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Rhodium(I)-Catalyzed Carbonyl Allenylation versus Propargylation via Redox Transmetalation Across Tetragonal Tin(II) Oxide[†]

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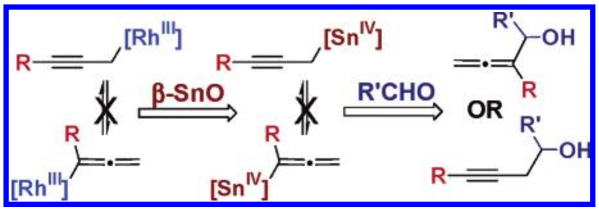
ABSTRACT



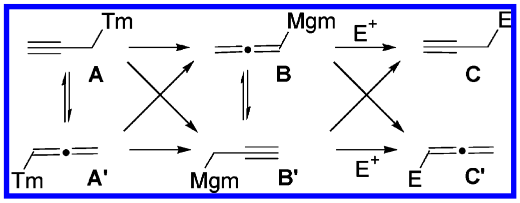
A reagent combination of β-SnO and catalytic [Rh(COD)Cl]$_2$ in THF–H$_2$O promotes the reaction of propargyl bromides and aldehydes and directs the regioselectivity toward the formation of either allenic alcohols or homopropargylic alcohols. This highly regioselective either/or transformation proceeds via a transmetalation from rhodium to tin, in which metallotropic rearrangement between a propargylmetal and allenylmetal is arrested.

An attractive choice in carbon−carbon bond forming strategies is to exploit the nucleophilic reactivity of an organo main group metal reagent, generated in situ via transmetalation from a catalytic organotransition metal partner. The selectivity in the end organic product is determined by the degree of control in all three reactions occurring in tandem.[1] Deployment of this strategy for the generation of a propargylmetal (Scheme 1) is expected to be complicated by metallotropic rearrangement (A to A′, B to B′), transmetalation selectivity (A to B/B′; A′ to B′/B), and selectivity during the reaction with electrophile (B to C/C′; B′ to C′/C).

For carbonyl compounds as the electrophile, Tamaru[2] and Marshall[3] elegantly demonstrated pathway A′ → B → C using a palladium to zinc/indium transmetalation strategy for the synthesis of homopropargyl alcohols. Tuning the regioselectivity to either allenic or homopropargyl alcohol (either C or C′) by the same set of transition metal and main group metal partners remains a pertinent challenge. We are pleased to achieve such an either/or regioselective transformation via redox−transmetalation from rhodium to tetragonal tin(II)-oxide (hereafter β-SnO) in the presence of water and to report our preliminary finding here.[4]

Enhancement of nucleophilic reactivity of organostannanes by water continues to evoke interest. Most recently, Li et

Scheme 1



[†] Presented in part at the Indo-US Conference on Recent Advances in Organometallic Catalysis & Olefin Polymerization, IIT Madras, Dec 10−12, 2003.

(1) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163.

(2) Tamaru, Y.; Goto, S.; Tanaka, A.; Shimuzu, M.; Kimura, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 878.

(3) Marshall, J. A.; Grant, C. M. *J. Org. Chem.* **1999**, *64*, 696.

10.1021/ol0493352 CCC: $27.50

al. speculated that an alkoxy or hydroxy pendant in R-Sn-$(OH)_3$ exerts electron donation to the vacant d orbital of tin, thereby stabilizing the species and consequently enhancing its reactivity.[5] Drawn by the bonding and structural similarities of β-SnO and hydrated tin(II) halides and the trihalostannous ion, we reasoned that transmetalation over β-SnO in the presence of water may generate intermediates that could be considered as surrogates of R-Sn$(OH)_3$ (Scheme 2).[6] In the present study we sought to explore whether such an intermediate is capable of arresting the metallotropic rearrangement in the case of an ambident nucleophile like propargylmetal.[7]

Scheme 2. Transmetalation from R-Tm to β-SnO

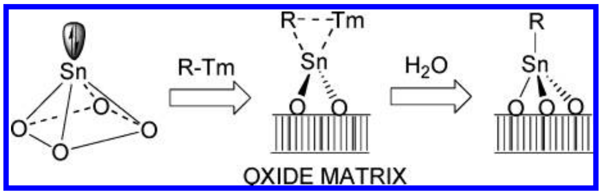
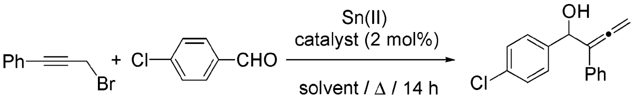


