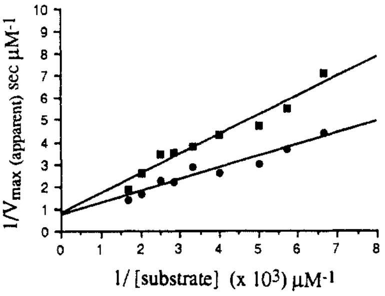

Figure 3. Replot of the apparent V_{max} values obtained from the Lineweaver-Burk plots versus concentration to provide the true V_{max} value as $1/(y$ intercept) and K_m values as $-1/(x$ intercept) (■ = fixed concentrations of diene; ● = fixed concentrations of dienophile).

rangement at 110 °C and subsequent trapping with methyl glycolate.[9] Only a single structural isomer was isolated from the Diels-Alder reaction with each of these dienes, and the endo conformation was assigned in both cases on the basis of nuclear Overhauser effect (NOE) cross peaks determined by 2D NOESY spectroscopy.[10] The isothiocyanate derivative of **6** was coupled to keyhole limpet hemocyanin (KLH), and the resulting protein conjugate **6b** was used to immunize Balb-c mice following a standard protocol.[11]

The kinetics of the Diels-Alder reaction of **1** with **2** were determined in 20 mM HEPES, 100 mM NaCl, pH 7.5 at 25 °C, both by HPLC[12] and by monitoring the change in absorbance at 247 nm.[13] One of 10 antibodies specific for hapten **6** (antibody 39, A11) demonstrated a large rate enhancement relative to the background reaction rate. The kinetics for this antibody-catalyzed reaction were determined by measuring the difference in initial rates between the catalyzed and background reactions. Catalysis of the Diels-Alder reaction by antibody 39, A11 was examined as a random, rapid equilibrium system, and Lineweaver-Burk plots were constructed by holding one substrate at a fixed concentration while varying the concentration of the second (Figure 2).[14] The apparent V_{max} values thus obtained were then plotted as a function of substrate concentration to give the true V_{max} as 1.35 µM s^{-1} and a k_{cat} value of 0.67 s^{-1} per binding site (Figure 3). The K_m values for diene **1** and dienophile **2** were determined to be 1130 and 740 µM, respectively. The apparent second-order rate constant, k_{cat}/K_m, is equal to 900 M^{-1} s^{-1} for the dienophile and 583 M^{-1} s^{-1} for the diene. The second-order rate constant for the background reaction, k_{uncat}, was found to be 1.9 M^{-1} s^{-1} in the reaction buffer at 25 °C and 0.002 M^{-1} s^{-1} in acetonitrile at 25 °C by using an integrated second-order rate equation and curve fitting with a nonlinear regression program.[15]

The dissociation constant of antibody 39, A11 for hapten **6** was measured by fluorescence quenching, and a K_D of 126 nM was determined by a Scatchard analysis.[16] The binding constant for the reaction product **3** was determined to be 10 µM by a similar analysis, indicating that while the product is bound approximately 100-fold less tightly than the hapten, the antibody binds the product **3** roughly 75 times tighter than either diene **1** or dienophile **2**. Currently we are investigating the mechanism of this antibody-catalyzed reaction with respect to stereochemistry, activation parameters, and the concerted nature of bond formation.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Division of Material Sciences and Division of Energy Biosciences, Office of General Life Sciences, Structural Biology Division, of the U.S. Department of Energy under Contract No. DE-AC03-76 SF00098 and the Lucille Markey Charitable Trust. We thank Denton Hoyer for his preliminary work on this project, Bob Simpson for his assistance with the NOESY spectra, and Jim Prudent for his assistance with antibody production.

Supplementary Material Available: Full experimental details for the synthesis of **3** and **6** as well as the experimental details for the kinetic measurements (14 pages). Ordering information is given on any current masthead page.

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(9) (a) Overman, L. E.; Taylor, G. F.; Petty, C. B.; Jessup, P. J. *J. Org. Chem.* **1978**, *43*, 2164-2167. (b) Hunig, S.; Kahanek, H. *Chem. Ber.* **1957**, *90*, 238.

(10) NOESY spectra were recorded on the UCB AMX 400-MHz instrument according to the following: Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370-388.

