Bismuth(III) Triflate in Organic Synthesis

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Keywords: Bismuth / Triflate / Catalysis / Organic synthesis

Bismuth(III) triflate is a new, cheap and environmentally friendly Lewis acid. The research presented in this microreview is devoted to the evaluation of the scope of the uses of bismuth(III) triflate in organic synthesis.

1. Introduction

The first synthesis of trifluoromethanesulfonic acid (triflic acid, TfOH) was reported half a century ago by Haszeldine et al.[1] Triflic acid is one of the most acidic monoprotic organic acids.[2] It forms water-stable salts with numerous metals[3] and can be considered as a super-acid.[4] Since the pioneering work reporting the use of silver(I) triflate as catalyst for polymerisation reactions,[5] metal triflates have received a lot of attention as Lewis-acid-type catalysts for organic synthesis and thus have been the subject of a large number of publications.[6] Bismuth stands out from other heavy elements (such as mercury, thallium and lead) due to its relatively non-toxic character.[7] This non-toxicity arises from the insolubility of its salts in neutral aqueous solutions such as biological fluids, which confers on bismuth the enviable status of being an "eco friendly" element likely to generate useful catalysts suitable for green chemistry. Unfortunately, due to its location in the periodic table next to the toxic heavy metals,[8] bismuth compounds were assumed to be toxic and hence the use of bismuth(III) salts, especially bismuth(III) triflate [$Bi(OTf)_3$] as catalysts for organic synthesis remained unexplored. The dawn of the use of $Bi(OTf)_3$ as a new catalyst has to be attributed to the seminal work of Dubac et al. who first established the Lewis

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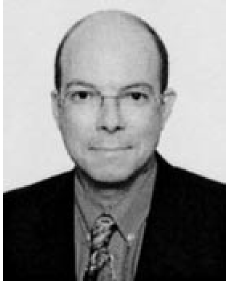

Christophe Le Roux was born in France in 1964. After a Masters degree in biochemistry obtained at Université Paul Sabatier in Toulouse, he decided to move to chemistry and received his doctorate in 1993 from the same University on the use of bismuth(III) salts as catalysts in organosilicon chemistry, under the supervision of Professor J. Dubac. He became interested in silicones during his post-doctoral research with Professor M. A. Brook at McMaster University (Hamilton, Canada). In 1995 he joined the Centre National de la Recherche Scientifique as a research assistant in the Laboratoire Hétérochimie Fondamentale et Appliquée (U.M.R. 5069, Dir. Dr. G. Bertrand). His main current research interests are focussed on electrophilic substitution, catalysis, green chemistry and industrial applications.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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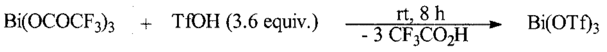
acid nature of Bi(OTf)$_3$.[8] At first glance its Lewis acid behaviour might be somewhat surprising since compounds of some of the elements of Group 15, such as phosphanes, are more commonly known for their Lewis base properties. In the case of bismuth, while relativistic effects are responsible for the stabilisation of the 6s orbital (weak Lewis base),[9] the Lewis acid behaviour can be related to the tendency for the extension of coordination around bismuth centre arising from the availability of unoccupied orbitals (d and/or Bi−X σ*),[10] this latter property being enhanced by strong electron-withdrawing groups (X = OTf).

As with previous reviews,[11] the aim of this article is focused on the state of the art of the applications of Bi(OTf)$_3$ in organic synthesis and, when possible, to compare its efficiency with that of other metal triflates.

2. Preparation of Bismuth(III) Triflate

Bi(OTf)$_3$ was first prepared by Verma et al. from triflic acid and bismuth(III) trifluoroacetate (Scheme 1).[12] The driving force of this reaction — a consequence of the reported inactivity of TfOH towards BiCl$_3$ in the preparation of Bi(OTf)$_3$ — is based on the higher acidic strength of TfOH compared to the CF$_3$CO$_2$H generated during the reaction.



$$\mathrm{Bi(OCOCF_3)_3} + \mathrm{TfOH\ (3.6\ equiv.)} \xrightarrow[\text{- 3 CF}_3\text{CO}_2\text{H}]{\text{rt, 8 h}} \mathrm{Bi(OTf)_3}$$

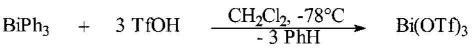
Scheme 1

In a separate procedure, the same authors prepared Bi(OTf)$_3$ starting from Bi$_2$O$_3$.[13] While Bi$_2$O$_3$ is one of the cheapest bismuth sources, this preparation still requires the use of an excess of triflic anhydride (Scheme 2).

$$\mathrm{Bi_2O_3} + \mathrm{Tf_2O\ (8\ equiv.)} \xrightarrow{\text{120 °C, 29 days}} \mathrm{Bi(OTf)_3}$$

Scheme 2

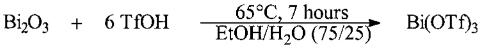
More recently our group proposed another strategy for the preparation of Bi(OTf)$_3$.[14] Inspired by an analogous method reported with trifluoroacetic acid,[15] the key point of our synthetic strategy is based on the acidic cleavage of the three carbon−bismuth bonds of triphenylbismuth by triflic acid in dichloromethane as solvent (Scheme 3). Modifications of this method with different solvents have also been reported.[16] A study of the hydration of Bi(OTf)$_3$ revealed that this compound can exist in three different hydrated forms: a nonahydrate, a tetrahydrate and a dihydrate.[17] The structures of the nona- and tetrahydrates have been determined by ab initio calculations[17] or X-ray diffraction.[18]



$$\mathrm{BiPh_3} + \mathrm{3\ TfOH} \xrightarrow[\text{- 3 PhH}]{\text{CH}_2\text{Cl}_2\text{, -78°C}} \mathrm{Bi(OTf)_3}$$

Scheme 3

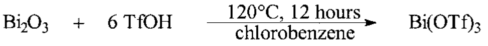
Recently, our group has discovered a "green" procedure for the synthesis of Bi(OTf)$_3$ starting from Bi$_2$O$_3$ and TfOH using an aqueous ethanol mixture as solvent.[19] Bi(OTf)$_3$·xH$_2$O (with $1 < x < 4$) is obtained after freeze-drying of the solution (Scheme 4).



$$\mathrm{Bi_2O_3} + \mathrm{6\ TfOH} \xrightarrow[\text{EtOH/H}_2\text{O (75/25)}]{\text{65°C, 7 hours}} \mathrm{Bi(OTf)_3}$$

Scheme 4

Very recently, a new and inexpensive method has been published by our group (Scheme 5).[20a] It uses Bi$_2$O$_3$ and TfOH as starting materials and chlorobenzene as solvent, which allows the recovery of Bi(OTf)$_3$·xH$_2$O (with $1 < x < 4$) simply by filtration.



$$\mathrm{Bi_2O_3} + \mathrm{6\ TfOH} \xrightarrow[\text{chlorobenzene}]{\text{120°C, 12 hours}} \mathrm{Bi(OTf)_3}$$

Scheme 5

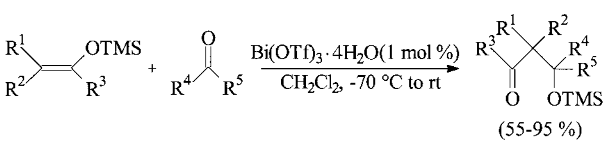
A survey of all the literature methods for the preparation of Bi(OTf)$_3$ indicates that the best method is the one starting from Bi$_2$O$_3$ and triflic acid in chlorobenzene.[20a] This procedure is suitable for small scale reactions as well as for the preparation of Bi(OTf)$_3$ on an industrial scale. Based on our knowledge, strictly anhydrous Bi(OTf)$_3$ cannot be obtained from any of the previously reported methods (even using triphenylbismuth) and in all cases a slight hydration of the catalyst [Bi(OTf)$_3$·xH$_2$O with $1 < x < 4$) has to be taken into account [for a discussion about the behaviour of water towards Bi(OTf)$_3$ and its hydrolysis, see Section 11 of this article].[20b] In addition, we strongly believe that such a hydrated form has been used in the majority of most of the previously reported works reviewed below. Thus, it seems to us that it would be desirable for future publications that Bi(OTf)$_3$ be replaced by Bi(OTf)$_3$·xH$_2$O ($1 < x < 4$).

3. Nucleophilic Additions

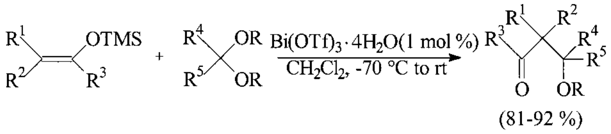
3.1. Aldol Reactions

The aldol reaction is considered to be one of the most important carbon-carbon bond-forming reactions in organic chemistry. Many metal derivatives, and especially metal triflates, have been reported to catalyse these reactions.

