i.d. column; 10:90 EtOAc/hexanes) to yield 100 mg (53%) of **2d** as a colorless oil (inseparable 1.5:1 mixture of diastereomers) [R_f 0.51; (40:60 EtOAc/hexanes); IR (neat) 1755 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) diastereomer A δ 7.39–7.27 (m, 5 H), 4.47–4.27 (m, 2 H), 3.06 (dd, J = 14.2, 4.4 Hz, 1 H), 2.97 (dd, J = 14.4, 7.1 Hz, 1 H) 2.48 (dd, J = 18.0, 6.8 Hz, 1 H), 2.22 (dd, J = 18.0, 7.2 Hz, 1 H), 1.39 (d, J = 6.8 Hz, 3 H); diastereomer B δ 7.39–7.27 (m, 5 H), 4.29–4.23 (m, 1 H) 4.10 (dd, J = 7.1, 3.7 Hz, 1 H), 3.17 (dd, J = 14.4, 3.7 Hz, 1 H), 2.94 (dd, J = 14.4, 7.1 Hz, 1 H), 2.56 (dd, J = 17.8, 10.7 Hz, 1 H), 1.90 (dd, J = 17.8, 10.7 Hz, 1 H), 1.43 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (75 MHz; $CDCl_3$) diastereomer A δ 216.3, 137.1, 129.5, 128.4, 126.6, 80.2, 71.7, 44.0, 37.1, 21.4; diastereomer B 215.9, 137.1, 129.6, 128.1, 126.5, 82.4, 72.0, 44.8, 37.2, 21.0; HRMS calcd for $C_{12}H_{14}O_2$ m/e 190.099 38, found m/e 190.09995] along with 10 mg 1,2-diphenylethane **5** (11%).

Preparation of Tetrahydro-2-(2-phenyl-2-oxoethyl)-4,4-dimethylfuran-3-one (2e). A 0.04 M solution of **1e** (108 mg, 0.41 mmol) in CH_2Cl_2 (10 mL) was treated with rhodium acetate (11 mg, 0.025 mmol) in CH_2Cl_2 (30 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g of silica gel; 15-mm i.d. column; 85:15 EtOAc/hexanes) to yield 17 mg (17%) of **2e** as a colorless oil [R_f 0.32 (15:85 EtOAc/hexanes); IR (neat) 1775, 1700 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.95–7.92 (m, 2 H), 7.62–7.26 (m, 3 H), 4.79 (d, J = 16.9 Hz, 1 H), 4.77 (d, J = 16.9 Hz, 1 H), 4.04 (t, J = 6.2 Hz, 1 H), 3.26 (dd, J = 18.0, 6.8 Hz, 1 H), 3.18 (dd, J = 18.0, 5.6 Hz, 1 H), 1.26 (s, 3 H), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 212.0, 195.5, 134.7, 133.7, 128.7, 127.9, 74.9, 72.9, 63.3, 50.1, 21.6, 16.6; HRMS calcd for $C_{14}H_{16}O_3$ m/e 232.109 94, found m/e 232.11008] accompanied by a large quantity of polar, uncharacterizable material.

Preparation of 2-Benzyl-3-coumaranone (2f). A 0.04 M solution of **1f** (215 mg, 0.85 mmol) in CH_2Cl_2 (21 mL) was treated with rhodium acetate (11 mg, 0.025 mmol) in CH_2Cl_2 (64 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g of silica gel; 15-mm i.d. column; 5:95 EtOAc/hexanes) to yield 152 mg (78%) of **2f** as a colorless oil: R_f 0.38 (15:85 EtOAc/hexanes); IR (neat) 1715 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.63–7.53 (m, 2 H), 7.32–7.21 (m, 5 H), 7.09–7.00 (m, 2 H), 4.77 (dd, J = 8.6, 3.6 Hz, 1 H), 3.34 (dd, J = 14.7, 3.6 Hz, 1 H), 2.98 (dd, J = 14.7, 8.6 Hz, 1 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 200.9, 172.5, 137.9, 136.0, 129.3, 128.4, 126.8, 124.2, 121.8, 120.9, 113.4, 85.7, 37.3; HRMS calcd for $C_{15}H_{12}O_2$ m/e 224.083 73, found m/e 224.084 06.

Preparation of 2-Benzyl-3-chromanone (2g). A solution of **1g** (123 mg, 0.46 mmol) in CH_2Cl_2 (15 mL) was treated with rhodium acetate (6 mg, 1.3×10^{-2} mmol) in CH_2Cl_2 (30 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (27 g of silica gel; 22-mm i.d. column; 5:95 EtOAc/hexanes) to yield 73 mg (67%) of **2g** as a colorless oil: R_f 0.34 (10:90 EtOAc/hexanes); IR (neat) 1730 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.28–7.16 (m, 7 H), 7.04–6.96 (m, 2 H), 4.46 (ddd, J = 8.4, 3.7, 2.7 Hz, 1 H), 3.55 (d, J_{AB} = 19.5 Hz, 1 H), 3.39 (d, J_{AB} = 19.4 Hz, 1 H), 3.21 (dd, J = 14.5, 3.7 Hz, 1 H), 3.01 (dd, J = 14.5, 8.4 Hz, 1 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 208.0, 153.6, 136.7, 132.9, 131.7, 129.5, 128.3, 126.7, 123.1, 121.7, 118.1, 82.8, 41.0, 37.1. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.70; H, 5.96.

