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LETTERS

Rhodium catalyzed conjugated addition of unsaturated carbonyl compounds by triphenylbismuth in aqueous media and under an air atmosphere

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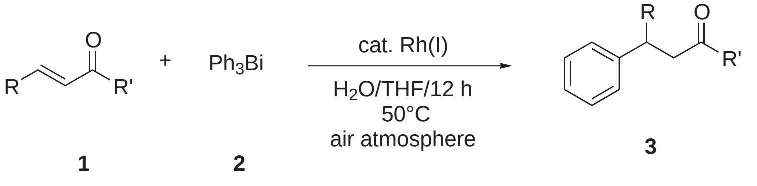
Abstract—In the presence of a rhodium catalyst, α,β-unsaturated esters and ketones react with triphenylbismuth in aqueous media and under an air atmosphere to give the corresponding conjugated addition products in high yields. © 2001 Published by Elsevier Science Ltd.

Recently interest has been growing in carrying out organic reactions in water because of its natural abundance and the inherent advantages of using water as a solvent. Various reactions that are traditionally carried out in organic solvent have now been equally successful or more effective in aqueous media.[1] Such developments are exemplified by the aqueous Barbier–Grignard type reactions that traditionally are considered highly sensitive towards water.[2] An important method that is closely related to Grignard reactions for forming carbon–carbon bonds is through the conjugated addition of an organometallic reagent to unsaturated carbonyl derivatives.[3] Such reactions are generally carried out by using copper reagents or catalysts.[4] As in the case of Grignard-type reactions, for conjugated additions based on organometallic reagents, it is generally accepted that strict anhydrous reaction conditions are required.

On the other hand, the significance of performing metal-mediated carbon–carbon bond formation reactions in water has been recognized recently.[5] While most attentions have been focused on Grignard-type reactions, the corresponding conjugated addition has been explored much less. Previously, Luche et al. reported a zinc–copper couple mediated conjugated addition of unsaturated carbonyl compounds and nitriles with alkyl iodides under sonication conditions in aqueous ethanol.[6] Giese and co-workers studied the diastereoselectivity of these reactions.[7] Recently, we reported a Grignard-type phenylation of aldehydes in water in which phenyltin derivatives (trimethyl and tributyl) reacted effectively with aldehydes in water and under an atmosphere of air to give nucleophilic addition products in high yields in the presence of a catalytic amount of rhodium catalyst.[8] The intriguing insensitivity of the rhodium catalytic system towards air and water led us to explore the potentials of other synthetically useful reactions under similar conditions.[9] Herein we wish to report that in the presence of a rhodium catalyst, α,β-unsaturated esters and ketones react with triphenylbismuth in aqueous media to give the corresponding conjugated addition products in high yields under an air atmosphere (Eq. (1)).[10]