Our group has examined the activity of Bi(OTf)$_3$ in aldol and aldol-type reactions.[21] Bi(OTf)$_3$·4H$_2$O, was found to be a very efficient catalyst for the Mukaiyama aldol-type reactions and showed higher catalytic activity than other metal triflates such as Sc(OTf)$_3$, Yb(OTf)$_3$ or Y(OTf)$_3$.[22a] Ketones, aldehydes and acetals may be used as electrophiles with aromatic and aliphatic silyl enol ethers to give the corresponding β-hydroxy or alkoxycarbonyl compounds in the presence of 1 mol % of the catalyst (Scheme 6 and 7 and Table 1). Furthermore, Bi(OTf)$_3$ proved to be a better catalyst for acetal than for aldehyde activation. The mechanism proposed involves a transmetallation reaction between Bi(OTf)$_3$ and the silyl enol ether leading to TMSOTf which could be the true catalyst for the reaction, the latter being a well-known activator of acetals in comparison to aldehydes.[22b]



Scheme 6



Scheme 7

Table 1. Catalytic activity of metal triflates for the reaction between 1-trimethylsilyloxycyclohexene and benzaldehyde

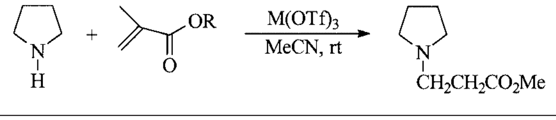
Entry	Cat.: $M(OTf)_3$ (mol %)	Conditions	Yield (%)
1	$Bi(OTf)_3$ (1)	−70 °C, 0.5 h	95
2	$Sc(OTf)_3$ (5)	−78 °C, 15 h	81
3	$Yb(OTf)_3$ (5)	−78 °C, 15 h	trace
4	$Y(OTf)_3$ (5)	−78 °C, 15 h	trace

3.2. Michael-Type Reactions

Another reaction which is also very important as a carbon−carbon bond-forming process in organic synthesis is the Michael reaction. The conjugate addition of amines to α,β-unsaturated esters yielding β-amino esters requires drastic reaction conditions. Various lanthanide triflates [$La(OTf)_3$, $Sm(OTf)_3$, $Yb(OTf)_3$] have been tested to catalyse the conjugate addition of benzylamine to α,β-unsaturated esters; 10% of catalyst was necessary and the reaction time was long.

Quite recently, $Bi(OTf)_3$ was found to be an excellent and reusable chemoselective catalyst for the Michael conjugate addition of aliphatic amines to α,β-ethylenic compounds under mild conditions.[23] Just 2 mol % of the catalyst was sufficient and the reaction time was shorter than with $Yb(OTf)_3$ as a catalyst, although overall yields were similar (Table 2).

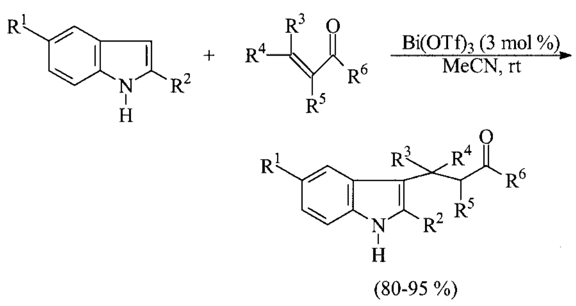
Table 2. Catalytic activity of metal triflates in the Michael addition



Entry	$M(OTf)_3$ (mol %)	Ethylenic compound	Time (h)	Yield[a] (%)
1	$Bi(OTf)_3$ (2)	Methyl acrylate	0.5	96
2	$Yb(OTf)_3$ (10)	Ethyl crotonate[b]	6	95

[a] Isolated yields. [b] Mainly the *trans* isomer.

$Bi(OTf)_3$ has also been used as a Lewis acid catalyst for the conjugate addition of indoles to α,β-enones giving 3-substituted indoles, which exhibit a range of biological activities.[24] Many methods have been reported for the preparation of these indole derivatives. With $Bi(OTf)_3$ as catalyst (3 mol %), these reactions proceed smoothly at room temperature in excellent yields with high selectivity using various α,β-unsaturated ketones such as cyclic and acyclic enones (Scheme 8).

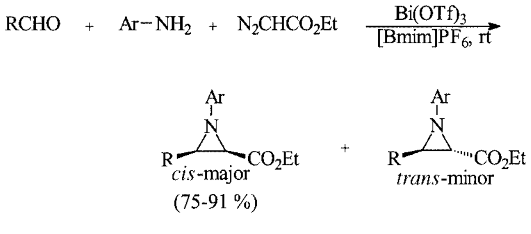


Scheme 8

3.3. Mannich-Type Reactions

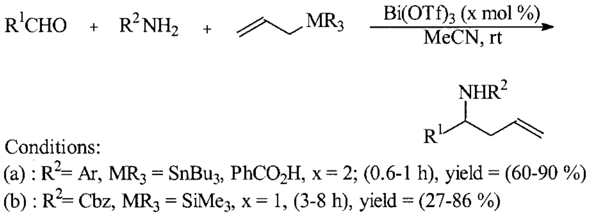
Aziridines are well-known carbon electrophiles that react with various nucleophiles leading to many biologically active compounds, such as various α,β-unsaturated amino esters. One of the most versatile methods for the preparation of aziridines is the nucleophilic addition of ethyl diazoacetate to imines. While several catalysts have been employed to promote these reactions, many of them cannot be carried out in a one-pot operation.

$Bi(OTf)_3$ has been used in an ionic liquid (IL) to catalyse the synthesis of *cis*-aziridine carboxylates through the one-pot coupling of an aldehyde, amine and ethyl diazoacetate under mild conditions.[25] The reaction was realised with a variety of aldehydes and amines at room temperature to produce the corresponding aziridine carboxylates in high yields and, in most cases, with high *cis* stereoselectivity (Scheme 9). Interestingly, the catalyst can be recovered from the IL and reused easily.



Scheme 9

$Bi(OTf)_3$ has also been used in combination with benzoic acid or sodium dodecylsulfate to catalyse the one-pot synthesis of homoallylamines. A variety of aldehydes and amines have been examined and the adducts were obtained in good to excellent yields (Scheme 10, conditions a).[26a]



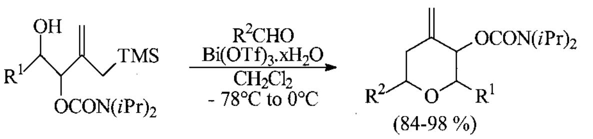
Scheme 10

More recently, a similar method was reported, the allylation of a variety of in situ generated N-protected aldimines being carried out with allyltrimethylsilane instead of allyltrimethylstannane catalysed by $Bi(OTf)_3$ without any additive (Scheme 10, conditions b).[26b]

3.4. Allylation Reactions

3.4.1. Intramolecular Sakurai Cyclisation

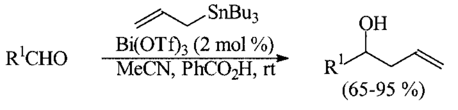
An efficient and stereoselective synthesis of polysubstituted tetrahydropyrans takes advantage of the Lewis-acid-catalysed intramolecular Sakurai cyclisation.[27] One problem, however, was the formation of a significant amount of desilylated product. A variety of Lewis acids were screened in an attempt to avoid this side reaction. Among all the catalysts, $Bi(OTf)_3$ gave the most satisfactory results and proved to be very efficient for this condensation, giving excellent yields and none of the desilylated by-products (Scheme 11).



Scheme 11

3.4.2. Allylation of Aldehydes

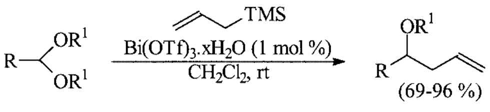
The allylation of aldehydes leading to the corresponding homoallyl alcohols has attracted much attention in organic synthesis. Several different metal-based Lewis acid catalysts are available for this reaction. Recently, lanthanide triflates in combination with rate-accelerating agents[28] such as benzoic acid and sodium dodecylsulfate (SDS)[29] as catalysts for this reaction have received considerable attention. The search for a cheaper and more efficient catalyst for this reaction led to the development of a catalytic system of $Bi(OTf)_3$ and benzoic acid (1 equivalent). This system proved to be economical, high yielding and a time-saving catalyst for the allylation of aldehydes.[26a] Indeed, the reactions were complete in 5−30 minutes with very good yields (Scheme 12). An added advantage is that the catalyst system can be recovered and reused.



