SYNLETT
Spotlight 142

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

Copper(II) Acetylacetonate: An Inexpensive Multifunctional Catalyst

Compiled by Antonio Carlos Bender Burtoloso

Antonio Carlos B. Burtoloso was born in Petrópolis (RJ), Brazil in 1976. He completed his B.Sc. in 2001 and his M.Sc. in 2002 at the Federal University of Rio de Janeiro. In 2002, he moved to Campinas (SP)-Brazil, where he is currently working for his Ph.D. under the supervision of Prof. Carlos Roque D. Correia at the State University of Campinas. His Ph.D. work is based on the investigation of new methodologies for the stereoselective synthesis of azetidines and azetidine alkaloids.

Instituto de Química, Universidade Estadual de Campinas, UNICAMP, C.P. 6154, CEP. 13083-970, Campinas, São Paulo, Brasil
E-mail: burtoloso@iqm.unicamp; E-mail: burtoloso@hotmail.com

Introduction

Copper(II) acetylacetonate [$Cu(acac)_2$] (Figure 1) is a soluble copper catalyst that has been widely employed in many types of reactions. It can be readily and easily prepared[1] from the reaction of acetylacetone with copper(II) sulfate in aqueous basic solution, and is isolated as a blue solid.

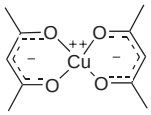
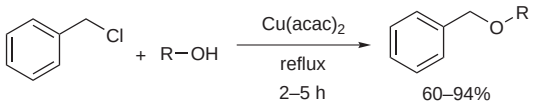


Figure 1 Copper(II) acetylacetonate

Although $Cu(acac)_2$ has been mostly used as catalyst in different reactions involving diazocompounds,[2] it is also described as a catalyst for other types of reactions such as benzylation of alcohols,[3] reduction of aromatic nitro compounds,[4] aziridination,[5,6] and epoxidation.[6] The easy access and low cost of copper(II) acetylacetonate, together with its varied applications as catalyst, make $Cu(acac)_2$ a powerful reagent in organic synthesis.

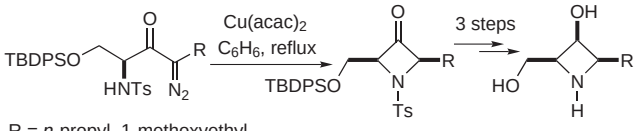
Abstract

(A) *Benzylation of Alcohols:*
Sirkecioglu and co-workers[3] have found that selective O-benzylation of primary hydroxy compounds can be performed in the presence of catalytic amounts of $Cu(acac)_2$ and benzyl chloride in good to high yields.



Alcohol (R-OH): *n*-octyl alcohol, cyclohexanol, cholesterol, benzyl alcohol, 4-hydroxybenzyl alcohol, 4-methoxybenzyl alcohol, ethylene glycol, propylene glycol, glycerol, 2-ethyl-1,3-hexanediol.

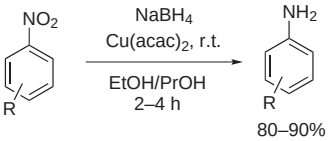
(B) *X–H Insertion Reactions:*
$Cu(acac)_2$ can catalyze many X–H (X = N, O, S, P, Se) insertion reactions. This scheme illustrates a recent example of an intramolecular N–H insertion reaction from diazoketones for the construction of fully substituted azetidines by Correia and Burtoloso.[7]



R = *n*-propyl, 1-methoxyethyl, methyl

61–65%
single isomers

(C) *Reduction of Aromatic Nitro Compounds:*
Hanaya and co-workers[4] reported a protocol for the reduction of aromatic nitro compounds to amines in high yields and in short reaction times in the presence of $NaBH_4$ and $Cu(acac)_2$ as catalyst.



