Nickel-Catalysed Reductive Cross-Coupling of Xanthate Esters and Iodoarenes

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One of the most frequently occurring class of compounds in nature are alcohols and thus their functionalization, in particular in C−C bond formation is very desirable. The comparatively low reactivity of alcohols in cross-coupling reactions often necessitates prefunctionalization.

An example for prefunctionalized alcohols used in C−C cross-coupling reactions are xanthate esters, which can be easily accessed together with a base, carbon disulfide and a alkyl halide. Typical cross-coupling reactions of xanthates are mediated by either organic radicals or a Ni(I) species.[1, 2] For the activation by organic radicals, radical precursors and possibly a photocatalyst are required. Activation by reduction with Ni(I) species is until now only possible by usage of aryl zinc reagents as coupling partners that lead to a diminished functional group tolerance.[3]

A recently reported C−S coupling of xanthates with acyl chlorides to from thioesters describes the activation of the xanthate ester by a Ni(I) species generated by the reduction of a Ni(II) precatalyst with zinc metal.[4] Application of these conditions to O-benzyl xanthates enables the direct coupling with iodoarenes to form diarylmethanes in good yields. (Figure 1)

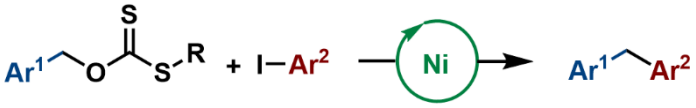

Figure 1. Nickel-catalyzed cross-coupling of xanthate esters and iodoarenes.

This cross-coupling reaction features a good functional group tolerance and catalyst loading as low as 1.5 mol% that is uncommon in reductive nickel-catalyzed transformations.

[1] B. A. Vara, N. R. Patel, G. A. Molander, *ACS Catal*. **2017**, *7*, 3955. [2] A. Cai, W. Yan, W. Liu, *J. Am. Chem. Soc.* **2021**, *143*, 9952. [3] J. J. Moneith, K. Scotchburn, L. R. Mills, S. A. L. Rousseaux, *Org. Lett.* **2022**, *24*, 619. [4] L. Tai, L. Chen, Y. Shi, L.-A. Chen, *Org. Chem. Front.* **2023**, *10*, 2505.