(11) Jacobs, J.; Schultz, P. G. *J. Am. Chem. Soc.* **1987**, *109*, 2174. Hybridomas were generated by standard methods using P-3 myeloma cells as the fusion partner and subsequently screened by ELISA for binding to the bovine serum albumin (BSA) conjugate of **6** and for inhibition of binding by free **6**. Antibodies were purified from ascites by protein A Sepharose 4B affinity chromatography and were determined to be >95% homogeneous by sodium dodecyl sulfate polyacrylamide gel electrophoresis with Coomasie blue staining.

(12) HPLC assays were carried out with a Microsorb C8 reverse-phase column with a gradient starting at 10% acetonitrile in 50 mM NaOAc at pH 5.0 and increasing to 40% acetonitrile over 6 min. Product formation was quantitated against the internal standard, 2,4-dinitrobenzoic acid. The retention time of the product formed in the catalyzed reaction is identical with that of the endo product.

(13) Reaction velocities were determined by measuring the difference in initial rates between the catalyzed and background reactions. All reactions were carried out at 25 °C in 20 mM HEPES, 100 mM NaCl at pH 7.5 with 1% acetonitrile, and all catalyzed reactions were run with 1 µM antibody 39, A11. Since the product and the dienophile have identical extinction coefficients at 247 nm (ϵ_{247} = 17 000), the loss in absorbance reflects the reaction of the diene (ϵ_{247} = 28 000) and represents the rate of the catalyzed reaction. Velocities were determined from the slope of the linear portion of the absorbance change at less than 3% completion.

(14) Segel, I.H. *Enzyme Kinetics*; John Wiley and Sons: New York, 1975; pp 273-283.

(15) Leatherbarrow, R. J. *Enzfitter Manual*; Elsevier Science Publishers: Amsterdam, 1987.

(16) Fluorescence quenching was measured in 20 mM HEPES, 100 mM NaCl at pH 7.5, 25 °C. The sample was excited at 280 nm, and fluorescence was detected at 340 nm. Data was analyzed according to the following: Taira, K.; Benkovic, S. J. *J. Med. Chem.* **1988**, *31*, 129-137.

New Approach to Boron-Stabilized Organometallics

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Boron-stabilized carbanions are versatile reagents that have found numerous synthetic applications.[1-3] They have been prepared via deprotonation of sterically hindered boranes[1] and stabilized alkyldialkoxyboranes[2] or via a boron-lithium exchange reaction.[3] We report herein a new general preparation of α-

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(1) (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Kow, R.; Rathke, M. W. *J. Am. Chem. Soc.* **1973**, *95*, 2715. (c) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 623. (d) Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 631. (e) Garad, M. V.; Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 637. (f) Wilson, J. W. *J. Organomet. Chem.* **1980**, *186*, 297. (g) Pelter, A.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 627. (h) Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 635. (i) Pelter, A.; Buss, D.; Pitchford, A. *Tetrahedron Lett.* **1985**, *26*, 5093. (j) Pelter, A.; Buss, D.; Colclough, E. *J. Chem. Soc., Chem. Commun.* **1987**, 297. (k) Pelter, A.; Smith, K.; Elgendy, S.; Rowlands, M. *Tetrahedron Lett.* **1989**, *30*, 5643, 5647.

(2) (a) Matteson, D. S.; Moody, R. J. *Organometallics* **1982**, *1*, 20. (b) Matteson, D. S.; Moody, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 3196. (c) Matteson, D. S.; Arne, K. H. *Organometallics* **1982**, *1*, 280. (d) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 230.

(3) (a) Cainelli, G.; Dal Bello, G.; Zubiani, G. *Tetrahedron Lett.* **1965**, 3429. (b) Zweifel, G.; Arzoumanian, H. *Tetrahedron Lett.* **1966**, 2535. (c) Zweifel, G.; Fisher, R. P.; Horng, A. *Synthesis* **1973**, 37. (d) Matteson, D. S. *Synthesis* **1975**, 147. (e) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 291.

