Bismuth(III) Trifluoromethanesulfonate: A Chameleon Catalyst for the Friedel–Crafts Acylation[☆]

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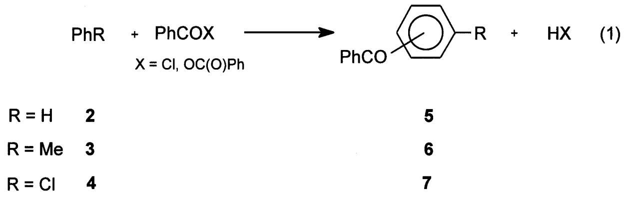
A mechanism for acylations catalyzed by bismuth(III) triflate (**1**) is proposed in the case of the benzoylation of benzene, toluene, and chlorobenzene. With Bz_2O as a reagent, **1** acts as a Lewis acid and allows the benzoylation of toluene. It is almost completely recovered after the reaction. With BzCl, **1** promotes an exchange reaction which generates BzOTf, which is the active species of the benzoylation. In this latter case, the reaction leads to the formation of TfOH which finally reacts with $BiCl_3$ to partially regenerate **1**. The power of the Bz_2O/**1** system is less than that of BzCl/**1**, which allows not only the benzoylation of toluene but also that of benzene and deactivated chlorobenzene. The activity of **1** is much higher than that of other metallic triflates previously reported, and is comparable with that of TfOH, however it also has the advantage that the triflate moieties are more easily recoverable.

The Friedel−Crafts (FC) acylation of aromatic compounds is one of the most important reactions in organic chemistry[1][2]. Traditionally, $AlCl_3$ is the Lewis acid promoter used, but the stoichiometric amounts required, due to the formation of a stable complex with the arylketone produced, leads to an environmentally hostile process with gaseous effluents and mineral wastes. Some catalysts, in particular metallic salts such as $FeCl_3$, $ZnCl_2$[3][4], and zeolites[5], have been reported, but their use is generally restricted to the acylation of activated aromatics. Brønsted acids, including superacidic systems[6] and sulfonic acids[7], are known to be efficient catalysts, in particular triflic acid[7a]. However, the latter is extremely hygroscopic and soluble in the reaction media, which seriously complicates its recovery in anhydrous form[8]. A decade ago, Olah and coworkers reported on the catalytic activity of triflates of boron, aluminum, and gallium[9]. These catalysts are highly sensitive to hydrolysis and, with 50% catalyst added, give a maximum yield of 72% in the benzoylation of toluene. Recently, aqueous stable metallic salts of triflic acid[10] or bis(trifluoromethylsulfonyl)amide[11] have been reported. Unfortunately, their activity is essentially limited to the acylation of activated aromatics. Nevertheless, hafnium triflate in the presence of excess lithium perchlorate[12a] and bromopentacarbonylrhenium (I)[12b] leads to the catalytic acylation of toluene in high yield (but that of benzene in low yield).

As early as 1994, our laboratory described the Lewis acid activity of bismuth trichloride towards the FC acylation[13][14]. As its catalytic power is restricted to the acylation of activated aromatics, we decided to replace the chlorine atoms by triflate groups, which are more electron withdrawing substituents. Bismuth(III) triflate (**1**) revealed a strong activity for the FC acylation[15], and allowed not only the acylation of aromatic ethers but also the benzoylation of benzene, toluene and halobenzenes. In the present paper we describe our mechanistic examination of this reaction, catalyzed by **1**, in the case of the benzoylation of benzene (**2**), toluene (**3**), and chlorobenzene (**4**).