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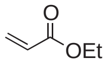
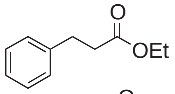
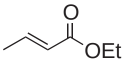
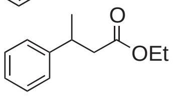
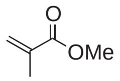
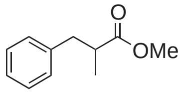
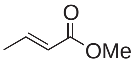
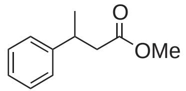
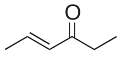
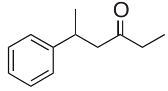
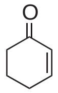
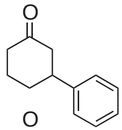
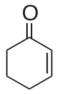
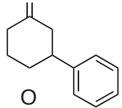
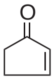
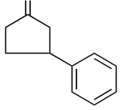
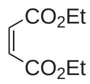
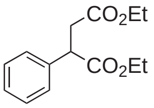
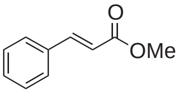
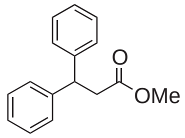
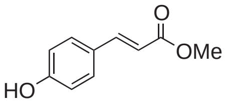
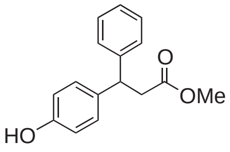
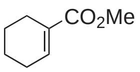
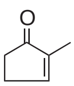
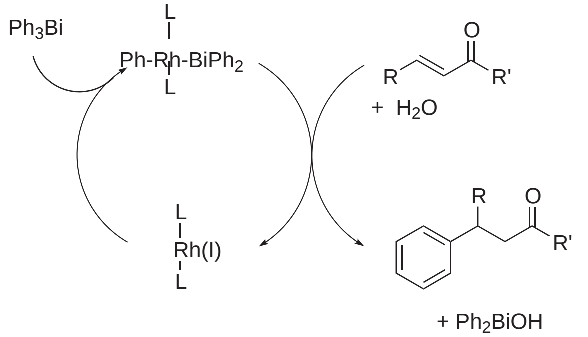
To begin our study, triphenylbismuth was stirred with ethyl acrylate and a catalytic amount of a $Rh_2(COD)_2Cl_2$ (5 mol%) at 50°C in water.[11] A complicated mixture was obtained (including mono- and bisphenylation products). However, when ethyl crotonate was used instead of acrylate, a smooth reaction occurred to give the conjugated product in 80% isolated yield (together with biphenyl). The reaction was equally successful at room temperature albeit took a much longer reaction time for a high conversion (2–3 days). Cationic $Rh(COD)_2BF_4$ was also effective as the catalyst. Various conjugated carbonyl compounds were thus examined under the same reaction conditions with $Rh_2(COD)_2Cl_2$ (Table 1). In all cases when a disubsti-

Table 1. Rhodium catalyzed reaction of triphenylbismuth with unsaturated carbonyl compounds in aqueous media

Entry	Carbonyl Derivative (**1**)	Product (**3**)	Yield (%)
1			11
2			80
3			70
4			80
5			70
6			84
7			40[a]
8			75
9			74
10			68
11			73
12			nr
13			nr

All reactions were carried out at 50ºC and yields were isolated ones after column chromatography on silica gel.
a: Carried out at room temperature and the yield was based on H NMR measurement of crude material.



Scheme 1. Tentative mechanism for the rhodium catalyzed conjugated addition of triphenylbismuth to unsaturated carbonyl compounds in aqueous media.

tuted unsaturated C=C was involved, the reaction proceeded smoothly to generate the desired conjugated addition product. Interestingly, the use of tri-substituted double bonds shut down the reaction completely. Both ketones (linear and cyclic) and esters are effective as the electron-withdrawing functional groups. The use of conjugated nitriles, acids, and aldehydes led to either the failure of the conjugated reaction or a mixture of a variety of products. Compounds bearing a hydroxyl group reacted as expected and did not require any protection (entry 11). Scheme 1 outlines a tentative mechanism in which rhodium serves as a catalyst for the conjugated addition.[12] In conclusion, a highly effective aqueous and air-stable rhodium catalyzed conjugated addition of α,β-unsaturated carbonyl compounds was developed by using triphenylbismuth. The scope, mechanism, and synthetic applications of this novel reaction are under investigation.

A typical experimental procedure is as follows: A mixture of cyclohex-2-en-1-one (100 mg, 1.04 mmol), triphenylbismuth (504 mg, 1.14 mmol), and bis(1,4-cyclooctadiene)dirhodium dichloride (25 mg, 5 mol%) in 4 mL water/THF (7:3) was capped and stirred at 50°C (oil bath temperature) for 12 h. Upon cooling, the reaction mixture was extracted with ether. The combined organic fractions were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 20:1 to 10:1) to give 3-phenylcyclohexanone (151 mg, 84% yield).

Acknowledgements

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