such time is reached, when the conditioning of aluminum oxide (after six or seven batches) suppresses this negative effect. Thus, the use of inert support materials achieves higher yields in shorter times. The conversion of selenium into selenophene is almost quantitative (based on selenium), since any unreacted selenium in one batch can be converted into selenophene in the next batch.

Registry No. Selenium, 7782-49-2; acetylene, 74-86-2; selenophene, 288-05-1.

Highly Chemoselective Reductions with PMHS and Palladium(0) Catalyst

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Transition-metal catalysts not only enhance reaction rates but very often significantly change the course of the uncatalyzed reaction, leading to different, and on occasion to completely opposite, regio- and stereochemical selectivities. The catalyzed reaction often also shows increased functional specificity, leading to enhanced chemoselectivity.[1]

The best examples of these properties of transition-metal catalysis are probably found in the literature of organic reduction chemistry, which is still a challenging and demanding area in synthetic chemistry, particularly when working with compounds having several reducible moieties. Fortunately, an astute choice of reducing agent and catalyst can often lead to sufficient chemoselectivity for practical synthesis, without resorting to complex masking procedures. In our recent work, tributyltin hydride reducing agent and $Pd(PPh_3)_4$ catalyst[2,3] were shown to selectively reduce allylic heterosubstituents and Michael acceptors in the presence of other easily reducible functionalities such as benzylic heterosubstituents, aldehydes, and ketones.

In this paper we report on a reducing system that has even greater chemoselectivity and can differentiate unprecedently between functional groups with a similar tendency to be reduced. It involves a Pd(0) catalyst and polymethylhydrosiloxane[4] (PMHS) as a hydride donor.

Surprisingly, although PMHS has been known and readily available for more than 35 years,[5] it has been almost entirely overlooked by organic chemists. There are only sporadic reports on its having been employed for reduction,[6] and then mainly to generate trialkyltin hydrides.[7] A closely related organosilicone olygomer, HSL-94, has been employed for ionic hydrogenation of alkenes, aldehydes, and ketones.[8]

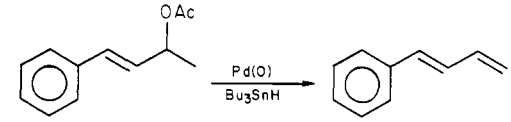
Although in general PMHS is a much weaker reducing agent than tributyltin hydride, when it is used to reduce (π-allyl)palladium intermediates it operates with equal efficiency, giving rise to reductive cleavage of allylic heterosubstituents[9] as shown in Table I.

PMHS is a more convenient reagent than Bu_3SnH, as it is more stable,[4] nontoxic,[10] and even less expensive. Moreover, it may be added to a reaction mixture in a single portion, and products are easily separated from the resulting polysiloxane byproducts by filtration or distillation.

It is important to note that this reaction may be carried out with palladium catalysts other than $Pd(PPh_3)_3$. It is conceivable, for example, that under reducing conditions, a Pd(0) catalyst may be generated in situ from a Pd(II) species. Indeed, identical synthetic results were obtained with $Pd(OAc)_2$ and triphenylphosphine at a 1:4 equivalent ratio were substituted for $Pd(PPh_3)_4$.

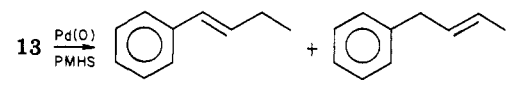
A study comparing the characteristics of PMHS and Bu_3SnH as hydride donors has revealed striking differences between the two, with PMHS offering much greater chemoselectivity. We point out four of the most significant findings.

A. Higher Selectivity with Regard to β-Hydride Elimination. Tributyltin hydride, a hydride donor of low basicity, is capable of reducing a large variety of multifunctional allylic heterosubstituents.[2] However, compounds possessing a relatively acidic hydrogen α to the allylic unit are incompatible with even this low basicity donor. In such compounds, the intermediate (π-allyl)palladium complex undergoes β-hydride elimination to yield the corresponding diene,[11] as shown in eq 1. When PMHS was employed, however, reduction of the allylic acetate was clean, with no apparent β-hydride elimination (eq 2).



