

A New Preparative Method for Allylic Indium(III) Reagents by Reductive Transmetalation of π -Allylpalladium(II) with Indium(I) Salts

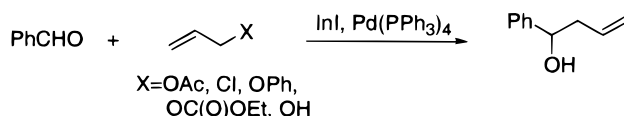
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ABSTRACT



A reductive transmetalation of the π -allylpalladium(II) complexes, generated in situ from a catalytic amount of a palladium(0) complex and a variety of allylic substrates, with indium(I) salts proceeded smoothly in various solvents, providing a new route for allylindium(III) reagents.

Over the past decade, organoindium reagents, in particular, allylic indium reagents, are of increasing interest in organic synthesis such as carbonyl allylation and allylindation of carbon–carbon multiple bonds.¹ In these reactions, high regio- and stereoselectivity have often been realized on the basis of the chelation of the indium atom with a hydroxyl or a carboxyl group in the substrates. The tolerance to water allows the wide use of allylindium reagents in aqueous media, and this property makes the reagents unique and important in respect to environmentally benign chemistry.² However, the preparative methods of allylindium(III) compounds are limited. Apart from the conventional transmetalation of allyllithium or allyl Grignard reagents with indium(III) halides,^{3,4} a more convenient and widely used

method is the oxidative addition of metallic indium⁵ or indium(I) iodide⁶ to allylic substrates. However, this method suffers from the restricted usability of both allylic substrates and solvents, i.e., the reaction proceeds only with allylic bromides or iodides⁷ in polar solvents.⁸ Here we report a new preparative method for allylic indium(III) reagents via a reductive transmetalation of a π -allylpalladium(II) complex with indium(I) salts, which enables the use of a wide variety of allylic compounds and solvents.

(1) (a) Cintas, P. *Synlett* **1995**, 1087–1096. (b) Marshall, J. A. *Chemtracts-Org. Chem.* **1997**, *10*, 481–496. For recent papers, see: (c) Hirashita, T.; Kamei, T.; Horie, T.; Yamamura, H.; Kawai, M.; Araki, S. *J. Org. Chem.* **1999**, *64*, 172–177. (d) Araki, S.; Kamei, T.; Igarashi, Y.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 7999–8002. (e) Klaps, E.; Schmid, W. *J. Org. Chem.* **1999**, *64*, 7537–7546 and references therein.

(2) (a) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023–2035. (b) Li, C.-J. *Tetrahedron* **1996**, *52*, 5643–5668. (c) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149–11176. (d) Paquette, L. A. In *Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing*; Anastas, P., Williamson, T., Eds.; Oxford University Press: New York, 1998.

(3) For example, see: Araki, S.; Horie, T.; Kato, M.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 2331–2334.

(4) Transmetalation of allylstannane with indium(III) chloride also gives allylindium(III): Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920–1921. Li, X.-R.; Loh, T.-P. *Tetrahedron: Asymmetry* **1996**, *7*, 1535–1538.

(5) Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831–1833. Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S.-J.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538–2542.

(6) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291–296.

(7) Allylic chlorides and phosphates are usable only in the presence of iodide salts such as sodium iodide via the in situ conversion to allylic iodides (see ref 5).

(8) Recently, Chan reported a new preparation of allylindium(I) via a transmetalation of allylmercury with metallic indium in water concerning the structural study of the allylindium reagents prepared in aqueous media: Chan, T.-H.; Yang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3228–3229.

Allyl acetate and indium(I) iodide were reacted with benzaldehyde in a Barbier-type manner in the presence of a catalytic amount (5 mol %) of tetrakis(triphenylphosphine)-palladium(0). The allylation proceeded smoothly at room temperature to give high yields of the corresponding homoallyl alcohol. Table 1 summarizes the results under various

Table 1. Palladium-Catalyzed Allylation of Benzaldehyde with Allyl Acetate and Indium Iodide^a

$$\text{PhCHO} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{OAc} \xrightarrow[\text{rt}]{\text{InI, Pd(PPh}_3)_4} \text{Ph}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}=\text{CH}_2$$

run	molar ratio ^b	solvent	time (h)	yield (%)
1	2/2/1	THF	1.5	86
2	1/1/1	THF	5	91
3	2/2/1	DMI	1	96
4	2/2/1	CH ₂ Cl ₂	3	68
5	2/2/1	THF/H ₂ O ^c	2	100
6	2/2/1	H ₂ O	5	96
7	2/2/1	MeOH	18	81
8	2/2/1	EtOH	24	100
9	2/2/1	Et ₂ O	72	26
10	2/2/1	benzene	48	8
11	2/2/1	hexane	72	8