The acylation of toluene, and more particularly that of benzene, is a much more difficult reaction than the acylation of aromatic ethers. Scandium triflate, known to be an efficient catalyst for the acetylation of aromatic ethers[10], was almost inactive for the benzoylation of **3** by BzCl: after 4 h only a 4% yield in methylbenzophenone (**6**) was real-

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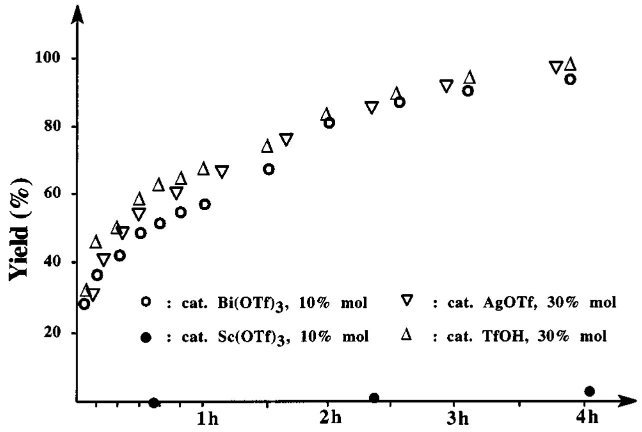
ized. Other rare earth triflates, such as those derived from cerium or ytterbium, were totally inactive for the same reaction. However, **1** (10 mol%) exhibited a strong catalytic activity giving a yield of 83% after 2 h, and 95% after 5 h of toluene reflux, with a *para* selectivity (*o-/m-/p-***6** = 19:2:79) (Eq. 1, R = Me). As triflic acid is known to catalyze the benzoylation of toluene[7a], we decided to compare the catalytic activity of **1** (10 mol%) and triflic acid (30 mol%) on this reaction. It appeared that the two rate curves presented a similar profile (Figure 1), with the same initial rate, and that the two catalysts led to the same *para* selectivity. Moreover, the yield in **6** was 32% after 5 min, i.e. about the amount corresponding to that of triflate introduced in the reaction. This suggested that a ligand exchange reaction might be occurring. Weight was given to this hypothesis by testing the catalytic activity of silver triflate, which is well known to give the triflate−chloride exchange (Eq. 2, M = Ag, $n = 1$)[7b][16]. With 30 mol% of AgOTf, a kinetic curve similar to the two previous examples has been obtained (Figure 1). Therefore, the first step of the mechanism of the **1**-catalyzed benzoylation of toluene is the reaction between this catalyst and BzCl (Eq. 2, M = Bi, $n = 3$), which generates $BiCl_3$ and a mixed anhydride, the benzoyl triflate (**8**).

Figure 1. Catalysis of the benzoylation of toluene. Conditions: temp. 110°C, reactants: benzoyl chloride (1 equiv.), toluene (10 equiv.), catalyst; yield in methylbenzophenone (**6**)

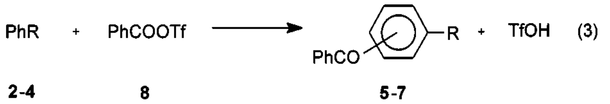


$$M(OTf)_n + n\ PhCOCl \rightarrow MCl_n + n\ PhCOOTf \qquad (2)$$

$n = 3$, M = Bi (**1**) Tf = SO_2CF_3
$n = 1$, M = Ag

Such ligand exchange has also been reported for thallium salts[17]. The similarity of the three kinetic curves (Figure 1) shows that the exchange reaction (Eq. 2) is very fast for AgOTf and **1** under the experimental conditions of the acylation reaction.

Sulfonic acid mixed anhydrides are known to be good acylating agents[16][18], especially those of triflic acid[16]. Consequently, we proposed the reaction of toluene with BzOTf (Eq. 3, R = Me) as the second step of the **1**-catalyzed benzoylation of this substrate.



2-4 **8** **5-7**

In support of this hypothesis, we observed that the performances of the **1**-catalyzed benzoylations[15] and those of BzOTf[16] towards benzene, toluene, and chlorobenzene were similar (Eq. 3). Therefore, the real catalyst of the reaction is triflic acid. This has also been proved by achieving the inhibition of the benzoylation of toluene (catalyzed by 10 mol% of **1**) using 30 mol% of 2,4,6-tri-*tert*-butylpyridine, added during the course of the reaction. The triflic acid formed is able to regenerate **8** from BzCl[16] (Eq. 4, step 3).