(1)

100%



(2)

68% 11%

B. Higher Stability of Both Hydride Donor and Catalyst. Reduction of allylic heterosubstituents with $Bu_3SnH/Pd(0)$ is efficient, particularly when formation of the (π-allyl)palladium intermediate is relatively fast at room temperature. However, when its formation is slow (e.g., when the allylic unit is sterically crowded), both catalyst and tributyltin hydride may deteriorate via competing processes, as indicated by evolution of hydrogen gas and precipitation of metallic palladium. This complication occurs when slow-reacting substrates such as geranyl acetate are reacted with Bu_3SnH. However, when PMHS is employed as the reducing agent, the reaction proceeds as expected (eq 3). Moreover, no gas evolution or color change was observed when solutions containing PMHS and $Pd(PPh_3)_4$ were stirred at room temperature for several days.

C. Differentiation between Allylic Heterosubstituent and Michael Acceptor. Electron-deficient double

(1) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.
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(8) Kursanov, D. N.; Parnes, Z. N.; Loim, M. M. *Synthesis* **1974**, 633.
(9) The use of a number of strong hydride donors for the Pd-catalyzed reduction of allylic heterosubstituents has recently been demonstrated: Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380 and ref 11c.
(10) Klyashchitskaya, A. L.; Krasovskii, G. N.; Fridlyand, S. A. *Gig. Sanit.* **1970**, *35*, 28-31; *Chem. Abstr.* **1970**, *72*, 124864.
(11) (a) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T., *Tetrahedron Lett.* **1978**, 2075. (b) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Ibid.* **1979**, 2301. (c) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Ibid.* **1980**, *21*, 27.

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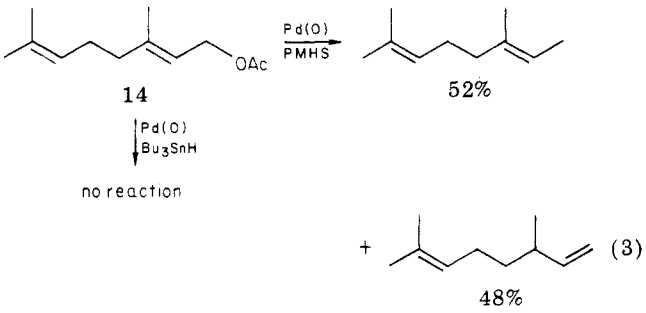
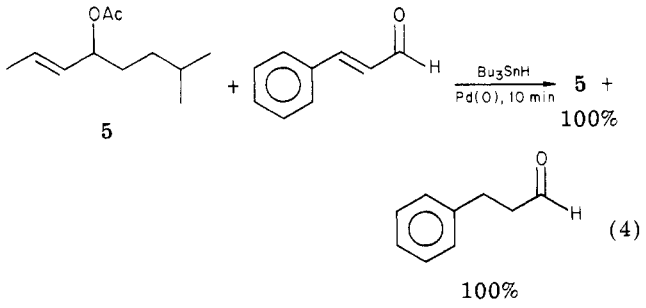
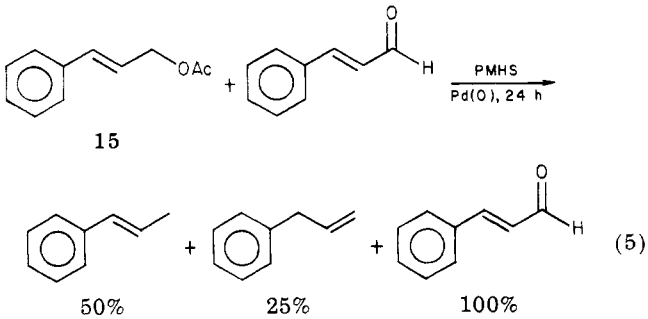


(3)

bonds are prone to rapid reduction with tributyltin hydride and Pd(0).[2,12] This process is much faster in many cases than the reduction of many allylic acetates. In fact, this rate differential can be utilized as a basis for chemoselectivity, as shown in eq 4.



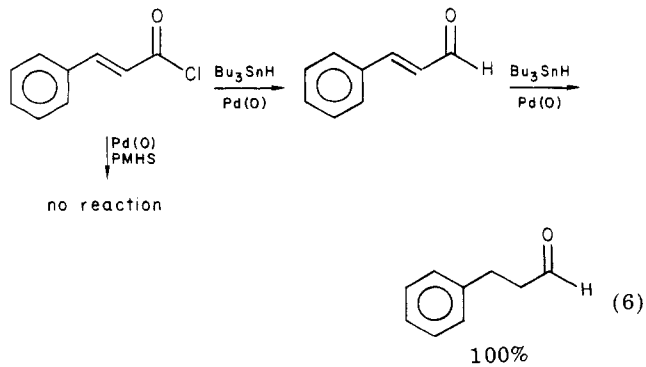
(4)



(5)

Interestingly, Michael acceptors, which are easily reduced with Bu_3SnH,[2] are not reduced by PMHS. Thus, complementary chemoselectivity can also be achieved, namely, reduction of allylic acetate in the presence of a α,β-unsaturated carbonyl compound, as illustrated in eq 5.

