The different ligands $Ph_2POEt$, $PhP(OMe)_2$, $Ph_2PNMe_2$, $PhP(NMe_2)_2$, and $P(NMe_2)_3$ were prepared according to classic methods.[24] The synthesis of ligand $Ph_2PN(i\text{-}Pr)_2$ is described below. Crude products were generally prepurified by Kugelrohr distillations on a Büchi GKR-50 apparatus. The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded respectively at 100, 25.144, 40, and 48 MHz on a Bruker AC 100 spectrometer. The NMR spectra were obtained from $CDCl_3$ solutions unless otherwise stated. Chemical shifts are given in parts per million relative to $Me_4Si$ for $^1H$ and $^{13}C$ and 85% $H_3PO_4$ for $^{31}P$ NMR spectra. Chemical shifts upfield of the standard are defined as negative; the coupling constants are given in hertz. Multiplicities are expressed as follows: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. In $^{13}C$ NMR spectra, basic DEPT sequence[25] was used to determine the structure of compounds **3-6**. The $^1H$ NMR peak areas are expressed as the number of hydrogen atoms (H). The IR spectra were obtained on a Perkin-Elmer Model 298 from neat liquid films. The analytical results agree with calculated values within 0.3%. Analytical gas-liquid chromatography (GLC) was performed on an Intersmat IGC 121 FL instrument with a flame-ionization detector and helium carrier gas (1.0-1.3 kg/cm$^2$) using a CP Sil 5 fused silica 20-m capillary column. Codimerization reactions were monitored on CPG capillary column by using undecane as internal standard. Calibration curves can be prepared by plotting peak areas against corresponding concentrations. CPG conditions: $P(H_2)$ and carrier gas, helium 1 bar; injector and detector temperature, 220 °C; isotherm for 3 min, linear temperature programmed from 35 to 120 °C by 7 °C/min; the different retention times in minutes are 10.76 (**3**), 8.45 (**4**), **5** 9.10 (**5**), 9.18 (**6**), and 9.55 (undecane).

**(*N,N*-Diisopropylamino)diphenylphosphine.** To a solution of *N,N*-diisopropylamine (5.05 g, 0.05 mol) and triethylamine (0.05 mol) in benzene (50 mL) was added dropwise a solution of chlorodiphenylphosphine (11.03 g, 0.05 mol) and benzene (20 mL) at room temperature under $N_2$ atmosphere. The resulting mixture was stirred and heated with reflux for 4 h and allowed to cool to room temperature. The triethylammonium chlorohydrate was collected on a glass filter and washed with diethyl ether. The combined organic phases were concentrated under vacuum to afford a viscous yellow oil, which crystallized from petroleum ether/diethyl ether in 1/1 ratio and in 89% chemical yield to give the product: mp 76-80 °C; $^1H$ NMR ($C_6D_6$) $\delta$ 1-1.40 (d, 6 H), 3.2-3.7 (m, 1 H), 7.1-7.6 (m, 10 H); $^{13}C$ NMR ($C_6D_6$) $\delta$ 24 (d, $^3J_{CP}$ = 6.3 Hz, $CH_3$), 47.8 (d, $^2J_{CP}$ = 8.4 Hz, CH), 128.2-133.4 (m, Ph); $^{31}P$ NMR ($C_6D_6$) $\delta$ 38. Anal. Calcd for $C_{18}H_{24}NP$: C, 75.79; H, 8.42; N, 4.91. Found: C, 75.95; H, 8.36; N, 4.69.

**TMVS and 1,3-Cyclohexadiene Codimerization.** The catalyst $Ni(COD)_2$ (2 mmol) and organophosphorus ligand (2 mmol) were dissolved in 2 mL of toluene under a $N_2$ atmosphere at room temperature. The solution was stirred for 10 min and then transferred into a glass reactor containing 1,3-cyclohexadiene (0.1 mol) and VTMS (0.1 mol). To the stirred mixture was added a (1 M) solution of $AlEt_2Cl$ (12 mmol) in toluene (12 mL). It is important that this sequence of events be adhered to strictly, otherwise the reaction fails to give any product. The mixture was stirred for 48 h at 50 °C. Workup consisted of the addition of $H_2O$ (10 mL) to the reaction mixture. Then the reaction products were extracted with diethyl ether (5 × 20 mL). The organic phase was dried over $Na_2SO_4$ and concentrated under vacuum, and the reaction products were distilled under vacuum on a spinning band column. *n*-Undecane was added to the products to follow the codimerization reaction, and the mixture was analyzed on GLC.