^a The reactions were carried out in a Barbier-type manner with Pd(PPh₃)₄ (5 mol %) at room temperature. ^b InI/allyl acetate/PhCHO. ^c Ratio 1/1.

reaction conditions.¹¹ The reaction could be carried out in a variety of solvents including THF, 1,3-dimethyl-2-imidazolidinone (DMI), and dichloromethane. Protic solvents such as water, methanol, and ethanol could also be used, although a somewhat longer reaction time was needed for the alcoholic solvents. Nonpolar solvents such as ether, benzene, and hexane gave poor yields of the product. As is shown in Table 2, various allylic compounds with different leaving groups

Table 2. Palladium-Catalyzed Allylation of Benzaldehyde with Various Allylic Substrates^a

$$\text{PhCHO} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{X} \xrightarrow[\text{THF, rt}]{\text{InI, Pd(PPh}_3)_4} \text{Ph}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}=\text{CH}_2$$

run	X	time (h)	yield (%)
1	OAc	1.5	86
2	Cl	1.5	100
3	OPh	1.5	89
4	OC(O)OEt	1.5	76
5	OH	13	76
6	SMe	17	43

^a The reactions were carried out in a Barbier-type manner with InI/allylic substrate/PhCHO (2/2/1) and Pd(PPh₃)₄ (5 mol %) in THF at room temperature.

are usable for this palladium-catalyzed allylation; in particular, allyl alcohol itself can be used. Other indium(I) salts

such as indium(I) bromide and indium(I) chloride are equally effective, and even metallic indium powder works as a reductant, although a much longer reaction time is required (Table 3). The satisfactory results with a combination of

Table 3. Comparison of Reducing Agents^a

$$\text{PhCHO} + \text{R}-\text{CH}=\text{CH}-\text{CH}_2-\text{OAc} \xrightarrow[\text{THF, rt}]{\text{M, Pd(PPh}_3)_4} \text{Ph}-\text{CH}(\text{OH})-\text{CH}(\text{R})-\text{CH}=\text{CH}_2$$

run	M	R	time	yield (%)
1	InI	H	1.5 h	84
2	InBr	H	1 h	84
3	InCl	H	4 h	51
4	In	H	6 d	48
5	In	Ph	8 d	92 (<i>anti</i> only)
6 ^b	InCl ₃ •(3–4)H ₂ O/Al	H	9 h	82

^a The reactions were carried out in a Barbier-type manner with M/allylic acetate/PhCHO (2/2/1) and Pd(PPh₃)₄ (5 mol %) in THF at room temperature, unless stated otherwise. ^b With InCl₃•(3–4)H₂O (1.1 mmol), Al (3.7 mmol), allyl acetate (1 mmol), PhCHO (1 mmol), and Pd(PPh₃)₄ (0.05 mmol).


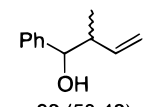
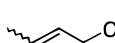
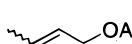
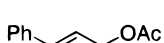
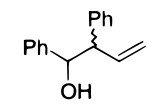
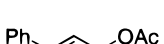
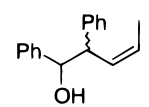

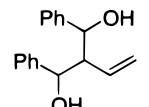
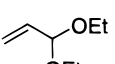
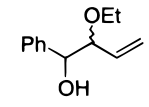
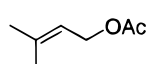
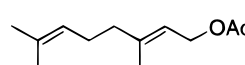
indium trichloride hydrate and metallic aluminum allow the use of this inexpensive indium source (entry 6).

Starting from α -methallyl chloride, crotyl chloride, or crotyl acetate, the branched homoallylic alcohol was obtained exclusively (Table 4, entries 1–3). Although the diastereoselectivities are slightly different, the results support the intermediacy of the common allylic indium species in these reactions. The α,γ -disubstituted allylic acetate also gave the γ -adduct stereoselectively (*Z* only) (entry 5). On the contrary, the vinyloxirane gave the branched allylic diol (α -adduct) exclusively in high yield (entry 6). With acrolein diethyl acetal, the α -adduct was obtained again in 91% yield, together with a small amount (9%) of the homoallylic diol. In the latter reactions, the products were formed *syn* selectively, suggesting that the intermediate indium reagents may exist as oxygen-chelated cyclic forms.^{1c} The γ,γ -disubstituted allylic acetates were unfortunately unsusceptible to conversion to the corresponding allylic indium reagents.