D. Differentiation between Allylic Heterosubstituents and Acyl Halides. Acyl halides are rapidly reduced to aldehydes with Bu_3SnH and a Pd(0) catalyst.[13] They react even faster than unsaturated carbonyl compounds, as exemplified by the stepwise reduction of cinnamoyl chloride (eq 6). Surprisingly, acyl halides cannot



(6)

be reduced with $PMHS/Pd(PPh_3)_4$. Moreover, addition of cinnamoyl chloride to a reaction mixture containing cinnamyl acetate, PMHS, and $Pd(PPh_3)_4$ immediately quenched the allylic reduction.

It seems reasonable to assume that the Pd(0) catalyst is irreversibly and rapidly trapped by oxidative addition of acyl chloride to form the corresponding acylpalladium chloride complex, which cannot be reduced by PMHS. This assumption is supported by the observation that addition of Bu_3SnH to the abovementioned, quenched reaction mixture resulted in rapid formation of cinnamaldehyde and dihydrocinnamaldehyde, along with complete reduction of the allylic acetate. Indeed, inhibition of catalytic activity by competitive complexation is a well-documented phenomenon. One of the earliest examples was reported by Kindler,[14] who found that *p*-nitrocinnamic acid, which is not reduced under transfer-hydrogenation conditions, will inhibit the reduction of *p*-methoxycinnamic acid when present in the reaction mixture. Similarly, aromatic aldehydes interfere with the reduction of nitro groups, probably by blocking the catalyst.[15]

In summation, this work has demonstrated that highly chemoselective reductions can be achieved by the proper choice of catalyst and hydride donor. Further studies on utilizing group 4A hydride donors in conjunction with transition-metal catalysts are currently under active investigation in our laboratories.

Experimental Section

General Methods. Melting points (uncorrected) were determined on a Büchi apparatus. Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrometer or on a Nicolet MX-1 FT spectrometer and are given in cm^{-1}. Proton NMR spectra were measured in deuteriochloroform (unless otherwise cited) on a Varian FT-80A or Bruker WH-270 NMR spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si, and the J values are given in hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened. Mass spectra were recorded on a Varian Mat 731 spectrometer. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254, No. 5549). Column chromatography separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh, No. 9385) under pressure (flash chromatography).[16] Preparative TLC was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254, No. 5717). Distillation of products were performed in a Kugelrohr apparatus, and the temperatures given are pot temperatures. GLC analyses were performed on a Hewlett-Packard 7260 (FI detector) chromatograph equipped with a $^1/_8$ in. × 6 ft column packed with 10% Carbowax-20 on Chromosorb W, or a $^1/_8$ in. × 6 ft column packed with 10% SE-30 on Chromosorb W; peak areas were measured by the cut-and-weigh method. Preparative GLC separations were performed on a Varian Aerograph 90P (TC detector) chromatograph equipped with a $^1/_2$ in. × 12 ft column packed with 10% Carbowax-20 on Chromosorb W or a $^3/_8$ in. × 12 ft column packed with 10% SE-30 on Chromosorb W.

Materials. Tetrahydrofuran was distilled over sodium benzophenoneketyl. Tetrakis(triphenylphosphine)palladium(0) was prepared from $PdCl_2$ as reported.[17] Palladium acetate was prepared from Pd metal.[18] Tri-*n*-butyltin hydride was prepared from polymethylhydrosiloxane[19] (Aldrich) and bis(tri-*n*-butyltin) oxide (Aldrich).

