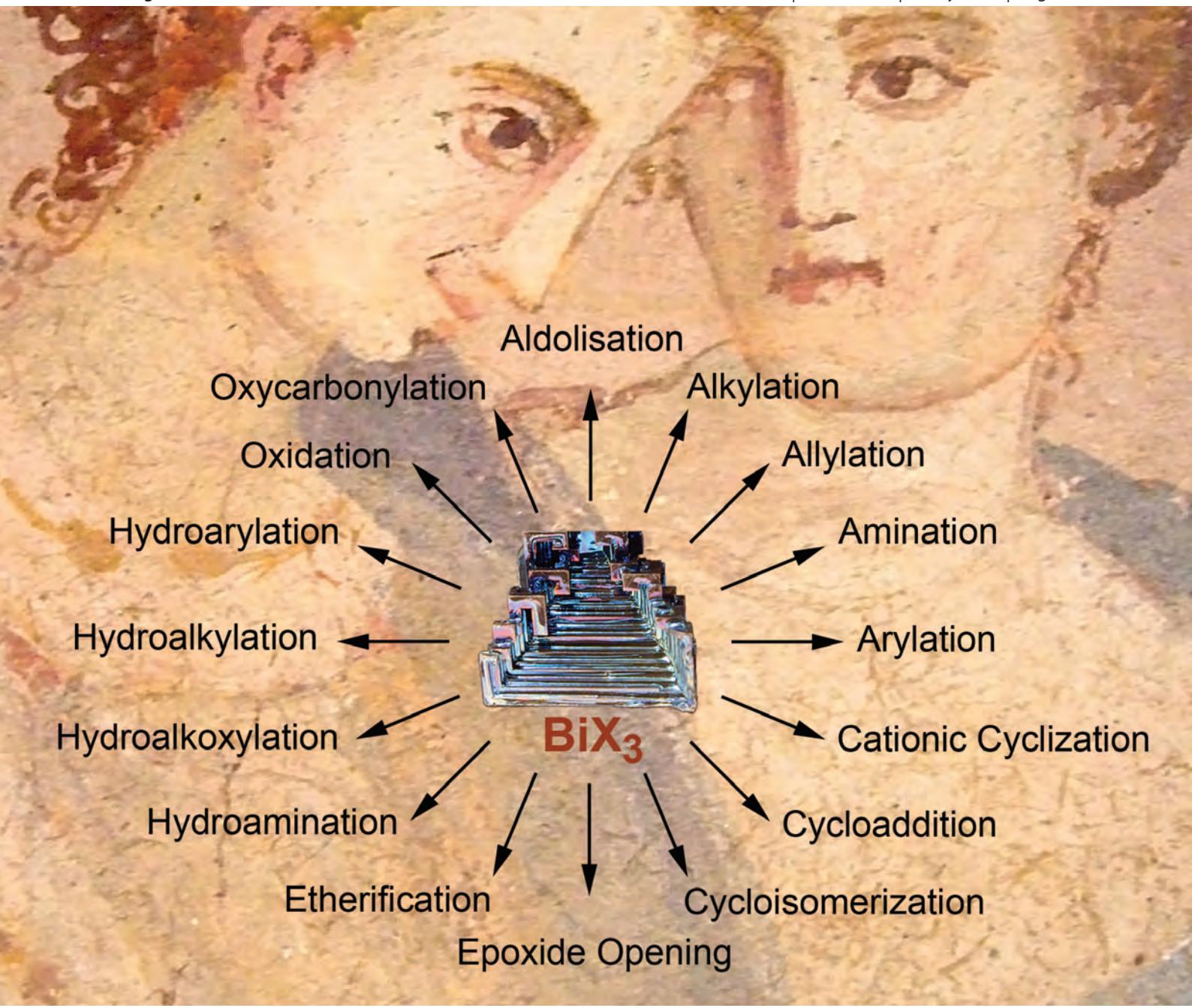


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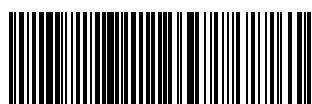
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Thierry Olevier

New trends in bismuth-catalyzed synthetic transformations



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New trends in bismuth-catalyzed synthetic transformations

Thierry Ollevier*

This review covers uses of bismuth catalysts since 2005 with a special emphasis on the emerging applications of such catalysts. Low toxicity, low catalytic loading, synergistic effects with other catalysts, and some hydrocompatibility properties confer to bismuth salts major advantages. The expanding activity in the field clearly highlights the growing potential of bismuth catalysts. The article is not a comprehensive review on bismuth catalysis but a selection of its most promising uses in challenging synthetic transformations.

1. Introduction

Bismuth is known as an environmentally benign element and has been used in a growing number of applications over the last few years. The role of bismuth(III) salts as Lewis acids has only been studied since the late 1980s. Pioneering work by Dubac, Wada and others paved the way to wide and general

methods using bismuth(III) catalysts.¹ The versatile use of bismuth salts in synthesis has clearly been highlighted by the increasing number of publications in the field. Low toxicity of bismuth salts, associated with low cost, make them attractive and practical catalysts. During the last decade, the chemical community finally began considering the previously under-used chemistry of organobismuth derivatives and bismuth catalysts. Now, many academic groups around the world are entering the area. As a result of increasing concern about green catalysts, bismuth catalysts have become a main focus.

Various books and reviews have been published in the field of bismuth catalysis.^{1,2} The present review covers uses of bismuth catalysts since 2005 with a special emphasis on the emerging applications in terms of efficiency and novelty.

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Thierry Ollevier

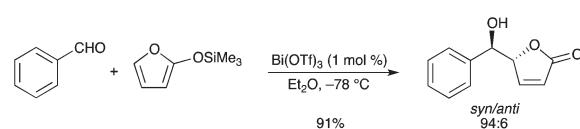
an Assistant Professor appointment (2001) at Université Laval, he became an Associate (2006) and is currently a Full Professor. Current research in his group aims at designing novel catalysts, developing catalytic reactions and applying these methods to chemical synthesis. He is active in the areas of Lewis acids, asymmetric catalysis, organic chemistry under aqueous conditions, and synthetic green chemistry.

2. Aldol reactions

Since the original work by Dubac in the bismuth-catalyzed Mukaiyama aldol reaction,^{1,2} considerable progress has been made in addressing a variety of more complex systems.

2.1. Vinylogous Mukaiyama aldol reaction

An efficient vinylogous Mukaiyama aldol reaction of 2-(trimethylsilyloxy)furan with various aromatic aldehydes mediated by Bi(OTf)₃ in a low catalyst loading (1 mol%) was developed by our group (Scheme 1).³ The reaction proceeds



Scheme 1



rapidly and affords the corresponding 5-(hydroxy(aryl)methyl)furan-2(5*H*)-ones in high yields with good to very good diastereoselectivities (dr up to >98:2). Such selectivities, albeit previously reported with other Lewis acids, could this time be achieved with a much lower catalyst loading. 5-(Hydroxy(alkyl)methyl)furan-2(5*H*)-ones derived from ketones could also be obtained with good diastereoselectivities.

2.2. Asymmetric Mukaiyama aldol reaction

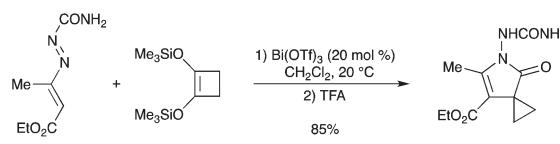
The development of organic reactions in aqueous media is essential because water is a key solvent for environmentally benign chemical synthesis. Catalytic asymmetric hydroxymethylation of silyl enolates with aqueous formaldehyde has been achieved using a chiral bismuth complex.⁴ Bismuth triflate was conjointly used with Bolm's ligand in dimethoxyethane–water solvent mixtures (Scheme 2). High enantioselectivities and high yields have been obtained. Kobayashi's work provided a new entry to "water-compatible Lewis acids".⁵

2.3. Crossed condensation of ketones and aldehydes

A cationic organobismuth perfluorooctanesulfonate (cat. A, Scheme 3) showed high catalytic activity in the one-pot synthesis of (*E*)- α,β -unsaturated ketones through highly selective crossed condensation of ketones and aldehydes in water (Scheme 3).⁶ The catalyst is air-stable and exhibits both acidic and basic characteristics.

2.4. Mukaiyama–Michael addition reaction

New spiro-cyclopropanated 1-aminopyrrol-2-ones were regioselectively prepared in high yields by Bi(OTf)₃-catalyzed one-pot Mukaiyama–Michael addition/cyclization/ring-contraction reactions of 1,2-bis(trimethylsilyloxy)cyclobutene with



Scheme 4

1,2-diaza-1,3-butadienes (Scheme 4).⁷ The reaction conditions are mild and the products were afforded with excellent yields.

