

copper(I), (II), and (III) oxidation states was operating (Scheme 12.2, Eq. 2).^[6b-d] ¹³C NMR kinetics experiments have also been recently reported supporting a Cu(I)/Cu(II)/Cu(III)/Cu(I) cycle (Eq. 3).^[6e]

In the presence of copper(I), terminal alkynes also underwent the oxidative homocoupling reaction to give symmetrical 1,3-diynes (in the presence of an equivalent or excess amount of copper(II) acetate) (Eglinton coupling reaction) (Scheme 12.3).^[8]

Beifuss and coworkers studied the Glaser-type reaction under different conditions and found that the yields of 1,3-diynes greatly depended on the nature of the base and ligand.^[9] The optimal catalytic system was found to consist of copper(I) chloride (2 mol %), bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,4-diazabicyclo[2.2.2]octane (DABCO) (1 equiv), and TMEDA (1.5 mol %) as the ligand. Aromatic alkynes could be oxidatively homocoupled in high yields at room temperature in acetonitrile (Scheme 12.4,

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