(12) Four, P.; Guibe, F. *Tetrahedron Lett.* **1982**, *23*, 1825.
(13) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.
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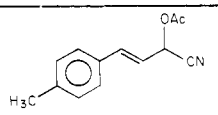
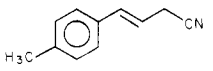
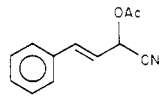
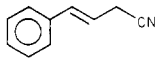
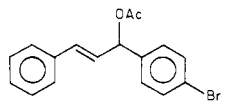
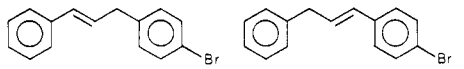
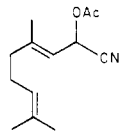
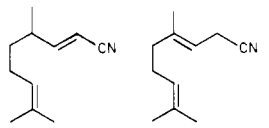
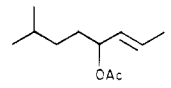
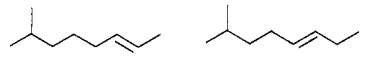
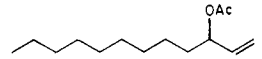
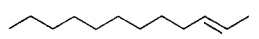
(17) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(18) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.
(19) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81.

Table I. Reductive Cleavage of Allylic Acetates with PMHS and $Pd(PPh_3)_4$

entry	starting material	Pd(0), mol %	PMHS, equiv	time	products	yield, %
1		3	1.8	1.5 h	 7	100
2	 2	4.6	2.2	20 min	 8	93
3	 3	6.7	2.4	7 h	 9a 1:1 9b	89
4	 4	3.5	2.5	48 h	 10a 10:1 10b	75
5	 5	4	2	4 days	 11a 1:1 11b	98
6	 6	8	3.7	1.5 h	 12	74

Substrates. Cyanohydrin acetates **1** and **2** were prepared from the corresponding aldehydes.[20] Substrate **3** was prepared from the corresponding bromochalcone.[20b] 1-Phenyl-3-acetoxy-1-butene (**13**)[21] was prepared by reduction of benzalacetone with $NaBH_4$, followed by acetylation. Geranyl acetate (**14**) and cinnamyl acetate (**15**) were prepared from the corresponding commercial alcohols.

2-Acetoxy-4,8-dimethyl-3,7-nonadienenitrile (4) (*E* + *Z* Isomers). The cyanohydrin of commercial citral (a 1:1 mixture of *E* + *Z* isomers) was acetylated by using acetic anhydride/pyridine: MS, *m/e* (relative intensity), M^+ 221 (17) 179 (11), 161 (3), 146 (3.5), 69 (100); IR, 2500, 2210, 1730, 1650, 1430, 1630, 1210, 1010, 930, 820; NMR, 5.99 (d, *J* = 9.4 Hz, 1 H), 5.35 (br d, *J* = 5.4 Hz, 1 H), 5.06 (m, 1 H), 2.16 (br s, 4 H), 2.11 (s, 3 H), 1.82 (s) and 1.81 (s) (together 3 H), 1.70 (s, 3 H), 1.61 (s, 3 H).

4-Acetoxy-7-methyl-2-octene (5) was prepared from crotonaldehyde and isoamylmagnesium bromide, and the resultant crude alcohol was acetylated, followed by Kugelrohr distillation (130 °C (0.2 torr)): NMR, 5.7 (m [seven lines], 1 H), 5.5 (m, 1 H), 5.2 (q, *J* = 6.8 Hz, 1 H), 1.6 (m, 2 H), 1.2 (m, 3 H), 0.9 (d, *J* = 6.1, 6 H); IR 2950, 1730, 1450, 1370, 1240, 1020, 970.

3-Acetoxy-1-dodecene (6) was prepared from decanal and vinylmagnesium chloride in THF solution followed by acetylation: IR 2900, 1730, 1520, 1320, 1180, 1020, 930; NMR, 5.75 (m, 1 H), 5.25 (m, 3 H), 2.0 (s, 3 H), 1.2 (m, 16 H), 0.9 (br t, 3 H).

General Procedure for the Palladium-Catalyzed Reduction of an Allylic Acetate Using Polymethylhydrosiloxane (PMHS).[22] PMHS was added to a THF solution (5 mL) containing the allylic acetate to be reduced (1–2 mmol) and 2–8 mol % of palladium catalyst. The solution was stirred at room temperature until no starting material could be detected by either TLC or GLC. The mixture was filtered through a short silica gel column with CH_2Cl_2, as eluent. Solvent was removed under reduced pressure, and products were purified either by Kugelrohr distillation or flash chromatography.