3. Epoxide opening reactions

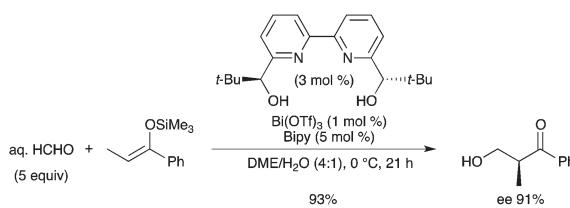
3.1. Organobismuth-catalyzed epoxide opening reaction

A related organobismuth triflate (cat. B, Scheme 3) was used as an air-stable catalyst for the epoxide opening reaction.⁸ It was found to exhibit high catalytic activity towards the ring opening reaction of epoxides in aqueous media with aromatic amines at room temperature (Scheme 5). The catalyst showed good stability, recyclability and reusability. The catalytic system afforded a simple and efficient method for the synthesis of β -amino alcohols.

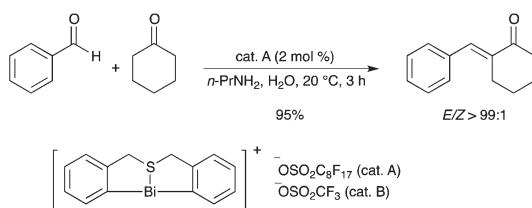
These air-stable hypervalent organobismuth(III) salts have also been used as catalysts for other reactions, such as the allylation reaction of aldehydes using tetraallyltin and the Mannich reaction in water.⁹

3.2. Asymmetric epoxide opening reaction

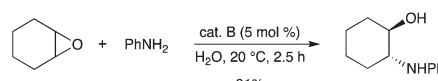
The use of Bi(OTf)₃ with Bolm's ligand has been successfully applied by Kobayashi in an asymmetric epoxide opening reaction with anilines in water.¹⁰ The reaction of aniline with *cis*-stilbene oxide occurred in pure water with sodium dodecylbenzene sulfonate (SDBS) as a surfactant and afforded the corresponding enantioenriched β -amino alcohol with a good enantioselectivity and a good yield (Scheme 6). Such applications are particularly important, as Bi(OTf)₃ itself is unstable in the presence of water,¹¹ but is stabilized by the basic ligands in such a way that hydrolysis is prevented.⁵



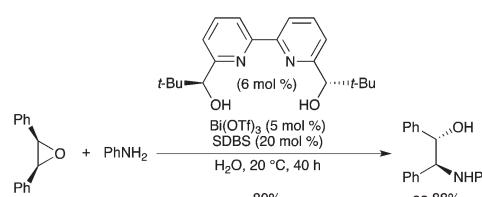
Scheme 2



Scheme 3



Scheme 5



Scheme 6



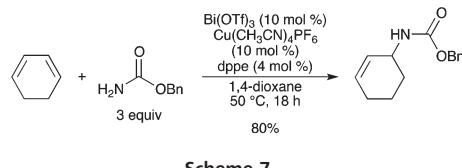
4. Hydroamination and amination reactions

4.1. Intermolecular hydroamination reactions

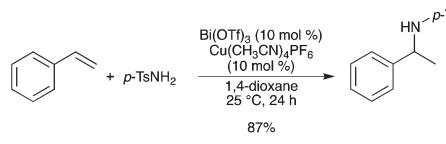
A $\text{Bi}(\text{OTf})_3\text{-Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ system efficiently promoted intermolecular 1 : 1 hydroamination of 1,3-dienes with various carbamates, sulfonamides, and carboxamides to afford allylic amines in good yields.¹² The reaction proceeded with 0.5–10 mol% catalyst loading in 1,4-dioxane (Scheme 7). This $\text{Bi}(\text{OTf})_3\text{-Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ system using a main group metal constitutes a new entry into a series of hydroamination catalysts. The hydroamination reaction gave unsatisfactory results with either $\text{Bi}(\text{OTf})_3$ or $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ alone. The combination of $\text{Bi}(\text{OTf})_3$ with MPF_6 ($\text{M} = [\text{Cu}(\text{CH}_3\text{CN})_4]$ or K) was essential to achieve high yields. The authors also suggested that PF_6^- , rather than Cu , plays an important role. Mechanistic studies suggested that the active species is cationic $\text{Bi}(\text{OTf})_2\text{PF}_6$ generated by cation exchange, which acts as a π -acid to activate 1,3-dienes to generate carbenium intermediates. The ability of Bi to interact with the carbonyl group of benzamide, chosen as the nucleophile, was confirmed by IR and NMR analysis.

The $\text{Bi}(\text{OTf})_3\text{-Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ system was further applied to hydroaminations of styrene with sulfonamides.¹³ With $p\text{-TsNH}_2$, the reaction proceeded smoothly at 25 °C and the corresponding product was obtained with a good yield (Scheme 8). However, due to limitations with the scope of the reaction, other metal triflates were also investigated. A new $\text{Hf}(\text{OTf})_4\text{-Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ system was found to be very efficient to promote the hydroamination of various vinyl arenes with electron-withdrawing groups. This method was successfully applied to sulfonamides, carbamates, and carboxamides.

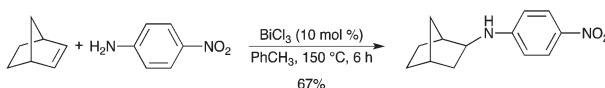
The BiCl_3 -catalyzed intermolecular hydroamination of norbornene with various aniline derivatives was studied.¹⁴ Hydroamination products were obtained as the major products



Scheme 7



Scheme 8



Scheme 9

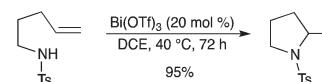
(Scheme 9). However, in some cases, hydroarylation occurred as a side reaction.

4.2. Intramolecular hydroamination reactions

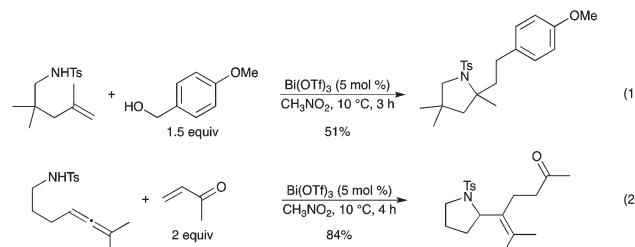
4.2.1. Hydroamination reaction of alkenyl sulfonamides. A catalytic intramolecular hydroamination of unactivated alkenyl sulfonamides was developed using $\text{Bi}(\text{OTf})_3$.¹⁵ The reaction proceeds under simple conditions and provides an easy access to 2-methylpyrrolidines in high yields (Scheme 10). Control experiments supported the hypothesis that the actual hydroamination catalyst might be HOTf generated from $\text{Bi}(\text{OTf})_3$.

$\text{Bi}(\text{OTf})_3$ was proven to be an effective catalyst for tandem hydroamination of amino-alkene and amino-allene derivatives with benzyl alcohols or vinyl ketones, affording functionalized *N*-heterocycles in good yields under mild conditions (Scheme 11).¹⁶ This method could be further applied to other types of amino-olefins, such as one-carbon-elongated amino-alkenes and trisubstituted ones.

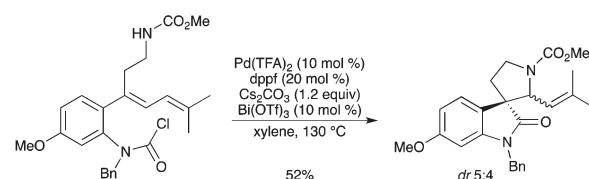
4.2.2. Heck hydroamination cascade reaction. The spiro (pyrrolidine-3,3'-oxindole) skeleton, found in hemiterpene spirooxindole alkaloids, was efficiently constructed by using a tandem Pd^0 -catalyzed Heck cyclization reaction and Bi^{III} -catalyzed hydroamination (Scheme 12).¹⁷ The spiro derivative could also be prepared from the same carbamoyl chloride in better yield and with better diastereoselectivity by a stepwise Pd^0 -catalyzed Heck reaction and $\text{Bi}(\text{OTf})_3$ -catalyzed hydroamination ($\text{Bi}(\text{OTf})_3$ (10 mol%), KPF_6 (10 mol%), 1,4-dioxane, 50 °C, 83%, dr 3 : 1).