Acknowledgment. We thank S. F. McHardy for assistance in carrying out this work. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and for a Summer Faculty Fellowship (T.H.E.). We also acknowledge the National Institutes of Health (BRSG Grant No. S07 RR07092) for partial support of this work and the Americal Cancer Society for a Junior Faculty Research Award (F.G.W.).

Registry No. **1a**, 91350-71-9; **1b**, 36901-15-2; **1c**, 139914-36-6; **1d**, 139914-37-7; **1e**, 139914-38-8; **1f**, 139914-39-9; **1g**, 139914-40-2; **2a**, 139914-41-3; **2b**, 139914-42-4; **2c**, 139914-43-5; **2d** (isomer 1), 139914-44-6; **2d** (isomer 2), 139914-45-7; **2e**, 139914-46-8; **2f**, 58202-26-9; **2g**, 139914-47-9; **3**, 139914-48-0; **4a** (isomer 1), 139914-49-1; **4a** (isomer 2), 139914-50-4; **4b** (isomer 1), 139914-51-5; **4b** (isomer 2), 139914-52-6; **5**, 103-29-7; 3-(benzyloxy)-2,2-dimethylpropionic acid, 36881-14-8; 3-(benzyloxy)propionic acid, 27912-85-2; 4-(benzyloxy)butyric acid, 10385-30-5; 3-(benzyloxy)butyric acid, 1135-38-2; 2,2-dimethyl-3-(phenacyloxy)propionic acid, 139914-53-7; 2-(benzyloxy)benzoic acid, 14389-86-7; 2-(benzyloxy)phenylacetic acid, 22047-88-7; rhodium acetate, 15956-28-2.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **1a–g**, **2a–g**, and **3** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Mild and Stereoselective Hydroborations of Functionalized Alkynes and Alkenes Using Pinacolborane

Charles E. Tucker, Jessica Davidson, and Paul Knochel*,[1]

The Willard H. Dow Laboratories, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

Received November 5, 1991

Alkane and alkeneboronic esters are useful intermediates in organic synthesis.[2] They can be prepared by several methods,[2] notably by hydroboration using catecholborane.[3] This direct preparation often requires harsh reaction conditions (100 °C for alkenes and 70 °C for alkynes). Furthermore, it leads to water-sensitive[3a-c] *B*-alkyl- and alkenylcatecholboranes of variable thermal stability.[4] Their transesterification to more stable boronic esters via intermediate boronic acids is often necessary if further transformations have to be performed with conservation of the boronic ester functionality.[2g] We report herein a new hydroboration reagent, pinacolborane (1), which is easy to prepare and adds with excellent regio- and stereoselectivity to alkynes under very mild conditions (25 °C, several hours). The reagent displays a good chemoselectivity and can also be used to add to olefins.

Thus, the addition of borane–dimethyl sulfide (10.0 M solution in Me_2S, 1 equiv) to a solution of pinacol (1 equiv)

(1) Present address: Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein Str., D-3550 Marburg, Germany.

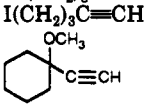
(2) (a) Matteson, D. S. *Tetrahedron* **1989**, *45*, 1859. (b) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535. (c) Matteson, D. S. *Acc. Chem. Res.* **1988**, *21*, 294. (d) Roush, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348. (e) Roush, W. R.; Moriarty, K. J.; Brown, B. B. *Tetrahedron Lett.* **1990**, *31*, 6509. (f) Roush, W. R.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 1143. (g) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (h) Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309. (i) Hoffmann, R. W.; Landmann, B. *Tetrahedron Lett.* **1983**, *24*, 3209. (j) Hoffmann, R. W.; Landmann, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 437. (k) Hoffmann, R. W.; Dresely, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 189. (l) Hoffmann, R. W.; Dresely, S. *Tetrahedron Lett.* **1987**, *28*, 5303. (m) Hoffmann, R. W.; Dresely, S. *Synthesis* **1988**, 103. (n) Wuts, P. G. M.; Jung, Y. W. *J. Org. Chem.* **1988**, *53*, 5989. (o) Wuts, P. G. M.; Jung, Y. W. *J. Org. Chem.* **1988**, *53*, 1957. (p) Wuts, P. G. M.; Jung, Y. W. *J. Org. Chem.* **1991**, *56*, 365. (q) Brown, H. C.; Srebnik, M.; Cole, T. E. *Organometallics* **1986**, *5*, 2300. (r) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311. (s) Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868. (t) Brown, H. C.; Rangaishenvi, M. V. *Tetrahedron Lett.* **1990**, *31*, 7113, 7115.