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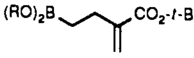
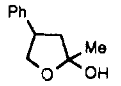
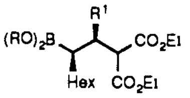
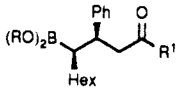
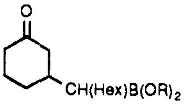
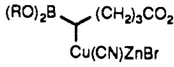
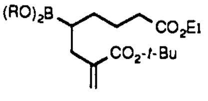
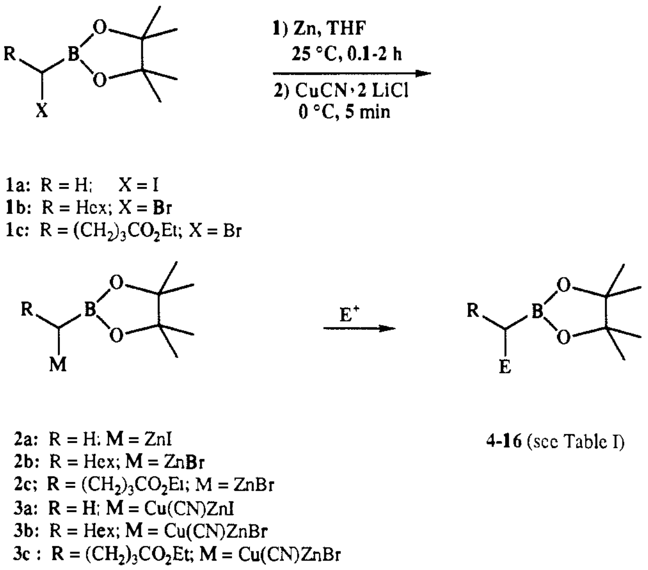
Table I. Products **4–16** Obtained by the Reaction of the α Zinc and Copper Pinacol Alkaneboronates **3a–c** with Electrophiles[5]

entry	copper reagent	electrophile	product		yield,[a] %
1	$(RO)_2BCH_2Cu(CN)ZnI$ (**3a**)	Me_3SnCl	$(RO)_2BCH_2SnMe_3$ (**4**)		87
2	**3a**	$MeSCH_2Cl$	$(RO)_2B(CH_2)_2SMe$ (**5**)		63
3	**3a**	*tert*-butyl α-(bromomethyl)-acrylate	 **6**		88
4	**3a**	benzylideneacetone	 **7**		67[b]
5	**3a**	1-naphthaldehyde	1-Naphth-CH(OH)CH_2OH (**8**)		93[b]
6	$(RO)_2BCH(Hex)Cu(CN)ZnBr$ (**3b**)	diethyl benzylidenemalonate		(**9**), R^1 = Ph	95
7	**3b**	diethyl hexylidenemalonate		(**10**), R^1 = Pent	86
8	**3b**	benzylideneacetone		(**11**), R^1 = Me	79
9	**3b**	cinnamaldehyde		(**12**), R^1 = H	57
10	**3b**	cyclohexenone	 **13**		74
11	**3b**	PhCOCl	$HexCH_2COPh$ (**14**)		74
12	**3b**	2-(bromomethyl)hexene	$H_2C{=}C(Bu)CH_2CH(OH)Hex$ (**15**)		93[b]
13	 **3c**	*tert*-butyl α-(bromomethyl)-acrylate	 **16**		83

[a] $(RO)_2$: pinacol. All yields reported refer to isolated yields of analytical pure products. Satisfactory spectral data (IR, ^1H and ^{13}C NMR, mass spectra, and high-resolution mass spectra) were obtained for all new compounds. [b] Product obtained after oxidative workup (30% H_2O_2, 5 M NaOAc, THF/ethanol).

Scheme I


1a: R = H; X = I
1b: R = Hex; X = Br
1c: R = $(CH_2)_3CO_2Et$; X = Br

2a: R = H; M = ZnI
2b: R = Hex; M = ZnBr
2c; R = $(CH_2)_3CO_2Et$; M = ZnBr
3a: R = H; M = Cu(CN)ZnI
3b: R = Hex; M = Cu(CN)ZnBr
3c : R = $(CH_2)_3CO_2Et$; M = Cu(CN)ZnBr

4-16 (see Table I)