Scheme 10

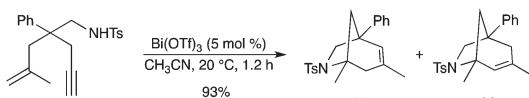


Scheme 11



Scheme 12





Scheme 13

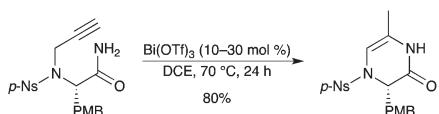
4.2.3. Tandem hydroamination reaction of amino-1,6-enynes. Bi(OTf)₃ efficiently catalyzed the cyclization of amino-1,6-enynes, leading to bicyclic amines (Scheme 13).¹⁸ The reaction drastically depended on the stability of the cationic intermediate formed after the addition of the alkene on the alkyne moiety.

4.3. Hydroamidation reaction

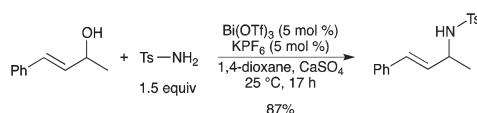
A highly selective 6-*exo*-dig cyclization of alkynylamides was described using Bi(OTf)₃.¹⁹ The synthesis of piperazin-2-ones was afforded by a 6-*exo*-dig intramolecular hydroamidation of 2-(prop-2-ynylamino)acetamides. The reaction with Bi(OTf)₃ proceeded slowly at room temperature and afforded the 6-*exo*-cyclized product as a single product (Scheme 14). It is noteworthy that the use of Bi(OTf)₃ resulted in the opposite regioselectivity to that of PtCl₂ leading to the 7-*endo*-dig cyclization. The mechanism occurs through initial π -activation of the triple bond, followed by nucleophilic addition of the amide to the internal carbon of the triple bond. Subsequent protodemetalation followed by isomerization of the exocyclic double bond to the endocyclic position gave the observed product. The authors noted that in a few cases of the bismuth-catalyzed cyclization, the addition of five equivalents of water or catalytic amounts of HOTf gave better yields as well as complete conversions.

4.4. Amination reactions

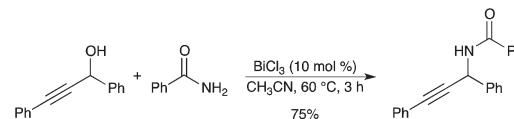
Bismuth catalysis is also suitable for the direct substitution of allylic, propargylic, and benzylic alcohols with sulfonamides, carbamates, and carboxamides under mild reaction conditions. A combination of Bi(OTf)₃ and KPF₆ (1–5 mol%) promoted the amination reactions at room temperature to give the products in up to 99% yield (Scheme 15).²⁰ According to the authors, the possibility that HOTf, generated from Bi(OTf)₃ and H₂O, promotes the reaction cannot be ruled out completely, even in the presence of a dessicant. However,



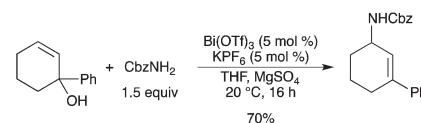
Scheme 14



Scheme 15



Scheme 16



Scheme 17

control experiments support the hypothesis that Bi(OTf)₃/KPF₆ functions as a combined catalyst.

Substitution of a propargylic alcohol with benzamide was promoted by BiCl₃ as the catalyst (Scheme 16).²¹ Under mild conditions, the corresponding amide was obtained in good yield.

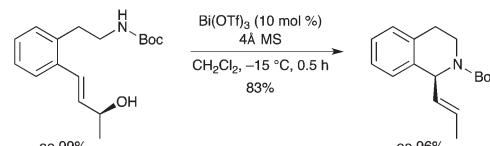
The Bi(OTf)₃–KPF₆ catalytic system was successfully used in an S_N' substitution of tertiary allylic alcohols with benzyl carbamate.²² The corresponding allylic carbamate was obtained in good yield (Scheme 17). A related S_N' hydroamination has also been reported in an intramolecular case using Bi(OTf)₃, in a moderate yield however.²³

4.5. Chirality transfer

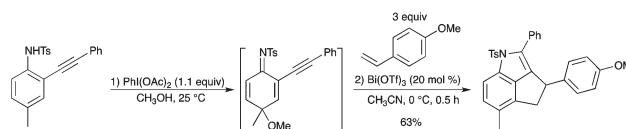
The Bi(OTf)₃-catalyzed intramolecular 1,3-chirality transfer reaction of chiral amino alcohols was developed to construct chiral 1-substituted tetrahydroquinolines (Scheme 18).²⁴ The mechanism was believed to involve σ -activation of the hydroxyl group with the Bi^{III} salt, followed by a concerted S_N2'-type substitution.

4.6. Cascade reaction

The oxidative dearomatization of *para*-substituted *o*-alkynylanilines affords 2-alkynyl cyclohexadienimines, which can act as an active substrate with electron-rich styrenes upon catalysis with Bi(OTf)₃ to give 3,4-dihydro-cyclopenta[c,d]indoles (Scheme 19).²⁵ After the first oxidation step and a work-up



Scheme 18



Scheme 19



process to remove methanol, the crude oxidative dearomatization mixture was used in the cascade reaction. The cascade reaction is metal-controlled; AgOTf provided tricyclic pyrrole derivatives instead of 3,4-dihydro-cyclopenta[c,d]indoles.

5. Alkylation reactions

5.1. Silyl-derived etherification reactions

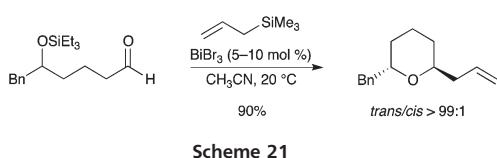
Various one-pot methods for the conversion of aldehydes to homoallylic ethers and esters catalyzed by Bi(OTf)₃ have been reported.²⁶ A wide variety of homoallylic ethers including allyl, benzyl and methyl ethers can be synthesized using allyltrimethylsilane and alkoxytrimethylsilanes in the presence of Bi(OTf)₃ (Scheme 20).

Bismuth salts have been proven to be efficient catalysts for stereoselective etherification reactions.²⁷ Evans reported that BiBr₃ could catalyze the reaction of δ -trialkylsilyloxy aldehydes and ketones, using various trialkylsilyl nucleophiles for the construction of *cis*- and *trans*-2,6-di- and trisubstituted tetrahydropyrans (Scheme 21). The authors demonstrated that the bismuth salt was acting as a Brønsted acid source. Other carbon nucleophiles, such as a propargyl trimethylsilane or an enoxy trimethylsilane, could be used. A related strategy using BiBr₃ and *tert*-butyldimethylsilane has been part of the total synthesis of (–)-mucocin.²⁷ Evans' protocol could be advantageously extended to a bromoenoxysilane in a polypropionate synthesis by Guindon.²⁸

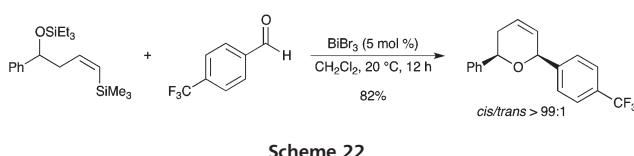
A tandem intermolecular addition/intramolecular silyl-Prins (silyl-modified Sakurai reaction-ISMS) reaction efficiently afforded *cis*-2,6-disubstituted dihydropyrans using 5 mol% of BiBr₃ in CH₂Cl₂ (Scheme 22).²⁹ The reaction occurred between δ -triethylsilyloxyvinyltrimethylsilanes and a variety of aldehydes to give good to excellent yields of dihydropyran



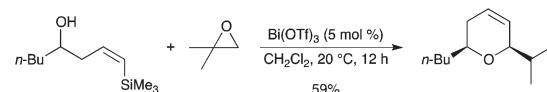
Scheme 20



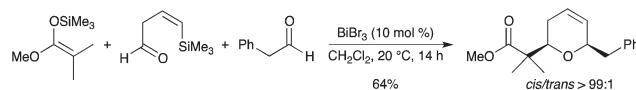
Scheme 21



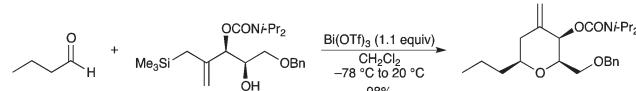
Scheme 22



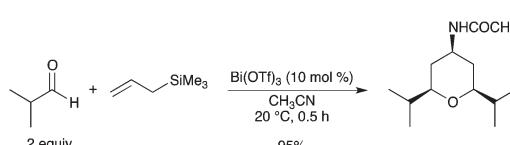
Scheme 23



Scheme 24



Scheme 25



Scheme 26

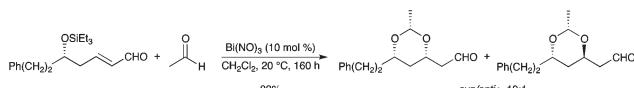
derivatives. The procedure is a mild alternative to the use of other Lewis acids such as BF₃·OEt₂ or TMSOTf and provides the dihydropyrans with an excellent diastereoselectivity.

