SYNLETT
Spotlight 449

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

Aluminum Trifluoromethanesulfonate

Compiled by Maretha du Plessis

Maretha du Plessis was born in Wellington, South Africa, in 1988. She received her B.Sc. in 2009, her honours degree in 2010, and earlier in 2013 her M.Sc. in organic chemistry, all with distinction, from the University of the Free State. She is currently working towards her Ph.D. under the supervision of Professor B. C. B. Bezuidenhoudt at the University of the Free State.

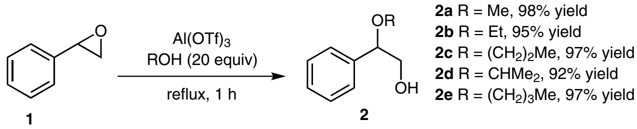
Faculty of Natural and Agricultural Sciences, University of the Free State, Bloemfontein 9300, South Africa
E-mail: 2006034538@ufs4life.ac.za

Introduction

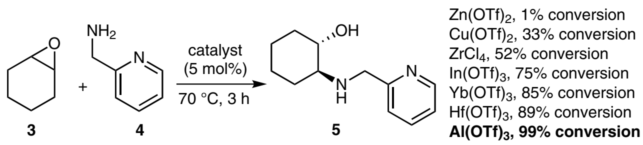
The synthesis of aluminum trifluoromethanesulfonate from aluminum trichloride and triflic acid was published by Olah et al.[1,2] in 1988. Aluminum triflate is a white solid with a high melting point[2] and acts as a strong, stable, oxophilic[3–5] Lewis acid that can easily be recycled and reused[6] due to its water-tolerant properties.[7] During initial investigations, aluminum trifluoromethanesulfonate was mainly used for Michael and Friedel–Crafts reactions, and it also functioned as a Lewis acid catalyst for the protection of alcohols, phenols, and thiophenols[8] with a variety of different protecting groups (i.e., methyl, ethyl, isopropyl, *tert*-butyl, acetyl, tetrahydropyranyl and tetrahydrofuranyl).[1,9,10] Recently, the utilization of aluminum trifluoromethanesulfonate has been studied in much more diversity, for example as a co-catalyst in metal-catalyzed reactions,[4,11] in the nucleophilic opening of epoxides,[5,12,13] cyclization,[14] substitution,[15] and other reactions.

Abstracts

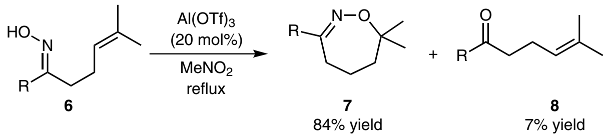
(A) Williams et al.[12] obtained excellent results (92–98% yield) in the ring opening of epoxides like styrene oxide with alcohols (ROH, R = C_1–C_4) and aluminum triflate to produce the monoethers of phenyl-substituted glycols. The ring opening of cyclohexene oxide also gave 83–89% yield utilizing only 0.002 mol% of triflate.



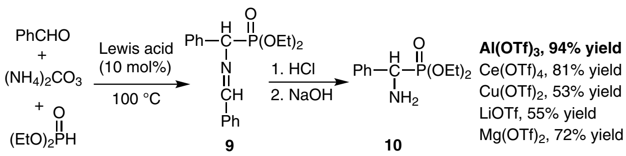
(B) Fringuelli et al.[5] and Williams et al.[13] extended the $Al(OTf)_3$-catalysed ring opening of epoxides to include the use of amines instead of alcohols and were able to isolate the aminoalcohols in good yield (75–90%). The opening of cyclohexene oxide with 2-picolylamine could be effected with $Al(OTf)_3$ at concentrations of 5 mol% leading to the product being obtained in 99% yield under solvent-free conditions.



