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Copper(II) Acetylacetonate: An Inexpensive Multifunctional Catalyst

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

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Introduction

Copper(II) acetylacetonate $[\text{Cu}(\text{acac})_2]$ (Figure 1) is a soluble copper catalyst that has been widely employed in many types of reactions. It can be readily and easily prepared¹ 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 $\text{Cu}(\text{acac})_2$ 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 $\text{Cu}(\text{acac})_2$ a powerful reagent in organic synthesis.

Abstract

(A) Benzylation of Alcohols:

Sirkecioglu and co-workers³ have found that selective O-benylation of primary hydroxy compounds can be performed in the presence of catalytic amounts of $\text{Cu}(\text{acac})_2$ 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:

$\text{Cu}(\text{acac})_2$ 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

(C) Reduction of Aromatic Nitro Compounds:

Hanaya and co-workers⁴ 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 $\text{Cu}(\text{acac})_2$ as catalyst.

(D) Cyclopropanation:

$\text{Cu}(\text{acac})_2$ catalyzes both intermolecular⁸ and intramolecular⁹ cyclopropanation of double bonds with diazo compounds.

(E) Aziridination of Olefins:

Kantam and co-workers³ have reported a novel recyclable catalytic system for aziridination of olefins using $\text{PhI}=\text{NTs}$ in the presence of $\text{Cu}(\text{acac})_2$ 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 $\text{Cu}(\text{acac})_2$ 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 $\text{Cu}(\text{acac})_2$ furnishes conjugated enynes under very mild conditions.¹¹

References

- (1) Preparation of $\text{Cu}(\text{acac})_2$: 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 $\text{CuSO}_4\cdot\text{H}_2\text{O}$ (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.
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