Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

gold catalysis oxidative rearrangement oxonium ylides M. XU, T.-T. REN, C.-Y. LI* (ZHEJIANG SCI-TECH UNIVERSITY, HANGZHOU, P. R. OF CHINA)

Gold-Catalyzed Oxidative Rearrangement of Homopropargylic Ether via Oxonium Ylide *Org. Lett.* **2012**, *14*, 4902–4905.

Homopropargylic Ether Rearrangement via Gold Catalysis

Significance: Gold catalysis has emerged as a powerful platform to conduct complex organic transformations. Specifically, the implementation of gold carbenoids has shown great promise in synthetic planning. These useful intermediates offer a convenient alternative to generate metal carbenes which are traditionally obtained from diazo compounds. The authors utilize these intermediates to synthesize α, β -unsaturated carbonyl compounds from homopropargylic ethers.

SYNFACTS Contributors: Mark Lautens, David A. Petrone Synfacts 2013, 9(1), 0060 Published online: 17.12.2012 **DOI:** 10.1055/s-0032-1317758; **Reg-No.:** L16012SF

Comment: The authors report a silver-assisted gold(I)-catalyzed carbonyl synthesis. In an effort to obtain cyclobutanes **3** via a [1,2]-shift mechanism (path d), the authors unexpectingly obtained the corresponding α,β -unsaturated carbonyl compounds **2**. Control experiments show that neither IMesAuCl, nor AgNTf₂ or HNTf₂ alone could catalyze the reaction. The scope of the reported reaction is quite broad; however, yields are generally moderate to good. In some instances cyclobutanones are obtained as the major product.