(dialkoxyboryl)alkyl zinc and copper organometallics as well as their reactivity toward various electrophiles. Thus, the insertion of zinc dust to the readily available α-halo boronic esters[4] **1** in THF proceeds smoothly (Zn (2–3 equiv); 0.1–2 h; >85% yield),[5] affording (α-(dialkoxyboryl)alkyl)zinc halides of type **2** (X = Br, I). This remarkably easy zinc insertion clearly reflects the participation of the dialkoxyboryl group in the formation of the organometallic. It should be noted that nonfunctionalized alkyl bromides do not react with zinc in THF, while alkyl iodides require a reaction temperature of 40–55 °C.[6] The addition of the THF soluble copper salt CuCN·2LiCl converts the zinc compounds **2** to the more reactive copper derivatives **3**. As shown in Table I,

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(4) (a) Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1977**, *42*, 3252. (b) Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Murahashi, S.; Sonoda, A. *J. Org. Chem.* **1977**, *42*, 4088. (c) Matteson, D. S.; Schaumberg, G. D. *J. Org. Chem.* **1966**, *31*, 726. (d) Matteson, D. S.; Cheng, T. C. *J. Org. Chem.* **1968**, *33*, 3055. (e) Matteson, D. S.; Arne, K. *J. Am. Chem. Soc.* **1978**, *100*, 1325. (f) Rathke, M. W.; Chao, E.; Wu, G. *J. Organomet. Chem.* **1976**, *122*, 145. (g) Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (h) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 1529. (i) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535.

(5) Typical procedure, preparation of 2-butyl-1-decen-4-ol (**15**): A three-necked, 25-mL flask equipped with a dropping funnel, an argon inlet, a low-temperature thermometer, and a magnetic stirring bar was charged with zinc dust (1.5 g, 23 mmol, Aldrich 325 mesh) flushed with argon, and the zinc was activated with dibromoethane[6] (200 mg, 1.1 mmol) in 2 mL of THF. Pinacol 1-bromoheptane-1-boronate (**1b**) (2.50 g, 7.4 mmol, 90% purity) in 4 mL of dry THF was added dropwise within 20 min at 22–25 °C. GLC analysis of a hydrolyzed aliquot indicates the completion of the reaction (in the case of **1c**, the reaction mixture was stirred for 2 h at 25 °C). The zinc dust was decanted and was transferred via syringe into a three-necked flask under argon at –20 °C containing a solution made of CuCN (720 mg, 8 mmol), LiCl (672 mg, 16 mmol, dried for 1 h at 120 °C under vacuum), and 10 mL of THF.[6] The reaction mixture was warmed up to 5 °C and was ready to use after 5 min at this temperature. It was cooled to –20 °C, and 2-(bromomethyl)-1-hexene (884 mg, 5 mmol) was added. The reaction mixture was allowed to warm up to 25 °C, stirred for 0.5 h, diluted with 100 mL of ether, and worked up as usual. After evaporation of the solvents, the pale yellow oil was dissolved in 10 mL of THF and 10 mL of ethanol. A sodium hydroxide solution (6 N NaOH, 3.3 mL) was added, followed by 30% H_2O_2 (4 mL). An exothermic reaction occurs and GLC analysis indicates completion of the reaction. The solvent was evaporated and the residue dissolved in 150 mL of ether. After a normal workup and evaporation of the solvent, the crude oil was purified by flash chromatography (solvent: hexane/ether 9/1) yielding 0.99 g of 2-butyl-1-decen-4-ol (**15**) (93% yield) as an analytically pure sample.

(6) (a) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. (b) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1988**, *29*, 2395. (c) Yeh, M. C. P.; Knochel, P.; Butler, W. M.; Berk, S. C. *Tetrahedron Lett.* **1988**, *29*, 6693. (d) Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* **1988**, *53*, 5789.