(3) (a) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1816. (b) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370. (c) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249. See also (d) Thaisrivongs, S.; Wuest, J. D. *J. Org. Chem.* **1977**, *42*, 3243. (e) Fish, R. H. *J. Org. Chem.* **1973**, *38*, 158. (f) Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966**, *88*, 4667. (g) For an excellent review on the preparation and reactivity of catecholborane see: Lane, C. F.; Kabalka, G. W. *Tetrahedron* **1976**, *32*, 981.

(4) (a) Matteson, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 4228. (b) Matteson, D. S.; Schaumberg, G. D. *J. Org. Chem.* **1966**, *31*, 726.

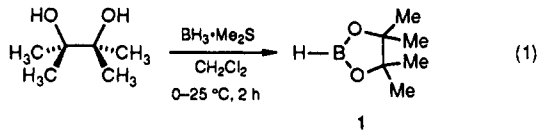
0022-3263/92/1957-3482$03.00/0

Table I. β-Alkenyl- and β-Alkylpinacolboranes 2 Prepared by the Hydroboration of Alkynes and Alkenes with Pinacolborane 1

entry	alkyne/alkene		product R¹	product R²	ratio 2:3:4	yield[a] (%)
1	HexC≡CH	**2a**	Hex	H	98:1:1	88
2	$Cl(CH_2)_3C{\equiv}CH$	**2b**	$Cl(CH_2)_3$	H	99:0.5:0.5	85
3	$I(CH_2)_3C{\equiv}CH$	**2c**	$I(CH_2)_3$	H	97:1:2	84
4		**2d**		H	100:0:0	85
5	PhC≡CH	**2e**	Ph	H	96:4:0 (91:9:0)[b]	64
6	$NC(CH_2)_3C{\equiv}CH$	**2f**	$NC(CH_2)_3$	H	97:0:3	79
7	t-$BuCO_2(CH_2)_3C{\equiv}CH$	**2g**	t-$BuCO_2(CH_2)_3$	H	95:2:3	78
8	PrC≡CMe	**2h**	Pr	Me	93:0:7 (60:0:40)[b]	75
9	PhC≡CMe	**2i**	Ph	Me	85:0:15 (73:0:27)[b]	69
10	1-ethynyl-1-cyclohexene	**2j**	1-cyclohexenyl	H	99:0:1	83
11	Oct-CH=CH_2	**2k**	pinacol decylboronate		99:–:1[c]	70
12	cyclohexene	**2l**	pinacol (cyclohexyl)boronate			73
13	norbornene	**2m**	*exo*-pinacol (2-norbonyl)boronate		>99:0:1[d]	54

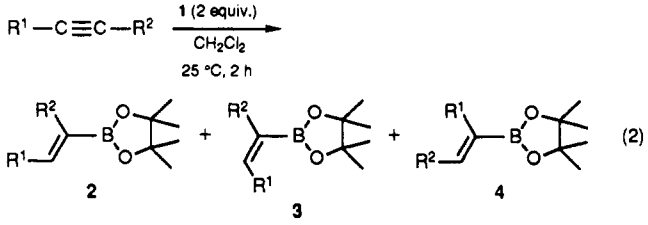
[a] All indicated yields refer to isolated yields of compounds being >99% pure by GC analysis. [b] Ratio of isomers obtained by using catecholborane (ref 2). [c] Ratio of terminal and internal regioisomers. [d] Exo–endo ratio of isomers.

in dry dichloromethane at 0 °C leads to a fast evolution of hydrogen, and after 1 h of stirring at 0 °C and 1 h at 25 °C the reagent 1 is ready to use (eq 1). This solution



(1)

1



(2)

2 3 4

of 1 in dichloromethane is stable at 25 °C for at least 2 weeks. It can be further purified by distillation (42–43 °C (50 mmHg); 63% isolated yield); however, for most applications this purification is not necessary. The addition of an alkyne (0.5 equiv) at 0 °C, followed by a few hours of stirring at 25 °C, affords (*E*)-pinacol (1-alkenyl)boronates **2** as the major stereoisomer. Minor amounts of the (*Z*)-pinacol (1-alkenyl)boronates **3** (0–4%) are also formed, and the regioisomer **4** is formed in variable amounts (0.15%), depending on the structure of the substrate (eq 2 and Table I).

