

SYNLETT Spotlight 118

Copper(II) Trifluoromethanesulfonate¹

Compiled by Manoj Kumar Gupta



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

M. K. Gupta was born in Uttar Pradesh state in India in 1978. He obtained his Bachelor's and Master's degrees in chemistry from Dr. Ram Manohar Lohiya Avadh University, Faizabad, Uttar Pradesh. He later completed a diploma course in Industrial Fermentation and Alcohol Technology from National Sugar Institute at Kanpur. After qualifying as a CSIR Junior Research Fellow, he joined the Director's research group at Indian Institute of Chemical Technology in Hyderabad, India. Currently, he is a second-year Ph.D. student in Dr. J. S. Yadav's research group. His research interest is focused on natural product synthesis, medicinal chemistry, peptide chemistry and development of novel synthetic methodologies.

Division of Organic Chemistry-I, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Fax +91(40)27160512; E-mail: mnj78@rediffmail.com; E-mail: gupta_iict@rediffmail.com

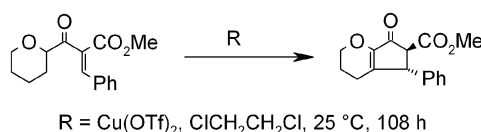
Introduction

Copper(II) trifluoromethanesulfonate is a mild and efficient catalyst and is commonly known as copper triflate. It is commercially available as a white powder and, when freshly prepared, it is in the form of a blue powder. It is prepared most conveniently from copper(II) carbonate and triflic acid (trifluoromethanesulfonic acid) in acetonitrile.² The freshly prepared salt is precipitated from Et₂O and is pale blue in colour. It is soluble in MeOH, EtOH, DMF, MeCN,

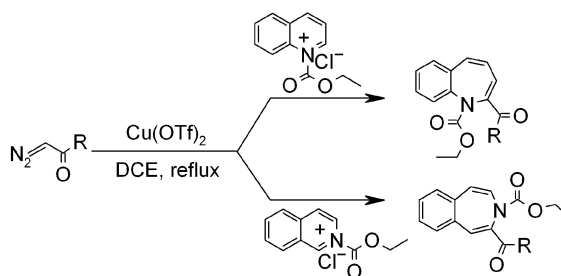
formamide, *i*-PrCN and acetone. It is moisture stable and can be handled in air for quick transfer. Pure samples are only mildly corrosive. It appears to be indefinitely stable in the absence of air, moisture and light. Copper triflate has been used extensively, effecting various organic transformations such as oxidative coupling,³ reactions of diazo-compounds,⁴ formation of oxazoles from ketones,⁵ and oxidation of alkyl radicals,² among others.⁶

Abstracts

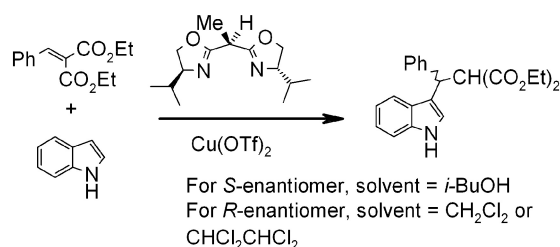
A) He et al. reported a mild and efficient copper(II) triflate-catalyzed procedure for the Nazarov cyclization of polarized divinyl ketones.⁷



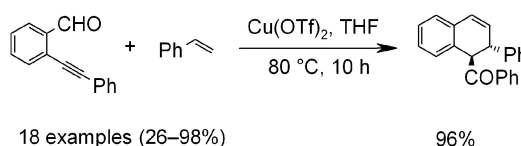
B) Our group reported unexpected ring expansion from activated quinoline and isoquinoline by using diazocarbonyl compounds via C–C insertion in the presence of 5 mol% of copper triflate to produce ethyl 1*H*-benzo[*b*]azepine-1-carboxylate and ethyl 3*H*-benzo[*d*]azepine-3-carboxylate, respectively, in excellent yields and with a high degree of selectivity.⁸ The products represent an important moiety in many pharmaceutically active naturally occurring molecules.^{9,10}



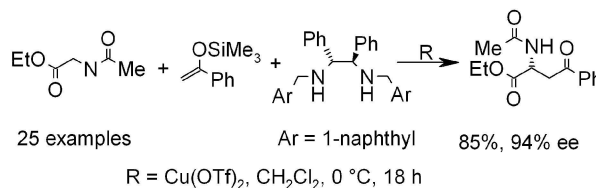
C) The combination of a bis(isopropylloxazole) and Cu(OTf)₂ proved to be an efficient catalyst in the asymmetric Friedel–Crafts reaction of indoles with arylidene malonates. In isobutanol, the *S*-enantiomer was obtained in up to 97% ee, while the opposite enantiomer was obtained in up to 78% ee in CH₂Cl₂ or 1,1,2,2-tetrachloroethane.¹¹



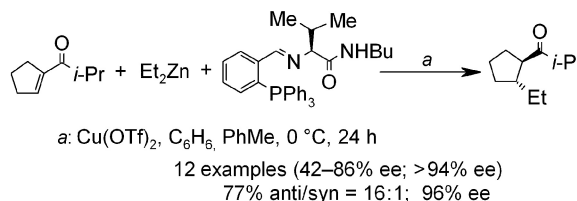
D) Asao and co-workers reported the [4+2] cycloaddition reaction between *o*-alkynyl(oxo)benzene and olefins in the presence of catalytic amount of Cu(OTf)₂. The reaction affords 1,2-dihydronaphthalene derivatives bearing an oxo function at the 1-position. The reaction proceeds most probably through the formation of benzo[*c*]pyrylium cupric ate complex.¹²