**2,4-Bis(trimethylsilyl)-1-butene (4)**: bp 38 °C (2 mm), $n^{20}_D$ 1.4381 [lit.[13] bp 70.71 °C (25 mm), $n^{20}_D$ 1.4382]; IR, strongest bands 1480, 1250, 920, 850-870, 760, 700 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.05 (s, 9 H), 0.13 (s, 9 H), 0.48-0.78 (m, 2 H), 1.93-2.32 (m, 2 H), 5.18-5.68 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ -1.71 ($Si(CH_3)_3$), -1.33 ($Si(CH_3)_3$), 15.9 ($CH_2$), 29.82 ($CH_2$), 154.9 (C) 122.25 (CH). Anal. Calcd for $C_{10}H_{24}Si_2$: C, 59.94; H, 11.98. Found: C, 59.69; H, 11.60.

**(*Z*)- and (*E*)-1,4-Bis(trimethylsilyl)-2-butenes (5, 6)**: bp 46 °C (2 mm), $n^{20}_D$ 1.4416, cis/trans ratio 1/2 [lit.[13] 90-91 °C (28 mm), $n^{20}_D$ 1.4412, cis/trans ratio 1/1]; IR, 3020, 1610, 1260, 1150, 1050, 810-870, 700 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ -0.02 (s, 9 H), 0.04 (s, 9 H), 1.49-1.55 (m, 4 H), 5.15-5.20 (m, 2 H); $^{13}C$ NMR (trans isomer **5**) $\delta$ -1.93 (s, $Si(CH_3)_3$), 22.83 ($CH_2$), 124.33 (CH); (cis isomer **6**) $\delta$ -1.70 (s, $Si(CH_3)_3$), 17.81 ($CH_2$), 123.12 (CH). Anal. Calcd for $C_{10}H_{24}Si_2$: C, 59.94; H, 11.98. Found: C, 59.71; H, 11.70.

**3-[1-(Trimethylsilyl)vinyl]-1-cyclohexene (3)**: bp 30-35 °C (0.5 mm), $n^{21}_D$ 1.4802; IR, 3020, 1450, 1410, 1250, 840, 690 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.35 (s, 9 H), 1.1-2.1 (m, 6 H), 2.80-3.04 (m, 1 H), 5.31-5.85 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) -0.85 ($SiMe_3$), 20.75 ($CH_2$), 25.06 ($CH_2$), 29.91 ($CH_2$), 40.98 (CH), 124.84 (CH), 127.44 (CH), 130.77 ($CH_2$), 156.02 (C). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.29; H, 11.10. Found: C, 73.13; H, 11.05.

**Registry No.** **1**, 592-57-4; **2**, 754-05-2; **3**, 110434-24-7; **4**, 53304-31-7; **5**, 16054-35-6; **6**, 16054-34-5; $Ph_2PN(i\text{-}Pr)_2$, 22859-57-0; $HN(i\text{-}Pr)_2$, 108-18-9; $Ph_2PCl$, 1079-66-9; $Ni(COD)_2$, 1295-35-8; $AlEt_2Cl$, 96-10-6; $PPh_3$, 603-35-0; $P(Ph\text{-}o\text{-}OMe)_3$, 4731-65-1; $PPh_2(CH_2)_2PPh_2$, 50819-15-3; $PhP(OMe)_2$, 2946-61-4; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; $Ph_2P(NMe_2)$, 6840-01-3; $PhP(NMe_2)_2$, 6143-71-1; $P(NMe_2)_3$, 1608-26-0; $Ph_2POEt$, 719-80-2; $NiCl_2$, 7718-54-9; $Ni(acac)_2$, 3264-82-2.

(24) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley-Interscience: New York, 1972; Vols. 4, 5.
(25) Doddrell, D. M.; et al. *J. Magn. Reson.* **1982**, *48*, 233.

