

# SYNLETT Spotlight 376

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Bis(trifluoromethanesulfonyl)imide

Compiled by Victor L. Rendina

Victor L. Rendina received his B.S. in Chemistry (2008) from the Ohio State University where he conducted research under the direction of Professor T. V. RajanBabu. He is currently pursuing his doctoral degree at Boston College with Assistant Professor Jason S. Kingsbury. His research is focused on the design of novel scandium catalysts for use in reactions of non-stabilized diazoalkanes.

Eugene F. Merkert Chemistry Center, Boston College, 2609 Beacon St., Chestnut Hill, MA 02467, USA  
E-mail: victor.rendina@bc.edu

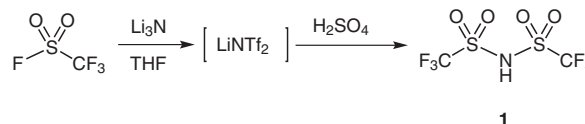


### Introduction

Bis(trifluoromethanesulfonyl)imide (**1**), or triflimide, is a commercially available Brønsted acid that has been applied to a broad range of organic transformations.<sup>1</sup> In addition to being an exceptionally potent Brønsted acid, the corresponding conjugate base is more commonly employed as a weakly coordinating counterion with a variety of metal and organic catalyst systems.<sup>2</sup> Experimental evidence indicates that triflimide is a weaker Brønsted acid in solution than the closely related triflic acid,<sup>3</sup> however, the lower charge density and greater steric encumbrance results in a less coordinating anion. Consequently, triflimide-based Lewis acids generally show higher activity than their corresponding triflate counterparts.<sup>4</sup>

### Preparation

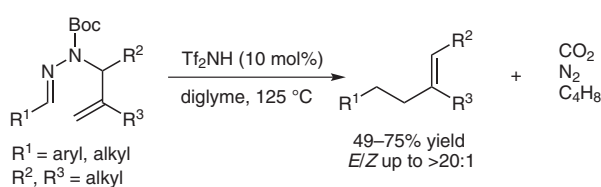
Triflimide was first prepared by stepwise addition of trifluoromethanesulfonyl fluoride to anhydrous ammonia.<sup>3</sup> It has also been prepared by the reaction of trifluoromethanesulfonyl fluoride with lithium nitride followed by vacuum distillation from concentrated sulfuric acid.<sup>5</sup> Lewis acids are commonly prepared by treating metal halides, carbonates, hydroxides, or oxides with aqueous triflimide.<sup>6</sup> Silver triflimide can also be utilized in salt metathesis reactions under anhydrous conditions.<sup>7</sup>



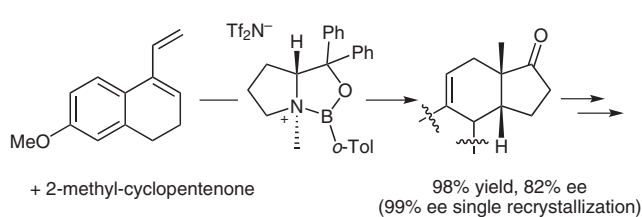
**Scheme 1** Preparation of bis(trifluoromethanesulfonyl)imide

### Abstracts

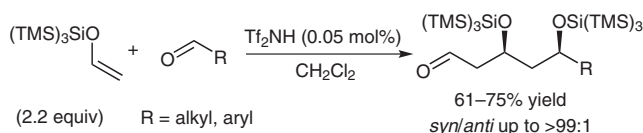
(A) Triflimide was found to be effective at promoting the [3,3]-sigmatropic rearrangement of Boc-protected *N*-allyl hydrazones.<sup>8</sup> The authors describe the newly forged C–C bond as traceless, since the functional groups utilized in the bond forming event are cleanly lost as volatile byproducts.



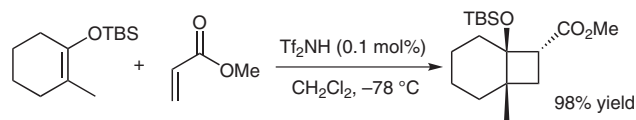
(B) Chiral proline-derived oxazaborolidinones, when treated with triflimide, generate highly efficient and enantioselective Diels–Alder catalysts.<sup>9</sup> A short enantioselective synthesis of estrone was disclosed that relies on a novel *N*-methyl-oxazaborolidinium triflimide catalyzed Diels–Alder reaction as key step.