Compared to catecholborane, pinacolborane (1) leads to a better regioselectivity and stereoselectivity (see Table I). The mild reaction conditions required for alkyne addition allow the presence of several functional groups such as a chlorine (entry 2), an iodine (entry 3), a nitrile (entry 6), an ester (entry 7), or an internal alkene (entry 10). The hydroboration of alkenes with 1 is also possible, and 1-decene is converted to pinacol decylboronate **3k** (2 equiv of 1, $ClCH_2CH_2Cl$, 50 °C, 48 h) in 70% yield (entry 11). Other alkenes such as cyclohexene (entry 12) and norbornene (entry 13) can be hydroborated with pinacolborane in a similar way. Attempts to prepare other diolboranes using benzopinacole or pinanediol for hydroborations were unsuccessful. Furthermore, pinacolborane (1) presents the advantage that most of the alkenyl pinacolboranes **2** obtained can be purified by flash chromatography[5] without appreciable decomposition (see Experimental Section). The use of less than 2 equiv of pinacolborane leads to incomplete reactions, and performing the reaction in the absence of solvents produces a mixture of isomers. Attempts to catalyze the reduction of either alkenes or alkynes using $RhCl(PPh_3)_3$ were not successful.[6]

In summary, we have demonstrated that the readily prepared pinacolborane 1 is a very efficient hydroboration reagent which may offer several advantages over catecholborane (milder reaction conditions, higher functional group tolerance, higher regio- and stereoselectivity, excellent stability of the resulting pinacol alkeneboronic esters) and should find wide use in organic synthesis.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-300 (300-MHz) spectrometer. FT-IR spectra were recorded on NaCl plates. IR values are given in cm^{-1}. All reactions were carried out under nitrogen. CH_2Cl_2 was dried and freshly distilled from CaH_2. The yields indicated are yields of isolated products purified by flash chromatography and having a purity greater than 99% as indicated by GC analysis (DB5 column, 15 m).

Starting Materials. All alkynes except 4-pentynyl 2,2-dimethylpropanoate were commercially available. 4-Pentynyl 2,2-dimethylpropanoate was prepared from the corresponding alcohol (PivCl (1.0 equiv), pyridine (1 equiv), CH_2Cl_2, 0–25 °C, 1 h; 95% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.13 (t, 2 H, J = 6.2 Hz), 2.26 (dt, 2 H, J = 2.7, 7.1 Hz), 1.99 (t, 1 H, J = 2.7 Hz), 1.89 (p, 2 H, J = 6.7 Hz), 1.18 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 178.4, 83.1, 68.9, 62.9, 38.8, 27.7, 27.2, 15.2.

Borane–methyl sulfide complex was purchased from Aldrich Chemical Co. as a 10 M solution in methyl sulfide and was used without titration.

Preparation of Pinacolborane (1). A solution of pinacol (20 mmol, 2.36 g) in dry CH_2Cl_2 (2 mL) was stirred and cooled to 0 °C. A solution of $BH_3{\cdot}SMe_2$ (20 mmol, 10.0 M in methyl sulfide) was added dropwise leading to effervescence. The reaction mixture was stirred for 1 h at 0 °C and was then warmed to 25 °C and stirred until no further evolution of hydrogen was observed (ca. 1 h). This solution can then be used directly for further reactions. Pure pinacolborane (containing less than 1% of Me_2S) can, however, be isolated by distillation as a clear oil (1.61 g; bp

(5) Still, W. C.; Kahn, M.; Mitra. A. *J. Org. Chem.* **1978**, *43*, 2923.
(6) (a) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. (b) Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280. (c) Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 5678. (d) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 395. (e) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (f) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, 1179.

42–43 °C (50 mmHg)). IR (CH_2Cl_2): 3272 (s), 2980 (s), 1530 (m), 1482 (s), 1333 (s), 1143 (s), 983 (s), 851 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.27 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 83.1, 24.5. ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 28.07.

Typical Procedure for the Hydroboration of Alkynes Using Pinacolborane. Preparation of (*E*)-Pinacol 5-Chloro-1-pentenyl)borane (2b). A clear solution of pinacolborane (20 mmol) in CH_2Cl_2 prepared as above was cooled to 0 °C, and 5-chloro-1-pentyne (10 mmol, 1.02 g) was slowly added. The reaction mixture was warmed to 25 °C and stirred for 7 h. GC analysis of a reaction aliquot shows the completion of the reaction. Ether (150 mL) was added, and the resulting solution was poured into a separatory funnel containing a saturated aqueous NH_4Cl solution (250 mL). The organic phase was washed quickly with a saturated aqueous NH_4Cl solution (100 mL) and dried over $MgSO_4$. The solvents were removed in vacuo, affording a residue which was purified by flash column chromatography (3% ether in hexane) providing the desired product as a clear oil (1.95 g; 85% yield). GC analysis indicates a *E*/*Z* ratio of >99:1 and the presence of <1% of the regioisomer.

