Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 48 (2007) 5963–5965
Tetrahedron Letters

# Iridium-catalyzed carbonyl allylation by allyl ethers with tin(II) chloride

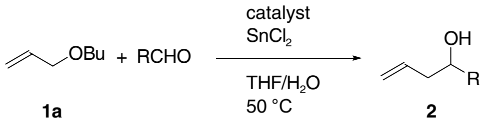
Yoshiro Masuyama* and Masanori Marukawa

*Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan*

Received 28 May 2007; revised 18 June 2007; accepted 21 June 2007
Available online 24 June 2007

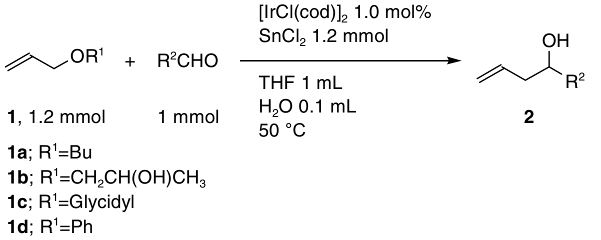
**Abstract**—3-Alkoxypropenes, namely allyl ethers such as allyl butyl ether, allyl 2-hydroxypropyl ether, and diallyl ether, serve as reagents for the allylation of aldehydes with tin(II) chloride in the presence of a catalytic amount of $[IrCl(cod)]_2$ in THF and $H_2O$ at 50 °C to produce the corresponding homoallylic alcohols.

Allyl ethers are poor reagents for palladium-catalyzed allylic alkylation[1] or carbonyl allylation[2] via the formation of a π-allylpalladium complex.[3] We have found that tin(II) chloride mediates the elimination of a poor leaving group, the hydroxy group, for preparing π-allylmetal intermediates from allylic alcohols and metal complexes in palladium,[4] rhodium,[5] or iridium-catalyzed[6] carbonyl allylations. Thus, we hoped that alkoxy groups of 3-alkoxypropenes, namely allyl ethers, would also be eliminated by tin(II) chloride to prepare π-allylmetal complexes. We here report that allyl ethers become versatile reagents for palladium, rhodium, or iridium-catalyzed carbonyl allylations through the mediation of tin(II) chloride.



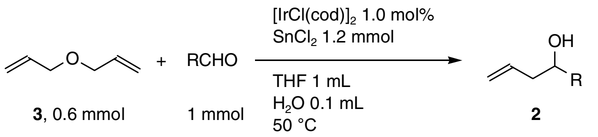
(1)

The reactivity of allyl butyl ether (**1a**) was investigated for the allylation of benzaldehyde or heptanal with tin(II) chloride in the presence of a catalytic amount of $PdCl_2(PhCN)_2$, $[RhCl(cod)]_2$, or $[IrCl(cod)]_2$ in THF–$H_2O$ at 50 °C (Eq. 1). The results are summarized in Table 1. A typical procedure (entry 3) is described in Ref. 8 $[IrCl(cod)]_2$ catalyst seems to be superior to $PdCl_2(PhCN)_2$ or $[RhCl(cod)]_2$ catalyst. No allylation occurred without both the catalysts and tin(II) chloride. The allylations at room temperature and those without $H_2O$ were quite slow.



(2)

The iridium-catalyzed allylations of some aldehydes with **1a** were carried out under the same conditions as those of entries 3 and 6 in Table 1 to produce the corresponding homoallylic alcohols **2** (Table 2, Eq. 2, entries 1–6). The allylation of cinnamaldehyde had a low yield at 50 °C in spite of consuming the aldehyde, and was slow at 25 °C (entries 2 and 3). The reactions of α-substituted aldehydes were quite slow (entries 5 and 6). Allyl 2-hydroxypropyl ether (**1b**), allyl glycidyl ether (**1c**), and allyl phenyl ether (**1d**) can also be used for the iridium-catalyzed carbonyl allylations (Table 2, Eq. 2, entries 7–15). The leaving ability of phenoxy group seems to be superior to that of alkoxy groups, similarly to the usual formation of π-allylmetal complexes (entries 14 and 15).[1]



(3)

---

* Corresponding author. Tel.: +81 3 3238 3453; fax: +81 3 3238 3361; e-mail: y-masuya@sophia.ac.jp

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.06.117

**Table 1.** Allylation of PhCHO and $CH_3(CH_2)_5CHO$ with **1a**

| Entry | R | Catalyst/mmol | Time (h) | **2**, Yield[a] (%) |
|---|---|---|---|---|
| 1 | Ph | $PdCl_2(PhCN)_2$/0.02 | 24 | 55 |
| 2 | Ph | $[RhCl(cod)]_2$/0.01 | 24 | 60 |
| 3 | Ph | $[IrCl(cod)]_2$/0.01 | 24 | 84 |
| 4 | $C_6H_{13}$ | $PdCl_2(PhCN)_2$/0.02 | 48 | 29 |
| 5 | $C_6H_{13}$ | $[RhCl(cod)]_2$/0.01 | 48 | 9 |
| 6 | $C_6H_{13}$ | $[IrCl(cod)]_2$/0.01 | 48 | 63 |