## Selective Hydroboration Studies with Acetoxyborohydride

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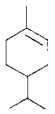
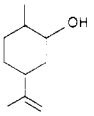
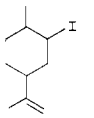
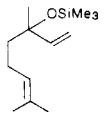
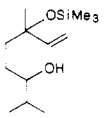
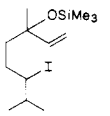
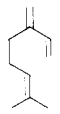
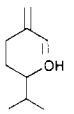
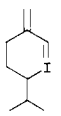
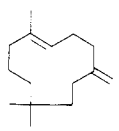
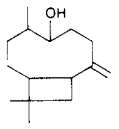
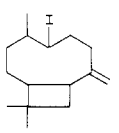
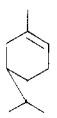
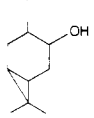
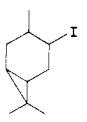
The remarkable facile monohydroboration of dienes, alkynes, or enynes has opened a new and convenient route to large number of unsaturated organoboranes. It is now possible with the choice of a suitable hydroborating reagent to selectively hydroborate either a mono- or disubstituted terminal double bond[1] of the diene or an internal carbon-carbon triple bond[2] or terminal double bond[3] of an enyne, and the diene containing terminal and internal carbon-carbon double bonds preferentially undergoes hydroboration at the terminal position.[4] This unique selectivity in hydroboration and the options for further manipulation of the intermediate organoboranes to a variety of organic molecules have recently been reviewed by us.[5] The lack of any general procedure for the hydroboration of an internal carbon-carbon double bond of a diene in the presence of terminal one prompted us to employ acetoxyborohydride ($CH_3COOBH_3^-$) as the hydroborating agent. It has been reported[6] that the reagent can tolerate some functional groups, is sluggish in hydroboration, and is convenient to prepare.

The acetoxyborohydride, as a hydroborating reagent, has a special significance for the synthesis of alkyl iodide via iodination since it gives mainly "$RBH_2$" and some "$R_2BH$" species.[6] The trialkylborane ($R_3B$) obtained from diborane has obvious disadvantage in iodination as only two alkyl groups are utilized in the formation of alkyl iodide.[7-10]

(1) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 644.
(2) Brown, H. C.; Campbell, J. B., Jr. *J. Org. Chem.* **1980**, *45*, 389.
(3) Brown, C. A.; Coleman, R. A. *J. Org. Chem.* **1979**, *44*, 2328.
(4) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Org. Chem.* **1978**, *43*, 1058.
(5) Suzuki, A.; Dhillon, R. S. *Top. Curr. Chem.* **1986**, *130*, 23.
(6) Narayana, C.; Periasamy, M. *Tetrahedron Lett.* **1985**, *26*, 1757.
(7) Brown, H. C.; Rathke, M. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 5038.
(8) Brown, H. C.; De Lue, N. R.; Kabalka, G. W.; Hedgecock, H. C., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 1290.
(9) Brown, H. C.; De Lue, N. R. *Synthesis* **1976**, 114.

0022-3263/88/1953-0187$01.50/0 

**Table I. Selective Hydroboration–Oxidation and Iodination with Acetoxyborohydride**

| entry | compd | product | isol yield, % |
|---|---|---|---|
| 1 |  |  | 87 |
| | |  | 69 |
| 2 |  |  | 83 |
| | |  | 64 |
| 3 |  |  | 81 |
| | |  | 61 |
| 4 |  |  | 89 |
| | |  | 68 |
| 5 |  |  | 88 |
| | |  | 70 |

The wastage of the third alkyl group is serious, if the starting alkene is expensive or obtained by multistep synthesis. To circumvent this difficulty the use of alkylborane for hydroboration, however, occasionally affords a mixture of alkyl iodides arising from the migration of both alkyl groups of hydroborating reagent and of an alkene. These problems thus stimulated us to employ acetoxyborohydride for hydroboration–iodination also to synthesize alkyl iodide in an enhanced yield. Moreover, the radio-iodine is now routinely used in therapeutic nuclear medicine.[10]

We are gratified to report here that acetoxyborohydride prepared at 0 °C from sodium borohydride and mercuric acetate in THF selectively hydroborates at room temperature the internal, more substituted, carbon–carbon double bond in preference to the terminal one (Table I). The reaction procedure is simple and alkaline hydrogen peroxide oxidation[11] or iodination[7] affords the corresponding alcohol or iodide in good yields based on reacted alkene (Table I). The workup leads to the separation of metallic mercury, which is conveniently separated, thus avoiding the wastage of expensive metal.