Analytical Data for Products 2a–2m Described in Table I. (*E*)-Pinacol 1-Octenylboronate (2a). A clear oil (2.09 g, 88%) was obtained from 1-octyne (10 mmol, 1.10 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2997 (s), 1639 (s), 1490 (s), 1384 (s), 1362 (s), 1270 (s), 1148 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.63 (dt, 1 H, *J* = 17.9, 6.4 Hz), 5.42 (dt, 1 H, *J* = 1.6, 17.9 Hz), 2.18–2.11 (m, 2 H), 1.43–1.38 (m, 2 H), 1.29–1.18 (m, 18 H), 0.87 (t, 3 H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 154.6, 119.1, (bs), 82.8, 35.8, 31.7, 28.9, 28.2, 24.7, 22.5, 14.0. MS (EI, 70 eV) *m*/*e* (rel int): 84 (42), 139 (68), 153 (100), 223 (53), 238 (13). HRMS calcd for $C_{14}H_{27}BO_2$: 238.2104. Observed: 238.2101.

(*E*)-Pinacol (5-Chloro-1-pentenyl)boronate (2b). A clear oil (1.95 g, 85%) was obtained from 5-chloro-1-pentyne (10 mmol, 1.02 g) after flash column chromatography (solvent, 3% ether in hexane). IR (neat): 2979 (s), 1640 (s), 1398 (s), 1364 (s), 1323 (s), 1165 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.57 (dt, 1 H, *J* = 17.9, 6.4 Hz), 5.47 (dt, 1 H, *J* = 1.5, 17.9 Hz), 3.50 (t, 2 H, *J* = 6.7 Hz), 2.30 (dq, 2 H, *J* = 1.5, 6.9 Hz), 1.89 (p, 2 H, *J* = 6.6 Hz), 1.26 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 151.7, 140.4 (bs), 83.0, 44.0, 32.6, 31.1, 24.7. ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 29.66. MS (EI, 70 eV) *m*/*e* (rel int): 41 (73), 69 (100), 85 (48), 144 (55), 153 (95), 215 (68), 230 (27). HRMS calcd for $C_{11}H_{20}{}^{11}B^{35}ClO_2$: 230.1245. Observed: 230.1256.

(*E*)-Pinacol (5-Iodo-1-pentenyl)boronate (2c). A clear oil (2.70 g, 84%) was obtained from 5-iodo-1-pentyne (10 mmol, 1.94 g) after flash column chromatography (solvent, 5% ether in hexane). IR (neat): 2978 (s), 1639 (s), 1368 (s), 1324 (s), 1165 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.55 (dt, 1 H, *J* = 18.0, 6.5 Hz), 5.49 (dt, 1 H, *J* = 1.5, 18.0 Hz), 3.17 (t, 2 H, *J* = 7.0 Hz), 2.26 (dq, 2 H, *J* = 1.2, 6.8 Hz), 1.95 (p, 2 H, *J* = 7.0 Hz), 1.26 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 151.4, 119.5 (bs), 82.8, 36.0, 31.7, 24.6, 5.8. MS (EI, 70 eV) *m*/*e* (rel int): 109 (71), 153 (61), 195 (46), 307 (41), 322 (48). HRMS calcd for $C_{11}H_{20}BIO_2$: 322.0601. Observed: 322.0602.

(*E*)-Pinacol [2-(1-Methoxycyclohexyl)ethenyl]boronate (2d). A clear oil (2.26 g, 85%) was obtained from 1-ethynyl-1-methoxycyclohexane (10 mmol, 1.38 g) after flash column chromatography (solvent, 5% ether in hexane). IR (neat): 2978 (s), 2933 (s), 1636 (s), 1448 (m), 1388 (s), 1376 (s), 1346 (s), 1324 (s), 1165 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.43 (d, 1 H, *J* = 18.6 Hz), 5.55 (d, 1 H, *J* = 18.6 Hz), 3.11 (s, 3 H), 1.79–1.67 (m, 2 H), 1.67–1.34 (m, 6 H), 1.27 (s, 12 H). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 75.5 MHz): δ 156.3, 117.4 (bs), 82.4, 75.6, 48.7, 32.9, 24.8, 24.0, 20.9. ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 30.84. MS (EI, 70 eV) *m*/*e* (rel int): 123 (100), 151 (73), 223 (43), 251 (33), 266 (13). HRMS calcd for $C_{15}H_{27}BO_3$: 266.2053. Observed: 266.2040.

(*E*)-Pinacol (2-Phenylethenyl)boronate (2e). A clear oil (1.74 g, 64%) was obtained from phenylacetylene (10 mmol, 1.02 g) after flash chromatography (solvent, 10% ether in hexane). IR (neat): 2978 (s), 1624 (s), 1577 (s), 1495 (s), 1386 (s), 1210 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.51–7.18 (m, 6 H), 6.18 (d, 1 H, *J* = 18.0 Hz), 1.31 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 149.5, 137.7, 130.9, 128.8, 128.5, 128.1, 128.0, 127.2, 127.0, 125.8, 116.7 (bs), 83.2, 24.7. ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 35.04. MS (EI, 70 eV) *m*/*e* (rel int): 130 (100), 144 (62), 230 (32). HRMS calcd for $C_{14}H_{19}BO_2$: 230.1478. Observed: 230.1471.

