

Efficient Preparation of Anhydrous Metallic Triflates and Triflimides under Ultrasonic Activation

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Several metallic triflates and triflimides, among them anhydrous salts, were prepared in high yields under ultrasonic activation from the corresponding metal powders and stoichiometric amounts of triflic or triflimidic acid in different

solvents. Different In^{III} and Bi^{III} salts were tested as catalysts in hydrothiolation of olefins and in hydroarylation processes, respectively.

Introduction

Metallic triflates M(OTf)_n and triflimides M(NTf₂)_n, as Lewis superacids, are now extensively used to efficiently catalyze various organic reactions such as Diels–Alder cycloadditions, enyne and diyne cycloisomerizations, aldol and Michael additions, Friedel–Crafts, and several other reactions.^[1] Their catalytic efficiency, as compared to those of classical Lewis acids such as AlCl₃ or ZnCl₂, has been highlighted by the possibility to work under low catalyst loading for high yields and selective processes, enabling in some cases to go from stoichiometric to catalytic reactions and in other cases to develop new original reactions.^[2] Apart from catalysis, lithium triflimide has found a large industrial application as electrolyte in fuel cells and in batteries for electric cars.^[3,4]

Classically, metallic triflates or triflimides can be prepared from metal oxides,^[5] hydroxides,^[6] carbonates,^[7] or halides,^[8] and triflic or triflimidic acid. These reactions are performed in water or in aqueous media and afford the corresponding hydrated salts. However, hydrated catalysts may not be convenient for reactions needing anhydrous conditions. Alternative preparations of anhydrous metallic triflates and triflimides solvated by organic solvent molecules have been reported by an electrochemical method^[9] and an oxidative dissolution of metal powders in DMSO under O₂.^[10] In the specific case of Bi^{III}, Bi(OTf)₃ has been prepared from BiPh₃ under anhydrous conditions.^[11]

The literature mentions only a few direct preparations of metallic triflates and triflimides by reaction of metals with

triflic and triflimidic acids.^[12] We present here a simple and efficient procedure for the preparation of metallic triflates and triflimides under ultrasonic activation involving the reaction of metal powders in the presence of stoichiometric amounts of the corresponding protic acids. The use of sonochemistry for efficient chemical synthesis is well documented and generally allows increasing reaction kinetics, reaction times, and product yields.^[13]

Results and Discussion

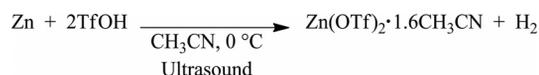
Preliminary tests were carried out with metallic zinc dust in the presence of two equivalents of triflic acid in acetonitrile under ultrasonic activation. The ultrasound waves were delivered by a sonotrode with a wavelength of 6 μm at a constant frequency of 20 kHz. The reaction was run at 0 °C, and the disappearance of the powder occurred within 30 min. Removal of the solvent and washing with dry diethyl ether afforded a white powder in a quantitative yield. The ¹⁹F NMR spectrum of the isolated Zn(OTf)₂ salt in [D₆]DMSO indicated a single singlet centered at –77.94 ppm and the ¹H NMR spectrum presented a singlet at 2.02 ppm attributed to the methyl group of the remaining coordinated acetonitrile. ¹H and ¹⁹F NMR spectroscopic analysis in the presence of 1-chloro-4-fluorobenzene as internal reference allowed to determine the salt composition as Zn(OTf)₂·1.6CH₃CN.

The process corresponds to a redox reaction between metallic zinc and triflic acid, involving hydrogen evolution as the only byproduct (Scheme 1).

In order to determine the effect of the amplitude of the ultrasound, the synthesis of zinc triflate was carried out under the same conditions at different wavelengths. As shown in Table 1, the amplitude had a low impact on the yield;

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Scheme 1.

however, the time of the experiment was considerably reduced by increasing the wavelength. In the absence of ultrasound irradiation, the amount of the zinc triflate salt formed was negligible (entry 5).