Extension of this work to a cascade reaction involving epoxide rearrangement³⁰ followed by a tandem addition/silyl-Prins reaction was reported by the same group.³¹ The cascade reaction sequence using isobutylene oxide afforded the pure *cis* isomer of the corresponding 2,6-disubstituted 3,6-dihydro-2*H*-pyran (Scheme 23). These studies indicate an initial Lewis acid/base interaction between Bi(OTf)₃ and the substrates providing HOTf *in situ*.

A related strategy has been reported with an initial Mukaiyama aldol reaction followed by a second addition/silyl-Prins step (ISMS).³² BiBr₃-mediated addition of silyl ketene acetals or silyl enol ethers to β,γ -unsaturated *cis*-4-trimethylsilyl-3-butenal provided an intermediate Mukaiyama aldol product containing a vinylsilane moiety tethered to a silyl ether (Scheme 24). The addition of a second aldehyde initiated a tandem sequence involving intermolecular addition followed by an ISMS reaction.

cis-Tetrahydropyrans have also been obtained in high yield via the intramolecular Sakurai allylation of a functionalized allylsilane with *n*-butyraldehyde in the presence of a stoichiometric amount of Bi(OTf)₃ (Scheme 25).³³

A diastereoselective synthesis of 4-amidotetrahydropyrans was achieved by a single-step Sakurai-Prins-Ritter reaction sequence in a tandem fashion by the reaction of an aldehyde and allyltrimethylsilane in acetonitrile using Bi(OTf)₃ as a catalyst (Scheme 26).³⁴



Scheme 27



Scheme 28

A diastereoselective construction of *syn*-1,3-dioxanes was reported *via* a bismuth-mediated two-component hemiacetal/oxa-conjugate addition reaction.³⁵ δ -Trialkylsilyloxy and δ -hydroxy α,β -unsaturated aldehydes and ketones react with alkyl aldehydes in a highly efficient and stereoselective manner (Scheme 27). Interestingly, the analogous process with nitric acid provided the 1,3-dioxane in significantly lower yield, illustrating the superiority of bismuth salts.

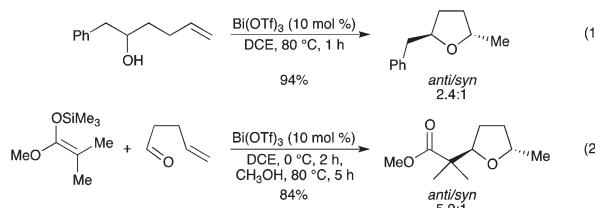
The same group reported a one-pot diastereoselective sequential two-component etherification, followed by an oxoconjugate addition.³⁶ The reaction of an anomeric acetal with a trimethylsilyloxy diene afforded a bis(tetrahydropyran) core used in the total synthesis of (+)-leucascandrolide A (Scheme 28). $\text{Bi}(\text{NO}_3)_3$ was used as a Brønsted acid source. The necessity of a dual Lewis and Brønsted acid catalyzed process to affect this type of sequential process was demonstrated.

5.2. Hydroalkylation reactions

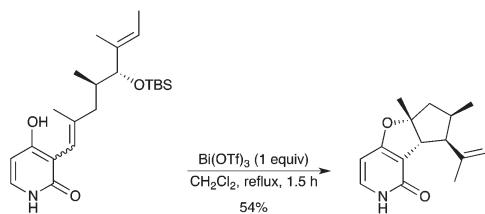
It was found that both terminal and internal olefins underwent a $\text{Bi}(\text{OTf})_3$ -catalyzed hydroalkylation to afford tetrahydrofurans in high yield with preference for the *anti* diastereoisomer (Scheme 29, eqn (1)).³⁷ A $\text{Bi}(\text{OTf})_3$ -catalyzed nucleophilic addition/hydroalkylation has also been disclosed for the coupling of a variety of nucleophilic partners and aldehydes, in the presence of a small amount of MeOH (Scheme 29, eqn (2)). Triflic acid was demonstrated to be the actual catalyst of the hydroalkylation step.

5.3. Tandem cationic cyclization

A pyridone alkaloid, citridone A, has been prepared in a highly stereoselective way by using a tandem cationic cyclization and heterocyclization promoted by bismuth (Scheme 30).



Scheme 29



Scheme 30

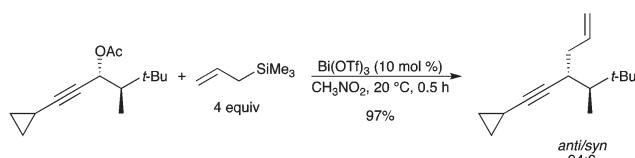
$\text{Bi}(\text{OTf})_3$ was the reagent of choice to avoid decomposition. The mechanism is believed to involve the formation of a bismuth amide complex, the ionization of the OTBS group, followed by internal etherification to quench an intermediately formed cation. $\text{Bi}(\text{OTf})_3$ was used in a stoichiometric quantity however.

5.4. Allylation reaction

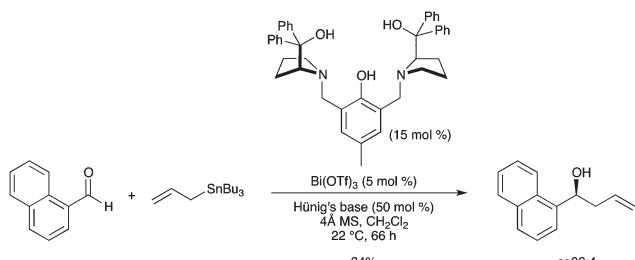
A highly diastereoselective $\text{Bi}(\text{OTf})_3$ -catalyzed reaction of chiral propargylic acetates with various weak carbon nucleophiles, *i.e.* silyl enol ethers, allyltrimethylsilane, and various arenes was disclosed.³⁹ Among a wide array of potential catalysts (such as FeCl_3 , InCl_3 , AuCl_3 , $\text{Cu}(\text{OTf})_2$), $\text{Bi}(\text{OTf})_3$ proved to be the most effective. Propargylic acetates react with high diastereoselectivity under $\text{S}_{\text{N}}1$ conditions to give the corresponding substitution products (Scheme 31).

5.5. Enantioselective allylation reaction

A highly enantioselective method for the catalytic addition of allyltributylstannane to aromatic aldehydes was developed by our group using $\text{Bi}(\text{OTf})_3$ and Trost's (*R,R*)-ProPhenol ligand.⁴⁰ The allylation of a variety of aromatic aldehydes afforded the desired homoallylic alcohols in good yields with enantioselectivities ranging from 93:7 to 96:4 er (Scheme 32). The reaction also proved to proceed in good yield and high enantioselectivity using naphthal carboxaldehydes or



Scheme 31



Scheme 32



heteroaromatic aldehydes as electrophiles. The conditions have also been applied to aliphatic aldehydes. In preliminary experiments, enantioselectivities up to 96:4 have been obtained. Characterization data from ^1H NMR spectroscopy and mass spectrometry have been provided as the first evidence of the pre-catalyst structure.

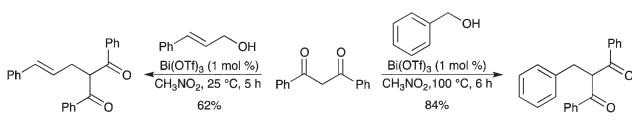
5.6. Benzylation reactions

An efficient bismuth-catalyzed direct benzylolation of 2,4-pentanediones was developed using various free benzyl alcohols and dicarbonyl compounds.⁴¹ The corresponding products of this direct C–C bond-forming reaction have been isolated in good to excellent yields. The procedure was extended to a direct allylic alkylation of 2,4-pentanediones affording the linear, unbranched products (Scheme 33). In this process, the only by-product was water.