Scheme 12

3.4.3. Allylation of Acetals

The allylation of acetals using organometallic reagents has attracted much attention as a useful synthesis of homoallyl ethers. Several catalysts, including some lanthanide triflates, have been used to promote this reaction. The allylation of dimethyl acetals was not successful even with 20 mol % $Yb(OTf)_3$, while it did occur in good yields with 10 mol % of $Sc(OTf)_3$. $Bi(OTf)_3$ was found to be superior in activity to the other triflates since only 1 mol % of $Bi(OTf)_3$ was needed.[30] The fact that $Bi(OTf)_3$ is much cheaper than $Sc(OTf)_3$ and less moisture-sensitive makes this procedure even more attractive (Scheme 13).

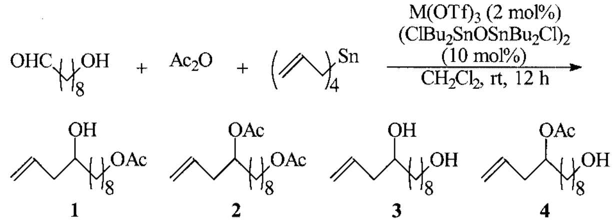


Scheme 13

3.4.4. Shotgun Process

The "shotgun process" is a new concept for one-pot reactions. It allows simultaneous multiple chemical transformations (here allylation and acylation) at different sites of a single substrate, with no protection/deprotection procedure being necessary. Several Lewis acids, including $Bi(OTf)_3$, have been used to illustrate the effectiveness of this protocol by a convenient synthesis of 9,11-dodecadien-1-yl acetate, a female sex pheromone of the red-bollworm moth.[31] The key step is the one-pot conversion of both an aldehyde and primary alcohol functionality into a homoallyl alcohol and a primary acetate, respectively (Table 3). It was found that

Table 3. Bismuth(III) triflate catalysis of the "shotgun process"[a]



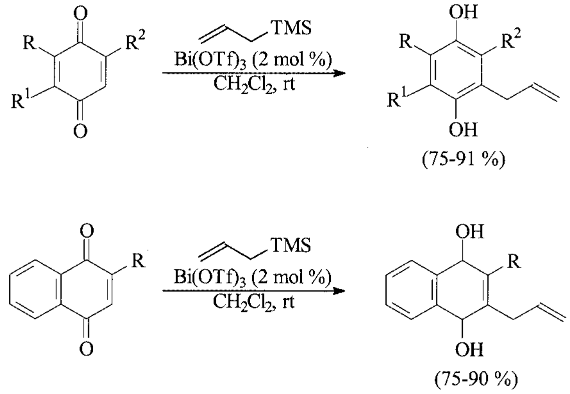
Entry[b]	$M(OTf)_3$	Products (%) 1	2	3	4
1	$Sc(OTf)_3$	88	8	1	0
2	$Bi(OTf)_3$	87	5	2	trace

[a] Reactions carried out with six equivalents of Ac_2O and 0.3 equivalents of tetraallyltin. [b] Isolated yields.

the combination of a Lewis acid (2 mol %) and 1,3-dichlorotetrabutyldistannoxane (10 mol %) as catalyst led to an almost perfect shotgun process (see also Section 8 of this article).

3.4.5. Allylation of Quinones

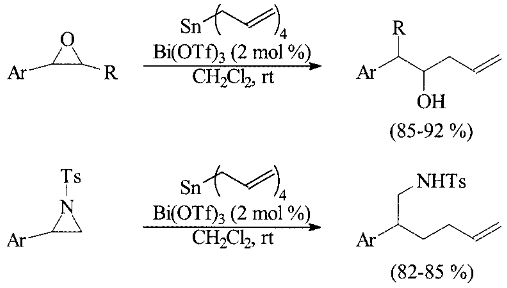
The allylation of quinones is an important reaction for the preparation of a variety of biologically active isoprenoid quinones and functionalised quinols which are useful as synthetic precursors to naturally occurring quinones and alkaloids. This allylation is generally carried out with allylsilanes in the presence of acid catalysts. Although a variety of catalysts have been reported for this allylation, they must be used in stoichiometric amounts and the reaction times are long. Quite recently, an efficient protocol for the allylation of quinones with allyltrimethylsilane using $Bi(OTf)_3$ (2 mol %) as the catalyst was reported (Scheme 14).[32] $Bi(OTf)_3$ was compared to others metal triflates such as $Yb(OTf)_3$, $In(OTf)_3$ and $Ce(OTf)_3$ and was found to be the most effective in terms of conversion and reaction rates. Similar yields and selectivity were also obtained when scandium triflate (5 mol %) was used under the same conditions.



Scheme 14

3.4.6. Allylation of Epoxides and Aziridines

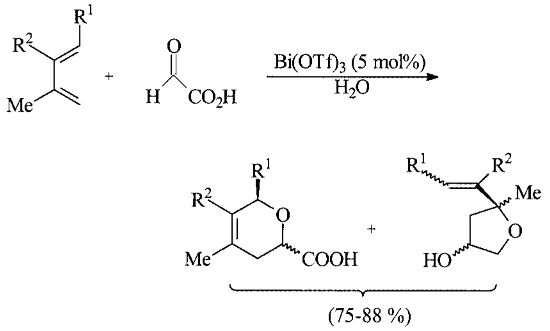
Epoxides and aziridines are well-known carbon electrophiles that react with a wide variety of nucleophiles and undergo regioselective ring-opening reactions. However, only a few methods are known for the efficient allylation of epoxides and aziridines with allylmetal reagents. Therefore, $Bi(OTf)_3$ was tested as a catalyst for the allylation of various aryl-substituted epoxides (Scheme 15).[33] In all cases, the reaction proceeded rapidly at room temperature with high selectivity. Arylaziridines also underwent cleavage in a regioselective manner. $Bi(OTf)_3$ was found to be a more effective catalyst than other metal triflates such as $Yb(OTf)_3$, $In(OTf)_3$ and $Ce(OTf)_3$.



Scheme 15

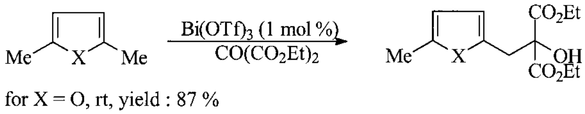
3.5. Ene Reactions

$Bi(OTf)_3$ was shown to significantly increase the dienophilic activity of carbonylated derivatives. Thus, its catalytic activity was evaluated in the carbonyl-Diels Alder reaction in water using glyoxylic acid as a dienophile with various dienes.[34] With some dienes, an α-hydroxy-γ-lactone was formed as a by-product which became the major product in some cases and even occasionally the sole product (Scheme 16). The formation of the lactone was explained by the rearrangement of the ene reaction product. There is a competition between the Diels Alder and ene reaction. Polar solvents could promote the ene selectivity, so it should be possible to carry out the *selective* synthesis of an α-hydroxy-γ-lactone by way of an ene reaction.



Scheme 16

An unusual high pressure reaction of 2,5-dimethylfuran with carbonyl compounds affording the “ene-type” products has been reported. Recently, the activity of $Bi(OTf)_3$ as catalyst for this reaction was compared to $SnCl_4$ and $ZnCl_2$ and it was found to be more active (Scheme 17).[35] The same authors have also studied the reaction between thiophene and pyrrole with diethyl mesoxalate.[35]



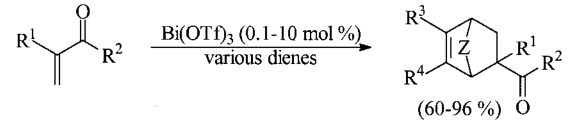
for X = O, rt, yield : 87 %
for X = S, 80 °C, yield : 56 %

Scheme 17

4. Cyclisation Reactions

4.1. Diels−Alder Reactions

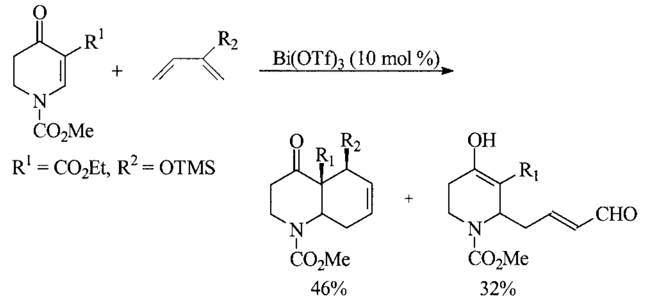
Among the various methods for the activation of dienes in a Diels−Alder reaction, Lewis acid catalysis is certainly the most important. Our group has reported the first example of a Diels−Alder reaction catalysed by Bi(OTf)$_3$,[36a] which showed high catalytic activity and regioselectivity in comparison with other Sc-, Ti-, Sm-, or Yb-based Lewis acids, which are well-known for their efficient catalytic activity (Scheme 18). Bi(OTf)$_3$ proved to be slightly more *endo* selective than Sc(OTf)$_3$. Further, no polymerisation of dienes or dienophiles was observed. Bi(OTf)$_3$ was also found to be superior to SnCl$_4$ and Cu(BF$_4$)$_2$.[36b]



