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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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SYNTHESIS AND UTILIZATION OF INDIUM (I) IODIDE FOR IN SITU FORMATION OF ENANTIOENRICHED ALLENYLINDIUM REAGENTS AND THEIR ADDITION TO ALDEHYDES: (2R,3S,4S)-1-(tert-BUTYLDIPHENYLSILYLOXY)-2,4-DIMETHYL-5-HEXYN-3-OL

[5-Hexyn-3-ol, 1-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-2,4-dimethyl-, (2R,3S,4S)-]
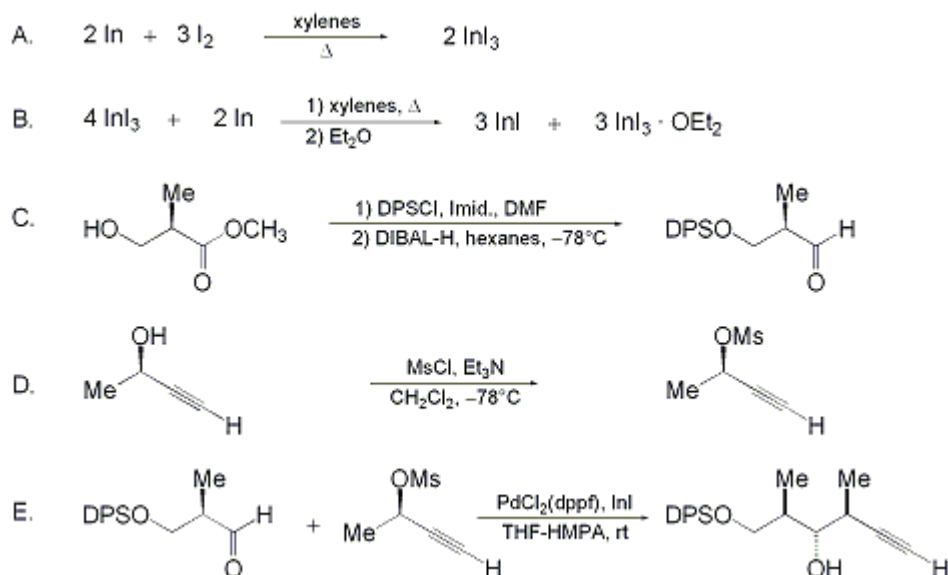
Submitted by Brian A. Johns, Charsetta M. Grant, and James A. Marshall[1] .
Checked by Edward B. Holson and William R. Roush.

1. Procedure

A. Indium(III) iodide . To a 1-L, oven-dried, round-bottomed flask flushed with argon and equipped with a magnetic stirrer is added xylenes (500 mL). The solvent is degassed (Note 1) and the flask is equipped with a reflux condenser. Indium powder (5.00 g, 43.6 mmol) (Note 2) is added to the vigorously stirring solution, followed by iodine (I$_2$, 16.57 g, 65.32 mmol). The mixture is stirred vigorously (Note 3) and heated at reflux (bath temp. ≈160-170°C) under argon for 1-1.5 hr or until the indium metal is consumed. When the metal is consumed, a crystal of iodine is added and stirring at reflux is resumed. The reaction is complete when the added iodine is not consumed after 15 min at reflux. The solution is filtered hot and allowed to cool to room temperature (Note 4). The resulting bright yellow crystals are filtered under nitrogen using a Schlenk filtration system (Note 5) and washed with two 10-mL portions of cold benzene to remove traces of I$_2$. The filtrate is concentrated to 1/4-1/3 volume (Note 6) and cooled to 0°C. The yellow precipitate is Schlenk-filtered under nitrogen and washed with cold benzene (10 mL). The product is dried under reduced pressure to yield 18.3 g (85%) of indium(III) iodide [In(III)I] (Note 7).