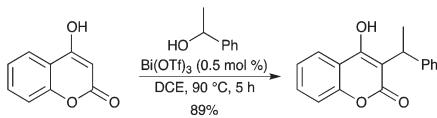
The $\text{Bi}(\text{OTf})_3$ -catalyzed benzylolation was successfully applied to 4-hydroxycoumarin for the synthesis of numerous differently substituted warfarin derivatives (Scheme 34).⁴²

A highly efficient $\text{Bi}(\text{OTf})_3$ -catalyzed benzylolation of arenes and heteroarenes has also been developed.⁴³ Several electron-rich arenes, such as 1-methylnaphthalene, gave the corresponding diarylmethane products in good to excellent yields (Scheme 35).

The benzylolation of several arenes was also performed by employing benzyl alcohol and benzyl acetate as the electrophiles (Scheme 36). Isolated yields of the products were



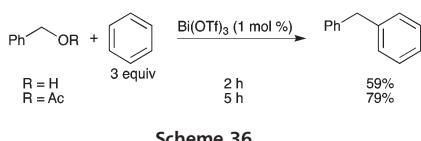
Scheme 33



Scheme 34



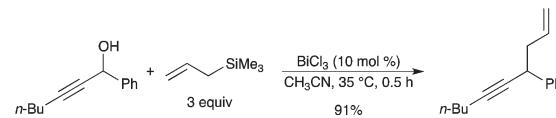
Scheme 35



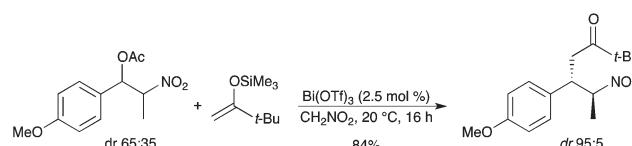
Scheme 36



Scheme 37



Scheme 38



Scheme 39

slightly lower for the benzyl alcohol as compared to the benzyl acetate.

A highly effective allylation reaction of substituted benzyllic alcohols with allyltrimethylsilane has been developed using BiCl_3 as the catalyst (Scheme 37).⁴⁴ $\text{Bi}(\text{OTf})_3$ was not effective as a catalyst under these conditions.

The reaction of allyltrimethylsilane with various propargylic alcohols was also mediated by BiCl_3 as the catalyst and the substituted 1,5-enynes were obtained in high yields (Scheme 38).²¹ BiCl_3 was also an efficient catalyst for the propargylation of several electron-rich arenes and heteroarenes.²¹

High facial diastereoselectivities were observed with acetates derived from chiral α -branched *para*-methoxybenzyllic alcohols.⁴⁵ The reaction with the silyl enol ether derived from *t*-butyl methyl ketone afforded the corresponding ketone with a good yield and a high diastereoselectivity (Scheme 39).

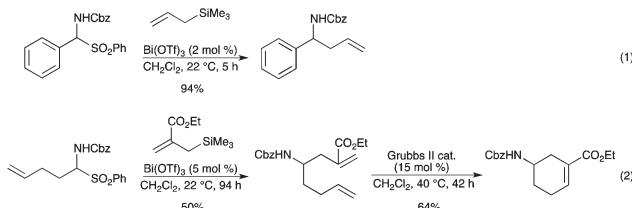
5.7. *N*-Alkoxy carbonyl amino sulfone allylation reactions

$\text{Bi}(\text{OTf})_3$ has been disclosed by our group to be an efficient catalyst in the Sakurai reaction of allyltrimethylsilanes with *N*-alkoxy carbonyl amino sulfones.⁴⁶ The reaction proceeded smoothly with a low catalyst loading of $\text{Bi}(\text{OTf})_3$ (2–5 mol%) to afford the corresponding protected homoallylic amines in very good yields (up to 96%) (Scheme 40, eqn (1)). The generality of our method was further extended to a functionalized allylsilane. Under the same conditions, the corresponding homoallylic amine was obtained and subsequently subjected to ring-closing metathesis using the second generation Grubbs' catalyst (Scheme 40, eqn (2)).

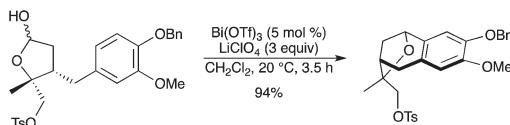
5.8. Allenylation reaction

A convenient method for the synthesis of the allenyl adduct of a hydrazinoester has been reported using allenyl pinacol

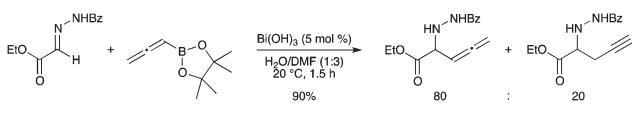




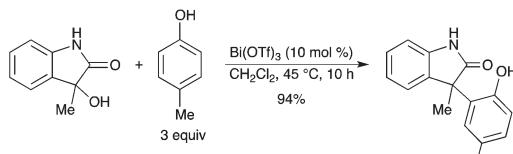
Scheme 40



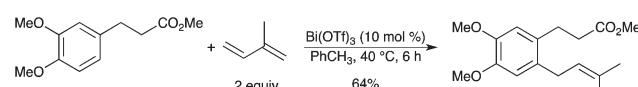
Scheme 44



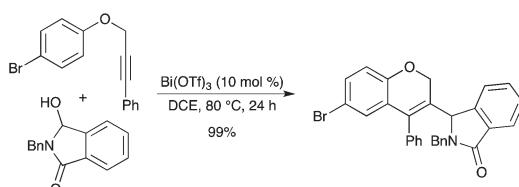
Scheme 41



Scheme 45



Scheme 42



Scheme 46

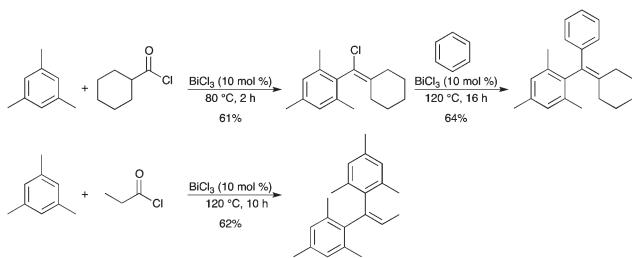
boronate and bismuth hydroxide as the catalyst.⁴⁷ The allenyl *vs.* propargyl adduct was produced preferentially using Bi(OH)₃ in a water-DMF solvent mixture (Scheme 41).

5.9. Prenylation reaction

Electron-rich aryl ethers and phenols react with isoprene in the presence of catalytic Bi(OTf)₃ to afford the corresponding prenylated or 2,2-dimethylchroman products in moderate to good yields (Scheme 42).⁴⁸ Prenylated aryl derivatives could also be obtained by Bi(OTf)₃-catalyzed [1,3]-rearrangement of aryl 3-methyl-2-butenoylethers.⁴⁹

6. Arylation and carboarylation reactions

In the presence of a catalytic amount of BiCl₃, the reaction of acyl chlorides or vinyl chlorides with arenes afforded 1,1-diarylalkenes (Scheme 43).⁵⁰ The procedure provides a one-pot method for the synthesis of 1,1-diarylalkenes. The reaction includes both the unusual formation of vinyl chlorides and the subsequent Friedel-Crafts-type vinylation of arenes catalyzed by BiCl₃.



Scheme 43

A new catalytic combination of 5 mol% of Bi(OTf)₃ with 3 equiv. of LiClO₄ as a co-catalyst was discovered to drive a Friedel-Crafts cyclization of a free lactol, as part of a stereocontrolled synthesis of (−)-platensimycin (Scheme 44).⁵¹ The cyclized product was obtained in 94% yield within 3.5 h. The combination of Bi(OTf)₃ with LiClO₄ was believed to generate a more reactive cationic species with the lactol toward nucleophilic ring closure.

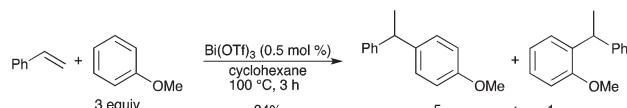
A Bi(OTf)₃-catalyzed Friedel-Crafts reaction of electron-rich aromatic compounds with 3-alkyl-3-hydroxy-2-oxindole has been developed (Scheme 45).⁵² It was found that In(OTf)₃ and Cu(OTf)₂ were equally efficient catalysts. Although, under similar conditions, 25–50 mol% of Ce(OTf)₃ and Sn(OTf)₂ provided high yields of the product, 10 mol% of these catalysts afforded decreased yields.

Bi(OTf)₃, as a borderline metal catalyst, was proven to work as a dual activator for alkynes and *N*,*O*-acetals *via* σ , π -chelation, which achieved a new carboarylation reaction of alkynyl-arenes with *N*,*O*-acetals (Scheme 46).⁵³ This reaction tolerated a wide range of alkynylarenes, particularly possessing non-protected heteroatoms, and various *N*,*O*-acetals.

