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An Efficient Method for the Preparation of Bismuth(III) Trifluoromethanesulfonate

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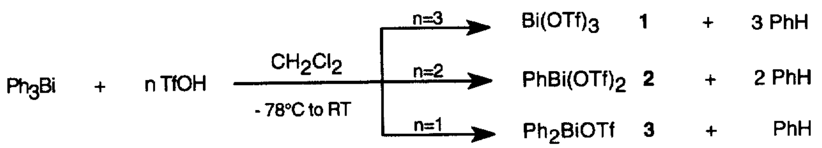
Abstract. *Bismuth(III) trifluoromethanesulfonate ($Bi(OTf)_3$ 1) can be easily prepared from the reaction of protiodemetallation of triphenylbismuth by a stoichiometric amount of trifluoromethanesulfonic acid. The intermediates $Ph_{3-n}Bi(OTf)_n$ [n=2(2), 1(3)] have been isolated. This process represents an improvement of the previously reported methods.*

Over the past few years, metallic triflates and especially rare earth triflates have been reported as new, efficient and water stable catalysts for organic synthesis.[1] On the other hand, bismuth(III) salts are attracting attention of an increasing number of chemists as catalysts.[2] Recently our laboratory reported the use of bismuth(III) triflate (**1**) as a new, water-stable and efficient catalyst for Friedel-Crafts,[3] Diels-Alder[4,5] and ene reactions.[5] In this paper we would like to report a new method for the preparation of **1**.

Usually, the preparation of metallic triflates involves the reaction of triflic acid on a metallic oxide,[1a,6] chloride,[7] carbonate,[8] sulfonate,[9] or carbide,[7a] and the reaction of silver triflate with a metallic halide.[10] In the litterature, three procedures describe the preparation of **1**. The first involves the addition of triflic acid on bismuth tris-trifluoroacetate,[11] the second refers to the addition of triflic anhydride on bismuth oxide.[12] A third publication reports the preparation of $Bi(H_2O)_9(OTf)_3$ from the reaction of a mixture of triflic acid and anhydride on bismuth oxide.[13] However these three methods suffer from some drawbacks. Effectively in all cases an excess of triflic reagent (an expensive product) has to be used and a long reaction time is sometimes necessary.[12] Our procedure[3a] is based on the direct reaction of triflic acid on commercially available triphenylbismuth (Eq. 1, $Tf = SO_2CF_3$).



(1)

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Protiodemetallation reactions of aryl-silicon, -germanium, -tin, -mercury and -lead compounds have been widely studied[14] and our method takes advantage of the very weak phenyl-bismuth bond energy (193 kJ/mol) which is one of the weakest aryl-element bonds.[15] Therefore, this process requires the use of only a stoichiometric amount of triflic acid and the by-product of the reaction is the volatile benzene.

Preparation of Bismuth(III) Triflate (**1**): In a 250 mL flask connected to an argon line were successively introduced 4.4 g (10 mmol) of triphenylbismuth and 100 mL of freshly distilled dichloromethane. Then the flask was immersed in an acetone/dry ice bath and 4.4 g (30 mmol) of triflic acid were introduced via a syringe under magnetic stirring. After 10 min the bath was removed and the reaction was stirred at room temperature for 10 h. The solid formed was filtered over a glass-frit funnel and washed once with 20 mL of dichloromethane. The very hygroscopic white powder obtained was heated at 50°C under reduced pressure. As proved by centesimal and TG analyses, **1** was isolated in its lower hydrated forms, mainly the tetrahydrated one[16] (6.48g; 89% yield). ^{13}C NMR (50.3 MHz, acetone-d_6): $\delta = 120$ ppm (quad.,$^1J_{^{13}C/^{19}F} = 321$ Hz); ^{19}F NMR (75.4 MHz, acetone-d_6): δ(from CF_3COOH) = 0.84 ppm; IR (nujol): $\nu = 3450\text{-}3550$ cm^{-1} (m), 1230-1290 (vs), 1180 (s), 1034 (s), 1028 (sh), 650 (sh), 643 (s).

Anhydrous **1** can be obtained by the same way, and directly used for a reaction after elimination of dichloromethane and benzene under reduced pressure.

Using two or one equivalent of TfOH respectively, the products **2** and **3** have been also isolated (white powders). NMR data (solvent acetone-d_6), **2**: ^1H (80 MHz): aromatic protons $\delta = 7.58$ (m, 1H), 8.28 (m, 2H), 9.28 (m, 2H); ^{13}C (50.3 MHz): $\delta = 121$ (quad.,$^1J_{^{13}C/^{19}F} = 321$ Hz), 130.4, 134.9, 139.1; ^{19}F (75.4 MHz): $\delta = 1.18$; **3**:[17] ^1H (80 MHz): aromatic protons $\delta = 7.45$ (m, 2H), 8.28 (m, 4H), 9.28 (m, 4H); ^{13}C NMR (50.3 MHz): $\delta = 120.8$ (quad.,$^1J_{^{13}C/^{19}F} = 321$ Hz), 129.7, 133.1, 138.2; ^{19}F (75.4 MHz): $\delta = 1.14$.

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