(*E*)-Pinacol (5-Cyano-1-pentenyl)boronate (2f). A clear oil (1.74 g, 79%) was obtained from 5-hexynenitrile (10 mmol, 0.93 g) after flash column chromatography (solvent, 10% ether in hexane). IR (neat): 2979 (s), 2247 (w), 1640 (s), 1399 (m), 1144 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.52 (dt, 1 H, *J* = 18.2, 7.6 Hz), 5.48 (dt, 1 H, *J* = 1.3, 18.2 Hz), 2.37–2.26 (m, 4 H), (p, 2 H, *J* = 7.4 Hz), 1.25 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 150.8, 121.1 (bs), 119.3, 83.2, 34.1, 24.7, 24.0, 16.4. MS (EI, 70 eV) *m*/*e* (rel int): 41 (100), 122 (93), 193 (62), 206 (58), 221 (22). HRMS calcd for $C_{12}H_{20}BNO_2$: 221.1587. Observed: 221.1585.

(*E*)-Pinacol [5-(Pivaloyloxy)-1-pentenyl]boronate (2g). A clear oil (2.32 g, 78%) was obtained from 4-pentynyl 2,2-dimethylpropanoate (10 mmol, 1.69 g) after flash column chromatography (solvent, 10% ether in hexane). IR (neat): 2978 (s), 1730 (s), 1640 (s), 1481 (s), 1368 (s), 1284 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.60 (dt, 1 H, *J* = 17.9, 6.4 Hz), 5.45 (dt, 1 H, *J* = 1.6, 17.9 Hz), 4.04 (t, 2 H, *J* = 6.4 Hz), 2.22 (dq, 2 H, *J* = 1.5, 6.7 Hz), 1.75 (p, 2 H, *J* = 6.5 Hz), 1.24 (s, 12 H), 1.17 (s, 9 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 178.6, 152.8, 119.4 (bs), 83.1, 63.7, 38.8, 32.1, 27.3, 27.2, 24.8. MS (EI, 70 eV) *m*/*e* (rel int): 57 (100), 281 (4), 296 (0.2). HRMS calcd for $C_{16}H_{29}BO_4H$: 297.2241. Observed: 297.2237.

(*Z*)-Pinacol 2-Hex-2-enylboronate (2h). A clear oil (1.58 g, 75%) was obtained from 2-hexyne (10 mmol, 0.82 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2979 (s), 1633 (s), 1449 (s), 1378 (s), 1165 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.36–6.25 (m, 1 H), 2.21–2.05 (m, 2 H), 1.75–1.64 (m, 3 H), 1.47–1.30 (m, 2 H), 1.24 (s, 12 H), 0.91 (t, 3 H, *J* = 7.9 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 146.3, 139.6, 126.3 (bs), 83.0, 82.9, 30.7, 30.1, 24.8, 23.1, 22.0, 13.9, 13.7. MS (EI, 70 eV) *m*/*e* (rel int): 84 (100), 101 (96), 153 (74), 195 (49), 210 (38). HRMS calcd for $C_{12}H_{23}BO_2$: 210.1791. Observed: 210.1773.

(*Z*)-Pinacol [2-(1-Phenyl)-2-propenyl]boronate (2i). A clear oil (1.68 g, 69%) was obtained from 1-propynylbenzene (10 mmol, 1.16 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 3023 (s), 1600 (s), 1493 (s), 1389 (s), 1272 (s), 1146 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.42–6.70 (m, 6 H), 2.00 (s, 1 H), 1.33 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.6, 142.4, 139.3, 138.0, 129.4, 129.1, 128.1, 127.8, 127.1, 125.9, 83.5, 83.4, 24.8, 24.7, 15.8. MS (EI, 70 eV) *m*/*e* (rel int): 49 (100), 229 (16), 244 (56). HRMS calcd for $C_{15}H_{21}BO_2$: 244.1635. Observed: 244.1641.

(*E*)-Pinacol [2-(1-Cyclohexenyl)ethenyl]boronate (2j). A clear oil (1.94 g, 83%) was obtained from 1-ethynyl-1-cyclohexene (10 mmol, 1.06 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2979 (s), 1632 (s), 1345 (s), 1294 (s), 1190 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.02 (d, 1 H, *J* = 18.3 Hz), 6.00–5.93 (m, 1 H), 5.43 (d, 1 H, *J* = 18.3 Hz), 2.16–2.12 (m, 4 H), 1.68–1.57 (m, 4 H), 1.27 (s, 12 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 153.2, 137.1, 134.1, 111.9 (bs), 82.9, 26.1, 24.7, 23.7, 22.3, 22.2 MS (EI, 70 eV) *m*/*e* (rel int): 134 (100), 190 (24), 219 (7), 234 (26). HRMS calcd for $C_{14}H_{23}BO_2$: 234.1791. Observed: 234.1777.