[a] Isolated yields based on aldehydes. The structures were confirmed by the comparison of spectroscopic values (IR and $^1H$ NMR) with those of authentic samples.[4,7]

**Table 2.** Iridium-catalyzed carbonyl allylation with **1**

| Entry | Allylic ether/mmol | $R^2$ | Time (h) | **2**, Yield[a] (%) |
|---|---|---|---|---|
| 1 | **1a**/1.2 | $4\text{-}ClC_6H_4$ | 24 | 71 |
| 2 | **1a**/1.2 | PhCH=CH | 24 | 32 |
| 3[b] | **1a**/1.2 | PhCH=CH | 72 | 33 |
| 4 | **1a**/1.2 | $PhCH_2CH_2$ | 24 | 63 |
| 5 | **1a**/1.2 | $c\text{-}C_6H_{11}$ | 48 | 8 |
| 6 | **1a**/1.2 | $PhCH(CH_3)$ | 48 | 19 |
| 7 | **1b**/1.2 | Ph | 46 | 85 |
| 8 | **1b**/1.2 | $4\text{-}ClC_6H_4$ | 45 | 63 |
| 9 | **1b**/1.2 | PhCH=CH | 48 | 25 |
| 10 | **1b**/1.2 | $PhCH_2CH_2$ | 48 | 60 |
| 11 | **1b**/1.2 | $C_6H_{13}$ | 48 | 48 |
| 12 | **1c**/1.2 | Ph | 24 | 74 |
| 13 | **1c**/1.2 | $C_6H_{13}$ | 24 | 57 |
| 14 | **1d**/1.2 | Ph | 24 | 91 |
| 15 | **1d**/1.2 | $C_6H_{13}$ | 24 | 93 |

[a] Isolated yields based on aldehydes. The structures were confirmed by the comparison of spectroscopic values (IR and $^1H$ NMR) with those of authentic samples.[4,7]

[b] The reaction was carried out at 25 °C.

Diallyl ether (**3**) can also be applied to the iridium-catalyzed carbonyl allylations, as summarized in Table 3 (Eq. 3). Both allyl moieties in **3** serve for the carbonyl allylation (entries 3–7). The allylation of benzaldehyde with **3** also proceeded using $PdCl_2(PhCN)_2$ or $[RhCl(cod)]_2$ as a catalyst to afford 1-phenyl-3-buten-1-ol (**2**, R = Ph) in 51% or 53% yield, respectively (entries 1 and 2). The use of four equimolar amounts of tin(II) chloride to **3** in the palladium-catalyzed allylation enhanced the yield (entry 1).

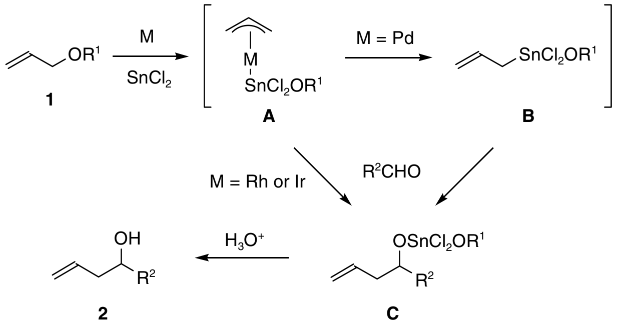
**Table 3.** Allylation of aldehydes with **3**

| Entry | aldehyde | Catalyst/mmol | Time (h) | **2**, Yield[a] (%) |
|---|---|---|---|---|
| 1 | PhCHO | $PdCl_2(PhCN)_2$/0.02 | 24 | 51(76)[b] |
| 2 | PhCHO | $[RhCl(cod)]_2$/0.01 | 24 | 53 |
| 3 | PhCHO | $[IrCl(cod)]_2$/0.01 | 24 | 69 |
| 4 | $4\text{-}ClC_6H_4CHO$ | $[IrCl(cod)]_2$/0.01 | 21 | 87 |
| 5 | PhCH=CHCHO | $[IrCl(cod)]_2$/0.01 | 46 | 38[c] |
| 6 | $Ph(CH_2)_2CHO$ | $[IrCl(cod)]_2$/0.01 | 24 | 94 |
| 7 | $C_6H_{13}$ | $[IrCl(cod)]_2$/0.01 | 24 | 64 |

[a] Isolated yields based on aldehydes. The structures were confirmed by the comparison of spectroscopic values (IR and $^1H$ NMR) with those of authentic samples.[4,7]

[b] The figure in parentheses is the yield with 2.4 mmol of $SnCl_2$.