Reduction of 1. PMHS (60 mg, 1 mequiv) was added to a THF (5 mL) solution containing **1** (118 mg, 0.55 mmol) and $Pd(PPh_3)_4$ (3 mol %). After 1.5 h the solution was treated as described above, and the product was Kugelrohr distilled (150 °C (0.4 torr)), producing 87 mg, (100% yield) of 4-(4-methylphenyl)-3-butenenitrile (**7**) as a white crystalline material: mp 55–56 °C; NMR, 7.3 (br s, 4 H), 6.50 (dt, *J* = 16, 1 Hz, 1 H), 5.95 (dt, *J* = 16, 6 Hz, 1 H), 3.30 (dd, *J* = 6, 1 Hz, 2 H), 2.3 (s, 3 H); MS, *m/e* (relative intensity) 157 (100), 156 (59), 142 (35), 130 (16), 129 (22), 115 (48), 105 (15), 91 (21), 77 (16); IR 3000, 2300, 1650, 1600, 1500, 1410, 1250, 1150, 1110, 800.

Reduction of 2. PMHS (96 mg, 1.6 mequiv) was added to a THF (5 mL) solution containing **2** (145 mg, 72 mmol) and $Pd(PPh_3)_4$ (39 mg, 4.6 mol %). After 20 min the mixture was worked up as described in the General Procedure, and the product was Kugelrohr distilled (123–130 °C (0.3 torr)), producing 96 mg (93% yield) of 4-phenyl-3-butenenitrile (**8**).[20b]

Reduction of 3. PMHS (83 mg, 1.4 mequiv) was added to a THF (5 mL) solution containing **3** (187 mg, 0.57 mmol) and $Pd(PPh_3)_4$ (44 mg, 6.7 mol %). It was stirred for 7 h under nitrogen and worked up as above (General Procedure). The product was Kugelrohr distilled (150 °C (0.3 torr)), producing 137 mg (89% yield) of two isomeric products, 1-phenyl-3-(4-bromophenyl-1-propene (**9a**) and 1-phenyl-3-(4-bromophenyl)-2-propene (**9b**) in a 1:1 ratio: IR 3000, 2950, 2900, 1750, 1600, 1500, 1450, 1420, 1400, 1070, 980, 820; MS, *m/e* (relative intensity) M^+ [274 (42), 272 (42)], 205 (30), 194 (45), 193 (94), 192 (22), 191 (18), 179 (16), 178 (38), 165 (13), 117 (12), 116 (29), 115 (100), 103 (14), 91 (36), 85 (15), 77 (13); NMR 7.27 (m, 9 H), 6.35 (d, *J* = 15.5 Hz) and 6.29 (d, *J* = 15.5 Hz) (together 1 H), 6.23 (dt, *J* = 15.5, 6.9 Hz) and 6.08 (dt, *J* = 15.5, 6.9 Hz) (together 1 H), 3.11 (d, *J* = 6.9 Hz) and 3.3 (d, *J* = 6.9 Hz) (together 2 H). The isomeric ratio (1:1) was determined from the HPLC chromatogram measured on a Waters-244-LC equipped with a SI-100-5μm column with CH_2Cl_2 at a flow rate of 1 mL/min. Retention times of the two isomers are 1.5 and 3 min.

Reduction of 4. PMHS (134 mg, 2.2 mequiv) was added to a THF (5 mL) solution containing **4** (196 mg, 0.85 mmol) and $Pd(PPh_3)_4$ (36 mg, 3.3 mol %). The solution was stirred for 48 h, after which no starting material was detected by GLC. The mixture was worked up as above, and the residue was Kugelrohr

(20) (a) Nudelman, A.; Keinan, E. *Synthesis* **1982**, 687. (b) Keinan, E.; Peretz, M. *J. Org. Chem.*, in press.
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(22) General procedures for reductions with $Bu_3SnH/Pd(PPh_3)_4$ are given in ref 2 and 3.

distilled (70 °C (5 torr)), affording 108 mg (75%) of two products: 4,8-dimethyl-2,7-nonadienenitrile (**10a**), and 4,8-dimethyl-3,7-nonadienenitrile (**10b**), at a 10:1 ratio: MS, *m/e* (relative intensity) M^+ (163 (7), 148 (15), 121 (22), 94 (26), 81 (23), 80 (11), 70 (29), 69 (100), 55 (78), 53 (22); IR 2500, 2200, 1620, 1450, 1370, 980, 820; NMR of **10a** 6.63 (dd, J = 16.4, 6.9 Hz, 1 H), 5.28 (dd, J = 16.4, 1.5 Hz, 1 H), 5.04 (br t, J = 7.0 Hz, 1 H), 2.32 (m [(seven lines], 1 H), 2.03 (m, 2 H), 1.69 (s, 3 H), 1.59 (s, 3 H), 1.38 (m, 2 H), 1.05 (d, J = 6.7 Hz, 3 H). The minor isomer (**10b**), was identified by its NMR absorptions[23] at 5.2 (m, 2 H) and 3.03 (d, J = 7.7 Hz, 2 H). The isomeric ratio (10:1) was determined by integration of the 270-MHz NMR spectral peaks at 6.63 and 3.03.