the reagents **3** react with a wide range of electrophiles in fair to excellent yields. Several reactive halides give the desired coupling products. Thus, the addition of **3a** to trimethyltin chloride (0.75 equiv; 25 °C, 0.5 h) affords the tin derivative **4** in 87% yield (entry 1). Reaction of **3a** with chloromethyl methyl sulfide gives the thio derivative **5** (0.75 equiv; −78 to 5 °C; 63% yield; entry 2). Allylation of **3a** with *tert*-butyl α-(bromomethyl)acrylate (0.72 equiv 0 °C, 0.1 h; 88% yield; entry 3) leads to the acrylate **6**. Michael addition of **3a** to benzylideneacetone (0.65 equiv; Me_3SiCl (1.1 equiv); −78 to 0 °C, 10 h; then 25 °C, 30 h) furnishes, after the oxidation[7] of the intermediate boronic ester (H_2O_2, 30%; NaOAc, 5 M; THF/EtOH; 25 °C, 3 h; 67% yield), the hydroxytetrahydrofuran **7**. In the presence of $BF_3 \cdot OEt_2$ (1.1 equiv),[8] the reagent **3a** adds readily to 1-naphthaldehyde (0.55 equiv; −70 to −30 °C, 1 h; then 5 °C, 10 h, and 25 °C, 3 h), and gives after oxidation (H_2O_2, 30%; NaOAc, 5 M; 1.5 h; 93% yield) the diol **8**. The 1,4-addition of **3b** to diethyl benzylidenemalonate (0.75 equiv; 25 °C, 10 h) produces *diastereospecifically*[9] the *syn*-γ-(dialkoxyboryl) malonate **9** in quantitative yield (entry 6). This reaction has some generality, and several β-phenyl-substituted Michael acceptors such as benzylideneacetone and cinnamaldehyde (entries 8 and 9) furnish diastereospecifically the 1,4-adducts **11** and **12** respectively in 79% and 57% yield. β-Alkyl-substituted Michael acceptors such as diethyl hexylidenemalonate or cyclohexenone[10] afford the addition products **10** and **13** as a mixture of diastereoisomers (ratio of 56:44 (86% yield) and 70:30 (74% yield) respectively). The benzoylation of **3b** (PhCOCl (0.75 equiv); 0 °C, 2 h) gives, after aqueous workup, heptyl phenyl ketone **14** (74%; entry 11). Finally, the high functional-group tolerance of organozinc halides has allowed the preparation of the ester-substituted boron-stabilized zinc and copper reagent **3c**.[11] Its allylation with *tert*-butyl α-(bromomethyl)acrylate (0.7 equiv; 0 °C, 0.5 h; 83% yield; entry 13) furnishes the polyfunctional boronic ester **16**.

In conclusion, we have developed a preparation of boron-stabilized zinc and copper organometallics, which, compared to the corresponding lithium derivatives, are able to accommodate functional groups. They display an excellent reactivity toward a broad range of electrophiles such as allylic halides, aldehydes, acyl chlorides, and various types of Michael acceptors. Further extensions of these studies are underway.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of 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. We also thank Dr. S.-H. Lee and R. Walawalkar for some preliminary experiments.

Supplementary Material Available: Typical experimental procedures and spectral data for new compounds (9 pages). Ordering information is given on any current masthead page.

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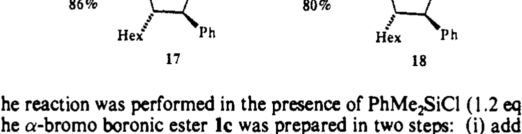
[7] Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 4306.

[8] Yeh, M. C. P.; Knochel, P.; Santa, L. E. *Tetrahedron Lett.* **1988**, *29*, 3887.

[9] The γ-(dialkoxyboryl) malonate **9** was oxidized (H_2O_2, 30%; NaOAc, 5 M; 25 °C, 1 h) to the lactone **17** (86% yield), which after deethylcarbonylation gave only the *trans*-lactone **18** (H_2O (2 equiv), DMSO, 140 °C, 6 h; 80%) as indicated by NOE experiments.



[10] The reaction was performed in the presence of $PhMe_2SiCl$ (1.2 equiv).

[11] The α-bromo boronic ester **1c** was prepared in two steps: (i) addition of $EtO_2C(CH_2)_3Cu(CN)ZnI$ to the pinacol dichloromethaneboronate (ref 4f; see also: Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039), (ii) followed by a Cl/Br exchange (LiBr, acetone, 25 °C). Overall yield: 54% (10-g scale).