B. Indium(I) iodide . To a 1-L, oven-dried, round-bottomed flask flushed with argon and equipped with a magnetic stirrer is added xylenes (400 mL). The solvent is degassed (Note 1) and the flask is equipped with a reflux condenser. Indium(III) iodide (18.30 g, 36.93 mmol) is added to the flask, and the mixture is stirred vigorously while indium powder (2.12 g, 18.46 mmol) (Note 2) is added. The mixture is stirred vigorously (Note 3) at reflux under argon for 18 hr. The resulting yellow suspension is allowed to cool to room temperature, diluted with ether (400-500 mL) and stirred for 1 hr. The resulting

burgundy precipitate is filtered under air and washed with ether (100 mL). The product is dried under reduced pressure to yield 6.14 g (92%) of indium(I) iodide . The filtrate is concentrated to dryness on a rotary evaporator, venting with nitrogen, to yield 14.4 g (105% based on eq B.) (Note 8) of recovered indium(III) iodide (Note 9).

C. (R)-3-(tert-Butyldiphenylsilyloxy)-2-methylpropanal . A 500-mL, oven-dried, round-bottomed flask equipped with a magnetic stirrer is charged with 10.00 g (84.67 mmol) of methyl (R)-(−)-3-hydroxy-2-methylpropionate (Note 10), and 100 mL of N,N-dimethylformamide (Note 11). The solution is cooled to 0°C and 14.4 g (211 mmol) of imidazole is added. Upon dissolution of the imidazole, 23.1 mL (88.9 mmol) of tert-butyldiphenylchlorosilane (DPSCl) (Note 12) is added dropwise via syringe. After 10 min, the cooling bath is removed and the solution is allowed to warm to room temperature for 2 hr. The reaction is quenched by the addition of 200 mL of pentane and 40 mL of water (H_2O). The layers are separated and the pentane layer is washed with brine (75 mL). The aqueous layer is extracted with pentane (3 × 75 mL), and the combined extracts are dried over anhydrous sodium sulfate (Na_2SO_4). Filtration and concentration under reduced pressure followed by purification by flash chromatography (Note 13) yield 29.9 g (99%) of methyl (R)-3-(tert-butyldiphenylsilyloxy)-2-methylpropionate as a clear oil (Note 14).

A 1-L, oven-dried, round-bottomed flask equipped with a magnetic stirrer is charged with 9.92 g (27.9 mmol) of methyl (R)-3-(tert-butyldiphenylsilyloxy)-2-methylpropionate and 200 mL of dry hexanes (Note 15). The solution is cooled to −78°C, and 31.5 mL (31.5 mmol) of 1 M diisobutylaluminum hydride (in hexane) (DIBAL-H) (Note 16) is added dropwise over 15 min via a syringe pump. After the addition is complete, the resultant solution is stirred at −78°C for 2 hr. The reaction is quenched by pouring the cold solution into 250 mL of saturated aqueous Rochelle's salt. Ether (300 mL) and H_2O (75 mL) are added and the biphasic mixture is stirred vigorously for 1 hr (Note 17). The layers are separated and the ether layer is washed with brine. The aqueous layer is extracted with ether (2 × 50 mL) and the combined extracts are dried over Na_2SO_4 . Filtration of the solution and concentration of the filtrate under reduced pressure followed by purification of the crude product by flash chromatography (Note 18) yields 7.85 g (86%) of (R)-3-(tert-butyldiphenylsilyloxy)-2-methylpropanal as a white solid (Note 19).

