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Quasi-nature catalysis: conjugated addition of unsaturated carbonyl compounds with aryl and vinyltin reagents catalyzed by rhodium in air and water

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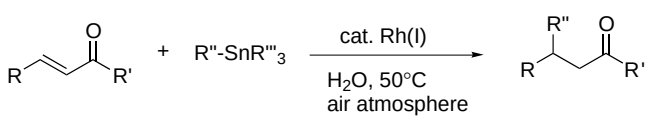
Abstract—In air and water, trialkylphenyl- or trialkylvinylstannanes react with α,β-unsaturated esters and ketones to give the corresponding conjugated addition products in high yields in the presence of a rhodium catalyst. © 2001 Published by Elsevier Science Ltd.

Recently, we have been interested in developing transition-metal catalyzed carbon–carbon bond formations under the quasi-nature conditions of air and water.[1] Such reactions have the advantages that (1) water-soluble substrates such as carbohydrates can be used directly without derivatization; (2) the aqueous catalyst solution can be recycled easily, and (3) it is more convenient for operations without the need for using an inert gas atmosphere. A general requirement for performing such reactions is that the reagent is air- and water-stable.

The use of tin and organotin compounds for synthetic purposes has been growing in scope.[2] This is due to their relatively high stability and the ability of tailoring chemo-, regio-, and stereoselectivities by combination of these reagents with appropriate catalysts. Widely recognized reactions attributed to the use of tin include tributyltin hydride based radical chemistry,[3] the Stille reaction,[4] allyltin chemistry,[5] and tin enolate chemistry.[6] More recently, transition-metal catalyzed carbonyl addition and conjugated additions involving organotin compounds were studied by Oi[7] and Yamamoto[8] under an inert gas atmosphere and anhydrous conditions. In particular, Oi[7b] and co-workers reported a conjugated addition of arylstannanes to unsaturated carbonyl compounds in dried THF, under nitrogen, in a sealed Schlenk tube, catalyzed by $[Rh(COD)(CH_3CN)_2]BF_4$ at 60°C, and was quenched by adding water.

On the other hand, the decreased reactivity and the relatively higher stability towards air and water of these reagents provides opportunities for performing reactions in aqueous media, such as the allylation[9] and aldol-type condensation,[10] and in air.[11,12] An important method for forming carbon–carbon bonds is through the conjugated addition of an organometallic reagent to unsaturated carbonyl derivatives.[13,14] Recently, we reported that α,β-unsaturated esters and ketones react with triphenylbismuth in aqueous media to give the corresponding conjugated addition products under an air atmosphere in the presence of a rhodium catalyst.[15] While the reaction provides the desired product effectively under the desired reaction conditions, it is not economical as three phenyl rings are involved in the triphenylbismuth reagents. Decreasing the amount of triphenylbismuth lowered the yield of the desired product considerably, which was in part due to the formation of biphenyl. In addition, most bismuth compounds are not readily available and are unstable towards air and water, which limits the application of the method. In order to overcome these problems, herein we found that the readily available and stable trialkylaryl- or trialkylvinyltin reagents **2** can be added efficiently to unsaturated carbonyl compounds **1**, generating the desired product **3** (upon the catalysis of rhodium) in air and water (Eq. (1)).[16]



1 **2** **3** (1)