Table 1. Preparation of zinc triflate under ultrasonic activation: influence of the ultrasound wavelength.^[a]

Entry	Wavelength [μm]	Reaction time [min]	Yield of isolated Zn(OTf) ₂ ·CH ₃ CN [%]
1	6	30	94
2	7.2	20	99
3	8.4	15	100
4	9.6	8	80
5	–	120	< 5

[a] Reactions carried out with Zn (1 mmol), TfOH (2 mmol) in dry MeCN (40 mL) at 0 °C.

The kinetic evolution of the reaction could be monitored by pH titration of aliquots of the reaction mixture (diluted in water) with a solution of sodium hydroxide. As illustrated in Figure 1, two jumps of pH were observed. The presence of triflic acid that was not consumed was responsible for the first one and allows the kinetic follow-up of the reaction. The second unexpected jump was shown to be due to the acidity of zinc triflate in aqueous media, by comparison with the titration of the isolated metallic salt alone. Other metallic triflates and triflimides also presented a similar behavior.

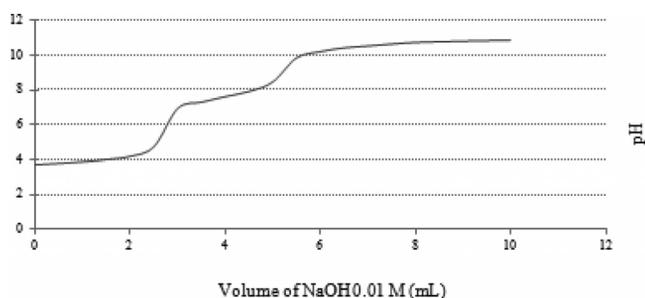
The preparation of zinc triflate could be carried out in different solvents. Thus, at a wavelength of 7.2 μm the differently solvated salts were formed almost quantitatively when water, acetonitrile, or DMF were used. The obtained salts were Zn(OTf)₂·4H₂O, Zn(OTf)₂·0.9CH₃CN, or Zn(OTf)₂·6DMF, respectively.

We further investigated the behavior of other metals under ultrasonic activation in the presence of triflic and triflimidic acids in acetonitrile, and the results of the syntheses of the corresponding triflates and triflimides are presented in Table 2.

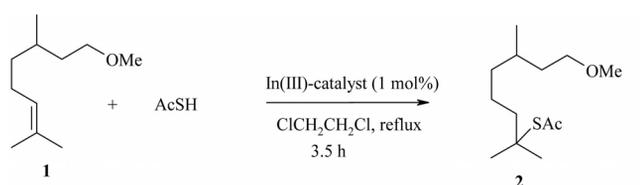
Table 2. Preparation of metallic triflates and triflimides under ultrasonic activation in acetonitrile.^[a]

Entry	λ [μm]	Metal	Acid (equiv.)	Reaction time [min]	δ (¹ H NMR) [ppm]	δ (¹⁹ F NMR) [ppm]	Product	Yield [%]
1	6	Zn	TfOH (2)	30	2.02	–77.94	Zn(OTf) ₂ ·1.5CH ₃ CN	94
2	7.2	Fe	TfOH (2)	90	1.75	–77.83	Fe(OTf) ₂ ·1.4CH ₃ CN	98
3	7.2	Sn	TfOH (2)	75	2.03	–77.88	Sn(OTf) ₂ ·2.5CH ₃ CN	30
4	7.2	In	TfOH (3)	60	1.80	–77.81	In(OTf) ₃ ·CH ₃ CN	30
5	6	Cu	TfOH (2)	35	2.05	–78.05	Cu(OTf) ₂ ·4.6CH ₃ CN	92
6	6	Bi	TfOH (3)	120	2.47	–77.83	Bi(OTf) ₃ ·0.9CH ₃ CN	50
7	7.2	Mn	TfOH (2)	40	1.75	–77.46	Mn(OTf) ₂ ·3.2CH ₃ CN	85
8	7.2	Zn	HNTf ₂ (2)	60	2.84	–78.85	Zn(NTf ₂) ₂ ·1.6CH ₃ CN	66
9	7.2	Fe	HNTf ₂ (2)	105	1.95	–78.81	Fe(NTf ₂) ₂ ·4.8CH ₃ CN	94
10	7.2	Mn	HNTf ₂ (2)	60	1.23	–78.98	Mn(NTf ₂) ₂ ·4.8CH ₃ CN	83

[a] Reactions run in MeCN at 0 °C. After consumption of the metal and the acid (by titration), the solvent was evaporated, the solid powder was washed with diethyl ether and dried under vacuum.