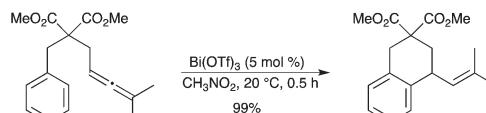
7. Hydroarylation and hydroalkylation reactions

Further studies by Rueping showed that the above-mentioned benzylic alcohol derivatives (Schemes 35 and 36) could be replaced by a styrene derivative.⁵⁴ A highly efficient

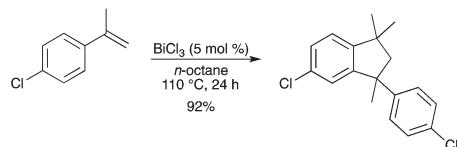




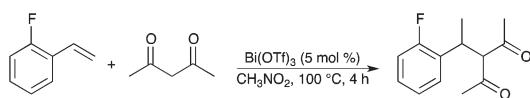
Scheme 47



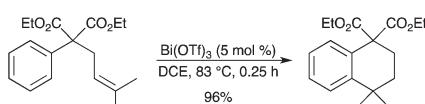
Scheme 51



Scheme 48



Scheme 49



Scheme 50

Bi(OTf)₃-catalyzed hydroarylation of various styrenes was then developed using arenes and heteroarenes (Scheme 47). The mild reaction conditions render this transformation an attractive approach to the valuable 1,1-diarylated alkanes.

BiCl₃ was also a catalyst for the hydroarylation of styrenes with electron-rich arenes and the Markovnikov adducts were selectively obtained in good to high yields.⁵⁵ Under arene-free conditions, the intermolecular hydroarylation of α -substituted styrenes and subsequent intramolecular hydroarylation produced the cyclic dimers of α -substituted styrenes in good yields (Scheme 48).

Rueping's procedure was then extended to the inter- and intramolecular hydroalkylation of styrenes using 1,3-dicarbonyl compound as the nucleophile.⁵⁶ An efficient Bi(OTf)₃-catalyzed hydroalkylation of various styrenes, norbornene, and cyclohexadiene derivatives was developed with different 2,4-pentanediones (Scheme 49).

An efficient intramolecular hydroarylation of non-activated substituted olefins with non-activated arenes has recently been disclosed.⁵⁷ The reaction could be carried out in the presence of 1–5 mol% Bi(OTf)₃ and allowed the preparation of various tetralin derivatives in good to excellent yields (Scheme 50). Although Sc(OTf)₃ and In(OTf)₃ could also efficiently catalyze the hydroarylation reaction, Bi(OTf)₃ was chosen because it is less toxic and shows high activity.

Intramolecular hydroarylation of allenes was achieved under very mild conditions using Bi(OTf)₃ as the catalyst (Scheme 51).⁵⁸ Interestingly, triflic acid did catalyze this reaction with almost the same yield as Bi(OTf)₃. The hydroarylation reaction is quite general and has been used for the synthesis of carbocycles and heterocycles without using noble metals and additional ligands.

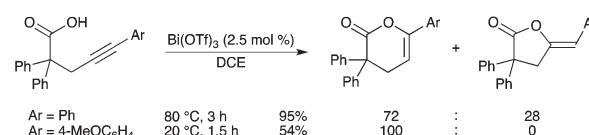
8. Oxycarbonylation reactions

8.1. Hydro-oxycarbonylation reaction

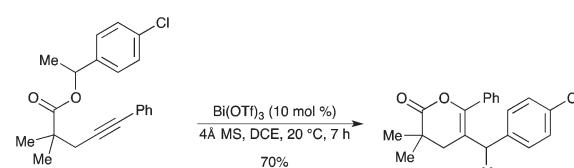
Bi(OTf)₃ was found to be a good catalyst for intramolecular addition of carboxylic acids to alkynes (hydro-oxycarbonylation), which afforded the corresponding 5- and 6-membered lactones in moderate to good yields under mild conditions (Scheme 52).⁵⁹ Bi^{III}, as a borderline-metal catalyst, was thought to act as a dual activator of both carboxylic and alkyne functions. Fe(OTf)₃ and Bi(OTf)₃ were found to be equally efficient to catalyze the transformation. The addition of the heteroatom seemed to mainly proceed at the alkynyl carbon attached to the aryl group.

8.2. Carbo-oxycarbonylation reaction

A Bi(OTf)₃-catalyzed intramolecular carbo-oxycarbonylation of alkynyl benzylic esters has been developed by the same authors.⁶⁰ This cyclization mainly afforded multisubstituted 6-membered lactones in good to high yields under mild conditions (Scheme 53). Evidence has been obtained to support an intramolecular mechanism.

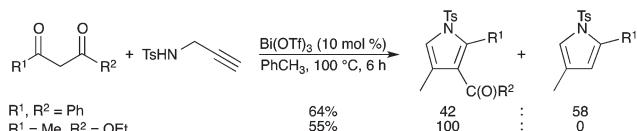


Scheme 52

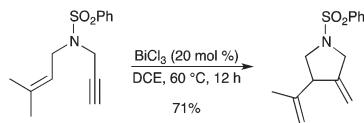


Scheme 53





Scheme 54



Scheme 57

9. Cycloisomerization reactions

9.1. Synthesis of pyrroles

Bi(OTf)₃ was found to be a good catalyst for the synthesis of substituted pyrroles from the readily accessible 2-propynyl-amine and methylene active compounds.⁶¹ The reaction could be applied to various β -dicarbonyl compounds (Scheme 54). However, when applied to β -keto esters, it is noteworthy that the reaction afforded 3-acylpyrroles only. A mechanism involving the formation of 3-aza-1,5-enyne, followed by cycloisomerization of the enyne moiety, has been demonstrated by the authors.

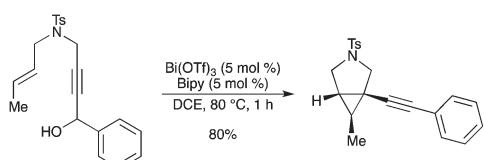
9.2. Dehydrative alkynylcyclopropanation reaction

A Bi^{III}-catalyzed dehydrative alkynylcyclopropanation of azabenzenes to give 1-alkynyl-3-azabicyclo[3.1.0]hexanes has been described by the same authors (Scheme 55).⁶² The stereochemistry of the adducts strongly depended on that of the starting azabenzenes. A dual coordination of the alkyne and the oxygen of the hydroxy group to the bismuth catalyst was believed to be essential.

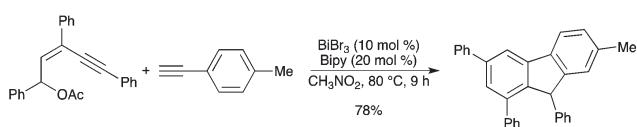
9.3. Enyne cycloisomerization reaction

A straightforward method for the synthesis of multisubstituted fluorenes with (Z)-pent-2-en-4-yl acetates and ethynylarenes was developed using BiBr₃ as a catalyst.⁶³ The domino reaction involves intermolecular electrophilic addition and cycloisomerization aromatization (Scheme 56). Compared with BiBr₃, other Bi salts as catalysts were less effective.

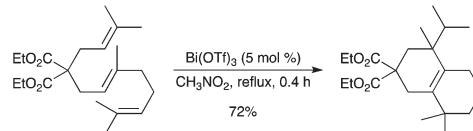
BiCl₃ was found to be an efficient catalyst for the cycloisomerization of 1,6-enynes (Scheme 57).⁶⁴ Electron-deficient alkynes appeared to be better substrates for the reaction.



Scheme 55



Scheme 56



Scheme 58



Scheme 59

9.4. Triene cycloisomerization reaction

Non-activated trienes were cyclized into polycyclic compounds in good to excellent yields under Bi(OTf)₃ catalysis in a biomimetic fashion.⁶⁵ The reaction showed broad generality and allowed for the formation of functionalized bicyclic to tetracyclic structures from simple precursors in a one-pot fashion (Scheme 58). A double cyclization occurred *via* the formation of cationic intermediates and involved a 1,2-methyl shift. It was proposed by the authors that the catalytic cycloisomerization process might proceed *via* a Lewis acid-assisted Brønsted acid-type activation. The cyclizations proceeded smoothly in 63–99% yields, leading to the formation of up to three cycles and three new C–C bonds in a single operation. Cycloisomerization of malonate-type highly substituted 1,6-dienes could also be catalyzed by Bi(OTf)₃ albeit in low yield.⁶⁶

9.5. Ketone cyclotrimerization reaction

Bi(OTf)₃ was found to efficiently catalyze the cyclotrimerization of acetophenones into 1,3,5-triarylbzenes in good yields (Scheme 59).⁶⁷ This method was also used for the conversion of *ortho*-substituted acetophenones, which do not readily undergo cyclotrimerization by other methods.