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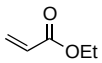
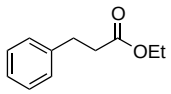
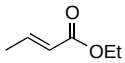
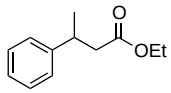
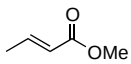
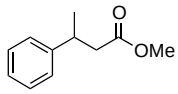
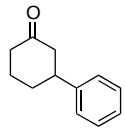
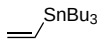
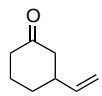
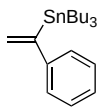
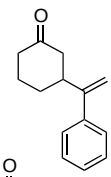
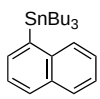
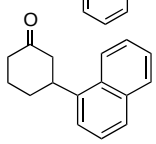
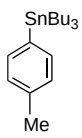
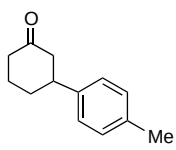
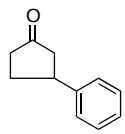
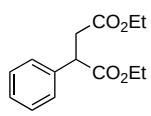
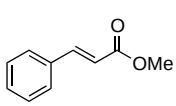
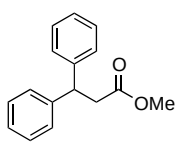
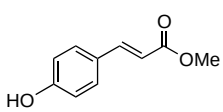
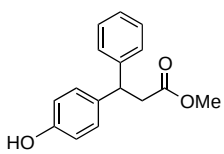
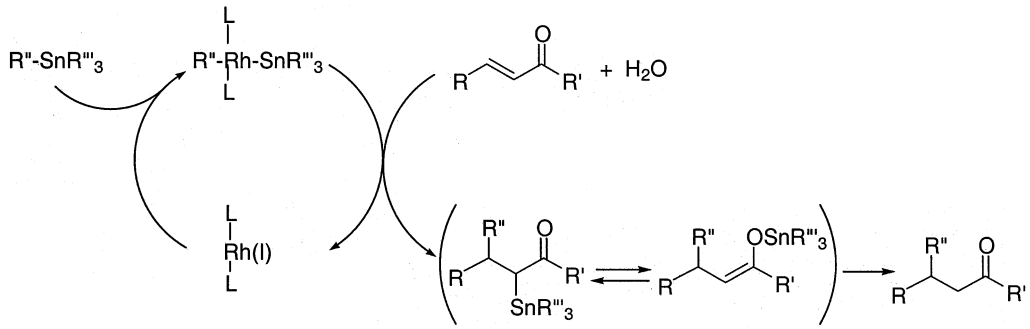
Table 1. Rhodium-catalyzed conjugated addition with aryl and vinylstannanes in aqueous media

Entry	Carbonyl Derivative (**1**)	Stannane(**2**)	Product (**3**)	Yield (%)
1		$PhSnMe_3$		57(2)
2		$PhSnMe_3$		65(64)
3		$PhSnMe_3$		67
4		$PhSnMe_3$		76(77)
5				30
6				50
7				65
8				61
9		$PhSnMe_3$		62(30)
10		$PhSnMe_3$		75
11		$PhSnMe_3$		77(91)
12		$PhSnMe_3$		62

All reactions were carried out at 50°C and yields were isolated ones after column chromatography on silica gel. Yields in parentheses are the ones reported by ref. 7b in anhydrous THF at 60°C under N_2.



Scheme 1. Tentative mechanism for the rhodium-catalyzed conjugated addition of aryl and vinylstannanes to unsaturated carbonyl compounds in air and water.

When trimethylphenylstannane was stirred with ethyl crotonate and a catalytic amount of a $Rh_2(COD)_2Cl_2$ (5 mol%) at 50°C in water, a smooth reaction occurred to give the conjugated product in 65% isolated yield. Unlike the triphenylbismuth reaction, virtually no biphenyl product was observed with the tin reagents. Various conjugated carbonyl compounds were thus examined under the same reaction conditions with $Rh_2(COD)_2Cl_2$ (Table 1). Simple ethyl acrylate also reacted to give the desired product (entry 1), which is in sharp contrast to the previous method[7b] in dried THF, where essentially no product was obtained on a similar substrate. In the triphenylbismuth reaction, only a very small amount of the desired product was obtained. Both ketones (linear and cyclic) and esters were effective as the electron-withdrawing functional groups. Compounds bearing a hydroxyl group reacted as expected and did not require any protection (entry 12). Scheme 1 outlines a tentative mechanism in which rhodium serves as a catalyst for the conjugated addition of vinyl and aryltin reagents. In conclusion, a convenient rhodium-catalyzed conjugated addition of α,β-unsaturated carbonyl compounds was developed by using trialkylvinyl- and trialkylphenylstannanes in air and water. 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), trimethylphenylstannane (275 mg, 1.14 mmol), and bis(1,4-cyclooctadiene)dirhodium dichloride (25 mg, 5% mol) in 4 mL of water 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 = 20:1–10:1) to give 3-phenylcyclohexanone (138 mg, 76% yield).