Reduction of 5. PMHS (126 mg, 2.1 mequiv) was added to a THF (5 mL) solution containing **5** (190 mg, 1.02 mmol), $Pd(PPh_3)_4$ (49 mg, 4 mol %), and PPh_3 (40 mg, 0.15 mmol), and the mixture was stirred for 4 days. Yield was determined by GLC, using allylbenzene as an internal reference. A purified sample was obtained by preparative GLC using an SE-30 column. **7-Methyl-2-octene (11a)**: NMR 5.00 (m, 2 H), 2.00 (m, 2 H), 1.63 (dd, J = 3.6, 1 Hz, 3 H), 1.26 (m, 5 H), 0.85 (d, J = 6.85 Hz, 6 H). **7-Methyl-3-octene (11b)**: NMR 5.00 (m, 2 H) 2.00 (m, 4 H), 1.26 (m, 3 H), 0.95 (t, J = 7.5 Hz, 3 H), 0.9 (d, J = 6.85 Hz, 6 H) (the isomeric ratio (**11a**:**11b** = 2:1) was determined by integration of the 270-MHz NMR spectral peaks at δ 1.63 (vinylic methyl) and 0.95 (allylic methyl)); MS, *m/e* (relative intensity) 126 (M^+) (27), 111 (10), 98 (8), 83 (17), 65 (70), 56 (100).

Reduction of 6. PHMS (163 mg, 2.6 mequiv) was added to a THF solution of **6** (140 mg, 0.62 mmol) and $Pd(PPh_3)_4$ (5 mol %). After 1 h, no starting material could be detected by GLC. The solution was treated as described in the General Procedure, affording 2-dodecene[24] (**12**), which was Kugelrohr distilled (120 °C (100 torr)): 82 mg, 79% yield; NMR, 5.4 (m, 2 H), 1.9 (m, 2 H), 1.6 (m, 3 H), 1.2 (br s, 14 H), 0.9 (br t, 3 H).

Reduction of 13. PMHS (132 mg, 2.2 mequiv) was added to a THF (5 mL) solution containing **13** (173 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (4.4 mg, 4 mol %). After 24 h, the solution was filtered through a silica gel column with CH_2Cl_2, solvent was removed under reduced pressure, and the products were Kugelrohr distilled (120 °C (100 torr)) to give 93 mg (79% yield) of 1-phenyl-1-butene[25a] and 1-phenyl-2-butene[25b] in a 6:1 ratio. The isomeric ratio was determined by integration of the 80-MHz NMR spectral peaks at δ 6.3 and 5.5.

Reduction of Geranyl Acetate (14). PMHS (105 mg, 1.75 mequiv) was added to a THF (5 mL) solution containing **14** (161 mg, 0.83 mmol), $Pd(PPh_3)_4$ (62 mg, 6 mol %), and PPh_3 (45 mg, 0.17 mmol), and the mixture was stirred for 5 days. The yield (100%) was determined by GC analysis usng a $^1/_8$ in. × 6 ft column packed with OV-1 at 80 °C and with *n*-octane as an internal reference. The products were isolated by preparative GC using a column packed with 20% SE-30 on Chromosorb W. **3,7-Dimethyl-1,6-octadiene**:[26] NMR 5.70 (ddd, J = 13.2, 9.4, 7.1 Hz, 1 H), 5.11 (m, 1 H), 4.95 (d, J = 13.2 Hz, 1 H), 4.92 (d, J = 7.1 Hz, 1 H), 2.44 (m [seven lines], 1 H), 2.14 (br q, J = 7 Hz, 2 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.31 (m, 2 H), 0.99 (d, J = 7 Hz, 3 H). **3,7-Dimethyl-2,6-octadiene**:[27] NMR 5.16 (br q, J = 6.0 Hz, 1 H), 5.06 (m, 1 H), 2.02 (m, 4 H), 1.68 (s, 3 H), 1.60 (s, 1 H), 1.59 (d, J = 6.0 Hz, 3 H). The isomeric ratio (48:52) was determined by GC.

