

Copper-Catalyzed Hydroxysulfidation of Alkenes using Disulfides

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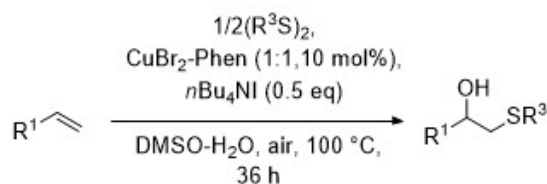
Transition metal-catalyzed carbon-sulfur bond formation is an important methodology in organic syntheses, and numerous procedures have been developed. In particular, herein produced organosulfur compounds are investigated for use as a convenient intermediate. The introduction of hydroxyl and sulfide groups into carbon double bonds has been reported by numerous researchers.

On the contrary, a reaction of alkenes with disulfides in AcOH affords β -acetoxysulfides whereas the synthesis of β -hydroxysulfides by a direct introduction of a hydroxyl-group cannot be achieved.¹ Therefore, the development of a transition metal-catalysis method introducing a free hydroxyl to an alkene is realized. In addition, a generating control of an active species such as a thiyl radical or a sulfenyl cation is an attractive synthetic method.

To solve the problem, it is required that a reaction proceeds via a radical process by a metal-catalyzed single-electron transfer. A combination of copper catalyst and additives was screened under aerobic conditions. Fortunately, a copper-catalyzed hydroxysulfenylation of alkenes was achieved using disulfides in the presence of *n*-Bu₄NI and H₂O. The procedure smoothly proceeded in air, and the corresponding β -hydroxysulfides were obtained with *regio*- and *anti*-selectivity in good yields.

Similarly, a reaction using diselenides effectively produced the expected β -hydroxyselenides. These reactions could consume both chalcogenide groups on dichalcogenides. The procedure also worked for hydrosulfenylation using thiols.

Herein, the developed methodology will be described.



1) N. Taniguchi, *J. Org. Chem.* **2006**, 71, 7874.