R^1, R^2, R^3, R^4 = H, Me, Et; Z = CH_2 or nothing
for R^1, R^3, R^4 = H, R^2 = Me and Z = CH_2 : *endo/exo* = 93/7

Scheme 18

More recently, Bi(OTf)$_3$ was tested as a catalyst along with other Lewis acids [BiCl$_3$, Yb(OTf)$_3$, Sc(OTf)$_3$, Cu(OTf)$_2$] for the intermolecular Diels−Alder cyclocondensation between *N*-methoxycarbonyl-2,3-dihydropyridin-4-one and trimethylsilyloxybutadienes in order to synthesise a highly functionalised *cis*-fused azadecalone.[37] With unactivated dienes the reaction doesn't work. However, trimethylsilyloxybutadienes led, in most cases, to the corresponding cycloadducts with the monocyclic enal (Scheme 19). The best chemical yield of the cycloadduct was obtained with Yb(OTf)$_3$.



Scheme 19

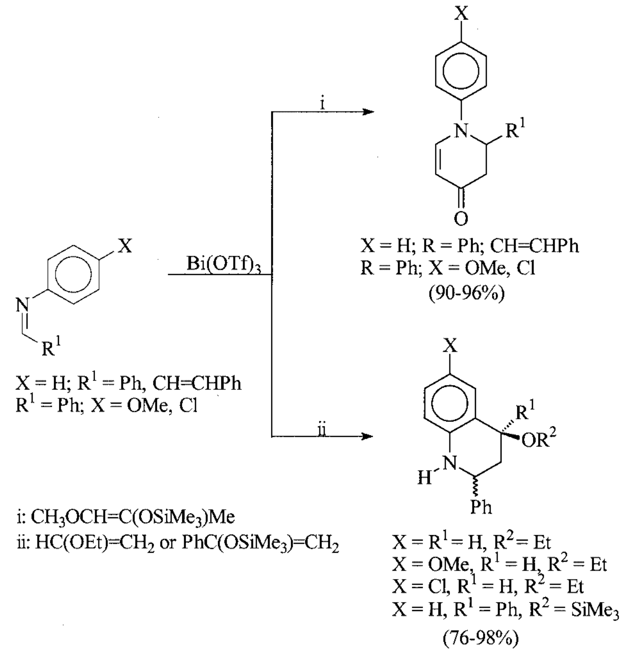
4.2. Hetero-Diels−Alder Reactions

4.2.1. Carbonyl-Diels−Alder Reactions

Bi(OTf)$_3$ has been found to catalyse carbonyl-Diels−Alder reactions in water with glyoxylic acid as the dienophile. In contrast to other Lewis acids [such as Sn(OTf)$_2$, Yb(OTf)$_3$, Nd(OTf)$_3$, Ce(OTf)$_3$ and Sc(OTf)$_3$], the strong catalytic power of Bi(OTf)$_3$ made it necessary to reduce the amount used as well as the reaction temperature. Bi(OTf)$_3$ enhanced the reaction rate but with some dienes the reaction led to a competitive formation of the ene reaction product (Scheme 16).[34]

4.2.2. Aza-Diels−Alder Reactions

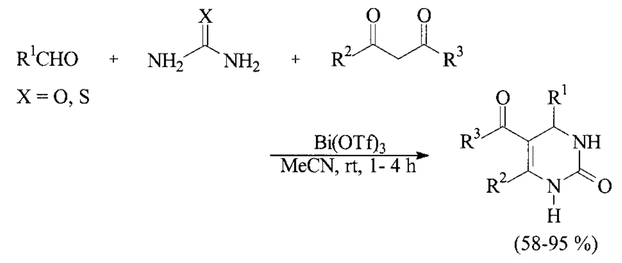
Although several Lewis acids are known to catalyse the hetero-Diels−Alder reaction involving imino-dienes or imino-dienophiles (aza-Diels−Alder reaction), a large amount of the catalyst is often necessary. Bi(OTf)$_3$ showed a higher activity than lanthanide triflates in catalysing the reactions of imines with Danishefsky's diene (Scheme 20).[38] Only 2 mol % of Bi(OTf)$_3$ led to the formation of the aza-Diels−Alder adducts in very high yield, in contrast to zinc chloride, which is required in stoichiometric amounts. In addition, the ZnCl$_2$ reaction takes significantly longer [36 h instead of 0.5−1 h with Bi(OTf)$_3$]. An added advantage of using Bi(OTf)$_3$ is that it allows for the possibility of one-pot procedures. The imine can be generated in situ from the corresponding aldehyde and amine followed by an imino Diels−Alder reaction. Tetrahydroquinolines have been synthesised by both methods.



Scheme 20

4.2.3. Biginelli Reactions

Bi(OTf)$_3$ was used (2 mol %) as an efficient Lewis acid catalyst for the Biginelli three-component, one-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.[39] Several aromatic and aliphatic aldehydes were examined. The reaction proceeded smoothly and rapidly to give the corresponding dihydropyrimidinones in good yield (Scheme 21).



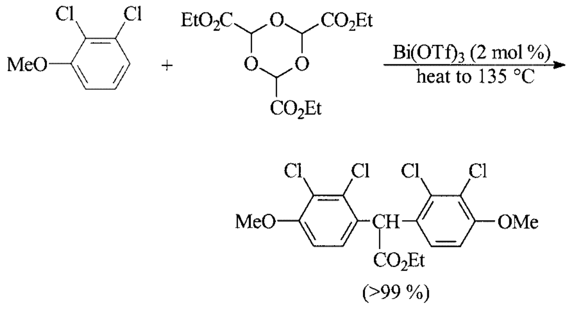
Scheme 21

5. Friedel−Crafts Reactions

Friedel−Crafts (FC) alkylation, acylation and sulfonylation reactions are important carbon-carbon bond-forming reactions in organic chemistry.[40] Since the seminal works of Charles Friedel and James Mason Crafts published in 1877, in which they report the use of $AlCl_3$ for alkylation reactions,[41] the search for more active catalysts, especially for acylation reactions, has continued. Due to increased environmental concerns, the search for "green" catalysts for the FC reaction has assumed new importance. While TfOH itself has been shown to be an active catalyst for the FC reaction,[42] Group XIII metal,[43] hafnium,[43e,43f,43h,44] tin(II),[43e] copper(II),[45] antimony(III),[43i] chlorotitanium,[46] rare-earth[47] and bismuth(III) triflates[48] have also been reported as active catalysts for FC reactions.

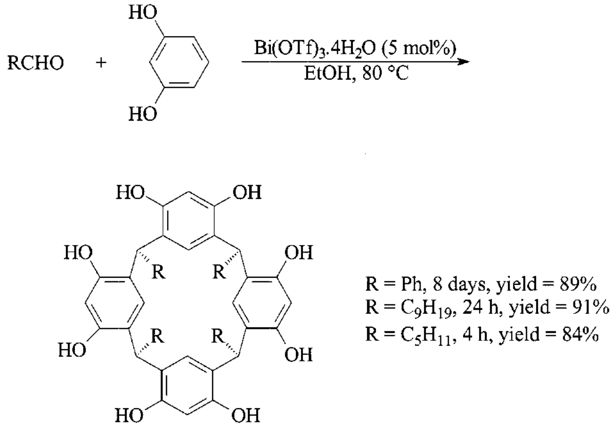
5.1. Alkylation Reactions

With industrial applications in mind (preparation of Aripiprazole), $Bi(OTf)_3$ has been used to catalyse a bis-arylation reaction between 2,3-dichloroanisole and trioxane derivatives (Scheme 22).[49] The catalytic activity of $Bi(OTf)_3$ has been reported to be similar to that of other metal triflates [$Hg(OTf)_2$, $Sc(OTf)_3$ and $Cu(OTf)_2$].



Scheme 22

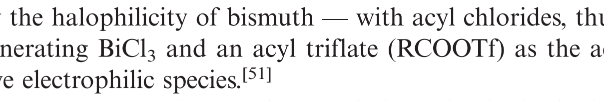
Very recently, the use of $Bi(OTf)_3$ as an efficient catalyst for the synthesis of resorcinarenes has been reported (Scheme 23).[50] The authors found that $Bi(OTf)_3$ is more efficient than $Yb(OTf)_3$.