$$TfOH + PhCOCl \rightarrow PhCOOTf + HCl \qquad (4)$$

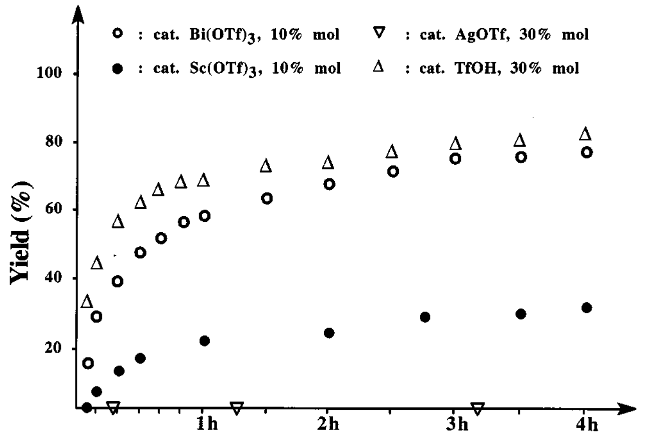
In the case of catalysis by AgOTf, silver was recovered as AgCl after the aqueous workup, because this chloride does not react with TfOH[19]. Conversely, the recovery of bismuth after the workup showed the presence of the $BiCl_3$-hydrolysis product, BiOCl, and also that of **1** as the major product (BiOCl/**1** = 1:2). The same mixture was obtained after the aqueous workup of the reaction between $BiCl_3$ and TfOH ($BiCl_3$/TfOH = 1:3) under the same conditions as those used for the benzoylation of toluene. This result indicates that TfOH reacts partially with $BiCl_3$ at the end of (or during) the benzoylation reaction (Eq. 5, step 4) leading to a 1:2 mixture of $BiCl_3$ and **1**; the transient formation of the mixed compound $Bi(OTf)_2Cl$ (Eq. 3, $n = 2$) is possible. It is known that a reaction occurs between $BiCl_3$ and fluorosulfonic acid, but that an excess of this acid is needed, and that the disubstituted product $Bi(SO_3F)_2Cl$ is more easily formed than $Bi(SO_3F)_3$[20].

$$BiCl_3 + n\ TfOH \rightarrow Bi(OTf)_nCl_{(3-n)} + nHCl \qquad (5)$$

These exchange reactions (Eqs. 2 and 5) seem to be controlled by the relative values of metal−oxygen and metal−chlorine bond energies. For bismuth, the two energies are close (D^0_{298} = 337 and 301 $kJmol^{-1}$, respectively)[21], and the exchange can take place in either direction (Eqs. 2 and 5). If the first is much lower than the second (Ag)[21] only the O/Cl exchange (Eq. 2) takes place with formation of **8**. On the contrary, if the metal−oxygen bond energy is much stronger than the metal−chlorine one (Sc)[21], this exchange reaction cannot take place, and the metallic triflate is inefficient in generating **8**.

Brønsted acids activate acid anhydrides more strongly than do Lewis acids. Surprisingly, $BiCl_3$ proved to be an efficient catalyst for the acylation of aromatic ethers by acid anhydrides[13][14]; however, $BiCl_3$ was inactive for the benzoylation of toluene by benzoic anhydride. Moreover, **1** turned out to be about five times more active than $Sc(OTf)_3$ for the acetylation of anisole by acetic anhydride ($MeNO_2$, 1 M; 50°C; results not shown). Then, we compared the catalytic activity of some metallic triflates towards the benzoylation of toluene by Bz_2O (Figure 2). While cerium-, ytterbium-, and silver triflates were inactive, $Sc(OTf)_3$ exhibited some activity. Again, **1** proved to be more effective than any of the metallic triflates tested, but gave a somewhat slower reaction than that catalyzed by TfOH, with the initial rate significantly lower; however, the yields after 4 h were close (78% with TfOH instead of 71% when catalyzed by **1**. For the benzoylation of toluene by Bz_2O in the presence of **1**, it would seem that the formation of the mixed anhydride **8** from **1** and, consequently, the catalysis by TfOH, are not taken into account. Another mechanistic possibility could be the catalysis by **1** itself as a Lewis acid. A set of experiments showed that, in this case, **1** is the true catalyst of the reaction, without formation of triflic acid.