Table 1. Activation of Phenylpropargyl Bromide **1** over Tin(II): Effect of Catalyst and Reaction Conditions



entry	conditions	yield (%)
1	$Pd_2(dba)_3$, $SnCl_2$, THF−H_2O (9:1)	0
2	$Pd_2(dba)_3$, β-SnO, THF−H_2O (9:1)	0
3	$PdCl_2(PPh_3)_2$, $SnCl_2$, THF−H_2O (9:1)	<5
4	$PtCl_2(PPh_3)_2$, $SnCl_2$, THF−H_2O (9:1)	<5
5	$NiCl_2(PPh_3)_2$, $SnCl_2$, THF−H_2O (9:1)	0
6	$RhCl(PPh_3)_3$, $SnCl_2$, THF−H_2O (9:1)	37
7	$[Rh(COD)Cl]_2$, $SnCl_2$, THF−H_2O (9:1)	38
8	$[Rh(COD)Cl]_2$, $SnBr_2$, THF−H_2O (9:1)	41
9	$[Rh(COD)Cl]_2$, β-SnO, THF−H_2O (9:1)	77
10	$[Rh(COD)Cl]_2$, β-SnO, THF	0
11	$[Rh(COD)Cl]_2$, β-SnO, DCM	0
12	$[Rh(COD)Cl]_2$, β-SnO, DCM−H_2O (9:1)	37
13	$[Rh(COD)Cl]_2$, β-SnO, MeOH−H_2O (9:1)	46
14	β-SnO, THF−H_2O (9:1)	0
15	$[Rh(COD)Cl]_2$, THF−H_2O (9:1)	0

Taking phenylpropargyl bromide **1** as the model substrate, a number of optimization experiments were carried out, varying the transition metal catalyst and tin(II) partner. Palladium(0/II), platinum(II), and nickel(II) catalysts resulted in no or negligible amount of desired product (either allenic or homopropargyl alcohol) (Table 1 entries 1−5). Since reaction of **1** with d^8/d^{10} complexes of palladium and platinum is well documented,[8] we ascribe the above failure to the poor ability of the organotransition metal species to transmetalate to the tin(II) partner. Gratifyingly transmetalation from Rh(I) to Sn(II) provided the desired allenic alcohol (entries 6−9, 12, and 13). Compared to other tin(II) partners, β-SnO was the best, affording exclusively the allenic alcohol in 77% yield (entry 9). Among the Rh(I)-complexes screened, $[Rh(COD)Cl]_2$ (where COD is cyclooctadiene) is found to be the best catalyst. The profound influence of water in the reaction may be noted: no reaction occurred in the absence of water (entries 10 and 11). Further, the carbonyl addition reaction between **1** and aldehyde is not promoted by either $[Rh(COD)Cl]_2$ or β-SnO alone (entries 14 and 15).

Motivated by these results, we extended the rhodium-catalyzed reaction of propargyl bromides **1**−**4** with various aldehydes to obtain the corresponding allenic alcohols in moderate to excellent yields (Table 2, entries 1−10).[9] No homopropargylic alcohols were observed in any of these cases.

It may be noted that allenic alcohols are versatile synthons in various stereoselective transformations leading to important organic intermediates such as amino alcohols, 1,2-diols, vinyl epoxides, vinyl cyclopropanes, and dihydrofurans.[10]

As reactions of propargyl and allenylstannanes with carbonyl compounds follow an S_E2' pathway, the allenic alcohol in the present case will arise from a propargyltin intermediate. The latter may originate from either an allenyl or propargylrhodium species. ^1H NMR monitoring of the reaction of **1** (0.02 mmol) with $[Rh(COD)Cl]_2$ (0.01 mmol) in $CDCl_3$ at 50 °C indicated a clear shift of the methylene signal of free bromide from δ (ppm) 4.17 to 2.17, indicating the formation of a propargylrhodium(III) intermediate. Wojcicki et al. also reported the formation of propargyl-

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(4) For allylic, aryl, and propargylic activation by Rh(I) complexes, see: (a) Chin, C. S.; Shin, S. Y.; Lee, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1323. (b) Li, C. J.; Meng, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9538. (c) Kayan, A.; Gallucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2001**, *630*, 44.

(5) Huang, T.; Meng, Y.; Venkatraman, S.; Wang, D.; Li, C. J. *J. Am. Chem. Soc.* **2001**, *123*, 7451.