Scheme 23

5.2. Acylation Reactions

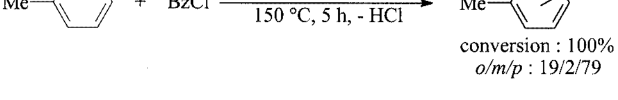
The use of $Bi(OTf)_3$ as a catalyst for FC acylation of anisole and aromatic compounds less electron-rich than anisole has been reported by our group (Scheme 24).[8] These results clearly showed that $Bi(OTf)_3$ is often more efficient than rare-earth triflates and much more active for the acylation of anisole than $BiCl_3$ when using acyl chlorides or acyl anhydrides. In addition, $Bi(OTf)_3$ has been found to be a moderately active catalyst for the intramolecular FC cyclisation of arylbutyric acids leading to 1-tetralone.[48c]



Scheme 24

From our mechanistic investigations it emerged that $Bi(OTf)_3$ behaves both as a Lewis acid with acid anhydrides and as a salt prone to undergo ligand exchange — driven by the halophilicity of bismuth — with acyl chlorides, thus generating $BiCl_3$ and an acyl triflate (RCOOTf) as the active electrophilic species.[51]

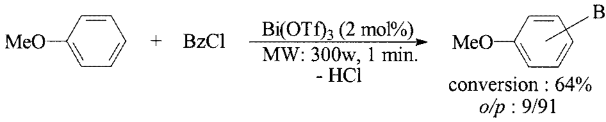
Very recently, $Bi(OTf)_3$ in association with ionic liquids (IL) has been reported to be a highly efficient catalyst for benzoylation reactions. The benzoylation of anisole and toluene can be carried out using only 1 mol % of the $Bi(OTf)_3$/IL catalytic system (Scheme 25).[52] Among all the ionic liquids screened, the best results were obtained with $Bi(OTf)_3$ dissolved in [emim][NTf_2] (with emim = 1-ethyl-3-methylimidazolium). This catalyst is currently the most powerful of all known bismuth-based catalysts.



Scheme 25

The $Bi(OTf)_3$-catalysed benzoylation of anisole under microwave (MW) irradiation led without temperature control to shorter reaction times due to the specific interaction of

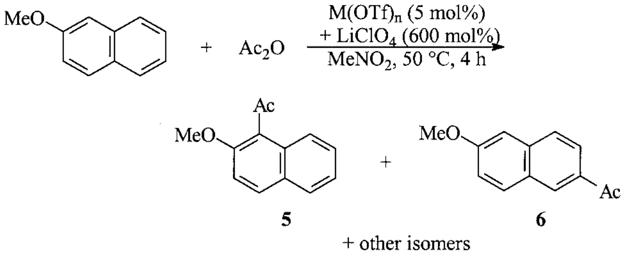
MW with the produced aryl ketone and especially with the catalyst−ketone complex (Scheme 26).[53]



Scheme 26

$Bi(OTf)_3$ in $MeNO_2/LiClO_4$ media has been reported to be a moderately active catalyst (when compared to other metal triflate catalysts) for the tandem acetylation of 2-methoxynaphthalene followed by the isomerisation of the resulting 1-acetyl-2-methoxynaphthalene to 6-acetyl-2-methoxynaphthalene, the latter being a well-known intermediate in the synthesis of the anti-inflammatory naproxen (Table 4).[43h,43i]

Table 4. Tandem acylation and isomerisation reactions

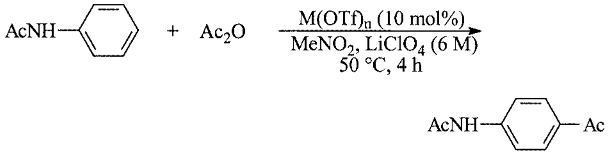


Entry	M(OTf)$_n$	Yield[a] of **5** (%)	Yield[a] of **6** (%)
1	$Bi(OTf)_3$	nd[b]	69
2	$Sb(OTf)_3$	nd	93
3	$Hf(OTf)_4$	nd	67
4	$Sc(OTf)_3$	14	62
5	$Ga(OTf)_3$	nd	92

[a] Yields determined by GC. [b] nd: not detected.

$Bi(OTf)_3$ in $MeNO_2/LiClO_4$ media has also been reported to be a moderately active catalyst (when compared to other metal triflate catalysts) for the acetylation of acetamides (Table 5).[43f,43g]

Table 5. Tandem acetylation of acetamide

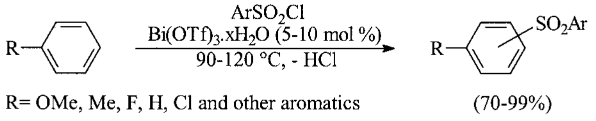


Entry	M(OTf)$_n$	Yield[a] of 4-acetylphenylacetamide
1	$Bi(OTf)_3$	59
2	$Sb(OTf)_3$	59
3	$Hf(OTf)_4$	44
4	$Sc(OTf)_3$	48
5	$Ga(OTf)_3$	93

[a] Isolated yields.

5.3. Sulfonylation Reactions

Our group has also reported the use of $Bi(OTf)_3$ for the catalysis of FC arylsulfonylation reactions of various aromatics (Scheme 27).[54] Our results clearly demonstrated that $Bi(OTf)_3$ is more active than $BiCl_3$ under conventional heating (oil bath) or under microwave irradiation and that it is also more active than other metal triflates. In contrast to the acylation reaction, where the activity of $Bi(OTf)_3$ proved to be identical (under the same molar ratio of triflate or its triflic acid equivalent) to that of AgOTf or TfOH for acyl chlorides,[51] the activity of $Bi(OTf)_3$ in sulfonylations is surprisingly far superior to that of AgOTf or TfOH.



Scheme 27

From a mechanistic point of view we have proposed that, in a first step, a ligand exchange might occur with acyl chlorides thus generating $BiCl_3$ and a sulfonyl triflate (RSO_2OTf) as the active electrophilic species.[48a,54a] In a second step, this species could react with the aromatic to generate the arylsulfone and TfOH. The key point here is that, unlike in the acylation reaction, TfOH is not an efficient catalyst for the arylsulfonylation reaction, as shown by ourselves and Effenberger et al.[42c,42d] Thus, regeneration of the sulfonyl triflate occurs partially by reaction of TfOH with $ArSO_2Cl$ (proton-mediated pathway) and we have shown that the main pathway for the regeneration of the sulfonyl triflate is the reaction of TfOH with $BiCl_3$ (bismuth-mediated pathway) leading to mixed chloro-triflate bismuth species, since the mixing of $BiCl_3$ and TfOH leads to an active system for the arylsulfonylation.[54b−54d] In addition, $Bi(OTf)_3$ has been used under microwave heating in the synthesis of diarylsulfones.[55]

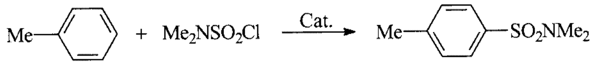
5.4. Sulfamoylation Reactions

The preparation of aromatic sulfonamides by the FC reaction between an alkanoyl sulfonyl chloride and an electron-rich aromatic has recently been reported (Table 6).[56] For this reaction the catalytic activity of indium(III) triflate has been reported to be much higher than that of $Bi(OTf)_3$ or other metal triflates.

5.5. Chlorosulfinylation Reactions

The catalytic activation of thionyl chloride by $Bi(OTf)_3$ has recently been reported and applied to the preparation of aryl sulfinyl chlorides (Table 7).[57] It has been shown that this procedure is restricted to electron-rich aromatics (such as aromatic ethers and mesitylene). The mechanistic investigation indicates that no ligand exchange occurs during the reaction.

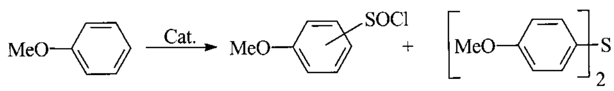
Table 6. Catalysis of the sulfamoylation of toluene



Entry	Cat.: M(OTf)$_3$ (20 mol %)	Yield of N,N-dimethyl-p-toluenesulfonamide[a] (%)
1	Bi(OTf)$_3$	19
2	In(OTf)$_3$	86
3	Sc(OTf)$_3$	19
4	Yb(OTf)$_3$	0
5	La(OTf)$_3$	0

[a] Isolated yields after 24 h heating at 100 °C.