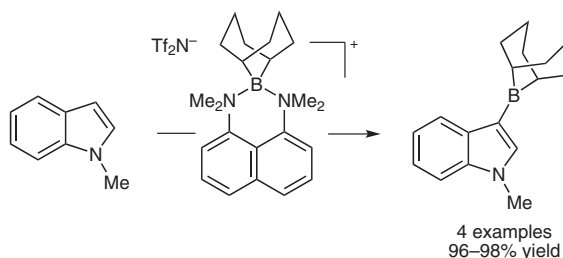
(C) Highly diastereoselective Mukaiyama cross-aldol reactions of aldehydes catalyzed by low loadings of triflimide have been reported.<sup>10</sup> In the presence of 2.2 equivalents of the silyl enol ether a diastereoselective cascade reaction resulting from double addition is observed. It is believed that the active catalyst is the Lewis acid  $\text{Tf}_2\text{NSi}(\text{TMS})_3$ , formed in situ following protodesilylation.



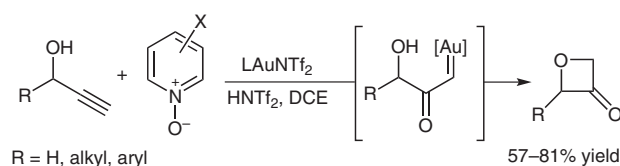
(D) The (2+2) cycloaddition of silyl enol ethers with  $\alpha,\beta$ -unsaturated esters proceeds with catalytic amounts of triflimide to produce substituted cyclobutanes.<sup>11</sup> Reaction with alkynyl esters affords the corresponding cyclobutenes. Like the aforementioned Mukaiyama aldol chemistry, the reaction is believed to proceed by way of a silicon-based Lewis acid generated in situ.



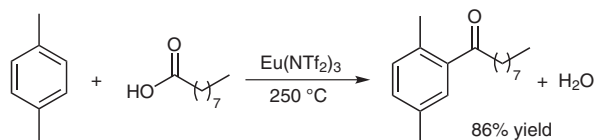
(E) Direct arene borylation with highly electrophilic boronium cations constitutes an efficient means to construct useful aryl–boron bonds in a single step.<sup>12</sup> When 9-BBN is treated with triflimide and then 1,8-bis(dimethylamino)naphthalene a relatively stable boronium salt complex results. The salt was fully characterized then applied to the borylation of several nitrogen heterocycles.



(F) Gold triflimide salts react with propargylic alcohols in the presence of substituted pyridine *N*-oxides to afford  $\alpha$ -oxo gold(III) carbene intermediates.<sup>13</sup> Intramolecular OH insertion affords functionalized oxetan-3-ones. The addition of stoichiometric amounts of triflimide prevents catalyst deactivation by the pyridine formed during oxidation.



(G) Historically, Friedel–Crafts acylation reactions are carried out with activated carboxylic acid derivatives and stoichiometric amounts of  $\text{AlCl}_3$ . Catalytic triflimide or triflimide-based Lewis acids have shown activity in intermolecular Friedel–Crafts acylations with carboxylic acids, producing water as the only stoichiometric byproduct.<sup>14</sup>



## References

- (1) J. Sun, *Triflimide*, In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, **2010**; <http://onlinelibrary.wiley.com/o/eros/articles/rn01222/frame.html>
- (2) Antoniotti, S.; Dalla, V.; Duñach, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 7860.
- (3) Foropoulos, J.; DesMarteau, D. *Inorg. Chem.* **1984**, *23*, 3720.
- (4) Mathieu, B.; Ghosez, L. *Tetrahedron* **2002**, *58*, 8219.
- (5) Conte, L.; Gambaretto, G.; Caporiccio, G.; Alessandrini, F.; Passerini, S. *J. Fluorine Chem.* **2004**, *125*, 243.
- (6) Earle, M. J.; Mcauley, J.; Ramani, A.; Seddon, R.; Thomson, J. M. US Patent 6,998,497, **2006**.
- (7) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.
- (8) Mundal, D. A.; Avetta, C. T.; Thomson, R. J. *Nature Chem.* **2010**, *2*, 294.
- (9) (a) Ryu, D.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388. (b) Canales, E.; Corey, E. J. *Org. Lett.* **2008**, *10*, 3271.
- (10) (a) Boxer, M. B.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 48. (b) Boxer, M. B.; Yamamoto, H. *Nat. Protoc.* **2006**, *1*, 2434.
- (11) (a) Inanaga, K.; Takasu, K.; Ihara, M. *J. Am. Chem. Soc.* **2005**, *127*, 3668. (b) Takasu, K.; Ishii, T.; Inanaga, K.; Ihara, M. *Org. Synth.* **2006**, *83*, 193.
- (12) Prokofjevs, A.; Kampf, J.; Vedejs, E. *Angew. Chem. Int. Ed.* **2011**, *50*, 2098.
- (13) (a) Ye, L.; He, W.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 8550. (b) Ye, L.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 3258.
- (14) Kawamura, M.; Cui, D.; Shimada, S. *Tetrahedron* **2006**, *62*, 9201.