D. (R)-3-Butyn-2-yl methanesulfonate . To a 1-L, oven-dried, round-bottomed flask flushed with argon and equipped with a magnetic stirrer is added dichloromethane (CH_2Cl_2, 713 mL) and (R)-(+)-3-butyn-2-ol (10.00 g, 143 mmol) (Note 20). The mixture is cooled to −78°C and triethylamine (Et_3N, 39.7 mL, 285 mmol) and methanesulfonyl chloride (16.6 mL, 214 mmol) are added. The resulting mixture is stirred at −78°C for 1 hr, then quenched with aqueous saturated sodium bicarbonate ($NaHCO_3$) solution and allowed to warm to room temperature. The layers are separated and the organic layer is washed with brine and concentrated under aspirator pressure (Note 21). The residue is diluted with 500 mL of ether and washed with water (20 mL) followed by brine (20 mL). The aqueous layer is extracted with ether (50 mL). The combined extracts are dried over anhydrous Na_2SO_4 and concentrated under aspirator pressure to yield 20.13 g (95%) of the methanesulfonate (Note 22). The material is used without further purification (Note 23).

E. (2R,3S,4S)-1-(tert-Butyldiphenylsilyloxy)-2,4-dimethyl-5-hexyn-3-ol . An oven-dried, 100-mL, one-necked flask, equipped with a magnetic stirring bar is purged with argon. The flask is charged with (R)-3-(tert-butyldiphenylsilyloxy)-2-methylpropanal (3.00 g, 9.19 mmol) and the (R)-methanesulfonate (1.50 g, 10.1 mmol). Tetrahydrofuran (THF, 29.4 mL) and hexamethylphosphoramide (HMPA, 7.4 mL) are added via syringe. To the solution is added PdCl$_2$(dppf) (335 mg, 0.46 mmol) (Note 24), immediately followed by indium(I) iodide (2.66 g, 11.0 mmol). The resultant dark suspension is stirred vigorously for 1 hr at which time the reaction is judged complete by TLC (Note 25). The reaction mixture is quenched by the addition of H_2O (30 mL), and ether (20 mL) is added. After being stirred for 2 min the layers are separated and the ether layer is washed with brine. The aqueous layer is extracted with ether (3 × 25 mL) and the combined extracts are dried over anhydrous Na_2SO_4 . Filtration of the solution and concentration of the filtrate under reduced pressure followed by purification of the crude product by flash chromatography on silica gel (Note 26) provide 2.64 g (76%) of (2R,3S,4S)-1-(tert-butyldiphenylsilyloxy)-2,4-dimethyl-5-hexyn-3-ol (Note 27) as a clear oil and 201 mg of the (2R,3R,4R) diastereomer (Note 28).

2. Notes

1. The commercial mixture of xylenes was used as received without further purification. Degassing was accomplished by bubbling argon through the solvent for 30 min.

2. Indium powder, −100 mesh, 99.99%, was purchased from Aldrich Chemical Company, Inc.

3. Vigorous stirring is very important. Use of a large stir bar for this reaction is crucial. During the course of the reaction the powdered indium metal may adhere to the sides of the flask. On occasion it was necessary to dislodge this powder from the walls of the flask. The flask was removed from the heat source, allowed to cool below reflux, and the walls of the flask were scraped with a metal spatula. *Caution should be exercised when performing this operation to avoid burns and the flask should be blanketed with argon to prevent solvent flash.* On a larger scale the submitters recommend use of a mechanical stirrer.

4. A coarse, 150-mL, fritted glass filter was used for the hot filtration. This filtration should be performed quickly, as precipitates form rapidly upon cooling. This filtration may be performed in the air without complication.

5. The product is very hygroscopic and should be handled under an inert atmosphere. The checkers found that inactive material was produced if the filtration was performed using a 150-mL fritted funnel under a blanket of nitrogen. The checkers subsequently performed this filtration under nitrogen using a Schlenk filtration system consisting of a 2-L, 24/40 three-necked flask, a 24/40 double male adapter, and a 400-mL 24/40 coarse fritted Schlenk filter. The reaction vessel is connected to one end of the double male adapter and the other end is quickly attached to the Schlenk filter system under a positive flow of nitrogen. The solution is poured onto the filter, and filtered into the three-necked flask via a vacuum system that is connected to one of the ports on the three-necked flask.

6. This step may be performed by using a rotary evaporator connected to a water aspirator, with a drying column inserted between the aspirator and the evaporator. The rotary evaporator is vented with nitrogen once the desired final volume is reached.