Table 7. Catalysis of the chlorosulfinylation of aromatics



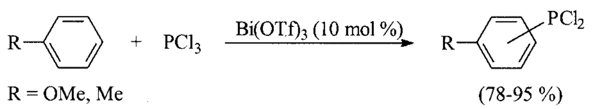
7 **8**

Entry	Cat.: M(OTf)$_3$ (2 mol %)	Yield of **7**[a] (%)	Yield of **8**[a] (%)
1	Bi(OTf)$_3$	99	traces
2	Sc(OTf)$_3$	14	40
3	Ce(OTf)$_4$ [b]	28	38
4	Yb(OTf)$_3$	traces	nd[c]
5	Sb(OTf)$_3$	75	4

[a] Yield determined by ^{1}H NMR spectroscopy. [b] Used as its hexahydrate. [c] Not detected.

5.6. Phosphonylation Reactions

The preparation of aryldichlorophosphanes through electrophilic addition of PCl$_3$ to electron-rich aromatics has been reported to be catalysed by Bi(OTf)$_3$ (Scheme 28).[58] The formation of diarylchlorophosphanes can be avoided by using a large excess of PCl$_3$.

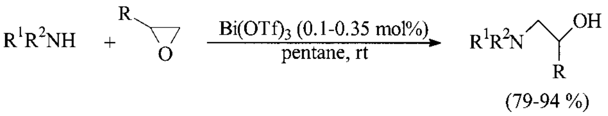


Scheme 28

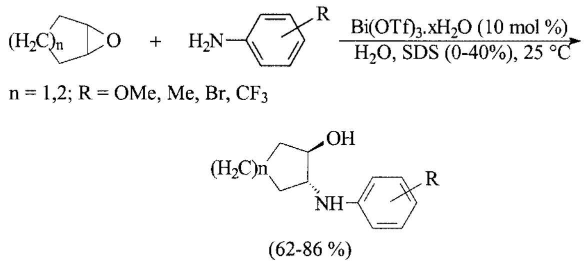
6. Reactions of Epoxides

6.1. Aminolysis of Epoxides

Aminolysis reactions of epoxides have been reported to be catalysed efficiently by Bi(OTf)$_3$.[59a] In all cases the reaction proved to be regioselective, leading exclusively to α-amino alcohols by nucleophilic attack at the less-hindered carbon (Scheme 29).[59a] Interestingly, Bi(OTf)$_3$ also proved to be efficient in the ring opening of *meso*-epoxides by anilines in water since Bi(OTf)$_3$ has been reported to be more efficient than TfOH (Scheme 30).[59b]

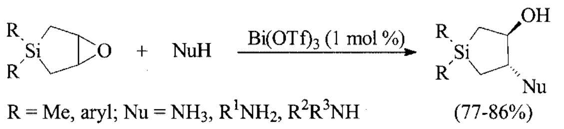


Scheme 29



Scheme 30

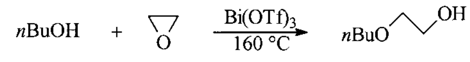
In the case of the aminolysis of epoxides derived from silacyclopentene, Bi(OTf)$_3$ proved to be an efficient catalyst since 1 mol % of Bi(OTf)$_3$ was sufficient to catalyse the reaction (Scheme 31).[59c]



Scheme 31

6.2. Alcoholysis of Epoxides

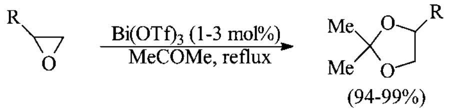
The Bi(OTf)$_3$-catalysed ring opening of ethylene oxide by n-butanol leading to n-butyl glycol has been patented recently (Scheme 32).[60]



Scheme 32

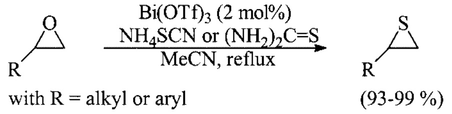
6.3. Conversion of Epoxides to 1,3-Dioxolanes

Epoxides have been successfully converted into 1,3-dioxolanes under Bi(OTf)$_3$ catalysis (Scheme 33).[61] As expected, Bi(OTf)$_3$ proved to be much more efficient for the catalysis of this transformation, especially when compared to other bismuth(III) salts such as BiCl$_3$ and Bi(OCOCF$_3$)$_3$. Surprisingly, no mention is made of the possible aldol condensation of acetone (used as solvent) catalysed by Bi(OTf)$_3$ especially under reflux conditions (such a side-reaction has frequently been observed in our group, even at room temperature).



Scheme 33

Epoxides have been reported to be efficiently converted into thiiranes with ammonium thiocyanate or thiourea, which is a less reactive source of sulfur, in the presence of catalytic amounts of $Bi(OTf)_3$ (Scheme 34).[62]

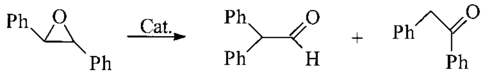


Scheme 34

6.4. Epoxide Rearrangements

$Bi(OTf)_3$ has recently been reported to be an efficient catalyst for the smooth rearrangement of various aryl-substituted epoxides, leading to carbonyl compounds in high yields after cleavage of the benzylic C−O bond followed by group migration (the decreasing ability of migration observed being: phenyl > hydrogen > alkyl).[63] $Bi(OTf)_3$ appears to be a powerful and regioselective catalyst for such transformations compared to other catalysts such as $BiOClO_4$. It is also more efficient than other commonly used Lewis acids such as $MgBr_2$ or BF_3 etherate which are required in excess amounts (Table 8).[64]

Table 8. Rearrangement of *trans*-stilbene oxide

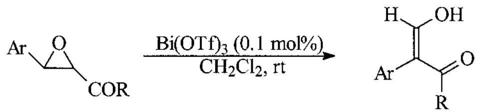


9 **10**

Entry	Cat. (mol %)	Yield of **9** (%)	Yield of **10** (%)
1	$Bi(OTf)_3 \cdot 4H_2O$ (0.1)	92	nd[a]
2	$BiOClO_4 \cdot xH_2O$ (20)	90[b]	nd
3	$[RhCl(PPh_3)_3]$ (2)	nd	88[c]

[a] nd: not detected. [b] See ref.[64a] [c] See ref.[64c]

Moreover, the catalytic efficiency of $Bi(OTf)_3$ can be better demonstrated in the case of the rearrangement of acyl epoxides since these latter lead to β-keto aldehydes (which exist in the enol form) which are prone to inhibit a Lewis-acid-type catalyst due to their intrinsic multi Lewis base character (Scheme 35).[63]



R = Me, C_6H_5, p-ClC_6H_4; yield = 89-92%

Scheme 35

7. Rearrangements

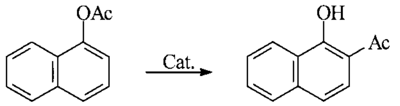
7.1. Rearrangement of Epoxides

See Section 6.

7.2. Fries Rearrangement

Another type of multi Lewis base character containing products can result from the Fries rearrangement, especially in the case of the ortho-Fries variety where 1-hydroxy-2-acyl aromatics are produced.[65] For this reaction $Bi(OTf)_3$ proved to be an efficient catalyst for the rearrangement of naphthyl acetate since its activity is only slightly lower than that of scandium triflate previously reported (Table 9). Moreover, we have discovered that $Bi(OTf)_3$ interacts with methanesulfonic acid (MSA) to form an efficient catalytic system via what we called a synergistic effect.

Table 9. Catalysis of the Fries rearrangement

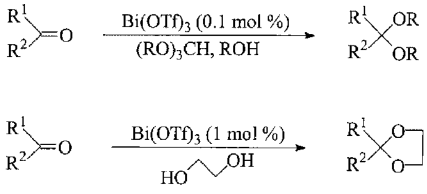


Entry	$M(OTf)_3$ (5 mol %)	Cat.: $M(OTf)_3$ Yield[b][c] (%)	Cat.: $M(OTf)_3$ + MSA[a] Yield[b] [c] (%)
1	$Bi(OTf)_3$	80 (40)	88 (70)
2	$Sc(OTf)_3$	93 (67)	74 (82)
3	$Y(OTf)_3$	0	90 (52)

[a] In our experiments MSA was used in 10 mol %. [b] Yield of 2-acetyl-1-hydroxynaphthalene after 5 hours heating. [c] Yield in parentheses is of 2-acetyl-1-hydroxynaphthalene after 1 hour heating.