Typical Procedure for the Hydroboration of Alkenes Using Pinacolborane. Preparation of Pinacol Decylboronate. To a solution of pinacolborane (1) (20 mmol) prepared in 1,2-dichloroethane (2 mL) was added 1-decene (10 mmol, 1.40 g). The reaction mixture was warmed to 40 °C and stirred for 48 h. GC analysis of a reaction aliquot shows the completion of the reaction. Ether (150 mL) was added, and the resulting solution was poured into a separatory funnel containing a saturated aqueous NH_4Cl solution (250 mL). The organic phase was washed quickly with a saturated aqueous NH_4Cl solution (100 mL) and dried over $MgSO_4$. The solvents were removed in vacuo, affording a residue which was purified by flash column chromatography (2% ether in hexane) providing the desired product as a clear oil (1.88 g; 70% yield). GC analysis indicates a regioisomer ratio of 99:1.

Pinacol Decylboronate (2k). A clear oil (1.88 g, 70%) was obtained from 1-decene (10 mmol, 1.40 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2994 (s), 1466 (s), 1371 (s), 1164 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.44–1.13 (m, 28 H), 0.87 (t, 3 H, *J* = 7.6 Hz), 0.78 (t, 2 H, *J* = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 82.7, 32.4, 31.9, 29.6, 29.4, 29.3, 29.3, 24.8, 24.0, 22.6, 14.0, 11.1 (bs). MS (EI, 70 eV)

m/e (rel int): 85 (53), 129 (100), 211 (13), 253 (52), 268 (33). HRMS calcd for $C_{16}H_{33}BO_2$: 268.2574. Observed: 268.2589.

Pinacol Cyclohexylboronate (2l). A clear oil (1.53 g, 73%) was obtained from cyclohexene (10 mmol, 0.82 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2978 (s), 1449 (s), 1371 (s), 1311 (s), 1258 (s), 1146 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.72–1.55 (m, 4 H), 1.40–1.27 (m, 6 H), 1.24 (s, 12 H), 1.04–0.93 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 82.6, 27.9, 27.1, 26.7, 24.7, 22.1 (bs). MS (EI, 70 eV) *m/e* (rel int): 124 (100), 129 (24), 195 (38), 210 (7). HRMS calcd for $C_{12}H_{23}BO_2$: 210.1791. Observed: 210.1783.

(*exo*)-Pinacol 2-Norbornylboronate (2m). A clear oil (1.20 g, 54%) was obtained from norbornene (10 mmol, 0.94 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2994 (s), 1452 (s), 1372 (s), 1266 (s), 1225 (s), 1187 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.29 (bs, 1 H), 2.22 (bs, 1 H), 1.58–1.42 (m, 4 H), 1.39–1.29 (m, 1 H), 1.29–1.13 (m, 15 H), 0.92–0.85 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 82.7, 38.7, 38.1, 36.7, 32.2, 29.3, 25.8 (bs), 24.7, 12.4 (bs). MS (EI, 70 eV) *m/e* (rel int): 136 (57), 165 (14), 207 (100), 222 (5). HRMS calcd for $C_{13}H_{23}BO_2$: 222.1791. Observed: 222.1785.

Registry No. 1, 25015-63-8; **2a**, 83947-55-1; **2b**, 126688-98-0; **2c**, 141091-29-4; **2d**, 141091-30-7; **2e**, 83947-56-2; **2f**, 141091-31-8; **2g**, 141091-32-9; **2h**, 141091-33-0; **2i**, 141091-35-2; **2j**, 141091-37-4; **2k**, 141091-38-5; **2l**, 87100-15-0; **2m**, 141091-39-6; **3e**, 74213-48-2; **4h**, 141091-34-1; **4i**, 141091-36-3; PivCl, 3282-30-2; BH_3·SMe_2, 13292-87-0; HexC≡CH, 629-05-0; $Cl(CH_2)_3C$≡CH, 14267-92-6; $I(CH_2)_3C$≡CH, 2468-55-5; PhC≡CH, 536-74-3; $NC(CH_2)_3C$≡CH, 14918-21-9; *t*-$BuOCO_2(CH_2)_3C$≡CH, 140872-91-9; PrC≡CMe, 764-35-2; PhC≡CMe, 673-32-5; OctCH=CH_2, 872-05-9; $HO(CH_2)_3C$≡CH, 5390-04-5; pinacol, 76-09-5; 1-ethynyl-1-methoxycyclohexane, 5240-36-8; 1-ethynyl-1-cyclohexene, 931-49-7; cyclohexene, 110-83-8; norbornene, 498-66-8.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of the products (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reversal of Regiochemistry of Wacker-Type Reactions Oriented by Heteroatoms