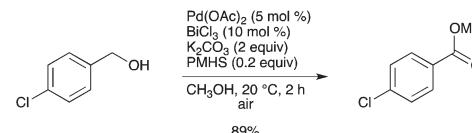
10. Oxidations

An efficient method for allylic oxidation of unsaturated steroids has been disclosed by Salvador.⁶⁸ Very good yields and high selectivity have been obtained, using *t*-BuOOH as the oxidant and various Bi^{III} salts as the catalysts. 17-Oxoandrost-5-en-3 β -yl acetate was smoothly converted into the corresponding enone (Scheme 60). Evidence was obtained that BiCl₃ was

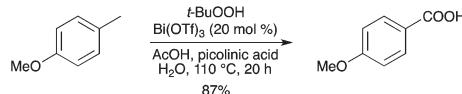




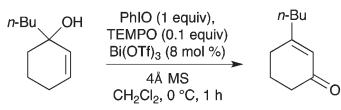
Scheme 60



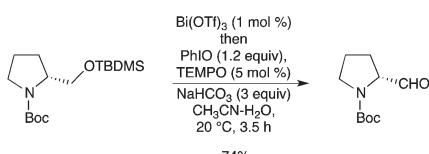
Scheme 64



Scheme 61



Scheme 62



Scheme 63

converted into BiOCl during the reaction. Recovered BiOCl gave identical reaction rates and isolated product yields.

In parallel, benzylic oxidation of methyl arenes with *t*-BuOOH in the presence of Bi(OTf)₃ gave the corresponding substituted benzoic acids (Scheme 61).⁶⁹ These results were consistent with the bismuth(III) acting as a Lewis acid and modifying the reactivity of the peroxide rather than acting in a Bi^{III}–Bi^V cycle. Other metal triflates, such as Hf(OTf)₄, Sc(OTf)₃ and Yb(OTf)₃, showed excellent catalytic activity as well for the oxidation of tetrahydronaphthalene into α -tetralone.

Bi(OTf)₃ was found to be an efficient catalyst for the oxidative rearrangement of tertiary allylic alcohols with the PhIO-TEMPO system (Scheme 62).⁷⁰ The bismuth(III) salt is believed to isomerize the allylic alcohol *via* an allylic cation, prior to oxidation. Good yields of 3-substituted cyclic enones were generally obtained.

A sequential one-pot deprotection–oxidation of primary and secondary *tert*-butyldimethylsilyl ethers was described using catalytic Bi(OTf)₃ and TEMPO in the presence of PhI(OAc)₂.⁷¹ Under such conditions, acid-sensitive substrates could be transformed into the corresponding aldehydes (Scheme 63).

In a palladium-catalyzed oxidative process, hydrosilane can serve as an activator of a palladium catalyst with bismuth(III) chloride, thus leading to a novel ligand- and silver-free palladium catalytic system for the facile oxidative esterification of a

variety of benzylic alcohols in good yields (Scheme 64).⁷² Other bismuth salts, except BiI₃, were also effective for the Pd-catalyzed oxidative esterification of *o*-tolylmethanol. This silver-free catalytic system has several advantages, *i.e.* being a ligand-free, environmentally benign system, and the possibility of directly using an air atmosphere as the terminal oxidant.

11. Other reactions

11.1. Glycosylation reaction

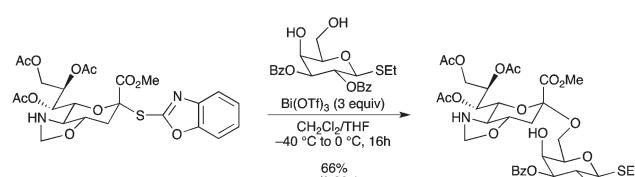
Glycosylation of a sialyl donor with a thioethyl galactosyl acceptor has been performed in the presence of Bi(OTf)₃ used in large excess *vs.* the sialyl donor (Scheme 65).⁷³ In this case, the desired disaccharide was obtained with nearly complete α -stereoselectivity ($\alpha/\beta = 20:1$). Activation with other Lewis acids led to decreased stereoselectivities.

11.2. Ritter reaction

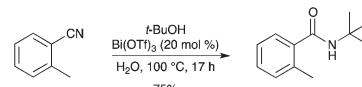
N-*tert*-Alkyl and aryl amides have been obtained by a Ritter reaction of various nitriles with tertiary alcohols in the presence of a catalytic amount of Bi(OTf)₃ (Scheme 66).⁷⁴ Presumably under these aqueous conditions, catalysis is effected by triflic acid.

11.3. Oxa- and thia-Pictet-Spengler reaction

Different isothiochroman or isochroman compounds have been synthesized from phenylethanethiol or phenylethanol and a series of benzaldehydes, in the presence of Bi(OTf)₃ (Scheme 67).⁷⁵

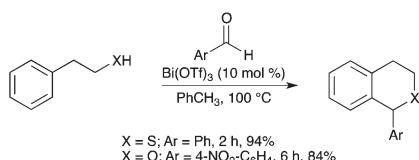


Scheme 65

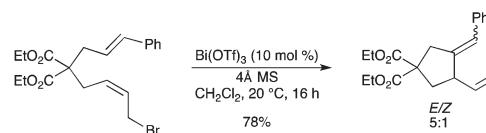


Scheme 66

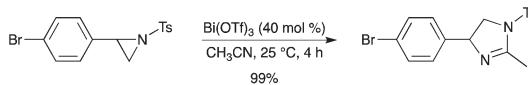




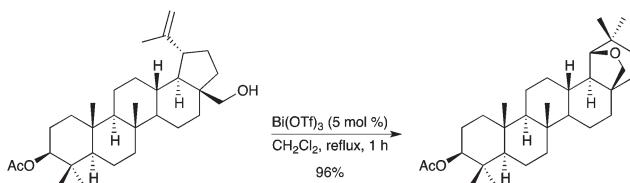
Scheme 67



Scheme 70



Scheme 68



Scheme 69

11.4. [3 + 2] Cycloaddition reaction

In parallel, the use of a nitrile as a nucleophile was also involved in the [3 + 2] cycloaddition of a series of substituted *N*-tosylaziridines with nitriles promoted by $\text{Bi}(\text{OTf})_3$.⁷⁶ Under these conditions, $\text{Bi}(\text{OTf})_3$ appeared to be the best promoter among various Lewis acids and various imidazolines were obtained under mild reaction conditions (Scheme 68).

11.5. Wagner–Meerwein rearrangement

The use of $\text{Bi}(\text{OTf})_3$ as a catalyst for the Wagner–Meerwein rearrangement of lupane derivatives with expansion of ring E and formation of an additional O-containing ring was reported.⁷⁷ This process has also been extended to other terpenes, such as (–)-caryophyllene oxide (Scheme 69). Evidence for a Brønsted acid species being the actual catalyst was provided by the authors. In related studies, $\text{Bi}(\text{OTf})_3$ was also used as a catalyst for the direct conversion of corticosteroids into highly functionalized 17-ketosteroids by cleavage of the C17-dihydroxyacetone side chain.⁷⁸ Participation of an *in situ* generated Brønsted acid species from $\text{Bi}(\text{OTf})_3$ was also pointed out for the opening of oleanolic hydroxy- γ -lactones into the corresponding 12-oxo-28-carboxylic acid derivatives.⁷⁹

11.6. Cationic cyclization *via* halide activation

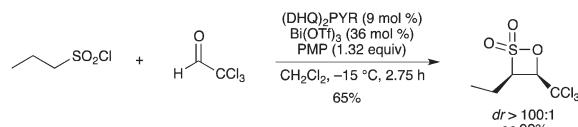
$\text{Bi}(\text{OTf})_3$ was used to catalyze 5-*exo*-trig cyclization *via* halide activation.⁸⁰ Employing 10 mol% $\text{Bi}(\text{OTf})_3$ with 4 \AA molecular sieves resulted in successful cyclization (Scheme 70). This study suggested that $\text{Bi}(\text{OTf})_3$ possesses interesting halophilic properties.

