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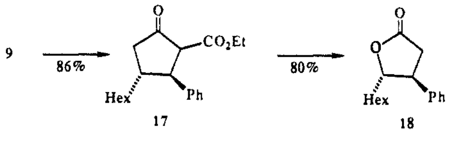
[7] Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 4306.

[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.

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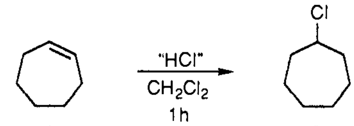
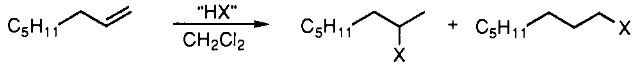
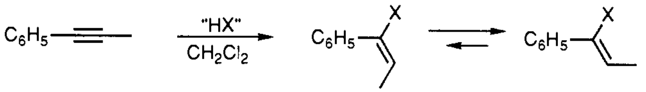


1		2
97%	HCl	0%
3%	HCl, SiO_2	62%
3%	$SOCl_2$, SiO_2	81%

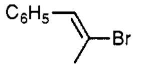


3		4	5
100%	HCl, 1 h	0%	
11%	HCl, Al_2O_3, 1h	60%	
6%	$(COCl)_2$, Al_2O_3	86%	
6%	HBr, 0.3 h	11%	83%
trace	HBr, SiO_2, 0.7 h	96%	0%
trace	$(COBr)_2$, Al_2O_3, 0.3 h	99%	0%
4%	PI_3, SiO_2, 0.3 h	78%	
9%	PI_3, Al_2O_3, 0.3 h	91%	

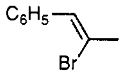
(*E*)-**7**, resulting from syn addition, was formed initially. In the presence of excess reagent, it rapidly equilibrated with the thermodynamically more stable *Z* isomer. Thus either isomer could be obtained in good yield by the proper choice of conditions.[8]



6		(*E*)-7	(*Z*)-7
100%	HCl, 1 h	0%	0%
44%	HCl, SiO_2, 1 h	39%	11%
0%	$(COCl)_2$, Al_2O_3, 0.3 h	85%	14%
0%	3 h	3%	96%
0%	HBr, 3h	29%	8%
0%	HBr, Al_2O_3, 0.3 h	14%	79%
2%	PBr_3, Al_2O_3, 3 h	82%	10%
0%	PBr_3 (xs), Al_2O_3, 3 h	4%	80%
6%	HI, 24 h	74%	19%
trace	AcI, Al_2O_3, 0.3 h	92%	6%

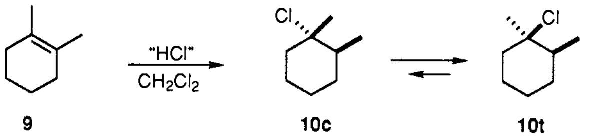


(*E*)-8



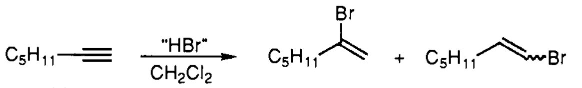
(*Z*)-8

Alkenes also undergo preferential syn addition. Being tetrasubstituted, 1,2-dimethylcyclohexene (**9**) undergoes rapid addition of HCl in solution.[2b,c] However, treatment with $(COCl)_2$ in the presence of alumina afforded adducts even more rapidly. Initially chloride **10c** predominated. However, since addition is reversible under these conditions, ultimately the known thermodynamic ratio **10c**:**10t** = 0.3[2c] was reached.



9		10c	10t
12%	HCl, 0.5 h	69%	14%
0%	$(COCl)_2$, Al_2O_3, 0.3 h	22%	73%

Simple treatment of 1-octene (**3**) or 1-phenylpropyne (**6**) with a saturated solution of HBr afforded, as expected, principally the radical addition product **5** (X = Br) or **8** (*E*, 18%; *Z*, 29%), respectively. However, similar treatment in the presence of silica gel or alumina resulted in almost *exclusive* formation of the ionic products **4** and **7** (X = Br).[9] Even more conveniently, treatment of alkene **3** or alkyne **6** with an HBr precursor such as $(COBr)_2$ or PBr_3 in the presence of alumina afforded the ionic product **4** or **7** (X = Br) in high yield. Once again, either the *E* or *Z* isomer of **7** could be obtained predominantly. Similar treatment with PI_3 or AcI readily afforded iodides **4** or **7** (X = I). The terminal alkyne **11**, which underwent only slow addition of HBr in solution, afforded bromide **12** in good yield on treatment with AcBr over alumina.



11		12	13
48%	HBr	8%	1%
14%	AcBr, Al_2O_3 (in C_5H_{12})	82%	3%

Silica gel and alumina surfaces presumably promote ionic addition through hydrogen-bonding interactions, which both polarize the HX bond and reduce entropy effects by bringing the two reactants together. Studies continue to delineate the mechanistic features of this highly useful procedure and extend it to additional unsaturated substrates and other electrophilic reagents.

Acknowledgment. Generous financial support by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of North Carolina Research Council is gratefully acknowledged.

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[7] In a typical experiment, 2 equiv of reagent was added to a stirred suspension of 2.5 g of Merck grade 40 silica gel or Fisher A540 alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h, in 5 mL of CH_2Cl_2 containing 1.0 mmol of the substrate. Yields were determined gas chromatographically. Comparable results were obtained on a preparative scale by adding the reagent as a 1.0 M solution to a stirred suspension of 25 g of adsorbent in 50 mL of CH_2Cl_2 containing 20 mmol of the substrate. Products were isolated by distillation or preparative gas chromatography and identified by IR and ^1H NMR spectroscopy.

[8] By contrast, alkyne **6** undergoes slow Lewis acid catalyzed addition of HCl or HBr in CH_2Cl_2 to give adducts (*E*)-**7** and (*Z*)-**7** in a ratio of 2.3 or 3.0, respectively: Marcuzzi, F.; Melloni, G. *J. Am. Chem. Soc.* **1976**, *98*, 3295–3300; *Gazz. Chim. Ital.* **1975**, *105*, 495–507.

[9] Similarly, the ratio of heterolytic to homolytic decomposition of peroxides is much greater on the highly polar surface of silica gel than in solution: (a) Leffler, J. E.; Barbas, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 7768–7773. (b) Lindley, S. M.; Flowers, G. C.; Leffler, J. E. *J. Org. Chem.* **1985**, *50*, 607–610.

Kinetic Resolutions of Chiral Unsaturated Alcohols That Cannot Be Resolved Efficiently via Enantioselective Epoxidation

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Received June 19, 1990

Katsuki/Sharpless epoxidations of allylic alcohols[1,2] perhaps constitute the single most important development in asymmetric induction during the last decade; certainly, they are among the most useful reactions for contemporary organic syntheses.[3,4] Protocols based upon asymmetric epoxidations also include some extremely valuable kinetic resolutions,[5] but there are restrictions that limit this approach. Specifically: (i) they do not work well for some allyl alcohol derivatives; (ii) they are not generally applicable to substrates other than allylic alcohols; and (iii) experimental procedures involved are moderately tedious because,

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[1] (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

[2] Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 247.

[3] Rossiter, B. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 193.

[4] Pfenninger, A. *Synthesis* **1986**, 89.

[5] (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (b) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Taktani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589. (c) Carlier, P. R.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 2978. (d) Dai, L.; Lou, B.; Zhang, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5195.

0002-7863/90/1512-7434$02.50/0