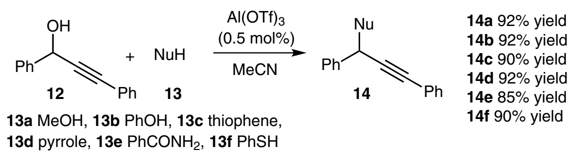
(C) Chaminade et al.[14] published the preparation of 1,2-oxaza heterocycles from unsaturated oximes through treatment of the substrate with different Lewis acid catalyst–solvent combinations. It was found that $Al(OTf)_3$ in nitromethane ($MeNO_2$) gave the best result for this transformation.



(D) Since naturally occurring 1-amino acids display a variety of biological activities and also act as plant-growth regulators and herbicides, Sobhani et al.[16] studied the synthesis of 1-aminophosphonates and found that $Al(OTf)_3$ could be applied as a catalyst in a one-pot synthesis of primary diethyl 1-aminophosphonates under solvent-free conditions.



(E) Gohain et al.[15] showed $Al(OTf)_3$ to be a highly efficient and relatively inexpensive catalyst for the direct nucleophilic substitution of propargylic alcohols forming carbon–carbon and carbon–heteroatom bonds.



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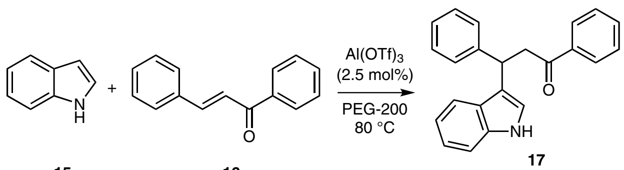
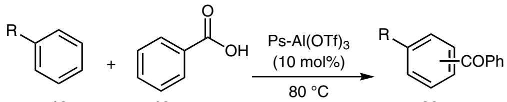
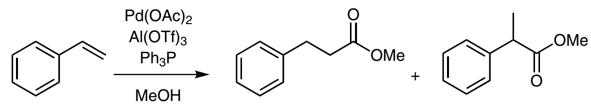
(F) Gohain et al.[17] reported a 'green' Friedel–Crafts, Michael-type addition of indole to α,β-unsaturated ketones catalyzed by $Al(OTf)_3$ in the recyclable solvent polyethylene glycol.



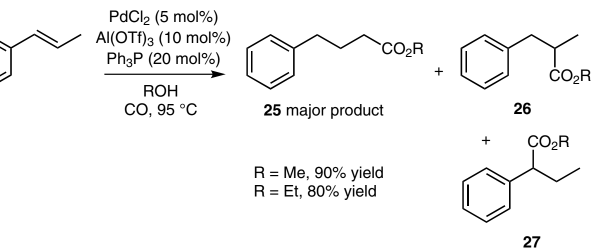
(G) Parvanak-Boroujeni and co-workers utilized polystyrene-supported aluminum triflate in the acylation of a range of aromatic substrates with benzoic acid and were able to obtain the corresponding benzophenones in excellent yields.[18]



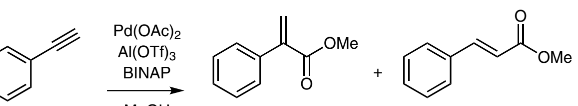
(H) Williams and co-workers discovered that aluminum triflate could be used as a highly active non-protic co-catalyst for the palladium-catalysed methoxycarbonylation of alkenes.[4] High conversions of up to 98% were obtained for the methoxycarbonylation of styrene with *l*/*b* ratios of up to 3:1. One of the main advantages of the Lewis acid co-catalyst is that it does not lead to phosphonium salt formation and depletion of the ligand, resulting in palladium 'fall-out' during these reactions.



(I) During the author's M.Sc. project, the utilization of $Al(OTf)_3$ as co-catalyst in alkoxycarbonylation was extended to include alkyl-substituted styrene substrates. In this regard, $PdCl_2$ was found to be more reactive than $Pd(OAc)_2$, and *trans*-*β*-methylstyrene could be transformed into its respective methyl and ethyl esters with up to 95% conversion, with the major products being linear in this instance.[19]



(J) The Williams group[11] found that the alkoxycarbonylation reaction could be extended to include alkynes when a bidentate ligand is utilized in the process. High conversions (100%) with very high *b*/*l* ratios (99:1) were obtained.



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