Surface-Mediated Reactions. 1. Hydrohalogenation of Alkenes and Alkynes

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Received May 21, 1990

Despite numerous implications to the contrary in introductory textbooks, electrophilic addition of hydrogen halides to unsaturated linkages is fraught with a number of experimental challenges. HCl does not add to alkenes at preparatively useful rates unless they are strained,[1] highly substituted,[2] or part of a styryl system.[3] HI adds more readily but is difficult to generate and expensive to obtain commercially.[4] Alkynes react with hydrogen halides more slowly. Moreover, since the initially formed vinyl halide undergoes addition more readily than the starting alkyne, it is often difficult to obtain the monoadduct in high yield. Although HBr adds readily to alkenes and alkynes, this is usually due to competing radical-chain addition to give the anti-Markovnikov product, which predominates unless stringent precautions are taken.[5] More generally, the generation and transfer of these hygroscopic, gaseous reagents is both inconvenient and difficult to perform stoichiometrically.

We report that the use of appropriate silica gel or alumina surfaces facilitates hydrohalogenation of alkenes and alkynes, making it possible to readily effect additions that otherwise occur slowly, if at all. Moreover, surface-mediated additions afford stereoselectivities often unattainable in solution. Finally, the use of various HX precursors in conjunction with silica gel or alumina is a convenient method for in situ generation of hydrogen halides that can be done easily and on a quantitative basis. Some typical examples follow.

Treatment of cycloheptene (**1**) with a saturated solution of HCl at −78 °C afforded no detectable reaction after 1 h. However, the simple addition of silica gel to the solution resulted in rapid conversion to chloride **2**. Similar behavior was observed for 1-octene (**3**) and 1-phenylpropyne (**6**), which also failed to react with HCl in solution, on adding alumina or silica gel to the reaction mixture.[6] Even more conveniently, simply adding an HCl precursor such as $SOCl_2$ or $(COCl_2)$ to a solution of alkene **1** or **3** or alkyne **6** containing a suspension of silica gel or alumina gave chloride **2**, **4**, or **7** (X = Cl) rapidly and in high yield.[7] Isomer

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[1] Schmerling, L. *J. Am. Chem. Soc.* **1946**, *68*, 195–196. Kwart, H.; Miller, R. K. *J. Am. Chem. Soc.* **1956**, *78*, 5008–5011. Stille, J. K.; Sonnenberg, F. M.; Kinstle, T. H. *J. Am. Chem. Soc.* **1966**, *88*, 4922–4925. Cristol, S. J.; Caple, R. *J. Org. Chem.* **1966**, *31*, 2741–2748. Brown, H. C.; Liu, K.-T.; *J. Am. Chem. Soc.* **1975**, *97*, 600–610.

[2] (a) Acharya, S. P.; Brown, H. C. *J. Chem. Soc., Chem. Commun.* **1968**, 305–306. (b) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 2445–2453. (c) Becker, K. B.; Grob, C. A. *Helv. Chim. Acta* **1973**, *56*, 2723–2732, 2733–2746. (d) Becker, K. B.; Boschung, A. F.; Geisel, M.; Grob, C. A. *Ibid.* **1973**, *56*, 2747–2759.

[3] (a) Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 2245–2248, 2248–2252. (b) Brown, H. C.; Rei, M.-H. *J. Org. Chem.* **1966**, *31*, 1090–1093.

[4] Consequently, a number of alternative approaches to hydriodination have been developed: (a) Stone, H.; Shechter, H. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, pp 543–544. (b) Landini, D.; Rolla, F. *J. Org. Chem.* **1980**, *45*, 3527–3529. (c) Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 319–320. (d) Irifune, S.; Kibayashi, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1988**, 366–369. (e) Pagni, R. M.; Kabalka, G. W.; Boothe, R.; Gaetano, K.; Stewart, L. J.; Conaway, R.; Dial, C.; Gray, D.; Larson, S.; Luidhardt, T. *J. Org. Chem.* **1988**, *53*, 4477–4482. (f) Reddy, C. K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919–1920.

[5] For reviews of radical addition of HBr, see (a) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 291–296. (b) Stacey, F. W.; Harris, J. F., Jr. *Org. React.* (*N.Y.*) **1963**, *13*, 150–376.

[6] Addition apparently occurs stepwise via a carbocationic intermediate since 1-octene (**3**) underwent some competing isomerization to (*E*)- and (*Z*)-2-octene.

0002-7863/90/1512-7433$02.50/0