SYNLETT Spotlight

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

Copper(II) Bromide

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Dedicated to the memory of my father, Sergey Makarov, M.D.

Aliis inserviendo ipse consumor

Introduction

Copper(II) bromide is a black crystalline powder with a melting point of 498 °C and a boiling point of 900 °C. It is soluble in water, alcohol and acetone; however, it is insoluble in benzene and ether. Copper(II) bromide can be obtained by the reaction of copper(II) oxide with hydrobromic acid or by the reaction of metallic copper with bromine.

Copper(II) bromide is a powerful brominating agent.\(^1\) It is also used as a catalyst in many organic reactions, including alkylation,\(^2\) amination,\(^3\) oxidation,\(^4\) multi-component reactions,\(^5\) and for the synthesis of ethers\(^6\) or esters.\(^7\)

Abstracts

(A) Shirinian and co-workers developed a regio- and chemoselective method for the bromination of 2,3-diarylcyclopent-2-en-1-ones with copper(II) bromide. Different brominated products can be obtained depending on the reaction conditions utilized in case of 2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-enone (1). The formation of 2 and 3 is suggested to proceed via the reaction of in situ generated enolates with cationic Cu–Br species while 4a and 4b are formed by S$_2$Ar.\(^8\)

(B) Zhou et al. described a mild and efficient method for the oxidation–bromination of isochromans 5 to afford the corresponding 2-(2-bromoethyl)benzaldehydes 6 in one step with an excess of copper(II) bromide.\(^9\)

(C) Recently, a green generic approach to complex α-amino carboxyls 8 via the CuBr$_2$-catalyzed coupling of carboxyls 7 and diverse secondary amines was described. The transformation is proposed to proceed via an α-bromo carboxyl species. The practical utility of this transformation was highlighted by one-step syntheses of two high-profile pharmaceutical agents, Plavix and amfepramone.\(^10\)
(D) Wang and co-workers reported a simple protocol for the synthesis of symmetric and unsymmetric (E)-2-ene-1,4-diones 10 by the reaction of acetophenones 9 with molecular iodine. The use of copper(II) bromide dramatically improved the yields of the desired products.11

(E) Chi and co-workers reported a CuBr2-catalyzed enantioselective oxidative cross-coupling reaction of tertiary amines 11 with aldehydes in the presence of a proline derivative as a chiral catalyst. The unstable aminaldehydes were reduced in situ by sodium borohydride to afford γ-amino alcohols 12 with good enantioselectivity.12

(F) An efficient and inexpensive Fe/CuBr2-catalyzed benzyla- tion of arenes and thiophenes under mild conditions was described. The method provides diarylmethanes 13 with good to excellent yields using the readily available benzyl alcohol 14 as a benzylating agent.13

(G) Yin and co-workers reported a mild method for the preparation of polysubstituted furans 16 via copper(II) bromide catalyzed rearrangement of furans 15. This protocol provides an efficient access to tetrasubstituted furans, which are usually synthesized through multi-step procedures utilizing harsher reaction conditions.14

(H) Deng and co-workers developed a method for copper(II) bromide promoted tetrahydrofuranylation of alcohols 17 with unsubstituted tetrahydrofuran 18. The protocol might be used for the protection of hydroxyl groups.15

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References