7. The checkers obtained 74-85% yields of indium(III) iodide .

8. The checkers obtained 86-93% yields of indium(I) iodide , and 98-113% yields of recovered indium (III) iodide etherate . The latter material was successfully recycled as described by the submitters (Note 9).

9. The recovered InI_3 can be used without further purification to generate additional InI. Procedure B was repeated with recovered InI_3 (14.4 g, 29.1 mmol), indium powder (1.7 g, 14.8 mmol) and degassed xylenes (320 mL) to yield 5.0 g (95%) of indium(I) iodide and 10.0 g (93%) of recovered indium(III) iodide .

10. Methyl (R)-(−)-3-hydroxy-2-methylpropionate was purchased from Sigma Chemical Company and refrigerated until used.

11. Anhydrous N,N-dimethylformamide was purchased from Aldrich Chemical Company, Inc.

12. tert-Butyldiphenylchlorosilane was purchased from United Chemical Technologies Inc.

13. The separation is achieved on a column of silica gel with pentane:ether (gradient 18:1 to 9:1) as the eluent.

14. The physical properties are as follows: $[\alpha]_D^{20} -16.4°$ (CHCl$_3$, *c* 2.8); ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.04 (s, 9 H), 1.16 (d, 3 H, J = 6.9), 2.72 (m, 1 H), 3.70 (s, 3 H), 3.73 (dd, 1 H, J = 9.9, 5.7) 3.84 (dd, 1 H, J = 9.9, 6.9), 7.36-7.46 (m, 6 H), 7.65-7.68 (m, 4 H) ; IR (film) cm^{-1}: 3071, 3050, 2955, 1746, 1111 . Anal. Calcd for $C_{21}H_{28}O_3Si$; C, 70.74; H, 7.92. Found: C, 70.73; H, 7.80.

15. Hexane was dried by storage over activated 4 Å molecular sieves.

16. The submitters indicated that 1.1 equiv of DIBAL-H was the optimal stoichiometry to ensure complete consumption of the starting methyl ester. If less was used, the aldehyde was not readily obtained in pure form. Excess DIBAL-H results in ≈5-10% overreduction to afford a small amount of the alcohol. However, the checkers found that the reaction did not go to completion under these conditions, and that it was very difficult to separate the aldehyde product from the ester starting material. Therefore, the checkers used 1.13-1.15 equivalents of DIBAL-H for complete reaction, and obtained the product aldehyde in 85-86% yield along with 12-13% yields of alcohol from overreduction. The checkers also obtained small amounts of ester **1** (2-5%, depending on the batch of DIBAL-H used). Ester **1** can be visualized by TLC (R$_f$ 0.65, 5% ether/ pentane), versus Rf's = 0.40 for the starting ester and product aldehyde (which do not separate under these conditions).
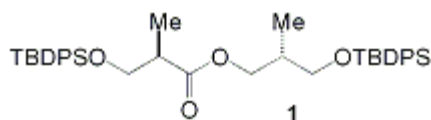
17. The biphasic mixture should be stirred until both layers are clear upon settling.

18. The separation is achieved on a column of silica gel with pentane:ether (gradient 18:1 to 9:1) as the eluent. If any methyl ester remains, the aldehyde can be further purified by recrystallization from hexanes.

19. The physical properties are as follows: $[\alpha]_D$ ^{20}−24.7° (CHCl$_3$, c 1.5); mp 63-64°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.04 (s, 9 H), 1.10 (d, 3 H, J = 6.9), 2.57 (m, 1 H), 3.84 (dd, 1 H, J = 10.5, 6.3), 3.91 (dd, 1 H, J = 10.5, 5.4), 7.37-7.47 (m, 6 H), 7.63-7.66 (m, 4 H), 9.77 (d, 1 H, J = 1.2) . Anal. Calcd for C$_{20}$H$_{26}$O$_2$Si: C, 73.57; H, 8.03. Found: C, 73.30; H, 7.93.