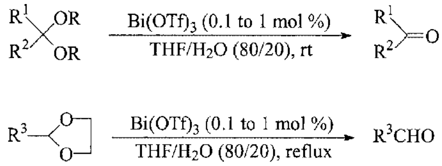
7.3. Beckmann and Schmidt Rearrangements

Mixtures of polyphosphoric acid (PPA) or K-10 clay (solid acid) and $Bi(OTf)_3$ have been reported to be efficient systems for the Beckmann and Schmidt rearrangements (Scheme 36 and 37).[66] Our recent findings with meth-



R^1 or R^2 = alkyl and/or aryl, R = Me, Et

Scheme 36



R^1, R^2 or R^3 = alkyl and/or aryl, R = Me, Et

Scheme 37

anesulfonic acid suggest that the system PPA/Bi(OTf)$_3$ might also be rationalised as a synergistic effect between both partners. Weight is given to this hypothesis since PPA on its own is reported to be less efficient than the PPA/Bi(OTf)$_3$ system for the Beckmann rearrangement.

8. Protection and Deprotection

Protective groups are very frequently used to protect a number of functional groups from side reactions during multi-step syntheses. A number of methodologies have been developed for the protection and deprotection of chemical functionalities.[67] Some of these transformations have been explored using Bi(OTf)$_3$ catalysis.

8.1. Protection and Deprotection of the Hydroxyl Group

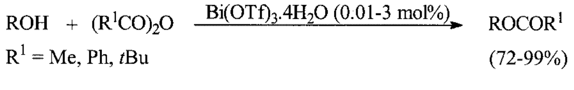
8.1.1. Acylation of Alcohols and Phenols

The catalytic acylation of alcohols and phenols has been the subject of a large number of studies using trimethylsilyl,[68] lithium,[69] scandium,[70] indium[71] and bismuth triflates[72] among many other catalysts. From all these results it can be seen that Bi(OTf)$_3$ is superior to other triflate-based catalysts for its efficiency [in some case only 0.005 mol % of Bi(OTf)$_3$·4H$_2$O is needed]. It has also been shown that Bi(OTf)$_3$ is one of the most efficient catalysts for the acylation and benzoylation of a wide set of alcohols and phenols (Scheme 38). Very interestingly, Bi(OTf)$_3$ can be used with the well-known acid-labile furfuryl alcohol. In some cases, Bi(OTf)$_3$ proved to be more efficient than Sc(OTf)$_3$ or TMSOTf. For example, pivaloylation under Bi(OTf)$_3$ catalysis was applied to a sugar having an acetal as a protecting group; the acetal does not survive when TMSOTf is used. Moreover, neither racemisation nor epimerisation of the substrate were detected during the acylation process.

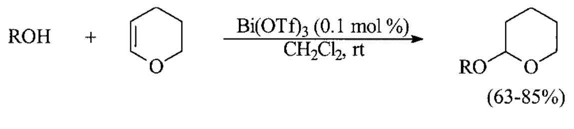
Based on these findings the activity of Bi(OTf)$_3$ has been extended to a large-scale acylation of alcohols and diols.[72c] Finally, mention has to be made of the interesting reaction called by the authors the "shotgun process".[31]

8.1.2. Formation and Cleavage of Tetrahydropyranyl (THP) Ethers

THP ethers are very often used as a protecting group for hydroxyl group. Such reactions with alcohols and phenols have been successfully catalysed by Bi(OTf)$_3$·4H$_2$O (Scheme 39).[73]

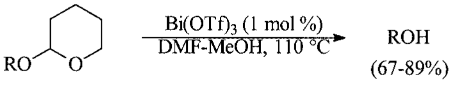


Scheme 38



Scheme 39

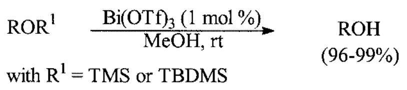
Moreover, Bi(OTf)$_3$·4H$_2$O was also effective in catalysing the cleavage of THP ethers to the corresponding alcohol (Scheme 40).[73] However, the experimental conditions seem to be more drastic than the ones reported with Sc(OTf)$_3$, which catalyses this transformation at room temperature.[74]



Scheme 40

8.1.3. Cleavage of Silyl Ethers

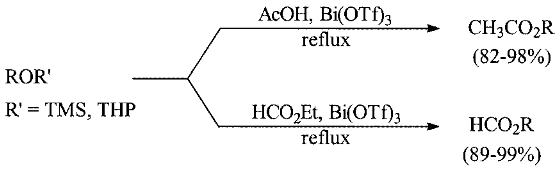
Bi(OTf)$_3$ has been reported to cleave a variety of silyl ethers derived from alcohols and phenols in good yields (Scheme 41). Unlike BiCl$_3$ or Bi(OCOCF$_3$)$_3$, Bi(OTf)$_3$ also cleaves TBDMS ethers.[75] It was shown by competition experiments that TMS ethers can be deprotected selectively in the presence of TBDMS ethers.



Scheme 41

8.1.4. Conversion of Trimethylsilyl and THP Ethers

The conversion of trimethylsilyl and THP ethers to acetate and formate esters has been reported to be efficiently catalysed by Bi(OTf)$_3$ (Scheme 42).[76] While the conversion of TMS requires only 3 mol % of Bi(OTf)$_3$, that of THP ethers requires 50 mol % of the triflate. Moreover, the chemoselective conversion of alcoholic TMS ethers to phenolic TMS or THP ethers has been reported.

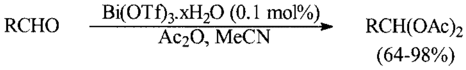


Scheme 42

8.2. Protection and Deprotection of a Carbonyl Group

8.2.1. Formation of Acylals

Recently, Bi(OTf)$_3$ has been reported as a highly powerful catalyst[77a] for the chemoselective synthesis of acylals from a variety of aromatic aldehydes. Its activity appears to be higher than that of copper(II)[77b] and scandium triflate (Scheme 43).[77c] Moreover, it has been shown that under solvent-free conditions (atom-economic conditions) higher yields could be obtained in shorter reaction times. While by-products were obtained in some cases, the sluggish formation of acylals from aliphatic aldehydes also occurred under Bi(OTf)$_3$ catalysis revealing the potentially chemoselective behaviour of $Bi(OTf)_3$. Aldehydes can also be chemoselectively protected in the presence of ketones under these conditions.

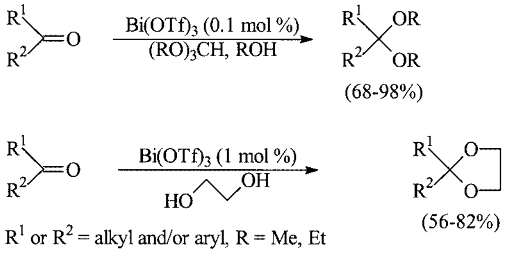


$$\text{RCHO} \xrightarrow[\text{Ac}_2\text{O, MeCN}]{\text{Bi(OTf)}_3.x\text{H}_2\text{O (0.1 mol\%)}} \text{RCH(OAc)}_2 \ (64\text{-}98\%)$$

Scheme 43

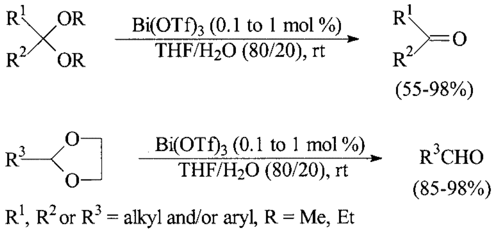
8.2.2. Formation and Cleavage of Acetals

Aldehydes and ketones are commonly protected as acetals in the course of total synthesis. $Bi(OTf)_3·4H_2O$ proved to be an efficient catalyst for the formation of acetals, ketals and 1,3-dioxolanes derived from a variety of aliphatic and aromatic aldehydes and ketones (Scheme 44).[78] It is noteworthy that $Bi(OTf)_3·4H_2O$ is also able to protect diaryl ketones, which are often resistant to other standard acetalisation conditions.



Scheme 44

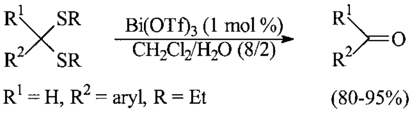
In addition, $Bi(OTf)_3$, $4H_2O$ also proved to be an efficient catalyst for the cleavage of a variety of acetals and ketals derived from alkyl and aryl aldehydes and ketones using as little as 0.1 mol % of the catalyst (Scheme 45).[79] Moreover, it has been shown that a chemoselective deprotection could be realized since tetrahydropyranyl and *tert*-butyldimethylsilyl ethers were resistant to this deprotection method.