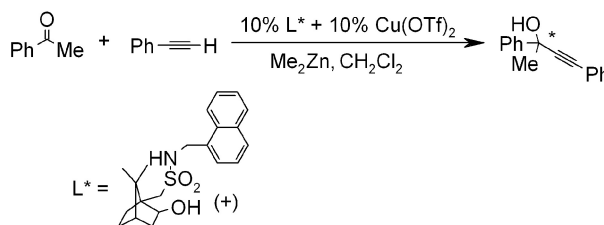
E) Kobayashi et al. developed catalytic asymmetric Mannich-type reactions of *N*-acyl esters with silyl enol ethers or alkyl vinyl ethers using Cu(OTf)₂-chiral diamine complexes as the catalyst.¹³ The reaction proceeded smoothly at 0 °C in most cases, and high yields and high diastereoselectivities were attained. This method is useful for the preparation of *N*-acetylated amino acid derivatives, which are often observed in biologically important compounds such as peptides and ceramide.¹⁴



F) Degrado et al. reported an efficient and highly selective Cu-catalyzed asymmetric conjugate addition of alkylzincs to trisubstituted cyclic enones. This transformation is catalyzed by Schiff base derivatives of a single amino acid that is commercially available and inexpensive (*L*- or *D*-valine). The ligand can be prepared and used directly, without isolation or purification, to afford products with high enantioselectivities.¹⁵



G) Lu et al. reported the smooth addition of phenylacetylene to aromatic ketones in the presence of catalytic amounts of Cu(OTf)₂ and camphorsulphonamide. The corresponding tertiary propargylic alcohols were obtained in high yields and with up to 97% ee. This reaction represents a highly enantioselective catalytic addition of dialkynyl zinc reagents to simple ketones.¹⁶



References

- (1) IICT Communication No. 050105
- (2) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.
- (3) Kobayashi, Y.; Taguchi, T.; Tokuno, E. *Tetrahedron Lett.* **1977**, *18*, 3741.
- (4) (a) Andrist, A. H.; Angello, R. M.; Wolfe, D. C. *J. Org. Chem.* **1978**, *43*, 3422. (b) Hubert, A. J.; Feron, A.; Warin, R.; Teyssie, P. *Tetrahedron Lett.* **1976**, *17*, 1317.
- (5) Nagayoshi, K.; Sato, T. *Chem. Lett.* **1983**, 1355.
- (6) (a) Yadav, J. S.; Reddy, B. V. S.; Baishya, G.; Narsaiah, A. V. *Chem. Lett.* **2005**, *34*, 102. (b) Yadav, J. S.; Reddy, B. V. S.; Satheesh, G. *Tetrahedron Lett.* **2003**, *44*, 8331. (c) Paraskar, A. S.; Dewkar, G. K.; Sudalai, A. *Tetrahedron Lett.* **2003**, *44*, 3305.
- (7) He, W.; Sun, X.; Frontoer, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 14278.
- (8) Yadav, J. S.; Reddy, B. V. S.; Gupta, M. K.; Prabhakar, A.; Jagadeesh, B. *Chem. Commun.* **2004**, 2124.
- (9) (a) May, J. A.; Zeidan, R. K.; Stoltz, B. M. *Tetrahedron Lett.* **2003**, *44*, 1203. (b) Guillou, C.; Beunard, J.-L.; Gras, E.; Thal, C. *Angew. Chem. Int. Ed.* **2001**, *40*, 4745. (c) Sha, C.-K.; Hong, A. W.; Huang, C.-M. *Org. Lett.* **2001**, *3*, 2177. (d) Jin, J.; Weinreb, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 2050.
- (10) (a) Johnson, R. E.; Busacca, C. A. (Sterling Drug, Inc.), US Patent 5098901, *Chem. Abstr.* **1992**, *117*, 7949j. (b) Croisier, P.; Rodriguez, L. (UCB, S.A.), Ger. Offen. 2733868 and 2733869, *Chem. Abstr.* **1978**, *88*, 152455g and 152456h. (c) Meschino, J. A. (McNeil Laboratories, Inc.); US Patent 3894072, *Chem. Abstr.* **1975**, *83*, 114031e.
- (11) Zhou, J.; Tang, Y. *Chem. Commun.* **2004**, 432.
- (12) Asao, A.; Kashara, T.; Yamamoto, Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 3504.
- (13) Kobayashi, S.; Matsubara, R.; Nakamura, Y.; Kitagawa, H.; Sugiura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2507.
- (14) (a) Helms, G. L.; Moore, R. E.; Niemczura, W. P.; Patterson, G. L. M.; Tomer, K. B.; Gross, M. L. *J. Org. Chem.* **1988**, *53*, 1298. (b) Kolter, T.; Sandhoff, K. *Angew. Chem. Int. Ed.* **1999**, *38*, 1532. (c) Dickson, R. C. *Annu. Rev. Biochem.* **1998**, *67*, 27. (d) von Dohren, H.; Keller, U.; Vater, J.; Zoehrer, R. *Chem. Rev.* **1997**, *97*, 2675.
- (15) Degrado, S. J.; Mizutani, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13362.
- (16) Lu, G.; Li, X.; Jia, X.; Chan, W. L.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 5057.