The most plausible catalytic cycle for the present palladium-catalyzed allylation is depicted in Scheme 1. The initially formed π -allylpalladium(II) complex is reductively transmetalated with indium(I) salts to give allylindium(III) species, which allylates benzaldehyde.⁹ This process has been confirmed by the following two experiments. Thus, the InI-mediated allylation of benzaldehyde with π -allylpalladium(II) chloride dimer in THF gave the homoallyl alcohol in 77% yield. Furthermore, the ¹H NMR spectrum of the allylindium compound, prepared in a Grignard-type manner from allyl chloride and indium(I) iodide in the presence of tetrakis-

(9) A pathway involving transient Pd–In complexes as intermediates has been suggested for the formation of allenylindium reagents from propargylic mesylates by Pd-catalyzed metalation with InI: Marshall, J. A.; Grant, C. M. *J. Org. Chem.* **1999**, *64*, 696–697. See also: Perez, I.; Sestelo, J. P.; Sarandeses, L. A. *Org. Lett.* **1999**, *1*, 1267–1269.

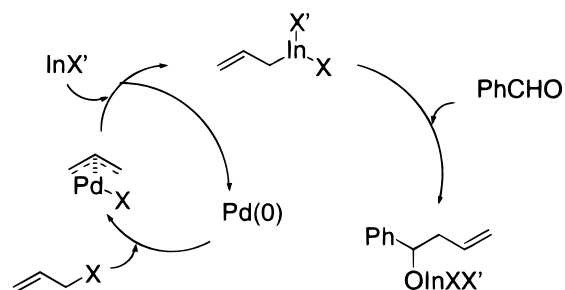
Table 4. Palladium-Catalyzed Allylation of Benzaldehyde with Substituted Allylic Compounds^a

run	allylic compound	product and yield (%) (<i>syn:anti</i>)
1		 92 (58:42)
2	 (<i>E:Z</i> =85:15)	96 (37:63)
3	 (<i>E:Z</i> =86:14)	98 (32:68)
4 ^b		 100 (14:86)
5 ^c		 79 (11:89)
6	 (<i>trans:cis</i> =31:69)	 80 (85:15) ^d
7 ^e		 91 (64:36)
8		0
9		0

^a Unless stated otherwise, the reactions were carried out in a Barbier-type manner with InI/allylic compound/PhCHO (1.5/1.2/1) and Pd(PPh₃)₄ (5 mol %) in THF at room temperature. ^b InI/allylic compound/PhCHO = 2/2/1. ^c InI/allylic compound/PhCHO = 2/1.2/1. ^d Diastereomeric ratio. ^e InI/allylic compound/PhCHO = 2/1/2. A small amount (9%) of the homoallylic diol was also obtained.

(triphenylphosphine)palladium (5 mol %) in DMF-*d*₇, revealed the allyl signals at δ 5.96 (1H), 4.67 (2H), and 2.08

Scheme 1



ppm (2H). These chemical shifts are in good accord to those of allylindium(III) diiodide prepared from allyl iodide and indium(I) iodide.⁶

Umpolung of π -allylpalladium(II) to allylmetals has been realized so far by using various reductants such as dialkylzinc and trialkylborane.¹⁰ The results described here demonstrate for the first time that indium(I) salts are also effective for this transformation. This new methodology expands the scope of usable allylic substrates and solvents and provides a convenient, efficient, and practical method for the preparation of allylindium(III) reagents.

Acknowledgment. We thank Professor Y. Tamaru of Nagasaki University for his generous sending the NMR data.

Supporting Information Available: Detailed experimental procedures and characterization data for the products in Table 4 and the ¹H NMR spectrum of the allylindium compound prepared in a Grignard-type manner. This material is available free of charge via Internet at <http://pubs.acs.org>. OL005610I

(10) For example, see: Tamaru, Y. *J. Organomet. Chem.* **1999**, 576, 215–231. See also: Kimura, M.; Kiyama, I.; Tomizawa, T.; Horino, Y.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **1999**, 40, 6795–6798 and references therein.

(11) **Typical experimental procedure** (Table 1, entry 1): To a mixture of indium(I) iodide (0.24 g, 1.0 mmol) and Pd(PPh₃)₄ (29 mg, 0.025 mmol) in THF (3 mL) were added allyl acetate (0.11 mL, 1.0 mmol) and benzaldehyde (0.052 mL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon. The reaction was monitored by TLC. After 1.5 h, the benzaldehyde was consumed. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was chromatographed on silica gel (CH₂Cl₂/hexane = 1/1) to give 1-phenyl-3-buten-1-ol (64 mg, 86% yield).