium 2 shows that it is possible to isolate the mononuclear form Bi^{3+} (hydrated) either in concentrated solution of a strong acid (TfOH),[3c,17] or by elimination of water (this work).

We think that the addition of ethanol in the present synthetic process promotes the shift of the equilibrium 2 towards formation of Bi^{3+} by leading to an homogeneous medium, and thus by avoiding any precipitate of ions **3** (or their derivatives). Moreover, it allows a lowering of the reaction temperature from 100 to 65°C. The formation of **2** when the reaction 1 is carried out in boiling water could be due to the decomposition of reaction intermediates rather than that of **1**. In fact, after 5 h in boiling water, **1** tetrahydrate gave only trace of **2**.

In a typical experiment, 2.293 g (4.92 mmol) of $\mathrm{Bi_2O_3}$ is added to 35 mL of a 75:25 (volumic ratio) mixture of ethanol/water. Then, 4.452 g (29.66 mmol) of TfOH is added all at once and the yellow suspension is magnetically stirred at 65°C during 3 h. After this time, a milky solution is obtained. Solvents and a possible trace of TfOH are evaporated under reduced pressure at a temperature not exceeding 50°C. Water (30 mL) is added to give a clear colorless solution which is submitted to freeze-drying (pressure: 4×10^{-3} mbar, temperature of the trap: −110°C). Thus, 6.727 g of a white solid is obtained. Analysis of this powder indicate the complete transformation of $\mathrm{Bi_2O_3}$ to **1** in weakly hydrated form (4% wt).[18] Yield: >99%. For IR, NMR, TGA and XRD data about **1**, see previous studies.[2a,3,4,6] Raman data of the hydrated form of **1** (powder): identical spectrum to that of **1**, $9\mathrm{H_2O}$.[3c]

In conclusion, bismuth(III) triflate (**1**) has been prepared by a new, cheap and environmentally friendly method which consists of the reaction of triflic acid on bismuth(III) oxide in an aqueous ethanolic solution. Reported for the first time with this type of salt, freeze-drying allows an almost complete dehydration of **1** without decomposition. The process is especially suitable for the future large scale preparation of this compound.

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