20. (R)-(+)-3-Butyn-2-ol was purchased from Aldrich Chemical Company, Inc., or DMS Fine Chemicals Inc.

21. Concentration of the crude mesylate under reduced pressure must be done with care to avoid loss of product due to volatility.

22. The physical properties are as follows: $[\alpha]_D$ ^{20}+108.4° (CHCl$_3$, c 2.39); ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.66 (d, 3 H, J = 6.8), 2.70 (d, 1 H, J = 2.0), 3.12 (s, 3 H), 5.29 (qd, 1 H, J = 6.8, 2.0) ; ^{13}C NMR (75 MHz, CDCl$_3$) δ: 22.3, 39.0, 67.4, 76.6, 80.1 .

23. The checkers found that the mesylate is unstable to storage and gave best results in the subsequent reaction with In(I)I if used immediately after preparation.

24. PdCl$_2$(dppf) was prepared according to the published procedure[2] from PdCl$_2$(NCPh)$_2$ and dppf ligand purchased from Aldrich Chemical Company, Inc. The commercially available PdCl$_2$(dppf) catalyst was also used, but the freshly prepared catalyst proved superior.

25. TLC analysis was performed on silica gel plates developed with hexanes:ether (3:1), R$_f$ = 0.47, and visualized with ceric(IV) sulfate / ammonium molybdate stain.

26. The separation is achieved on a column of silica gel (34 cm × 16 cm) with hexanes:ether (9:1) as the eluent.

27. The physical properties are as follows: $[\alpha]_D$ ^{20}−17.0° (CHCl$_3$, c 1.51); ^{1}H NMR (300 MHz, CDCl$_3$) δ: 0.86 (d, 3 H, J = 6.9), 1.07 (s, 9 H), 1.33 (d, 3 H, J = 7.5), 2.06 (m, 1 H), 2.15 (d, 1 H, J = 2.4), 2.71 (m, 1 H), 3.42 (m, 1 H), 3.44 (d, 1 H, J = 1.5), 3.71 (dd, 1 H, J = 10.2, 6.9), 3.78 (dd, 1 H, J = 10.2, 4.2), 7.37-7.46 (m, 6 H), 7.72-7.67 (m, 4 H) ; IR (film) cm^{-1}: 3493, 3305, 2931 ; ^{13}C NMR (75 MHz, CDCl$_3$) δ: 13.5, 17.9, 19.1, 26.8, 30.2, 38.9, 68.6, 70.2, 78.1, 85.0, 127.8, 129.8, 132.9, 135.6 . Anal. Calcd for C$_{24}$H$_{32}$O$_2$Si: C, 75.74; H, 8.47. Found: C, 75.74; H, 8.43.