Competition Experiments. A. Reduction of Allylic Acetate in the Presence of α,β-Unsaturated Aldehyde. PMHS (165 mg, 2.6 mequiv) was added to a THF solution containing cinnamyl acetate (**15**) (215 mg, 1.2 mmol), cinnamaldehyde (192 mg, 1.45 mmol), and $Pd(PPh_3)_4$ (53 mg, 4 mol %), and the solution was stirred under nitrogen for 24 h, after which no change was observed in cinnamaldehyde concentration (by GC analysis, 10% Carbowax column, 110 °C). No cinnamyl acetate could be detected. β-Methylstyrene and allylbenzene were present in a 2:1 ratio in 73% total yield (by GC analysis using acetophenone as an internal reference).

B. Reduction of α,β-Unsaturated Aldehyde in the Presence of Allylic Acetate. Bu_3SnH (0.40 mL, 1.6 mmol) was added over a period of 20 min to a THF solution containing cinnamaldehyde (149 mg, 1.13 mmol), 4-acetoxy-7-methyl-2-octene (**5**) (97 mg, 0.53 mmol), triphenylphosphine (16 mg, 0.06 mmol), $Pd(PPh_3)_4$ (81 mg, 6 mol %), and acetic acid (56 mg, 0.93 mmol). GC analysis revealed no change in the allylic acetate concentration. Cinnamaldehyde, however, was quantitatively converted into dihydrocinnamaldehyde (by GC analysis).

C. Reduction of Allylic Acetate in the Presence of Acyl Halide. PMHS (120 mg, 2 mequiv) was added to a THF (5 mL) solution containing cinnamyl acetate (150 mg, 0.85 mmol) and $Pd(PPh_3)_4$ (60 mg, 6 mol %). Slow formation of allylbenzene and β-methylstyrene was observed by GC analysis. After 30 min, cinnamoyl chloride (100 mg, 0.6 mmol) was added. No additional reduction of the cinnamyl acetate could be observed by GC within the next 5 h. Upon addition of Bu_3SnH (0.25 mL, 1 mmol), immediate formation of cinnamaldehyde and dihydrocinnamaldehyde was observed together with continuing reduction of cinnamyl acetate into β-methylstyrene and allylbenzene.

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Registry No. **1**, 81981-13-7; **2**, 79265-03-5; **3**, 86668-24-8; (*E*)-**4**, 86668-25-9; (*Z*)-**4**, 86668-26-0; **5**, 86668-27-1; **6**, 86668-28-2; **7**, 81981-14-8; **8**, 16170-45-9; **9a**, 86668-29-3; **9b**, 86668-30-6; **10a**, 86668-31-7; **10b**, 6250-73-3; **11a**, 86668-32-8; **11b**, 86668-33-9; **12**, 1652-96-6; **13**, 86668-34-0; **14**, 105-87-3; **15**, 103-54-8; PMHS, 9004-73-3; $Pd(PPh_3)_4$, 14221-01-3; cinnamaldehyde, 104-55-2.

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Resolution of Chiral Alcohols with Mandelic Acid

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Our continued interest in the area of asymmetric induction has led us to explore new and convenient methods for the resolution of chiral alcohols. Current methods concentrate on the formation of salts between chiral amines and the monophthalate esters and of diastereomeric esters through reaction with chiral acids.[1] The former method is limited by the rather large spatial separation of the chirality in the amine and alcohol moieties. Available acids that are generally effective for the latter technique are represented by camphanic acid[2] and α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher's reagent)[3] although use of these as well as other acids is hampered by inaccessibility and/or high cost. It occurred to us that mandelic acid[4] might well serve this purpose, notwithstanding the potential during esterification for racemization and self-condensation of this acid to form the

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(4) Mandelate esters of racemic alcohols have been prepared previously (in unspecified yields), and the diastereomers were shown to the be easily separable by gas chromatography (Cross, J. M.; Putney, B. F.; Bernstein, J. *J. Chromatogr. Sci.* **1970**, *8*, 679). However, a preparative separation followed by hydrolysis afforded alcohol with only moderate optical purity. No evidence was presented regarding the possibility of epimerization either during the esterification or the GC analysis, which in either case would have led to crossover of the alcohols.

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