SYNLETT
Spotlight 213

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

Copper(I) Iodide

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Introduction

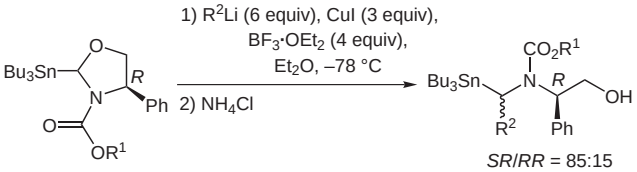
The first recorded attempt at making an organocopper was Buckton's use of diethylzinc on CuCl in the 1850s.[1] From that time, copper halides and consequently CuI have found widespread use in synthetic organic chemistry. Indeed, copper iodide, also called cuprous iodide, acts as a useful precursor of organocopper compounds which due to their unique chemoselectivity and reactivity occupy a special place in organic synthesis.[2–4] Furthermore, the effectiveness of CuI as catalyst or co-catalyst for cross-coupling reactions has been widely reported in the literature.[5,6]

The utilisation of CuI also encompasses a broad range of chemical transformations like construction of heterocycles,[7–9] iodination reations,[10] click chemistry[11] or multicomponent coupling reactions.[12–14]

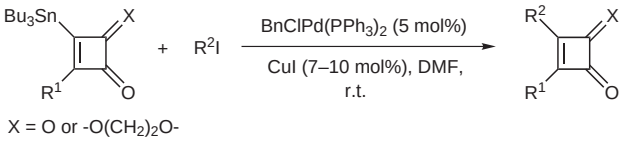
CuI is commercially available as an off-white solid but samples with time are often tan due to impurities. A dissolution–precipitation process with water in the presence of NaI or KI is used to purify CuI.[15,16] The colourless CuI is then stored under argon and protected from light to avoid decomposition.

Abstracts

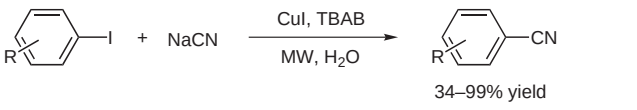
(A) *Preparation of Chiral Tributylstannyl-α-Amino Alcohols:*
Ring-opening of 2-tributylstannyloxazolidines by organocopper reagents in the presence of $BF_3{\cdot}OEt_2$ affords the corresponding tributylstannyl-α-amino alcohols in moderate to excellent yields.[17] This reaction proceeds in a diastereoselective fashion in favour of the *anti* isomer (dr close to 85:15).



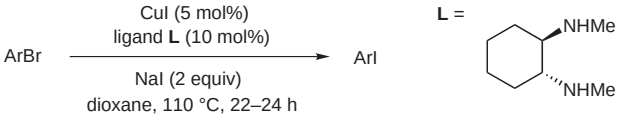
(B) *Modified Stille Cross-Coupling:*
In 1990, Liebeskind et al. highlighted the beneficial effect of catalytic copper iodide on the Stille reaction.[18] 3-Stannylcyclobutenediones and stannylcyclobutenedione monoacetals undergo efficient palladium-catalysed cross-coupling reactions with organic iodides.



(C) *Preparation of Aryl Nitriles:*
A rapid cyanation of aryl iodides under microwave activation occurs by using inexpensive NaCN as the cyanide source, and CuI as an additive. The reaction is performed in water, and tetrabutylammonium bromide is used as a phase-transfer catalyst.[19]



(D) *Iodination Reaction:*
In the presence of a catalyst system comprising CuI and a 1,2- or 1,3-diamine ligand, aryl or heteroaryl bromides are converted into the corresponding iodides in excellent yields (93–100%).[10] This method can also be applied to halogen exchange in vinyl bromides.



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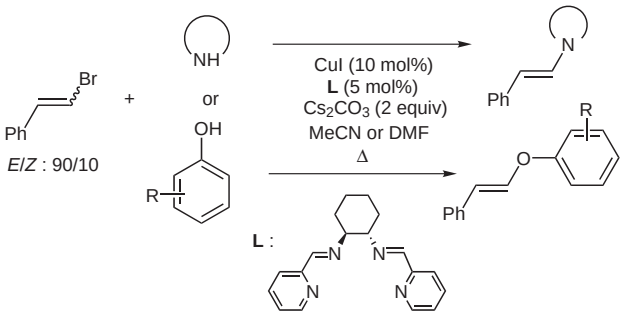
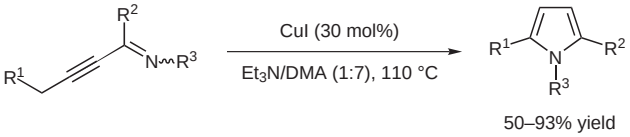
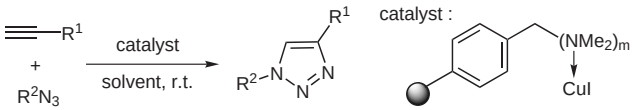
(E) *Vinylation Reaction:*
CuI, in combination with tetradentate ligand **L**, represents a remarkable catalyst system for vinylation reactions.[20] Under this set of conditions, both azoles and substituted phenols can be coupled with β-bromostyrene. While this protocol is effective for the vinylation of (*E*)-β-bromostyrene, the *Z*-isomer leads mainly to byproducts due to its lower reactivity.



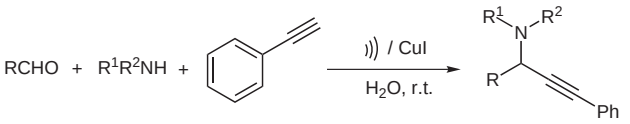
(F) *Construction of Substituted Pyrroles:*
A general and practical method for the construction of 2-monosubstituted and 2,5-disubstituted pyrroles via a CuI-assisted cycloisomerisation of readily available alkynyl imines has been recently reported.[7] This approach has also been extended to the synthesis of fused aromatic heterocycles containing a pyrrole ring.



(G) *Huisgen Cycloaddition:*
Fixation of CuI on Amberlyst A-21 furnishes an efficient heterogeneous catalytic system for the Huisgen's [3+2] cycloaddition between azides and alkynes. Furthermore, this polymer-supported catalyst can be reused for several cycles without decreased reaction yields in triazoles.[21]



(H) *Synthesis of Propargylamines:*
Propargylamines can be synthesised through a three-component coupling reaction of an aldehyde, an alkyne and an amine under ultrasound conditions.[14] Addition of CuI, as a catalyst, dramatically increases the yields (up to 98% yield).



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