Tetrahedron Letters 46 (2005) 787–789

Tetrahedron Letters

Rhenium complex-catalyzed allylation of aldehydes with allyltributylstannane

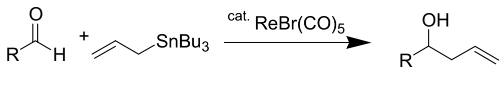
Yutaka Nishiyama,* Fujio Kakushou and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan

Received 1 November 2004; revised 29 November 2004; accepted 3 December 2004
Available online 19 December 2004

Abstract—It was confirmed that the rhenium complex, $ReBr(CO)_5$, catalyzed the allylation of aldehydes with allyltributylstannane to give the corresponding homoallylic alcohols in moderate to good yields. Similarly, the reaction of aldehydes with enol silyl ether was efficiently promoted by the rhenium catalyst to afford the corresponding β-hydroxy carbonyl compounds.

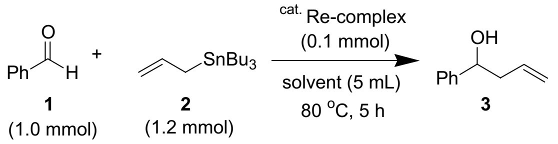
The allylation of carbonyl compounds with organoallylic compounds, such as allyltrialkyl- and allyltriarylstannane, has been widely utilized as a method for the preparation of homoallylic alcohols, which are useful intermediates for the construction of complex molecules and important building blocks for the synthesis of natural products in organic synthesis.[1] Although some Lewis acids catalyzes this reaction,[2] Lewis acids containing boron, aluminum, titanium, and tin are extremely moisture sensitive, and there is increasing interest in the development of a new catalyst, which is air-stable and water-tolerant compound. We have recently shown the hitherto unknown capacity of the rhenium complex, which is an air-stable and water-tolerant compound, as an efficient catalyst for the alkylation of arenes with alkyl halides.[10,11] Now it was found that rhenium complex acts as a catalyst for the allylation of aldehydes with allyltributylstannane (Scheme 1).



Scheme 1.

To determine the optimized reaction conditions, benzaldehyde (**1**) was allowed to react with allyltributylstannane (**2**) under various reaction conditions, and these results are shown in Table 1. The yield of 1-phenylbut-3-ene-1-ol (**3**) was dramatically affected by the solvent and rhenium complex used in the reaction. When an aromatic hydrocarbon, such as toluene or benzene, was used as a solvent, the allylation of **1** with **2** efficiently proceeded to give **3** in good yields (entries 1 and 2). In chlorinated hydrocarbon solvents such as 1,2-dichloroethane and $CHCl_3$, which were often utilized in the rhenium-catalyzed reaction, the allylation of **1** with **2** also occurred and **3** was obtained in 72% and 54% yields, respectively (entries 7 and 8). Whereas the use of coordinating solvents, such as THF, acetonitrile or methanol,

Table 1. Rhenium-catalyzed allylation of benzaldehyde with allyltributylstannane



Entry	Re complex	Solvent	Yield (%)[a]
1	$ReBr(CO)_5$	Benzene	83
2	$ReBr(CO)_5$	Toluene	80
3	$ReCl(CO)_5$	Benzene	75
4	$ReBr(CO)_4(PPh_3)$	Benzene	27
5	$Re_2(CO)_{10}$	Benzene	Trace
6	$CpRe(CO)_3$	Benzene	Trace
7	$ReBr(CO)_5$	CH_2ClCH_2Cl	72
8	$ReBr(CO)_5$	$CHCl_3$	54
9	$ReBr(CO)_5$	THF	0
10	$ReBr(CO)_5$	CH_3CN	0
11	$ReBr(CO)_5$	CH_3OH	23

[a] GC yields.