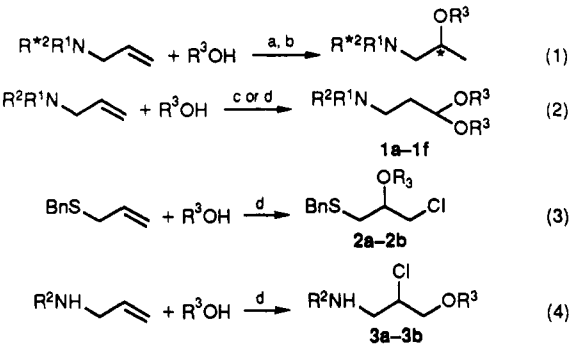
Jin-yu Lai, Xiao-xin Shi, and Li-xin Dai*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China

Received July 25, 1991 (Revised Manuscript Received January 6, 1992)

As one of the most widely used organometallic reactions, the Wacker process plays a very important role not only in the petrochemical industry but also in synthetic chemistry and especially in the synthesis of fine chemicals.[1-3] Although the application of this process is well-known with regard to the production of acetaldehyde from ethylene, the corresponding reactions of higher olefins usually afford methyl ketones rather than aldehyde, following the Markovnikov rule of addition.[2] Only a few reports have appeared of preferential aldehyde formations, and most of these involve olefins bearing an electron-withdrawing group wherein the direction of polarization of the terminal double bond is altered.[4] Because the formation of aldehydes and their derivatives via the attack at the terminal carbon of a terminal double bond is one of the important processes currently attracting attention in synthetic organic chemistry,[5] we report here a heteroatom-oriented Wacker-type reaction resulting in acetal as the main reaction product rather than the usual methyl ketone product.

During the course of studying the asymmetric oxypalladation of allylamine (eq 1),[6] we discovered that the addition of lithium or strontium carbonate changed the reaction course from eq 1 to eq 2, affording dimethyl acetal



(a) Li_2PdCl_4, K_2CO_3, (b) $NaBH_4$/THF, (c) Li_2PdCl_4, Li_2CO_3, or $SrCO_3$, (d) 10% Li_2PdCl_4/300% $CuCl_2$

as the major product rather than the expected 2-methoxypropylamine. We then examined this reaction with various substrates under the typical conditions of the Wacker process, using Li_2PdCl_4 with excess cupric chloride as cooxidant. The results of these reactions are listed in Table I, and the following conclusions can be drawn.

In the presence of $CuCl_2$, all reactions proceeded in the mode of a Wacker-type reaction. The difference in products (acetal, ketal, or chloro ether) is due to the directing influence of the heteroatoms. In the case of allyl and butenyl tertiary amines (entries 1–7) and of butenyl and pentenylsulfides (entries 9, 10), the acetals were obtained exclusively in good yields with no evidence of the formation of ketal. For allylic substrates with heteroatoms of stronger coordinating ability (S ≫ NH > N), the stabilized intermediates of the Wacker reactions were intercepted by Cu(II) to afford alkoxychlorinated products (chloro ethers, entries 11–14).

According to the regiochemistry of oxypalladation of allylic and homoallylic systems,[7,8] the nucleophile would be expected to attack the inner carbon atom of the double bond of allyl amines or sulfides and the external carbon atom of the double bond of the 3-butenylamine, 3-butenyl sulfide, or 4-pentenyl sulfide.[9] The above regiochemistry of the palladation reaction holds true in the presence of Cu(II) in several systems. Thus, for entries 7, 9, and 10, the nucleophiles were directed to the external carbon atom of the double bond of 3-butenylamine and sulfide and of

(1) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R.; Kojer, H. *Angew. Chem.* **1958**, *71*, 176. (b) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sabel, A. *Ibid.* **1962**, *74*, 93.

(2) For comprehensive reviews, see: (a) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, 1980. (b) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic: New York, 1971. (c) Heck, R. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985.

(3) Tsuji, J. *Synthesis* **1984**, 369.

(4) (a) Nogami, J.; Ogawa, H.; Miyamoto, S.; Mandai, T.; Wakabayashi, S.; Tsuji, J. *Tetrahedron Lett.* **1988**, *29*, 5181. (b) Alyea, E. C.; Dias, S. A.; Ferguson, G.; McAlees, A. J.; McCrindle, R.; Roberts, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 4985. (c) Hosokawa, T.; Shinohara, T.; Ooka, Y.; Murahashi, S.-I. *Chem. Lett.* **1989**, 2001. (d) Base, A. K.; Krishnan, L.; Wagle, D. R.; Menhas, M. S. *Tetrahedron Lett.* **1986**, *27*, 5955. (e) Feringa, B. I. *J. Chem. Soc., Chem. Commun.* **1986**, 909.

(5) Hosokawa, T.; Murahashi, S.-I. *Acc. Chem. Res.* **1990**, *23*, 49.

(6) Dai, L. X.; Lai, J. Y.; Shi, X. X. To be published.

(7) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

(8) (a) Holton, R. A.; Kjonaas, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 4177. (b) Holton, R. A. et al. *J. Organomet. Chem.* **1977**, *142*, C15.

(9) Zhang, Y. Z.; Shi, X. X.; Dai, L. X. *Acta Chem. Sinica*, in press.

0022-3263/92/1957-3485$03.00/0