Figure 2. Catalysis of the benzoylation of toluene. Conditions: temp. 110°C, reactants: benzoic anhydride (1 equiv.), toluene (10 equiv.), catalyst, yield in methylbenzophenone (**6**)



The presence of an intermolecular carbonyl−bismuth interaction has already been observed between MeCOCl and $BiCl_3$, and showed a down-field shift of the ^{13}CO magnetic resonance signal ($\Delta\delta = 6$)[13b]. A comparable deshielding has also been observed for an intramolecular carbonyl−bismuth coordination[22]. The NMR study of Bz_2O in the presence of $BiCl_3$ and **1** (Table 1) proved the existence of an intermolecular interaction between the carbonyl oxygens of Bz_2O and bismuth atoms in these compounds.

Table 1. ^{13}C-NMR data for mixtures of Bz_2O and $BiCl_3$ or $Bi(OTf)_3$ (**1**)[a]

Mixtures	δ $^{13}C{=}O$	$\Delta\delta$[b]
Bz_2O	164	
$Bz_2O + BiCl_3$[c]	171	7
$Bz_2O + Bi(OTf)_3$[c]	177	13

[a] Chemical shifts relative to TMS (ppm); solvent: $MeNO_2$; external ref: C_6D_6; temperature: 297 K. − [b] $\Delta\delta = \delta$ CO(mixture) − δ CO (Bz_2O). − [c] Molar ratios: $Bz_2O/BiCl_3$ or $Bi(OTf)_3$ = 1:1

The benzoylation of benzene (**2**) and chlorobenzene (**4**) was carried out by the two systems BzCl/**1** and Bz_2O/**1**. The benzoylation of benzene by Bz_2O in the presence of 10% of **1** gave 8% of benzophenone (**5**) after 22 h refluxing. In contrast the use of the BzCl/**1** system, generates **8** and TfOH: the benzoylation of **2** by this system led to **5** in an isolated yield of 78% after 15 h at reflux (Eqs. 1 and 3, R = H). In the same way, the benzoylation of chlorobenzene (**4**) by Bz_2O in the presence of 10% of **1** did not proceed at all after 12 h at 110°C, in contrast to the use of the BzCl/**1** system, which gave the chlorobenzophenone (*o-/p-***7** = 13:87) in yield of 69% after 15 h at the same temp. (Eqs. 1 and 3, R = Cl).

Finally, at the time of the benzoylation of **3** by Bz_2O, **1** can be recovered easily from the crude reaction mixture.

In summary, the catalytic activity of **1** in the FC benzoylation of toluene using Bz_2O can be attributed to the Lewis acidity of the bismuth center. This activity is a consequence of the three electronegative triflate ligands. **1** is nearly as efficient as triflic acid itself for this reaction and is the most efficient of the metallic triflates tested. **1** is a more efficient catalyst with BzCl as the acylating reagent, in that it allows the benzoylation of benzene and that of deactivated chlorobenzene in a convenient yield. By reversible exchange of triflate groups, it acts as generator of a mixed anhydride (benzoyl triflate) responsible for the benzoylation reaction. In this case, TfOH is the true catalyst of the reaction, and the activity of **1** is higher than that of other metallic triflates $M(OTf)_3$ previously reported (M = Al, Ga, Ln, or Sc). **1** brings a marked advantage, particularly with respect to TfOH, because of the ease of the recovery of the very expensive triflate moiety after the workup.

Lastly, since bismuth is the least toxic of the heavier elements[23] and is inexpensive, bismuth(III) salts, particularly bismuth triflate (**1**), are new and powerful catalysts for the old challenge that the FC acylation reaction constitutes. Further studies on the application of the present catalyst **1** to other reactions are in progress.

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Experimental Section

General: All starting materials were purchased commercially except the bismuth(III) trifluoromethanesulfonate (**1**). The products (**5**−**7**) of benzoylation reactions were identified and their isomeric composition determined by a comparison of their spectral data (NMR, GCMS) with those of authentic samples. − GC: Hewlett Packard 6890 chromatograph equipped with a 30 × 0.32 × 0.25 column (methyl silicone doped with 5% phenyl silicone; temperature conditions: 125°C to 300°C, 10°C/min). − GCMS: Hewlett-Packard MS 5989 apparatus (EI 70 eV) equipped with a GC 5890 chromatograph.