---

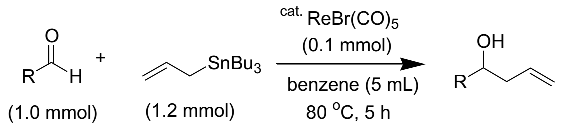
* Corresponding authors. Tel.: +81 6 6368 1121; fax: +81 6 6339 4026; e-mail: nishiya@ipcku.kansai-u.ac.jp

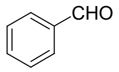
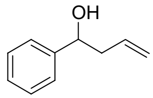
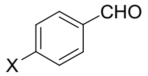
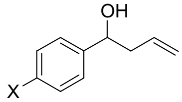
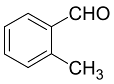
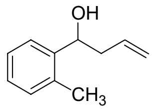
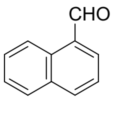
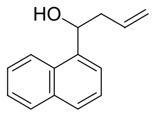
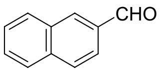
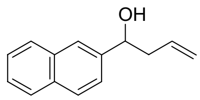
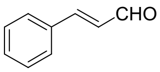
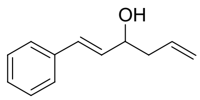
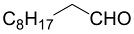
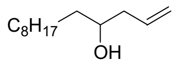
0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.12.022

caused a distinct decrease in the yield of **3** (entries 9–11). $ReBr(CO)_5$ and $ReCl(CO)_5$ showed a high catalytic activity in the reaction (entries 1 and 3). The replacement of one of the electron withdrawing carbonyl ligands by electron donating phosphine ligand led to a decrease in the yield of the allylated product (entry 4). The rhenium carbonyl complexes, such as $Re_2(CO)_{10}$ and $CpRe(CO)_3$, did not exhibit the same catalytic activity in the reaction (entries 5 and 6).

In order to understand the scope and limitations of the allylation of aldehydes with allyltributylstannane (**2**), various aldehydes were reacted with **2** in the presence of a catalytic amount of $ReBr(CO)_5$ at 80 °C and the results were shown in Table 2. For the 4-methyl-, 4-methoxy-, 4-chloro-, 4-bromo-, and 4-nitro- benzaldehydes, allylation of the aldehydes with **2** efficiently proceeded under the same reaction conditions as that of the benzaldehyde to give homoallylic alcohols in 56–82% yields (entries 2–6). Similarly, the sterically congested substrate such as 2-methylbenzaldehyde was allylated with **2** to give 1-*o*-tolyl-but-3-en-1-ol in 79% yield (entry 7). 1-(Naphthalen-1-yl)- and 1-(naphthalen-2-yl)but-3-en-1-ol were also synthesized by this method in 68% and 99% yields, respectively (entries 8 and 9). The allylation of an α, β-unsaturated aldehyde such as cinnamylaldehyde with **2** efficiently proceeded to afford the homoallylic alcohol in 80% yield (entry 10). For aliphatic aldehydes, the yield of the allylated product was markedly decreased, however the yield of the product was improved by the extending of reaction time (15 h) (entry 11). In contrast to that of aldehyde, for ketones, the allylation did not proceed under the same reaction conditions as that of the aldehydes.

Table 2. Rhenium-catalyzed allylation of aldehydes with allyltributylstannane



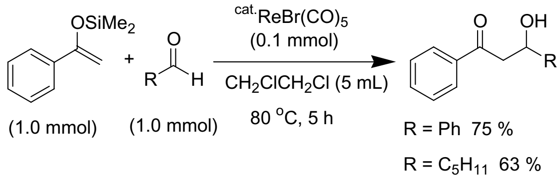
Entry	Aldehyde	Product	Yield (%)[a]
1			83(78)
			
2	X = CH_3		82(75)
3	OCH_3		68(61)
4	Cl		76(70)
5	Br		65(32)
6	NO_2		56(50)
7			79(74)
8[b]			68(65)
9			99(96)
10[b]			80(72)
11[b]			72(67)

[a] GC yields based on aldehyde. The number of parenthesis shows the isolated yield.

[b] For 15 h.

Although we cannot show the reaction pathway for the rhenium-catalyzed allylation of aldehydes with allyltributylstannane in detail, the following reaction pathway was proposed for the reaction. It has already been reported that the coordinative unsaturated 16-electron complex was generated by the dissociation of carbon monoxide from $ReBr(CO)_5$ under toluene reflux conditions.[14] Based on the information, we suggest that the first step of the present allylation of aldehydes is the generation of a 16-electron rhenium species by the dissociation of carbon monoxide from 18-electron rhenium complex, $ReBr(CO)_5$. The coordinative unsaturated rhenium species generated in situ acts as a Lewis acid for the allylation of aldehyde with allyltributylstannane.