28. The (2R,3R,4R) diastereomer results from partial racemization of one or both of the allenylmetal intermediates. This point was confirmed by comparison to authentic material as the (S)-MPA ((S)-(2-methoxy)phenylacetic acid-Mosher's acid) derivative. The optical rotations of these compounds are small, and thus correlation by comparison of $[\alpha]_D$ ^{20} values is unreliable.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.
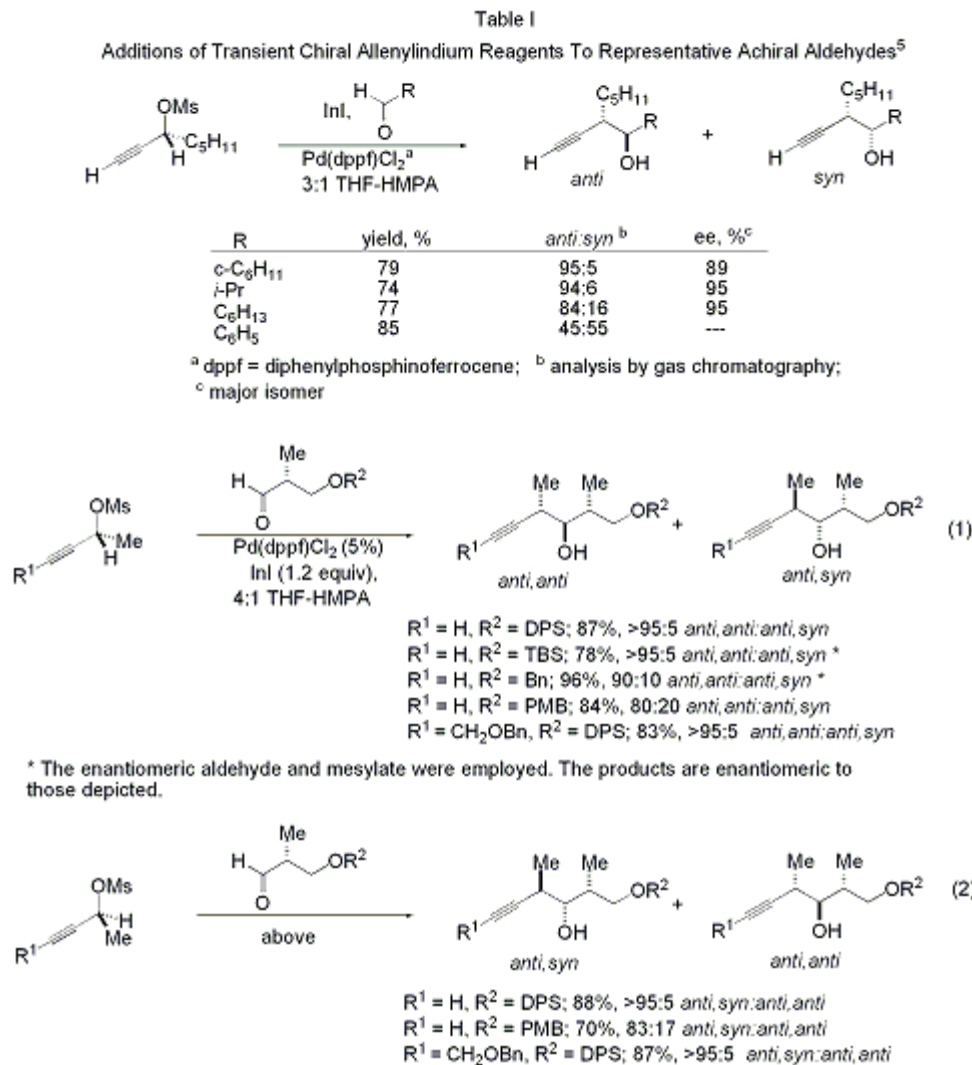
3. Discussion

Chiral allenylmetal compounds provide convenient access to enantioenriched homopropargylic alcohols through S$_E$2' additions to aldehydes.[3] The syn adducts can be obtained through addition of allenyl tributylstannanes in the presence of stoichiometric boron trifluoride etherate (BF$_3$·OEt$_2$). The use of allenylmetal halides derivatives of Sn, Zn, and In lead to the anti diastereomers. The former additions proceed through an acyclic transition state whereas the latter are thought to involve a cyclic transition state, thus accounting for the difference in diastereoselectivity.

The present method is practical and efficient as it employs readily available enantioenriched propargylic alcohols[4] as precursors to the allenylindium reagents. With achiral aldehydes the

diastereoselectivity is high for branched aldehydes, moderate for unbranched aldehydes, and low for benzaldehyde (Table I).[5] With chiral α-methyl aldehydes[6] the additions proceed under effective reagent control to afford anti adducts of high ee and with excellent diastereoselectivity (eq. 1 and 2). Comparable results were obtained with 3:1 dimethyl sulfoxide - tetrahydrofuran (DMSO-THF) as the solvent.