11.7. Co-catalysis

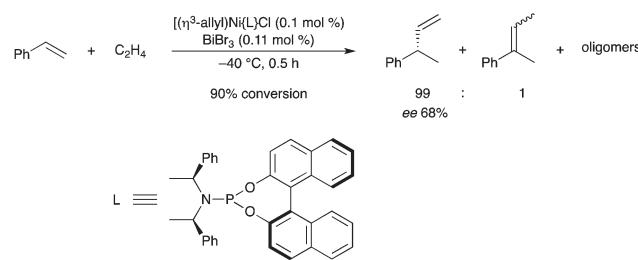
Cooperative catalytic action of a chiral nucleophilic tertiary amine (the cinchona alkaloid derivative dihydroquinine 2,5-diphenyl-4,6-pyrimidinediyl diether $[(\text{DHQ})_2\text{PYR}]$) and $\text{Bi}(\text{OTf})_3$, in the presence of 1,2,2,6,6-pentamethylpiperidine (PMP), was proposed in the [2+2]-cycloaddition of sulfenes and aldehydes.⁸¹ The reaction of propanesulfonyl chloride with chloral provided the disubstituted β -sulfone with high diastereo- and enantioselectivity (Scheme 71). $\text{Bi}(\text{OTf})_3$ provided better yields (47–87%) than $\text{In}(\text{OTf})_3$ (28–69%), whereas in terms of enantioselectivity a clear-cut trend is not obvious.

Bismuth salts have been studied for their ability to activate chiral nickel catalysts in the chemo- and enantioselective hydrovinylation of styrene.⁸² BiBr_3 was very efficient in the activation of the Ni complex, resulting in high conversion (Scheme 72). The Ni catalyst is activated by the Bi^{III} salt, which can abstract the chloride ligand. Substantial increase of the catalytic activity of the nickel complex was also possible using InI_3 or InBr_3 as activators.

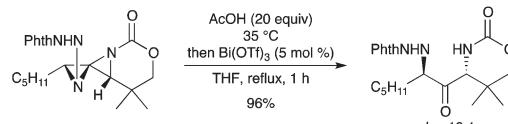
A variety of 1,4-diazaspiro[2.2]pentanes were converted to the corresponding 1,3-diaminated ketone products *via* treatment with HOAc , followed by addition of 5 mol% of $\text{Bi}(\text{OTf})_3$ (Scheme 73).⁸³ The authors obtained the evidence that the role



Scheme 71

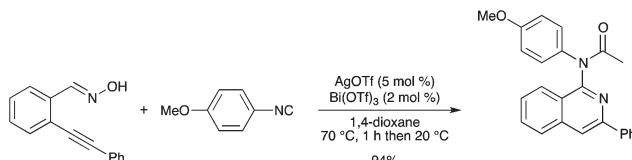


Scheme 72



Scheme 73





Scheme 74

of $\text{Bi}(\text{OTf})_3$ might be to simply generate small amounts of HOTf .

An efficient one-pot tandem reaction of 2-alkynylbenzaldioximes with isocyanides co-catalyzed by AgOTf and $\text{Bi}(\text{OTf})_3$ has been developed, which affords *N*-(isoquinolin-1-yl)formamides in good to excellent yields (Scheme 74).⁸⁴ AgOTf was effective for the generation of the intermediate isoquinoline *N*-oxides, $\text{Bi}(\text{OTf})_3$ being a catalyst for the further reaction with the isocyanide.

11.8. Michael addition reaction

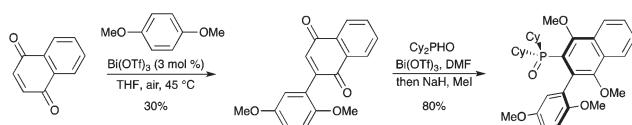
$\text{Bi}(\text{OTf})_3$ -catalyzed Friedel–Crafts alkenylation, followed by air oxidation, allowed the preparation of 2-arylnaphthoquinones. Conjugate addition of dicyclohexylphosphine oxide to the obtained product was also catalyzed by $\text{Bi}(\text{OTf})_3$ (Scheme 75).⁸⁵ Both arylation and phosphorylation reactions could be run in one-pot, however a better overall yield was obtained when isolated 2-arylnaphthoquinone was used.

11.9. Enantioselective cyclization

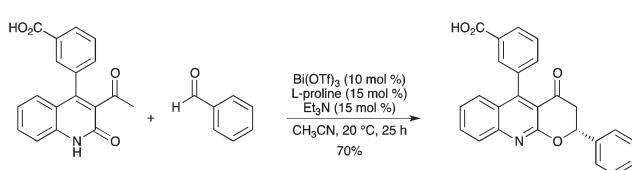
The synthesis of (2*R*)-2,5-diaryl-2,3-dihydropyrano[2,3-*b*]quolin-4-ones was recently achieved by the reaction of 3-acetyl-4-aryl-carboxylic acid and an aldehyde, in the presence of $\text{Bi}(\text{OTf})_3$ and L-proline (Scheme 76).⁸⁶ A $\text{Bi}(\text{OTf})_3$ -L-proline complex is believed to be formed *in situ*.

11.10. Synthesis of furans

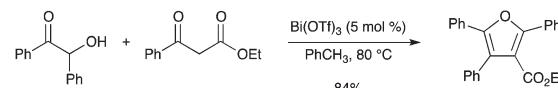
$\text{Bi}(\text{OTf})_3$ was found to be an effective catalyst for a tandem condensation/cyclization reaction of acyloins and β -diketones or β -keto esters to afford highly substituted furans in good to excellent yields (Scheme 77).⁸⁷



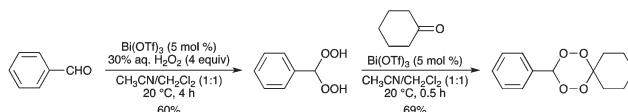
Scheme 75



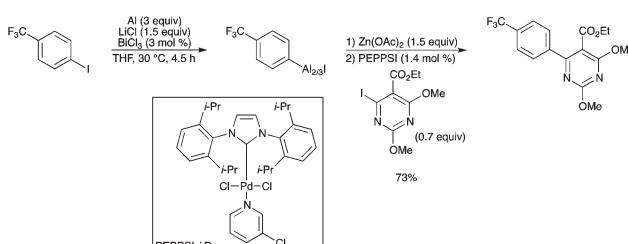
Scheme 76



Scheme 77



Scheme 78



Scheme 79

11.11. Synthesis of peroxides

$\text{Bi}(\text{OTf})_3$ was found to be an efficient and mild catalyst for the synthesis of both 1,1-dihydroperoxides, and symmetrical and unsymmetrical 1,2,4,5-tetraoxanes (Scheme 78).⁸⁸ TfOH was not as efficient as $\text{Bi}(\text{OTf})_3$ as a catalyst for both reactions.

11.12. Preparation of functionalized organoaluminiums

BiCl_3 was proved to be efficient for the generation of functionalized arylaluminium halides.⁸⁹ BiCl_3 , used as an additive (3 mol%), allowed the direct insertion of aluminium powder in the presence of Me_3SiCl (3 mol%) and LiCl (3 equiv.). Several functionalized unsaturated substrates readily underwent an Al insertion with BiCl_3 as a catalyst, followed by transmetalation with a Zn salt and Pd-catalyzed cross-coupling, to generate the desired product (Scheme 79). However, the aluminium insertion in the presence of an ester or an amide functional group did not lead to satisfactory yields with BiCl_3 . Interestingly, Bi did not insert into the aryl iodide under the standard reaction conditions.

12. Conclusions and future challenges

Catalytic transformation using bismuth is clearly an emerging area. The growing amount of activities in the field and the resulting constant need for knowledge developments make this review an essential update in organic synthesis using bismuth catalysis. Synergistic effects with other Lewis acids have also been recently highlighted. The discovery that some bismuth salts could be used as Lewis acids under aqueous conditions finally opened the door to designing catalysts and to broadening the concept of hydrocompatible Lewis acids,



which has since been applied to various reaction types. Moreover, the use of bismuth catalysts has definitively contributed to the area of environmentally benign catalysts, known as green catalysts. These are fascinating developments since such green catalysts are now widely appreciated and new reactions and catalysts are being designed and published on a regular basis. The current developments allow us to demonstrate that bismuth chemistry truly is an emerging field. Efficient catalytic transformations using bismuth are definitively high potential processes, which encompass asymmetric catalysis using chiral bismuth(III) complexes as one of their most promising challenges to reach. The expanding activity in the field clearly highlights the growing potential of bismuth catalysts. Research in this area will contribute to meeting some of the remaining challenges of synthetic organic chemistry.

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