The sluggish approach of acetoxyborohydride leads to its selectivity; thus boron–hydrogen of the reagent adds to the reactive more substituted carbon–carbon double bond of the diene. It has been reported[12] earlier that caryophyllene affords exclusively caryophyllene alcohol after the participation of the strained, more reactive *E*-trisubstituted double bond in preference to the exocyclic carbon–carbon double bond. However, no general procedure was available where the reagent preferentially hydroborates the internal carbon–carbon double bond in presence of terminal one. Recently, dibromoborane–dimethyl sulfide has been reported to discriminate between the two terminal carbon–carbon double bonds and preferentially hydroborates the one which is disubstituted,[1] but its selectivity for internal carbon–carbon double bond has not been reported. The remarkable selectivity shown by acetoxyborohydride made it possible for the first time to exclusively hydroborate the internal carbon–carbon double bond of a diene. The reagent may parallel in selectivity with that of $BHBr_2{\cdot}SMe_2$ for which the studies are being undertaken.

The hydroboration–iodination of the dienes has also demonstrated similar selectivity. The alkyl iodide formed after iodination leads to considerable improvements in the yield, thus enhancing the synthetic utility of the reagent.

Moreover, the cyclopropane present in $\Delta^3$-carene does not undergo reduction or ring cleavage and tolerates the reagent and the reaction conditions, thus demonstrating its application in a variety of organic molecules.

In conclusion the convenient preparation of acetoxyborohydride, its mildness, simple reaction procedure, recovery of expensive mercury, remarkable selectivity, and its utility in the synthesis of alkyl halide make it a valuable hydroborating reagent for synthetic purposes. The sluggish approach of the acetoxyborohydride is attributed to the mesomeric effect of oxygen of the acetoxy group and we are investigating its reactivity toward the carbon–carbon double bond present in the vicinity of functional group.

## Experimental Section

**Materials and Methods.** General experimental manipulations were followed as outlined in chapter 9 of ref 11. All glassware, syringes, and needles were oven-dried at 140 °C for several hours, assembled hot, and cooled under dry nitrogen gas. All reactions were carried out under nitrogen till the oxidation or iodination stage.

Commercially available samples (Aldrich, Fluka) of limonene, linalool, and myrcene were purified by passing over a bed of silica gel and distilled over lithium aluminum hydride (except linalool) prior to use. Caryophyllene and $\Delta^3$-carene were gifts from Hokkaido University, Japan, and Malti-Chem Research Centre, Baroda, respectively, and purified over silica gel. The hydroxyl group of linalool was protected as trimethylsilyl ether according to the literature procedure.[13] Sodium borohydride and mercuric acetate were procured from Romali and Sarabhai M. Chemicals, respectively.

NMR spectra were recorded on a R-22 Hitachi (90 MHz) or Varian EM-390 Perkin-Elmer (90 MHz) NMR spectrometer with $CCl_4$ as the solvent. All chemical shifts are reported in parts per

(10) Kabalka, G. W. *Acc. Chem. Res.* **1984**, *17*, 215 and references cited therein.

(11) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

(12) Rao Ramana, V. V.; Devaprabhakra, D. *Tetrahedron* **1978**, *34*, 2223.

(13) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley-Interscience: New York, 1981.

million (δ scale) by employing $Me_4Si$ or $CHCl_3$ (entry 2, Table I) as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 843-IR spectrophotometer.

Column chromatography was performed on silica gel (60–120 mesh) impregnated with silver nitrate (10%). TLC was done on glass plates coated with silica gel-G impregnated silver nitrate (10%).