(6) (a) Sinha, P.; Roy, S. *Organometallics* **2004**, *23*, 67. (b) Banerjee, M.; Roy, S. *Chem. Commun.* **2003**, 534. (c) Sinha, P.; Roy, S. *Chem. Commun.* **2001**, 1798.

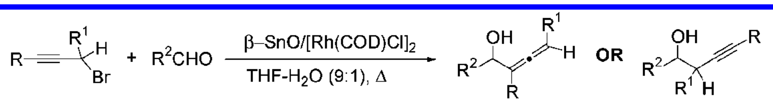
(7) Earlier attempts in this regard have been to vary process parameters such as temperature, solvent, or additive or to execute a further transmetalation involving tin−tin, tin−indium, tin−lithium, and tin−boron. See: (a) Masuyama, Y.; Watabe, A.; Ito, A.; Kurusu, Y. *Chem. Commun.* **2000**, 2009. (b) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550. (c) Marshall, J. A.; Grant, C. M. *J. Org. Chem.* **1999**, *64*, 696. (d) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441. (e) Corey, E. J.; Yu, C. M.; Lee, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 878.

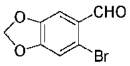
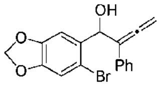
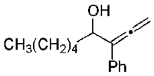
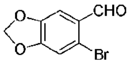
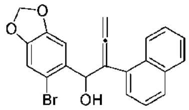
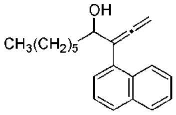
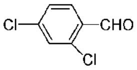
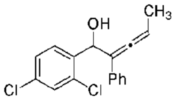
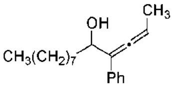
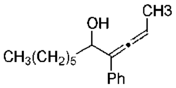
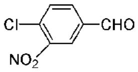
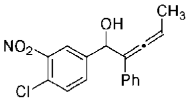
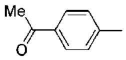
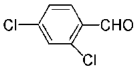
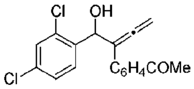
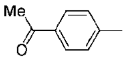
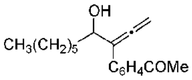
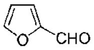
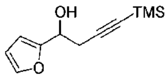
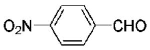
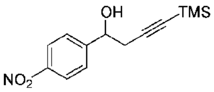
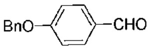
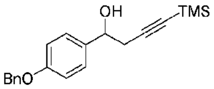
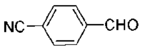
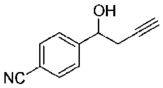
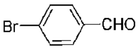
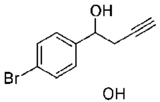
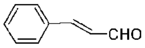
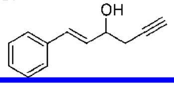
(8) (a) Ogoshi, S.; Nishida, T.; Shinagawa, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 7164. (b) Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *Chem. Commun.* **1995**, 2485.

(9) **Representative Experimental Procedure.** A mixture of 4-chlorobenzaldehyde (71 mg, 0.5 mmol) and (3-bromo-prop-1-ynyl)-benzene (195 mg, 1 mmol) in THF (2 mL) was slowly added to a stirred solution containing β-SnO (101 mg, 0.75 mmol) and $[Rh(COD)Cl]_2$ (5 mg, 0.02 mmol) in THF (2.5 mL) and H_2O (0.5 mL), which was previously refluxed for 30 min. The suspension was refluxed at 70 °C under an inert atmosphere for 14 h (TLC monitoring on silica gel, eluent ethyl acetate−hexane 1:9 v/v). An aqueous solution of NH_4F (15%, 10 mL) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 10 mL), washed with water (2 × 10 mL) and brine (2 × 10 mL), and dried over magnesium sulfate. Solvent removal followed by column chromatography (eluent *n*-hexanes−ethyl acetate; gradient elution) afforded pure 1-(4-chloro-phenyl)-2-phenyl-buta-2,3-dien-1-ol (99 mg, 77% with respect to aldehyde).

(10) (a) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590.