Bismuth(III) Trifluoromethanesulfonate (**1**): This compound was prepared following our procedure from triphenylbismuth and triflic acid[15a], and characterized by its spectroscopic data. − ^{13}C NMR (50.3 MHz, [D6]acetone): $\delta = 120$ ($^1J_{^{13}C/^{19}F} = 321$ Hz, quad.). − ^{19}F NMR (75.4 MHz, [D6]acetone): $\delta = 0.84$. − IR (nujol): $\tilde{\nu}$ = 3450−3550 cm^{-1} (m), 1230−1290 (vs), 1180 (s), 1034 (s), 1028 (sh), 650 (sh), 643 (s). **1** is water stable, and the existence of hydrated forms has been shown[24][25]. The catalyst used for the reactions described here was mainly the tetrahydrated form, for which the crystal structure has been established by X-ray diffractometry[25].

Typical Procedure for Kinetic Experiments: Compound $\mathbf{1}\cdot 4\ H_2O$ (600 mg, 0.823 mmol), Bz_2O (1.86 g, 8.23 mmol), tetradecane (850 mg, 4.28 mmol), and **3** (7.58 g, 82.3 mmol) were added together in a 50-ml flask. The flask was surrounded by a condenser then heated in an oil bath (110°C). The evolution of the reaction was monitored by analyzing an aliquote (quenched by triethylamine) of the reaction mixture by GC. The yield in methylbenzophenone (**6**) and the isomeric ratios were determined using tetradecane as an internal standard.

Typical Procedure for the Benzoylation of Toluene (**3**) *with Benzoic Anhydride:* Compound **1**·4 H_2O (1.16 g, 1.6 mmol), Bz_2O (3.62 g, 16 mmol), and **3** (2.95 g, 32 mmol) were added together in a 20-ml flask. the flask was surrounded by a condenser, then heated in an oil bath (110°C). After 5 h, 20 ml of dichloromethane were added and the reaction mixture was extracted with 6% aqueous HCl (2 × 10 ml). The aqueous layers were mixed. The residual benzoic acid was extracted by 10 ml of dichloromethane. The aqueous layer was submitted to evaporation of water under reduced pressure up to 60°C. Mass of **1** obtained: 1.02 g (88% recovery). The combined organic phases were dried ($MgSO_4$) and concentrated. The crude mixture was purified by flash chromatography (silica, pentane/ether, 9:1) to give **6** (2.35g, 75% yield from Bz_2O; *o-/m-/p-***6** = 19:3:78). − ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, Me, *o-* **6**), 2.42 (s, Me, *p-* **6**), 7.2−7.8 (m, Ph). − GCMS: *m/z* (%) = *o-* **6**: 196 (M^+, 60), 195 (100%), 119 (24), 105 (55), 91 (41), 77 (89); *p*-**6** 196 (57) [M^+], 181 (12), 119 (100%), 105 43), 91 (41), 77 (61).

Typical Procedure for the Benzoylation of Toluene (**3**) *with Benzoyl Chloride:* Compound **1**·4 H_2O (1.02 g, 1.4 mmol), BzCl (1.97 g, 14 mmol), and **3** (2.58 g, 28 mmol) were added together in a 20-ml flask. The flask was surrounded by a condenser then heated in an oil bath (110°C). After 5 h, the reaction mixture was treated following the same workup as given above. After evaporation of the aqueous layers and drying of the residue under reduced pressure up to 100°C, 0.71 g of a white solid was recovered, and identified by X-ray powder analysis[25] as a mixture of BiOCl and **1** (89% recovery towards Bi). A Cl analysis of this solid using silver nitrate allowed the molar ratio BiOCl/**1** = 1:2 to be determined.

Following the same workup as before, **6** was isolated in 95% yield from BzCl (*o-/m-/p-***6** = 22:2:76).

☆ Dedicated to Professor *P. Jutzi* on the occasion of his 60th birthday.

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