Table I

Table I
Additions of Transient Chiral Allenylindium Reagents To Representative Achiral Aldehydes[5]

R	yield, %	anti:syn[b]	ee, %[c]
c-C$_6$H$_{11}$	79	95:5	89
i-Pr	74	94:6	95
C$_6$H$_{13}$	77	84:16	95
C$_6$H$_5$	85	45:55	---

[a] dppf = diphenylphosphinoferrocene; [b] analysis by gas chromatography; [c] major isomer

R[1] = H, R[2] = DPS: 87%, >95:5 anti,anti:anti,syn
R[1] = H, R[2] = TBS: 78%, >95:5 anti,anti:anti,syn *
R[1] = H, R[2] = Bn: 96%, 90:10 anti,anti:anti,syn *
R[1] = H, R[2] = PMB: 84%, 80:20 anti,anti:anti,syn
R[1] = CH$_2$OBn, R[2] = DPS: 83%, >95:5 anti,anti:anti,syn

* The enantiomeric aldehyde and mesylate were employed. The products are enantiomeric to those depicted.

R[1] = H, R[2] = DPS: 88%, >95:5 anti,syn:anti,anti
R[1] = H, R[2] = PMB: 70%, 83:17 anti,syn:anti,anti
R[1] = CH$_2$OBn, R[2] = DPS: 87%, >95:5 anti,syn:anti,anti

The described preparation of InI is a modification of a 3-step literature procedure in which indium shot is hammered into indium foil and heated with iodine to form InI$_3$.[7] The InI$_3$ is then heated with excess indium foil to form In$_2$I$_4$ (as a complex of InI[InI$_3$]).In a third step, the In$_2$I$_4$ is treated with diethyl ether whereupon it disproportionates to insoluble InI and soluble InI$_3$ etherate that are separated by filtration.

The present procedure combines the second and third steps, thus avoiding handling of the hygroscopic intermediate In$_2$I$_4$ complex. It also demonstrates efficient recycling of the recovered InI$_3$ etherate. Commercial InI, available from Aldrich Chemical Company, Inc., can be used in the allenylindium procedure with comparable results but at greater expense. The InI prepared as described is an easily handled free-flowing powder, whereas the commercial product consists of small beads that must be crushed before use.

An alternative preparation of enantioenriched anti-homopropargylic alcohols along similar lines uses Et$_2$Zn to effect in situ transmetallation of an allenylpalladium intermediate from a propargyl

mesylate and 2.5 mol % of Pd(OAc)$_2$·PPh$_3$ in the presence of an aldehyde (Table II).[8] The two methods are comparable.

Table II

Table II.
Additions of Transient Allenylzinc Reagents to Representative Achiral Aldehydes[8]

R	yield, %	anti:syn [a]	ee, % [b]
c-C$_6$H$_{11}$	75	95:5	90
i-Pr	75	95:5	92
C$_6$H$_{13}$	74	88:12	95
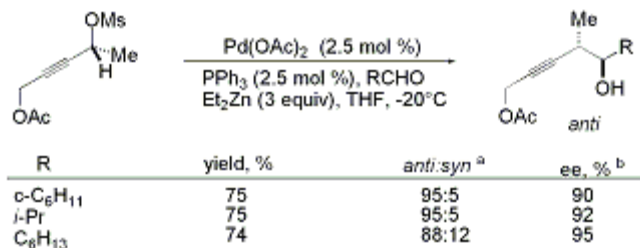
[a] analysis by gas chromatography; [b] major isomer