Table 2. Rh(I)-Catalyzed Carbonyl Allenylation/Propargylation



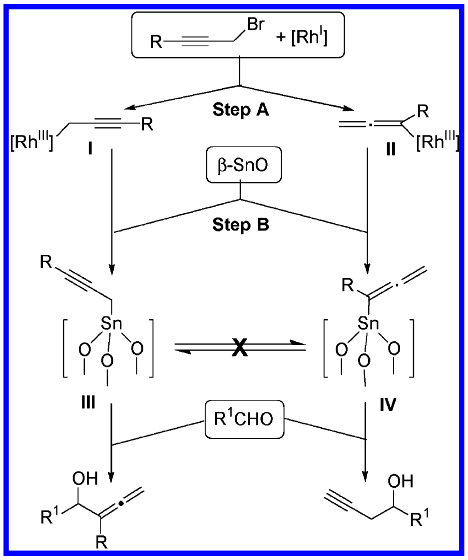
entry	halide	R	R^1	aldehyde	alcohol	time (h)	yield (%)
1	**1**	Ph	H			5	72
2	**1**	Ph	H	CH$_3$(CH$_2$)$_4$CHO		4	81
3	**2**	napthyl	H			7	67
4	**2**	napthyl	H	CH$_3$(CH$_2$)$_5$CHO		5	62
5	**3**	Ph	Me			3	66
6	**3**	Ph	Me	CH$_3$(CH$_2$)$_7$CHO		4	78
7	**3**	Ph	Me	CH$_3$(CH$_2$)$_5$CHO		5	92
8	**3**	Ph	Me			6	42
9	**4**		H			12	57
10	**4**		H	CH$_3$(CH$_2$)$_5$CHO		6	73
11	**5**	TMS	H			8	55
12	**5**	TMS	H			7	58
13	**5**	TMS	H			5	60
14	**6**	H	H			10	57
15	**6**	H	H			8	62
16	**6**	H	H			7	61

rhodium(III) products from the oxidative addition reactions of Rh($SbPh_3$)$_3$(CO)X (X = Cl, Br) with phenyl propargyl halides.[11] We therefore propose that the carbonyl allenylation reactions proceed by the pathway A → B′ → C′ (Scheme 1).

The Rh(I) to β-SnO transmetalation selectivity from propargylrhodium to propargyltin prompted us to explore next the fate of an allenylrhodium(III) in the reaction. Reactions of trimethylsilylpropargyl bromide **5** with Wilkinson's catalyst at ambient temperature in methylene chloride showed the formation of an allenylrhodium(III) species.[12] In a representative experiment trimethylsilyl propargyl bromide **5** (0.05 mmol) and Wilkinson's catalyst (0.01 mmol) were allowed to react for 6 h in methylene chloride, followed by concentration and addition of hexane to precipitate a yellow-brown solid. ^{1}H NMR of the solid showed the signal due to the allenyl proton of the intermediate at δ 5.3, in contrast to the methylene proton signal of free bromide **5** at δ 3.9. Most interestingly, further reaction of **5** and **6** with aldehydes in the presence of β-SnO and catalytic [Rh(COD)-Cl]$_2$ afforded the corresponding homopropargylic alcohols in moderate to good yields (Table 2, entries 11−16). No allenic alcohols were observed in any of these cases. This suggests a transmetalation selectivity from allenyl rhodium(III) to allenylltin(IV) and the likely reaction pathway to be A′ → B → C (Scheme 1).

In summary, we have developed a rhodium(I)-catalyzed highly regioselective either/or transmetalation strategy for the synthesis of allenic and homopropargyl alcohols, which are key intermediates in organic synthesis. Although a mechanistic rationale is yet to develop, the likely bond-forming steps are shown in Scheme 3.

Scheme 3



The remarkable ability of Rh(I) to facilitate a regioselective oxidative addition reaction (step A) generating either a propargylrhodium or an allenylrhodium species (**I** or **II**) is one of major factors in controlling the regioselectivity in the end organic product. Equally important is the redox transmetalation step from rhodium to β-SnO (step B) to generate the corresponding organotin(IV) intermediate (**III** or **IV**) in which the metallotropic rearrangement is completely arrested. Further work is underway to establish the exact nature of the tin(IV) intermediate and to understand the stereoelectronic factors that stabilize such intermediates and thereby arrest the metallotropic rearrangement between propargylmetal and allenylmetal.

Acknowledgment. We thank CSIR for financial support and a senior research fellowship to M.B.

Supporting Information Available: Experimental procedures including spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0493352

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[11] Kayan, A.; Wojcicki, A. *Inorg. Chim. Acta* **2001**, *319*, 187.
[12] Kayan, A.; Galluci J. C.; Wojcicki, A. *Inorg. Chem. Commun.* **1998**, *1*, 446.