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References

1. Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997. See also: Li, C. J. *Chem. Rev.* **1993**, *93*, 2023; Li, C. J.; Chan, T. H. *Tetrahedron* **1999**, *55*, 11149; Li, C. J. *Tetrahedron* **1996**, *52*, 5643.
2. (a) Davies, A. G. *Organotin Chemistry*; John Wiley & Son: New York, 1997; (b) Omae, I. *Organotin Chemistry*; Elsevier: New York, 1989; (c) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: Stoneham, 1986; (d) Smith, P. J. *Chemistry of Tin*; Blackie Academic & Professional: New York, 1997; (e) *Chemistry of Tin*; Harrison, P. G., Ed.; Chapman and Hall: New York, 1989; (f) Bristow, G. S. *Aldrichim. Acta* **1984**, *17*, 75.
3. (a) Curran, D. *Synlett* **1991**, 107; (b) Giovannini, R. *Synlett* **1995**, 973; (c) Pereyre, M. *Tetrahedron Lett.* **1970**, 3653; (d) Sato, T. *Synlett* **1995**, 965; (e) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986; (f) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622; (g) Porter, N. *J. Am. Chem. Soc.* **1989**, *111*, 8311; (h) Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 7283.
4. (a) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771; (b) Mitchell, T. N. *Synthesis* **1992**, 803.
5. (a) Thomas, E. J. *Main Group Met. Chem.* **1996**, *19*, 307; (b) Yamamoto, Y. *Aldrichim. Acta* **1987**, *20*, 45; (c) Tagliavini, G. *Rev. Silicon, Germanium, Tin Lead Compd.* **1985**, *8*, 237.
6. (a) Groger, H.; Vogl, E. M.; Shibasaki, M. *Chem. Eur. J.* **1998**, *4*, 1137; (b) Mukaiyama, T.; Kobayashi, S. *Org. React. (NY)* **1994**, *46*, 1; (c) Shibata, I.; Baba, A. *Org. Prep. Proc. Int.* **1994**, *26*, 85.
7. (a) Oi, S.; Moro, M.; Ono, S.; Inoue, Y. *Chem. Lett.* **1998**, 83; (b) Oi, S.; Moro, M.; Inoue, Y. *Chem. Commun.* **1997**, 1621.
8. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.
9. (a) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191; (b) Uneyama, K.; Kamaki, N.; Moriya, A.; Torii, S. *J. Org. Chem.* **1985**, *50*, 5396; (c) Petrier, C.; Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 1449.
10. Chan, T. H.; Li, C. J.; Wei, Z. Y. *J. Chem. Soc., Chem. Commun.* **1990**, 505.
11. Meng, Y.; Li, C. J. *J. Am. Chem. Soc.* **2000**, *120*, 9538.

12. For other water and air tolerant transition-metal catalyzed reactions reported from this group, see: Venkatraman, S.; Li, C. J. *Org. Lett.* **1999**, *1*, 1133; Venkatraman, S.; Li, C. J. *Tetrahedron Lett.* **2000**, *41*, 4831; Li, C. J.; Meng, Y.; Yi, X. H.; Ma, J. H.; Chan, T. H. *J. Org. Chem.* **1998**, *63*, 7498; Wang, D.; Chen, D. L.; Haberman, J. X.; Li, C. J. *Tetrahedron* **1998**, *54*, 5129; Li, C. J.; Meng, Y.; Yi, X. H.; Chan, T. H. *J. Org. Chem.* **1997**, *62*, 8632; Li, C. J.; Wang, D.; Chen, D. L. *J. Am. Chem. Soc.* **1995**, *117*, 12867.
13. Taylor, R. J. K. *Synthesis* **1985**, 364.
14. For reviews, see: Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; Wiley: New York, 1980; Lipshutz, B. H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; p. 283. For other examples of transition-metal catalyzed conjugated additions, see: Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S.; Shim, S. C. *J. Org. Chem.* **1995**, *60*, 883; Ikeda, S.; Cui, D. M.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4712; Sawamura, M.; Hamashima, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8295; Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259; Ohe, T.; Wakita, T.; Motofusa, S.; Cho, C. S.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2149.
15. Venkatraman, S.; Li, C. J. *Tetrahedron Lett.* **2001**, *42*, 781.
16. Recently, rhodium-catalyzed conjugated additions on α,β-unsaturated esters with arylboronic acids were reported in aqueous dioxane under an inert gas atmosphere. Sakuma, S.; Sakai, M.; Itooka, R.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 5951; Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716 and references cited therein.