

# An inexpensive and simple process for the preparation of antimony(III) and bismuth(III) triflates

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## Abstract

A new process for the preparation of antimony and bismuth(III) triflates has been found. This process is based on the reaction of triflic acid on metal oxide using chlorobenzene as a solvent. Due to its simplicity, this process can be useful for the laboratory scale as well as the industrial preparation of these metal triflates.

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## 1. Introduction

Trifluoromethanesulfonic acid (TfOH), which can be considered as a superacid [1], is one of the most acidic monoprotic organic acids [2] and readily forms stable salts with numerous metals [3]. The use of metal triflates such as copper(II) triflate [4], bismuth(III) triflate (BIT) [5,6], antimony(III) triflate (SBT) [7,8] and rare earth metal triflates (RET) [9] as catalysts for organic synthesis has received a lot of attention and therefore has been the subject of numerous publications. Among all metal triflates, SBT [7,10–14] and BIT [5,15–23] are receiving increasing attention from chemists due to their interesting catalytic properties. However, these new triflates are not yet commercially available due to the lack of clean and industrially viable synthetic methods for their preparation. The preparation of bismuth and antimony triflates from expensive and toxic triphenylbismuth [24] and triphenylantimony [7] has been reported. Therefore, we were interested in finding a procedure for their preparation that would ideally use a cheap and non-toxic

source of these metals in combination with a safe and practical procedure.

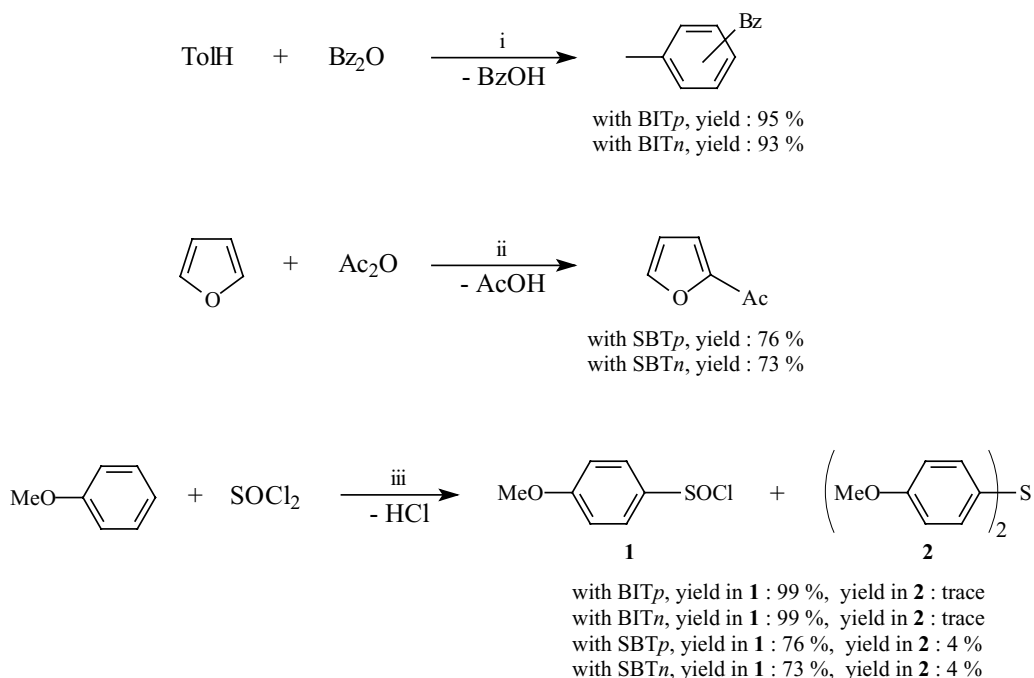
## 2. Experimental

### 2.1. General

Metal oxides were used as received. Triflic acid was distilled over concentrated sulphuric acid and kept under argon. Chlorobenzene was distilled over phosphorous pentoxide prior to use. Antimony(III) and bismuth(III) triflates used as reference compounds were prepared according to published procedures, respectively [7,24]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 250 and 100 MHz, respectively, at 25 °C and were referenced to external SiMe<sub>4</sub> ( $\delta = 0.00$ ). <sup>19</sup>F NMR spectra were recorded at 75 MHz, respectively, at 25 °C and were referenced to external CF<sub>3</sub>CO<sub>2</sub>H ( $\delta = 0.00$ ). GC analyses were performed using a Hewlett Packard 6890 chromatograph equipped with a 30 × 0.32 × 0.25 column (methyl silicone doped with 5% phenyl silicone; temperature conditions: 125–300 °C, 10 °C/min). Raman spectrum were recorded on a Dilor XY apparatus equipped with a CCD detector. X-ray powder diffraction data were recorded at room

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Scheme 1. (i) TolH/Bz<sub>2</sub>O = 2/1 (molar ratio), BIT = 10 molar percentage towards the minor reagent, reflux, 5 h, in both experiments the ortho/meta/para ratios of the obtained methylbenzophenones were 19:2:79 and were determined by GC; (ii) furan/Ac<sub>2</sub>O = 1/2 (molar ratio), SBT = 5 molar % towards the minor reagent, furan (*c* = 1 M) towards MeNO<sub>2</sub>, rt, 4 h, yields determined by GC; (iii) anisole/SOCl<sub>2</sub> = 1/10 molar ratio), BIT or SBT = 2 molar percentage towards the minor reagent, -5 °C, 5 h, yields determined by <sup>1</sup>H NMR.

temperature with a high resolution diffractometer (Seifert XRD 3000), equipped with an incident-beam monochromator to select monochromatic copper *K*α<sub>1</sub> radiation. To prevent hydration, the sample was kept in a nitrogen atmosphere by using an airtight sample holder.