80–90%

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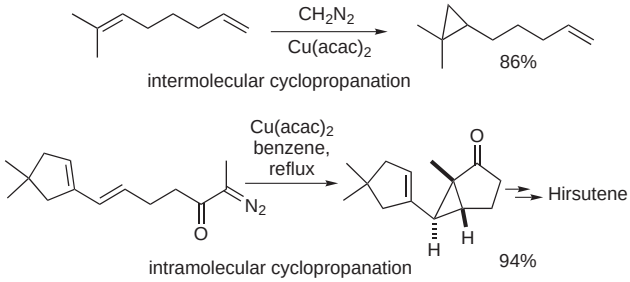
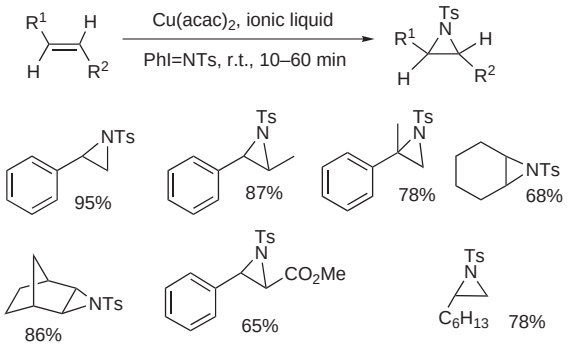
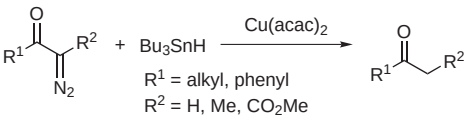
(D) *Cyclopropanation:*
$Cu(acac)_2$ catalyzes both intermolecular[8] and intramolecular[9] cyclopropanation of double bonds with diazo compounds.



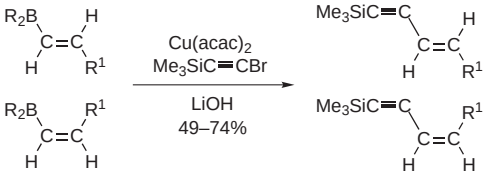
(E) *Aziridination of Olefins:*
Kantam and co-workers[5] have reported a novel recyclable catalytic system for aziridination of olefins using PhI=NTs in the presence of $Cu(acac)_2$ immobilized in ionic liquids. This methodology furnishes aziridines in good yields and with fast reaction rates.



(F) *Reduction of α-Diazo Carbonyl Compounds:*
Diazo carbonyl compounds are reduced in the presence of $Cu(acac)_2$ and Bu_3SnH.[10]



(G) *Synthesis of Conjugated Enynes from Alkenyldialkylboranes:*
The cross-coupling reaction of (*E*)- and (*Z*)-1-alkenyldialkylboranes with (trimethylsilyl)ethynyl bromide in the presence of $Cu(acac)_2$ furnishes conjugated enynes under very mild conditions.[11]



References

(1) Preparation of $Cu(acac)_2$: Copper(II) acetylacetonate was prepared by reaction of $CuSO_4$ with equimolar quantities of acetylacetone and NaOH in aqueous solution. After the subsequent addition of acetylacetone (1 equiv) and $CuSO_4 \cdot H_2O$ (0.5 equiv) in basic solution with stirring, a blue precipitate was obtained. The precipitate was filtered, dried in vacuum and recrystallized from glacial AcOH to give blue needles: (a) Graddon, D. P. *J. Inorg. Nucl. Chem.* **1960**, *14*, 161. (b) For another experimental procedure, see: Peacock, R. D. *J. Chem. Educ.*; **1971**, 48, 133.

(2) For many applications of $Cu(acac)_2$ in reactions with diazo compounds, see: Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds From Cyclopropanes to Ylides*; Wiley: New York, **1998**.

(3) Sirkecioglu, O.; Karliga, B.; Talinli, N. *Tetrahedron Lett.* **2003**, *44*, 8483.

(4) Hanaya, K.; Muramatsu, T.; Kudo, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2409.

(5) Kantam, M. L.; Kavita, V. N. B.; Haritha, Y. *Synlett* **2004**, 525.

(6) Aggarwal, V. K. *Synlett* **1998**, 329.

(7) Burtoloso, A. C. B.; Correia, C. R. D. *Tetrahedron Lett.* **2004**, *45*, 3355.

(8) Solomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.

(9) Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6353.

(10) Tan, Z.; Qu, Z.; Chen, B.; Wang, J. *Tetrahedron* **2000**, *56*, 7457.

(11) Hoshi, M.; Shirakawa, K. *Synlett* **2002**, 1101.