References and Notes

1. Department of Chemistry, University of Virginia, Charlottesville, VA 22901.
2. (a) Heck, R. F. "Palladium Reagents in Organic Synthesis"; Academic Press: London, 1985; p. 17; (b) Hiyashi T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158-163.
3. Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
4. These can be prepared by a) asymmetric dihydroxylation of allylic chlorides followed by acetonide formation and elimination with BuLi; b) catalytic asymmetric transfer hydrogenation and c) reduction of alkynones with chiral metal hydrides. (a) Marshall, J. A.; Jiang, H. *Tetrahedron Lett.* **1998**, *39*, 1493; Yadav, J. S.; Chander, M. C.; Rao, C. S. *Tetrahedron Lett.* **1989**, *30*, 5455; (b) Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738; (c) Marshall, J. A.; Wang, X. -j. *J. Org. Chem.* **1991**, *56*, 3211.
5. Marshall, J. A.; Grant, C. M. *J. Org. Chem.* **1999**, *64*, 696.
6. Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pilli, R.; Badertscher, U. *J. Org. Chem.* **1985**, *50*, 2095; Wasicak, J. T.; Donaldson, W. A. *Tetrahedron: Asymmetry* **1998**, *9*, 133; Roush, W. R.; Palkowitz, A. D.; Palmer, M. A. J. *J. Org. Chem.* **1987**, *52*, 316.
7. This procedure is a modification of the method of Tuck: Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.
8. Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1998**, *63*, 3812.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Indium (I) iodide:
Indium iodide (8);
Indium iodide (InI) (9); (13966-94-4)

(2R,3S,4S)-1-(tert-Butyldiphenylsilyloxy)-2,4-dimethyl-5-hexyn-3-ol:
5-Hexyn-3-ol, 1-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-2,4-dimethyl-, (2R,3S,4S)- (14); (220634-80-0)

Indium (III) iodide:
Indium iodide (8);

Indium iodide (InI$_3$) (9); (13510-35-5)

Indium (8, 9); (7440-74-6)

Iodine (8, 9); (7553-56-2)

(R)-3-(tert-Butyldiphenylsilyloxy)-2-methylpropanal:
Propanal, 3-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-2-methyl-, (2R)- (12); (112897-04-8)

Methyl (R)-(−)-3-hydroxy-2-methylpropionate:
Propanoic acid, 3-hydroxy-2-methyl-, methyl ester, (R)- (10); (72657-23-9)

N,N-Dimethylformanide: CANCER SUSPECT AGENT:
Formanide, N,N-dimethyl- (8, 9); (68-12-2)

Imidazole (8);
1H-Imidazole (9); (288-32-4)

tert-Butyldiphenylchlorosilane:
Silane, chloro(1,1-dimethylethyl)diphenyl- (9); (58479-61-1)

Methyl (R)-3-(tert-butyldiphenylsilyloxy)-2-methylpropionate:
Propanoic acid, [[(1,1-dimethylethyl)diphenylsilyl]oxy]-2-methyl-, methyl ester, (2R)- (13); (153775-90-7)

Diisobutylaluminum hydride: DIBAL-H:
Aluminum, hydrodiisobutyl- (8);
Aluminum, hydrobis(2-methylpropyl)- (9); (1191-15-7)

(R)-3-Butyn-2-yl methanesulfonate:
3-Butyn-2-ol, methanesulfonate, (2R)- (12); (121887-95-4)

(R)-(+)-3-Butyn-2-ol:
3-Butyn-2-ol, (+)- (9); (42969-65-3)

Triethylamine (8);
Ethanamine, N,N-diethyl- (9); (121-44-8)

Methanesulfonyl chloride (8, 9); (124-63-0)

Hexamethylphosphoramide: HIGHLY TOXIC; CANCER SUSPECT AGENT:
Phosphoric triamide, hexamethyl- (8, 9); (680-31-9)

[1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium:
Palladium, [1,1'-bis(diphenylphosphino)ferrocene-P,P']dichloro- (10); (72287-26-4)

Bis(benzonitrile)dichloropalladium(II):
Palladium, bis(benzonitrile)dichloro- (8, 9); (14220-64-5)

1,1'-Bis(diphenylphosphino)ferrocene (dppf):
Phosphine, 1,1'-ferrocenediylbis[diphenyl- (8);
Ferrocene, 1,1'-bis(diphenylphosphino)- (9); (12150-46-8)