**General Procedures. Hydroboration.** The acetoxyborohydride (20 mmol) was prepared according to the literature procedure[6] as follows: A dry 100 mL flask equipped with magnetic stirring bar, septum inlet, and reflux condenser was flushed with nitrogen. The flask was charged under nitrogen with sodium borohydride (20 mmol) followed by the addition of 40 mL of dry THF via syringe. The flask is immersed in an ice bath, and 10 mmol of mercuric acetate was added slowly under a blanket of nitrogen. The contents were allowed to stir for 1 h at 0 °C. The reaction mixture was brought to room temperature, and the diene (30 mmol) was added dropwise. The contents were further stirred for 16 h at room temperature for complete hydroboration.

**Oxidation.** The organoborane prepared as above in THF was cooled to 0 °C and 8 mL of 3 M aqueous sodium hydroxide was added slowly to the reaction mixture. Hydrogen peroxide, 8 mL of 30% aqueous solution, was introduced dropwise to the stirred reaction mixture. The temperature was then raised slowly, and the reaction mixture was heated at 70 °C for 1 h, during which the mercury coagulated. The contents were brought to room temperature, decanted to separate mercury, and saturated with sodium chloride. Isolation of the product was accomplished by pouring the cooled, two-phase reaction mixture into a separatory funnel, and the aqueous layer was extracted with ethyl ether (3 × 20 mL). The combined THF–ethyl ether extract was washed with water (2 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The product was isolated by column chromatography over silver nitrate (10%) impregnated silica gel using hexane/ether (5%).

**Iodination.** To a solution of organoborane prepared as above from acetoxyborohydride (20 mmol) was added iodine (25 mmol) all at once at room temperature, followed by the dropwise addition of 10 mL of 3 M solution of sodium hydroxide in methanol (30 mmol). After stirring for 10 min at room temperature the reaction mixture was decanted from mercury and poured into 50 mL of cold water containing 1 g of sodium thiosulfate to remove excess iodine. The aqueous layer was extracted with ether (3 × 20 mL). The combined THF–ether layer was dried and distilled and the product isolated as above.

**Spectral Data.** Alcohol (entry 1): $^1H$ NMR 4.70 (s, 2 H), 3.45–3.75 (m, 1 H), 2.20–2.50 (br, 1 H exchangeable), 1.73 (s, 3 H), 0.97 (d, $J$ = 7 Hz, 3 H); IR (neat, $cm^{-1}$) 3380, 1640, 1450, 1370, 1020, 880. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.79; H, 11.59.

**Iodo compound (entry 1):** $^1H$ NMR 4.80 (s, 2 H), 3.40–3.70 (m, 1 H), 1.70 (s, 3 H), 0.97 (d, $J$ = 6 Hz, 3 H); IR (neat, $cm^{-1}$) 1640, 882. Anal. Calcd for $C_{10}H_{17}I$: C, 45.47; H, 6.49. Found: C, 45.65; H, 6.41.

**Alcohol (entry 2):** $^1H$ NMR 5.97 (m, 1 H), 5.20 (m, 2 H), 3.85 (br, 1 H exchangeable), 3.35 (m, 1 H), 1.20 (s, 3 H), 0.88 (d, $J$ = 6 Hz, 6 H); IR (neat, $cm^{-1}$) 3320, 2920, 1635, 1450, 1360, 1040. Anal. Calcd for $C_{13}H_{28}SiO_2$: C, 63.88; H, 11.54. Found: C, 63.70; H, 11.69.

**Iodo compound (entry 2):** $^1H$ NMR 6.0 (m, 1 H), 5.20 (m, 2 H), 2.91–3.20 (m, 1 H), 1.31 (s, 3 H), 0.97 and 1.0 (2 s, 6 H); IR (neat, $cm^{-1}$) 2930, 1640, 1450, 1370, 1040. Anal. Calcd for $C_{13}H_{27}OSiI$: C, 44.06; H, 7.67. Found: C, 44.21; H, 7.54.

**Alcohol (entry 3):** $^1H$ NMR 6.20 (m, 1 H), 5.03 (m, 4 H), 3.55 (m, 1 H), 2.40 (br, 1 H exchangeable), 1.0 (d, $J$ = 7 Hz, 6 H); IR (neat, $cm^{-1}$) 3350, 1637, 1470, 1455, 890. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.98; H, 11.62.