Figure 1. Titration during the sonochemical preparation of Zn(OTf)₂.

The catalytic activity of In(OTf)₃·MeCN obtained by ultrasonic activation was compared to that of a commercial In^{III} salt and to the In(OTf)₃·7DMSO prepared according to ref.^[10] in the regioselective addition of thioacetic acid to non-activated olefins (Scheme 2).^[14] The functionalization of citronellyl methyl ether (**1**) in refluxing dichloroethane with 5 mol-% of catalyst led to complete conversion in less than 1 hour to form quantitatively 8-methoxy-2,6-dimethyloctan-3-yl ethane thioate (**2**) with the three In^{III} catalysts. For a more accurate comparison, the reactions were then run with only 1 mol-% of catalyst and stopped after 3.5 h. Whereas a 50% conversion of **1** to **2** was attained with In(OTf)₃·CH₃CN, conversions of only 30 and 28% were reached with commercial indium triflate and In(OTf)₃·7DMSO, respectively. These results, indicating the higher



	Conversion of 1	Yield of 2
Catalyst: In(OTf) ₃ ·CH ₃ CN (prepared <i>via</i> ultrasound)	51%	50%
In(OTf) ₃ ·7DMSO (ref 10)	28%	27%
Commercial In(OTf) ₃	30%	29%

Scheme 2.

Table 3. Sonochemical preparation of bismuth salts from different acids.^[a]

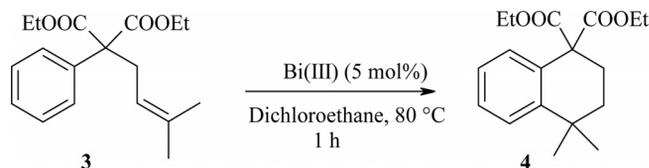
Entry	Protic acid	p <i>K</i> _a ^[12]	Bismuth salt obtained	Yield [%]
1	(CF ₃ SO ₂) ₂ NH (A-1)	< -14	Bi[N(SO ₂ CF ₃) ₂] ₃ ·1.3CH ₃ CN (Bi-1)	99
2	CF ₃ SO ₃ H (A-2)	-14	Bi(OSO ₂ CF ₃) ₃ ·0.9CH ₃ CN (Bi-2)	91
3	(CH ₃ C ₆ H ₄ SO ₂) ₂ NH (A-3)	-0.5	Bi[N(SO ₂ C ₆ H ₄ CH ₃) ₂] ₃ ·2.5CH ₃ CN (Bi-3)	35
4	<i>p</i> -CF ₃ C ₆ H ₄ CO ₂ H (A-4)	3.6	Bi(OCOC ₆ H ₄ CF ₃) ₃ ·2.5CH ₃ CN (Bi-4)	63
5	<i>p</i> -FC ₆ H ₄ CO ₂ H (A-5)	4.14	Bi(OCOC ₆ H ₄ F) ₃ ·8.3CH ₃ CN (Bi-5)	59

[a] General conditions: Bi (3 mmol), acid (9 mmol) in CH₃CN (30 mL) under ultrasonic activation ($\lambda = 7.2 \mu\text{m}$) for 3 h.

catalytic activity of the sonochemically prepared catalyst, were interpreted by the lower coordinating ability of MeCN to the metal center, as compared to water or DMSO.

In order to evaluate the possibilities of the sonochemical method for the preparation of metallic salts of less protic acids, a series of Bi^{III} salts derived from acids having different p*K*_a values was prepared. As illustrated in Table 3, aside from the high yields obtained for Bi(NTf₂)₃ and Bi(OTf)₃ (entries 1, 2), the methodology allowed the synthesis of Bi^{III} bis(*p*-tolylsulfonyl)imide (entry 3) as well as that of Bi^{III} carboxylates derived from *p*-trifluoromethylbenzoic acid and *p*-fluorobenzoic acid, with p*K*_a values of 3.6 and 4.14 respectively.^[15]

These different Bi^{III} salts, as well as the corresponding protic acids, were tested as catalysts for the recently reported intramolecular Friedel–Crafts alkylation of substrate **3** to bicyclic compound **4** (Scheme 3).^[16]



Scheme 3.