Scheme 45

8.2.3. Cleavage of Thioacetals

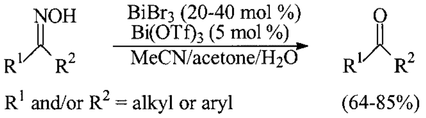
The efficient deprotection of thioacetals in the presence of catalytic amounts of $Bi(OTf)_3$ has been reported and applied to the synthesis of benzodiazepines (Scheme 46).[80]



Scheme 46

8.2.4. Cleavage of Ketoximes

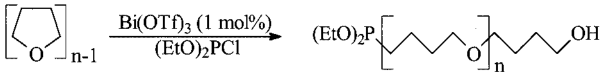
Very recently the deprotection of ketoximes has been reported with $BiBr_3/Bi(OTf)_3·4H_2O$ as the catalyst system (Scheme 47).[81]



Scheme 47

9. Polymerisation

In the field of polymer chemistry, $Bi(OTf)_3$ has been patented as a catalyst for the cationic polymerisation of THF using selected phosphorus compounds [such as $(EtO)_2PCl$] as initiators (Scheme 48).[82] Interestingly, the polymerisation of THF using rare-earth triflates led to a polymer with a higher molecular weight (M_w around 20000) than those obtained from the reaction catalysed by $Bi(OTf)_3$ (M_w = 6600).



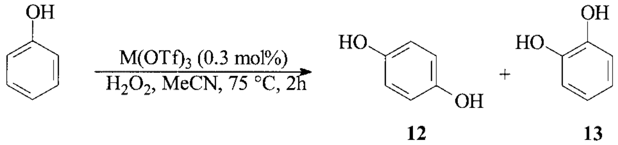
Scheme 48

10. Oxidation Reactions

10.1. Hydroxylation of Phenolic Compounds

In order to produce hydroquinone, $Bi(OTf)_3$ has been used to catalyse the reaction between hydrogen peroxide and phenol in the presence of benzophenone.[83] Its catalytic

Table 10. Metal-triflate-catalysed hydroxylation of phenol



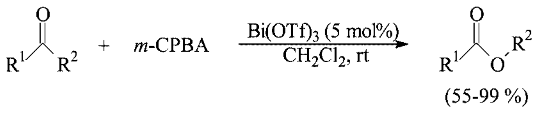
Entry	$M(OTf)_3$	Yield[a] of **12** (%)	Yield[a] of **13** (%)	Ratio **12**:**13**
1	$Bi(OTf)_3$	18.5	22	0.84
2	$Sc(OTf)_3$	33.5	35	0.96
3	$Yb(OTf)_3$	45	39.5	1.14

[a] Isolated yields.

efficiency and selectivity proved to be less than that of rare-earth triflates (Table 10).

10.2. Baeyer–Villiger Oxidation

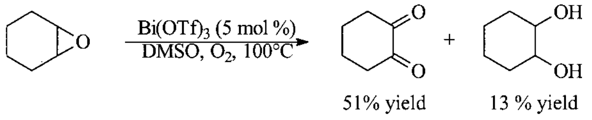
The Baeyer–Villiger oxidation of carbonyl compounds has been reported to be catalysed by Bi(OTf)$_3$ leading to esters or lactones by the activation of m-chloroperbenzoic acid (*m*-CPBA) (Scheme 49).[84]



Scheme 49

10.3. Oxidation of Epoxides

Very recently Bi(OTf)$_3$ has been reported to be an interesting catalyst for the oxidation of internal epoxides leading mainly to α-diketones using DMSO/O$_2$ (Scheme 50).[85] From a mechanistic point of view, in a first step DMSO is proposed to act as the oxidizing agent for the Lewis-acid-activated epoxide, leading to an α-ketol intermediate, while in a second step molecular oxygen is involved in a redox process. Such a redox step would involve Bi^{III}/Bi^0 or Bi^{III}/Bi^I reduction and has been proposed to explain the formation of the α-diketone through the α-ketol intermediate. Finally, the presence of water due to the hygroscopic nature of Bi(OTf)$_3$ has been proposed to rationalize the formation of 1,2-cyclohexanediol.

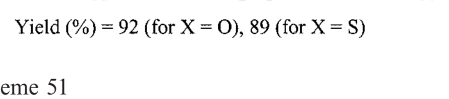


Scheme 50

11. Miscellaneous Reactions

11.1. Cleavage of Ethers

Bi(OTf)$_3$ has been reported as a catalyst for the cleavage of *tert*-butyl ethers derived from furan and thiophene compounds (Scheme 51).[86] It has to be pointed out that, in contrast to conventional Lewis acids (AlCl$_3$, TiCl$_4$), the use of Bi(OTf)$_3$ is compatible with furan derivatives (the compatibility of bismuth salts towards furan derivatives has been previously reported by our group using BiCl$_3$).[87]

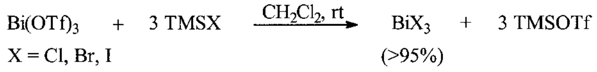


Yield (%) = 92 (for X = O), 89 (for X = S)

Scheme 51

11.2. Ligand-Exchange Reaction

Bi(OTf)$_3$ has been found to give a quantitative ligand exchange with trimethylhalosilane leading quantitatively to TMSOTf (Scheme 52).[20b]

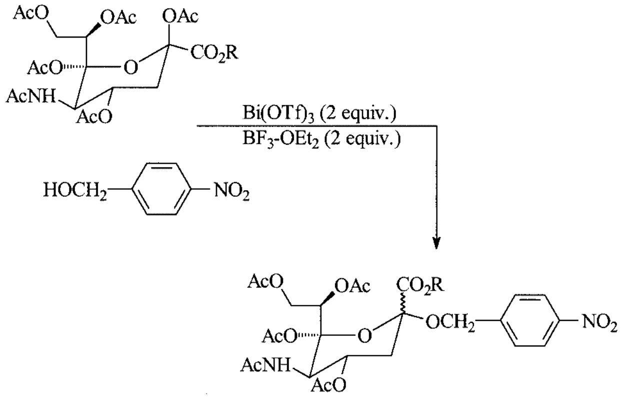


$$\underset{X = Cl, Br, I}{Bi(OTf)_3} + 3\,TMSX \xrightarrow{CH_2Cl_2,\ rt} \underset{(>95\%)}{BiX_3} + 3\,TMSOTf$$

Scheme 52

11.3. Glycosylation Reaction

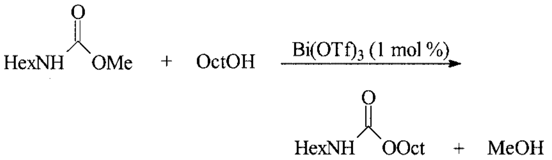
Very recently, a combination of Bi(OTf)$_3$ and boron trifluoride etherate has been reported to be an interesting promoter for the glycosylation of sialyl acetates (Scheme 53).[88]



Scheme 53

11.4. Transcarbamoylation Reactions

Bi(OTf)$_3$ has been reported to be a very efficient catalyst in the transcarbamoylation reaction of *N*-alkyl *O*-alkyl carbamates (Scheme 54).[89] Moreover, Bi(OTf)$_3$ was found to be superior to other metal triflates (such as rare-earth triflates) or tin-based catalysts. An added advantage of this method is that isocyanates were not detected during the reaction.



Scheme 54

11.5. Hydrolysis of Bi(OTf)$_3$

The hydrolysis of Bi(OTf)$_3$ has been studied by our group.[19] From our results it appears that Bi(OTf)$_3$ is prone to a reversible hydrolysis leading to cationic species such as Bi$_6$O$_n$(OH)$_{12-2n}$ (Scheme 55).[90a] This hydrolysis leads to the quantitative formation in water of triflic acid.[19] Therefore, the behaviour of $Bi(OTf)_3$ in water is completely different from that of rare-earth triflates, which are non-hydrolysable catalysts,[90b] and such a behaviour of $Bi(OTf)_3$ should be kept in mind for future work.

$$x\ Bi^{3+} + y\ H_2O \rightleftharpoons Bi_x(OH)_y^{(3x-y)+} + y\ H^+$$

Scheme 55

Conclusion and Future Directions

In summary, it appears that $Bi(OTf)_3$ can be considered as a new and efficient Lewis-acid-type catalyst for a number of reactions involving various Lewis bases as substrates. The relatively low cost and high catalytic efficiency of $Bi(OTf)_3$ makes it similar to rare-earth triflates. The catalytic efficiency of $Bi(OTf)_3$ in stereoselective synthesis still remains to be explored. The small number of publications reporting catalysis by $Bi(OTf)_3$ compared to that of rare-earth triflates indicates that the dawn of the use of $Bi(OTf)_3$ in organic synthesis has just begun. There is no doubt that $Bi(OTf)_3$ will emerge as a new, powerful and environmentally friendly Lewis acid catalyst for synthetic methodologies needed for green chemistry.

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