As an application of the rhenium-catalyzed reaction, the reaction of enol silyl ethers with an aldehyde in the presence of the rhenium catalyst was next examined. The treatment of the enol silyl ether derived from acetophenone with benzaldehyde gave 3-hydroxy-1,3-diphenylpropan-1-one in 75% yield (Scheme 2). Similarly, 3-phenyl-2-hydroxy-1-phenyloctan-1-one was obtained by the reaction of enol silyl ether derived from acetophenone with hexanal in moderate yield.



Scheme 2.

In summary, it was found that a rhenium complex catalyzed the allylation of aldehyde with allyltributylstannane and the Mukaiyama-type aldol reaction of enol silyl ether with an aldehyde to give the corresponding homoallylic alcohols and β-hydroxy carbonyl compounds in moderate to good yields. The application of the catalytic use of a rhenium complex in organic synthesis is now in progress.

References and notes

1. See recent reviews: (a) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 2; (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207; (c) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31; (d) Thomas, E. J. *Chem. Commun.* **1997**, 411.
2. Recently, it has been shown that borane,[3] aluminum,[4] silver,[5] titanium,[6] zirconium,[7] ytterbium,[8] and rhodium[9] complexes are capable of catalyzing the allylation of carbonyl compounds with organoallylstannane.
3. Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490.
4. Marx, A.; Yamamoto, H. *Synlett* **1999**, 584.
5. Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723.
6. (a) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001; (b) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467; (c) Gauthier, D. R., Jr.; Carreira, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2363.
7. (a) Bedeschi, P. B.; Casolari, S.; Costa, A. L.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7897; (b) Casolari, S.; Cozzi, P. G.; Orioli, P.; Tagliavini, E.; Umani-Ronchi, A. *Chem. Commun.* **1997**, 2123.
8. (a) Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639; (b) Aspinall, H. C.; Greeves, N.; McIver, E. G. *Tetrahedron Lett.* **1998**, *39*, 9283.
9. Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131.
10. Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2779.
11. Although many studies on the high valent rhenium-oxo-catalyzed transformations of organic compounds have been reported,[12] few have addressed the catalytic use of low-valent rhenium species in organic reactions.[13]
12. For recent reviews, see; (a) Herrman, W. A. In *Organic Peroxygen Chemistry*; Herrman, W. A., Ed.; Springer: Berlin, 1993; 164, p 130; (b) Kusama, H.; Narasaka, K. *J. Synth. Org. Chem.* **1996**, *54*, 644; (c) Espenson, J. H. *Chem. Commun.* **1999**, 479; (d) Adam, W.; Mitchell, C. M.; Saha-Moller, C. R.; Weichold, O. *J. Am. Chem. Soc.* **1999**, *121*, 2097; (e) Jacob, J.; Espenson, J. H. *Chem. Commun.* **1999**, 1003; (f) Jeon, H.-J.; Hguyen, S. T. *Chem. Commun.* **2001**, 235; (g) Kennedy-Smith, J. J.; Nolin, K. A.; Gunterman, H. P.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 4056; (h) Gable, K. P.; Brown, E. C. *J. Am. Chem. Soc.* **2003**, *125*, 11018; (i) Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 15760; (j) Gable, K. P.; Brown, E. C. *Synlett* **2003**, 2243; (k) Kennedy-Smith, J. J.; Young, L. A.; Toste, F. D. *Org. Lett.* **2004**, *6*, 1325; (l) Sherry, B. D.; Loy, R. N.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4510; (m) Cardona, F.; Soldaini, G.; Goti, A. *Synlett* **2004**, 1553, and references cited therein.
13. (a) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1988**, *29*, 3833; (b) Kusama, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2379; (c) Koga, Y.; Kusama, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 475; (d) Hua, R.; Tian, X. *J. Org. Chem.* **2004**, *69*, 5782, and Ref. 10,12b.
14. (a) Jolly, P. W.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5259; (b) Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3149; (c) Zingales, F.; Sartorelli, U.; Canziani, F.; Raveglia, M. *Inorg. Chem.* **1967**, *6*, 154.