**Iodo compound (entry 3):** $^1H$ NMR 6.20 (m, 1 H), 5.0 (m, 4 H), 3.1 (m, 1 H), 1.03 (d, $J$ = 7 Hz, 6 H); IR (neat, $cm^{-1}$) 2920, 1640, 1460, 892. Anal. Calcd for $C_{10}H_{17}I$: C, 45.47; H, 6.49. Found: C, 45.61; H, 6.58.

**Alcohol (entry 4):** $^1H$ NMR 4.90 and 5.0 (2 s, 2 H), 3.90 (br, 1 H exchangeable), 3.60–3.75 (m, 1 H), 1.10 (d, $J$ = 7 Hz, 3 H), 0.90 (s, 6 H); IR (neat, $cm^{-1}$) 3320, 1640, 882, 837. Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 80.85; H, 11.57.

**Iodo compound (entry 4):** $^1H$ NMR 4.90 and 5.0 (2 s, 2 H), 3.5 (m, 1 H), 1.10 (d, $J$ = 7 Hz, 3 H), 0.90 (s, 6 H); IR (neat, $cm^{-1}$) 1640, 882. Anal. Calcd for $C_{15}H_{25}I$: C, 54.22; H, 7.58. Found: C, 54.04; H, 7.69.

**Alcohol (entry 5):** $^1H$ NMR 3.40 (m, 1 H), 3.10 (br, 1 H, exchangeable), 1.05 (s, 3 H), 1.0 (s, 3 H), 0.90 (d, $J$ = 7 Hz, 3 H), 0.50–0.84 (m, 2 H); IR (neat, $cm^{-1}$) 3350, 2920, 1370, 1355, 1140. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.75; H, 11.94.

**Iodo compound (entry 5):** $^1H$ NMR 3.40–3.60 (m, 1 H), 1.03 (s, 3 H), 1.0 (s, 3 H), 0.93 (d, $J$ = 7 Hz, 3 H), 0.55–0.84 (m, 2 H); IR (neat, $cm^{-1}$) 2930, 1370, 1360. Anal. Calcd for $C_{10}H_{17}I$: C, 45.47; H, 6.49. Found: C, 45.23; H, 6.58.

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**Registry No.** Limonene, 138-86-3; limlonene (alcohol), 619-01-2; limonene (iodo compound), 110851-26-8; silated linalool, 59632-77-8; silated linalool (alcohol), 110851-25-7; silated linalool (iodo compound), 110851-27-9; myrcene, 123-35-3; myrcene (alcohol), 24202-03-7; myrcene (iodo compound), 110851-28-0; caryophyllene, 87-44-5; caryophyllene (alcohol), 69855-00-1; caryophyllene (iodo compound), 110851-29-1; 3-carene, 13466-78-9; 3-carene (alcohol), 16725-98-7; 3-carene (iodo compound), 110851-30-4; acetoxyborohydride, 71604-09-6.

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# Palladium-Catalyzed Syn 1,4-Additions of Silyl-Derived Carboxylates and Phenoxides to Cyclopentadiene Monoepoxide. A Stereo- and Regiocontrolled Route to Differentially Protected *cis*-2-Cyclopentene-1,4-diols[1]

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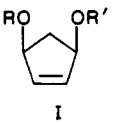
Cyclopentanoids are known to the synthetic practitioner as pivotal ingredients in the total synthesis of many biologically important molecules.[2] A recent escalation in their use has actuated the search for more elegant routes to these highly functionalized compounds. Toward this end, we now report that unsymmetrically protected versions of *cis*-2-cyclopentene-1,4-diol (I) can be conveniently prepared from cyclopentadiene monoepoxide in just one step. Our involvement in this area stems from a continued synthetic fascination with carbocyclic nucleosides.




I

Previously, we communicated[3] an especially direct route to the monoesters (**2a**) and symmetrical diesters (**2b**) of

(1) Presented in part by D.R.D. at the Pacific Conference on Chemistry and Spectroscopy (Western Regional Meeting), October 9–11, 1985, San Francisco, CA.

(2) For a review, see: Harre, M.; Raddatz, P.; Walenta, R.; Winterfeldt, E. *Agnew. Chem., Int. Ed. Engl.* **1982**, *21*, 480.

(3) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5615.

0022-3263/88/1953-0189$01.50/0 