

(Z)-Alkenyl Sulfides

Convenient and Efficient Diastereoselective Preparation of Functionalized Z-Alkenyl Sulfides

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Abstract: We have developed an efficient and convenient regio- and stereoselective reduction of the alkynyl sulfides with pinacolborane in the presence of copper(I) chloride to produce (Z)-alkenyl sulfides in good and very good yields. The function-

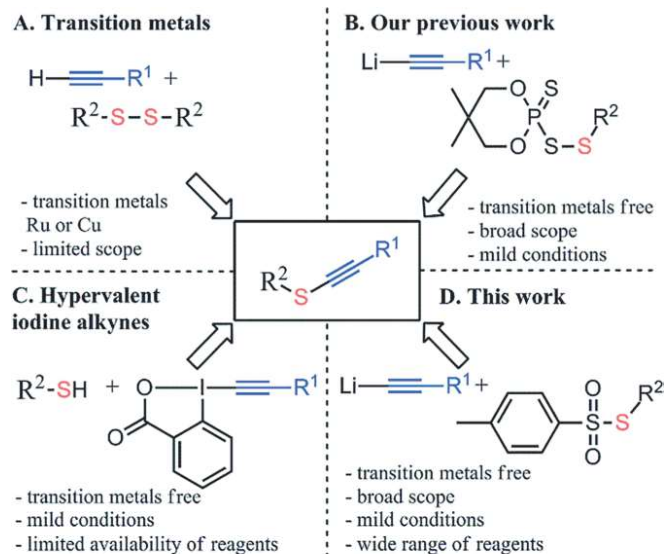
alized alkynyl sulfides are readily available based on the reaction of lithium acetylides with thiosylates under mild conditions.

Introduction

The continuously increasing range of applications for organo-sulfur compounds has expanded into different fields, from organic synthesis to material science.^[1] Among S-containing building blocks, one unique functional group is alkynyl sulfides, which contain two carbon atoms connected by a triple bond that are directly substituted with a sulfur atom. The reactivity of this functionality can be useful in organic synthesis. Alkynes have been applied in bulk chemical syntheses based on acetylene gas,^[2] in the stereoselective construction of the carbon backbones of natural products^[3] and in the metal complex-catalyzed cyclization reactions.^[4] In short, alkynyl sulfides can bring together the advantages of sulfur atoms with the exceptionally rich chemistry of alkynes.

Reported methods for the preparation of alkynyl sulfides include reactions based on transition-metal catalysts, such as the copper-catalyzed carbon sulfur coupling between terminal alkynes and disulfides^[5] or the use of catalytic rhodium for C–S bond formation by C–H and S–S bond metathesis^[6] (Scheme 1). Both alkyne and thiol groups are inherently nucleophilic, thus the umpolung of one of them is necessary for the construction of an alkynyl sulfide. This often requires the use of unselective reagents and harsh reaction conditions, which are not always compatible with sensitive functional groups.^[7] Recently, Waser and co-workers developed a thiol-alkynylation procedure that uses hypervalent iodine (ethynylbenziodoxolone, EBX) as the alkyne transfer reagent.^[8] This method is highly chemoselective, and a wide range of functional groups are tolerated under the developed conditions. However, the problems associated with

the preparation of the hypervalent iodine alkyne transfer reagents are the major disadvantage of the designed transformation. There are also scattered examples in the literature of alkynyl sulfides preparation based on the reaction of thiosylates with lithium acetylides.^[9,10b] Other practical procedures involve the reaction of a lithium acetylide and an activated thiol or disulfide.^[10]



Scheme 1. Previously reported methods for the synthesis of alkynyl sulfides (A–C) and our newly developed approach (D).

Results and Discussion

Previously, we demonstrated the synthesis of functionalized alkynyl sulfides based on the reaction of lithium acetylides with 5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-disulfanyl derivatives.^[11] These disulfanyl derivatives of phosphorodithioic acid are also convenient substrates for the preparation of α -sulfenylated carbonyl compounds,^[12] functionalized phosphorothioates^[13] as well as symmetrical and unsymmetrical trisulfanes.^[14] The above transformations are based on the elec-

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