## 2.2. Typical procedure for the preparation of BIT

A 250 ml schlenk was charged under argon with 4.19 g (9 mmole) of bismuth oxide and 60 ml of anhydrous chlorobenzene. Then 8.48 g (56.5 mmole, 6.27 equivalent towards bismuth oxide) of anhydrous TfOH was added via a syringe and the yellow suspension was vigorously magnetically stirred and heated in a thermostated oil bath at 120 °C for 12 h.<sup>1</sup> After this time, the resulting white suspension, was cooled to room temperature and filtered under argon over a glass-fritted funnel and the filtrate was put aside.<sup>2</sup> Then, the solid was washed with 50 ml of anhydrous chlorobenzene and the remaining solvent was removed under high vacuum

to give 12.4 g of Bi(OTf)<sub>3</sub>·*x*H<sub>2</sub>O<sup>3</sup> whose characteristics (IR, <sup>13</sup>C and <sup>19</sup>F NMR, Raman, DRX), obtained after hydration of an aliquot, were identical to the ones recorded from a pure sample of Bi(OTf)<sub>3</sub>·9H<sub>2</sub>O prepared from a known procedure [26]. Following our procedure, the preparation of BIT has been successfully realised on a kilogram scale.

## 2.3. Typical procedure for the preparation of SBT

Following the same procedure 11.1 g (of Sb(OTf)<sub>3</sub>·*x*H<sub>2</sub>O (1 < *x* < 4) were obtained as an off-white powder after removal of the chlorobenzene.<sup>4</sup> Powder DRX study (i) proved the complete disappearance of antimony(III) oxide and (ii) proved to be an inappropriate technique for the analysis of SBT due to the fast hydrolysis of this salt under our conditions. However, NMR and IR data proved to be similar to the ones obtained from a reference sample.

<sup>1</sup> In all our experiments the suspension was heated for 12 h. However, based on our observations the reaction time may change from one oxide to another and should therefore be optimized.

<sup>2</sup> It should be noted that most of the slight excess of TfOH used can be found in the chlorobenzene recovered after filtration and thus can be recycled very easily.

<sup>3</sup> The water content has been estimated to be 8.6 w/w % (Karl Fisher). Thus, the structure of the product is Bi(OTf)<sub>3</sub>·*x*H<sub>2</sub>O with 3 < *x* < 4 with the previously described tetrahydrated form [25] being one of the major components.

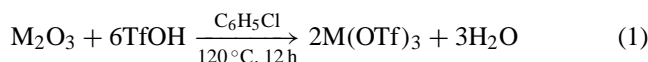
<sup>4</sup> In some cases the triflate formed spontaneously stuck to the schlenk glasses. In this case the chlorobenzene containing triflic traces had to be removed via syringe and the washing step was carried out using the same method. Finally, the drying step was similar to the one reported in Section 2.2.

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta = 120.5$  ppm (quad,  $J_{13\text{C}/^{19}\text{F}} = 322$  Hz);  $^{19}\text{F}$  NMR (DMSO- $d_6$ ):  $\delta = 2.5$  ppm; IR (nujol):  $\nu = 3474(\text{w})$   $\text{cm}^{-1}$ , 1306(vs), 1278(vs), 1257(vs), 1176(s), 1056(m), 1039(m), 648(w). For unknown reasons, micro-analysis of this compound gave incoherent results. Finally, the water content has been estimated ( $\text{Sb}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ , with  $1 < x < 4$ ) using the method previously reported [27].

### 3. Results and discussion

Metal oxides appeared to be the best compromise between ease of handling, cost and commercial availability. A new preparation of  $\text{Bi}(\text{OTf})_3$  bismuth(III) triflates has been recently proposed by us [27]. While this method advantageously uses cheap and non-toxic bismuth oxide as the bismuth source, one major drawback of this method is the use of special conditions for the drying of the product (freeze-drying) since aqueous ethanol is used as a solvent. Moreover, we have found that this method failed when applied to the preparation of  $\text{Sb}(\text{OTf})_3$ .

The method reported here is based on the simple reaction between bismuth or antimony oxides with a stoichiometric amount of TfOH using anhydrous chlorobenzene as a solvent at a temperature of  $120^\circ\text{C}$  (Eq. (1)). After 12 h, the corresponding metal triflate can be easily obtained in pure form. In each case, the powder obtained was analysed in order to confirm (i) the complete disappearance of the starting metal oxide (proved by powder DRX) and (ii) the formation of the corresponding metal triflate proved by comparison with an authentic sample (NMR analysis).



Finally, the catalytic activities of BIT and SBT were evaluated by studying standard reactions previously reported such as the benzylation of toluene catalysed by BIT [28], the acetylation of furan catalysed by SBT [11], and the chlorosulfonylation of anisole catalysed by both BIT and SBT [29]. As reported below (Scheme 1), bismuth and antimony triflates prepared from triphenyl metals (previous method noted BIT $p$  or SBT $p$ ) gave almost similar results with the ones obtained with bismuth and antimony triflates prepared from our new process (new method noted BIT $n$  or SBT $n$ ). Such results can be seen as an indirect evidence for the success of our synthetic process.

### 4. Conclusion

In conclusion we have found a new, cheap and practical methodology for the preparation of antimony(III) and bismuth(III) triflates based on the direct reaction of triflic acid on the appropriate metal(III) oxide in chlorobenzene. This new procedure is especially useful for the preparation

of SBT. The extension of this process to the preparation of other metal triflates is under investigation.

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