The cyclization was run with 5 mol-% of catalyst in dichloroethane at 80 °C for 1 hour. As illustrated in Figure 2, the cyclization was only efficient in the case of the catalysis by Bi(NTf₂)₃ and Bi(OTf)₃ or by the corresponding protic superacids. No reactivity was observed with the other salts or protic compounds, indicating the strong influence of the anion in these carbon–carbon coupling reactions catalyzed by Lewis acids. Moreover, it is remarkable to see that better results were obtained with Bi^{III} triflate and triflimide salts than with the superacids.

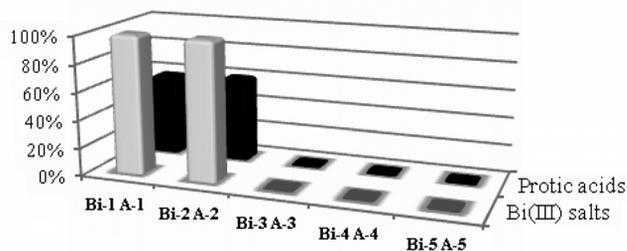


Figure 2. Yield of **4** after 1 hour of reaction of **3** catalyzed by Bi^{III} salts (5 mol-%) or by the corresponding protic acids (5 mol-%), according to Scheme 3 and Table 3.

Conclusions

We describe a new, simple, rapid, and efficient method of an alternative preparation of several metallic triflates and triflimides, which allows to obtain anhydrous, highly active, and useful catalysts. Furthermore, this method enables easy scale-up procedures and is compatible with several solvents. The activity of the In(OTf)₃ prepared by the sonochemical method was higher than that of the corresponding commercial compound. The high activity of the sonochemically prepared Bi(OTf)₃ and Bi(NTf₂)₃ in the catalysis of a Friedel–Crafts alkenylation process was also established.

Experimental Section

Representative Procedure for the Preparation of Metallic Salts by Using Ultrasound: The metal (3 mmol), freshly distilled acetonitrile (30 mL), and the acid (9 mmol) were introduced under nitrogen into a 100 mL vial flashed with nitrogen. The sonotrode was dipped in the solution, and ultrasound (amplitude: 7.5 μm) was applied by using the sonometer (UIP1000 hd Hielsher) until the complete disappearance of the metal. The solution was filtered, the solvent was evaporated, and the metal salt was washed three times with Et₂O and analyzed by ¹H and ¹⁹F NMR spectroscopy with 1-chloro 4-fluorobenzene as standard to evaluate the amount of coordinated solvent.

General Procedure for the Hydrothiolation Reaction: Citronellyl methyl ether (5 mmol), thioacetic acid (5 mmol), and In(OTf)₃ (0.05 mmol) were stirred in dichloroethane (5 mL) heated to reflux. The progress of the reaction was monitored by GC analysis. After 3.5 h, the reaction was quenched with distilled water, and the mixture was extracted with Et₂O. The organic layer was washed with saturated aqueous NaHCO₃ and dried with MgSO₄. The solvent was evaporated, the product was purified by column chromatography, analyzed by ¹H and ¹³C NMR spectroscopy and mass spectrometry, and compared to an authentic sample.

General Procedure for the Friedel–Crafts Reaction: Phenylprenyl- (ethyl malonate) (1 mmol) and Bi(OTf)₃ (0.05 mmol) were heated to 80 °C for 1 h in anhydrous dichloroethane under nitrogen. The reaction was quenched with ice water, and the mixture was extracted with Et₂O and brine. The organic layer was concentrated under reduced pressure, the product was purified by column chromatography, analyzed by ¹H and ¹³C NMR spectroscopy and mass spectrometry, and compared to an authentic sample.

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