COPPER CATALYZED 1, 4-BROOK REARRANGEMENT OF \(\alpha, \beta\)-UNSATURATED ACYLSILANE

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Since its discovery in 1958,[1] the Brook rearrangement has been widely used in organic synthesis.[2] Among the multiple possibilities of this rearrangement, the regioselective formation of silyl enol ethers was initially reported in the late 60’s.[3] Among the few reported examples of 1,4-Brook rearrangement on silyl enol ethers,[4] only one of them used copper catalysis,[5] and none of them has been applied to \(\alpha, \beta\)-unsaturated acylsilane

We propose hereby the extension of 1,4-Brook rearrangement to \(\alpha, \beta\)-unsaturated acylsilane through the catalytic addition of a copper-silicon species. Such addition generates a nucleophilic copper intermediate, which will eventually trap an electrophilic species, e.g. a proton in this work. In addition, we highlight the selectivity towards the 1,4-rearrangement as no 1,2-Brook rearrangement is observed.

This reaction allows us to obtain a stereogenic center, moreover the nucleophilic copper intermediate formed allows us to consider the use of other electrophiles such as allylic halides, carbonyl electrophiles (acyl halides, ketones,…) and even a dual catalysis process with palladium.