[c] The reaction was carried out at 25 °C.



**Scheme 1.**

A plausible mechanism is illustrated in Scheme 1. Alkoxy groups such as butoxy, 2-hydroxypropoxy, glycidyloxy, and allyloxy would function as leaving groups with the assistance of tin(II) chloride in the formation of π-allylmetal complexes **A** from allyl ethers **1**. And then the π-allylrhodium or -iridium complexes **A** (M = Rh or Ir) might directly react with aldehydes to produce 3-buten-1-ols **2**, similarly to the rhodium- or iridium-catalyzed carbonyl allylation by allylic alcohols with tin(II) chloride,[5,6,9,10] and π-allylpalladium complexes **A** (M = Pd) might be transformed into allyltin intermediates **B** that would cause nucleophilic attack to aldehydes to produce 3-buten-1-ols **2**, similarly to the palladium-catalyzed carbonyl allylations by allylic alcohols and esters with tin(II) chloride.[2,11] In the case of diallyl ether (**3**), a second allyl moiety ($R^1$ = allyl) in **C** would be converted to a π-allylmetal complex with the assistance of another tin(II) chloride to cause second nucleophilic addition to aldehydes.

## References and notes

1. (a) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 8, p 799; (b) Tsuji, J. In *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; Wiley: New York, 1995; p 290.
2. (a) Masuyama, Y. *J. Synth. Org. Chem. Jpn.* **1992**, *50*, 202; (b) Masuyama, Y. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 3, p 255; (c) Tamaru, Y. In *Perspectives in Organopalladium Chemistry for the XXI Century*; Tsuji, J., Ed.; Elsevier Science: Switzerland, 1999; p 215; (d) Tamaru, Y. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, 2002; p 1917.
3. For the allylic alkylation with a view to palladium-catalyzed deallylation of allyl alkyl ethers, see: Tsukamoto, H.; Kondo, Y. *Synlett* **2003**, 1061, and references cited therein.
4. Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577.
5. Masuyama, Y.; Kaneko, Y.; Kurusu, Y. *Tetrahedron Lett.* **2004**, *45*, 8969.
6. Masuyama, Y.; Chiyo, T.; Kurusu, Y. *Synlett* **2005**, 2251.
7. Ito, A.; Kishida, M.; Kurusu, Y.; Masuyama, Y. *J. Org. Chem.* **2000**, *65*, 494.
8. To the solution of **1a** (1.2 mmol), benzaldehyde (1.0 mmol) and tin(II) chloride (1.2 mmol) in THF (1 mL) and $H_2O$ (0.1 mL) was added $[IrCl(cod)]_2$ (0.01 mmol), and then the

solution was stirred at 50 °C for 24 h. The reaction mixture was diluted with $Et_2O$ (120 mL) and washed successively with aq 10% HCl solution (20 mL), aq $NaHCO_3$ solution (20 mL), $H_2O$ (20 mL), and brine (20 mL). The extracts were dried over anhydrous $MgSO_4$. After evaporation of solvents, purification by column chromatography (silica gel, hexane/EtOAc = 8:1) and/or HPLC (Japan Analytical Industry Co. Ltd., LC-908, JAIGEL-2H; $CHCl_3$) afforded 1-phenyl-3-buten-1-ol (**2**, R = Ph) as a colorless oil in 84% yield.

9. For direct carbonyl allylations by stoichiometric π-allylmetal compounds, see: (a) Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593; (b) Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434; (c) Sato, Y.; Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 1624.
10. For the suggestion of direct carbonyl allylations with the σ- or π-allylpalladium complexes prepared in situ catalytically, see: (a) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641; (b) Wallner, O. A.; Szabo, K. J. *J. Org. Chem.* **2003**, *68*, 2934; (c) Solin, N.; Kjellgren, J.; Szabo, K. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3656; (d) Hopkins, C. D.; Malinakova, H. C. *Org. Lett.* **2004**, *6*, 2221.
11. For other transition metal-catalyzed carbonyl allylations via transmetalations, see: (a) Sebelius, S.; Wallner, O. A.; Szabo, K. J. *Org. Lett.* **2003**, *5*, 3065; (b) Jang, T.-S.; Keum, G.; Kang, S. B.; Chung, B. Y.; Kim, Y. *Synthesis* **2003**, 775; (c) Hirashita, T.; Kambe, S.; Tsuji, H.; Omori, H.; Araki, S. *J. Org. Chem.* **2004**, *69*, 5054; (d) Kimura, M.; Shimizu, M.; Tanaka, S.; Tamaru, Y. *Tetrahedron* **2005**, *61*, 3705, and references cited therein.