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Tetrahedron Letters 46 (2005) 6247–6251

Tetrahedron Letters

# Barbier coupling in water: $SnCl_2$-mediated and $Co(acac)_2$-catalyzed allylation of carbonyls

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Received 11 May 2005; revised 5 July 2005; accepted 14 July 2005

**Abstract**—$Co(acac)_2{\cdot}2H_2O$ efficiently catalyzes $SnCl_2$-mediated Barbier coupling in water between carbonyls, including aromatic, aliphatic and α,β-unsaturated aldehydes, ketones, sugars and allyl bromide to afford the corresponding homoallylic alcohols in high yields. The catalyst was reused for several cycles with consistent activity.

The Barbier reaction[1] is a century old C–C bond forming reaction involving a coupling reaction between a carbonyl function and an organic halide mediated by a metal to afford the corresponding alcohol. Its synthetic utility was overtaken mainly by Grignard and related organometallic reactions, largely because the classical Barbier reactions suffered from the problems of interference from a host of side reactions especially reductions and couplings (cf. pinacol coupling of carbonyls and Wurtz coupling of halides)[2] in organic solvents. Significantly, if it is carried out in an aqueous medium, the desired product is obtained, almost quantitatively, if not exclusively. This realization gained momentum through the elegant contributions of Luche,[3] Nakami,[4] Benezra,[5] Li and Chan,[2,6] Whitesides,[7] Roy[8] and Liu and Guo.[9] An important incentive in this development is that the solvent water satisfies the demands of 'Green Chemistry.'[10] The developments in Barbier reactions in water are: (i) a large number of reagents and reaction protocols have been developed for the synthesis of homoallylic alcohols,[3–9] (ii) many metals viz. aluminium,[11] indium,[6a,12] antimony,[6g] bismuth,[13] lead,[14] manganese,[6e] magnesium,[6f] zinc,[15] tin,[2,16] cadmium,[17] gallium[18] and copper[9a] have been reported to be effective. Being heterogeneous in nature, metal-mediated reactions often pose operational problems (e.g., stirring), in addition, the conversion of starting materials to the products can be incomplete presumably because of passivity of the catalyst caused by oxo or hydroxo metal coating in the course of the reaction. The use of hydrobromic acid[4a,b] or ultrasonication together with saturated aqueous $NH_4Cl$/THF[3] to activate the metal, improves the yields. Our experience in catalytic organic transformations[19] in conjunction with information in recent publications[2–9,11–18] on metal mediated C–C bond forming reactions, suggested to us that a combination of a water-soluble reductive salt (e.g., $SnCl_2$) as a mediator and an appropriately water soluble, redox active, reusable metal complex as the catalyst would perhaps serve as a general activator for the metal. The bimetallic nature of the reagent and the significant effect of water to facilitate the reaction by in situ generation of reactive hydrated/hydroxyl organotin species are important. A suitable catalyst would be cost effective, reusable over several cycles of reactions and have appreciable shelf life, some solubility in water without decomposition or hydrolysis and easily accessible variable oxidation states. An appropriate catalyst is essential since in water, $SnCl_2$ alone cannot mediate the desired reaction.

Four recent reports using Pd(II),[20] Cu(II)[8a,9a] or Ti(III)[9b] as efficient catalysts are of direct relevance to the present work. However, Pd and Ti based catalysts are expensive, the former also needing biphasic conditions, while $TiCl_3$ has inherent stability problems and requires careful handling. The Cu(II) catalyzed reactions were conducted under nitrogen since the active catalyst Cu(I) is prone to easy oxidation. $TiCl_3$ is not efficient for ketones[9b] and Cu(II) is poor in allylation of aldehydes, RCHO, with R being cinnamyl, *n*-hexyl or

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*Keywords*: Cobalt(II) acetylacetonate; Allylation; Water; Carbonyl; Ketones; Sugars.

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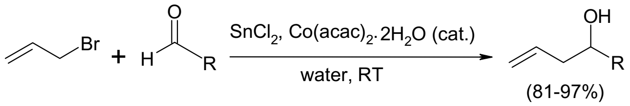
doi:10.1016/j.tetlet.2005.07.060

2-furyl.[9a] Moreover, it is not clear if carbohydrate allylation would be possible with these catalysts.

We now disclose our results on the Barbier allylation of a variety of substrates using $SnCl_2/Co(acac)_2·2H_2O$ as the reagent system.[21] Incidentally, we have reported a very easy access[22] to metal acetylacetonates including $Co(acac)_2·2H_2O$. The chosen catalyst has easily accessible variable oxidation states, the required solubility in water with no apparent hydrolysis and is capable of acting as a Lewis acid (Scheme 1).



**Scheme 1.**

**Table 1.** $SnCl_2$-mediated and $Co(acac)_2$-catalyzed carbonyl allylation

| Entry | Substrate | Product | Time (h) | Yield%[a] |
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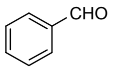
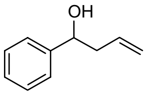
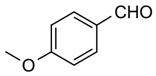
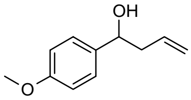
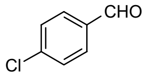
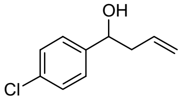
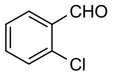
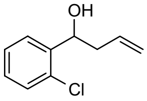
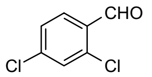
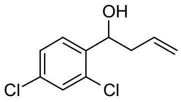
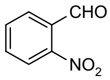
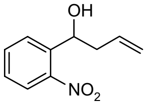
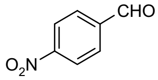
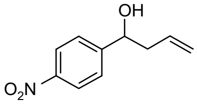
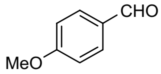
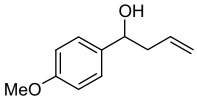
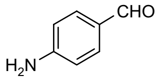
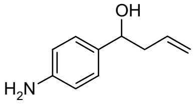
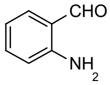
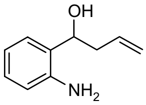
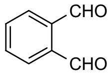
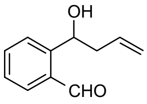
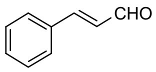
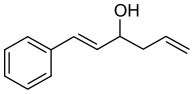
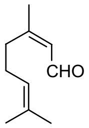
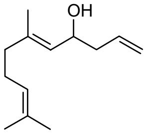
| 1 |  |  | 6 | 97 |
| 2 |  |  | 6 | 93 |
| 3 |  |  | 6 | 91 |
| 4 |  |  | 6 | 94 |
| 5 |  |  | 6 | 93 |
| 6 |  |  | 6 | 96 |
| 7 |  |  | 6 | 94 |
| 8 |  |  | 6 | 92 |
| 9 |  |  | 6 | 95 |
| 10 |  |  | 6 | 91 |
| 11 |  |  | 6 | 90 |
| 12 |  |  | 8 | 92 |
| 13 |  |  | 8 | 85 |