Communications

Hydroboration of Olefins with Catecholborane at Room Temperature in the Presence of *N,N*-Dimethylacetamide

Christine E. Garrett and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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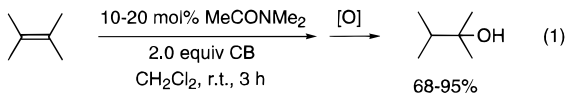
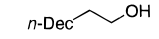
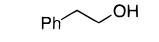
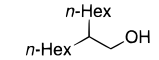
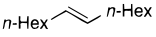
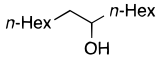
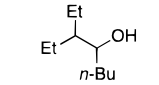
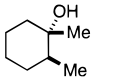
In comparison with boron hydrides such as BH_3−THF or 9-BBN,[1] catecholborane (CB) is much less reactive toward olefins, typically requiring elevated temperatures (70−100 °C) for addition.[2,3] During the past decade, a number of catalysts for the hydroboration of olefins with catecholborane have been reported. Virtually all of the work has focused on transition metal- and lanthanide metal-based systems,[4−6] due in part to their potential for effecting enantioselective catalysis.[5,7] In this paper, we report that hydroboration of mono-, di-, tri-, and tetrasubstituted olefins proceeds efficiently at room temperature upon treatment with catecholborane in the presence of 10−20 mol % *N,N*-dimethylacetamide (eq 1).



(1)

Reaction of an olefin with catecholborane (2 equiv) and *N,N*-dimethylacetamide (10−20 mol %) in CH_2Cl_2 for 3 h at room temperature, followed by an oxidative workup, provides the desired alcohol in good yield (Table 1).[8−11] The hydroborations of alkyl- and aryl-substituted terminal olefins afford the primary alcohols preferentially (Table 1, entry 1, 94:6;[12] entry 2, 85:15), with regioselectivity similar to that observed with BH_3−THF (94:6 and 80:20, respectively[1]). Reactions of 1,1-disubstituted (Table 1, entry 3), 1,2-disubstituted (Table 1, entry 4), trisubstituted (Table 1, entry 5), and tetrasubstituted (entry 6) olefins also proceed cleanly under the standard conditions. The stereochemistry of the product illustrated in entry 6 (Table 1) establishes that the boron hydride adds in a cis fashion to the olefin.

Table 1. Hydroboration of Olefins with Catecholborane in the Presence of *N,N*-Dimethylacetamide[a] (Eq 1)

Entry	Substrate	Product[b]	Yield (%)[c]
1			95
2			88
3			78
4			79
5			71
6			68[d]

[a] Amount of *N,N*-dimethylacetamide used: entries 1−4, 10 mol %; entries 5−6, 20 mol %. [b] Less than 3% of any other isomer is observed, except for entry 1 (94:6, primary:secondary) and entry 2 (85:15, primary:secondary). [c] Average of two runs. [d] The modest yield may be due in part to the volatility of the product alcohol.

In two instances, we have isolated *B*-alkylboronic esters from the unoxidized reaction mixtures (eqs 2 and 3).[13] ^{11}B NMR spectroscopy reveals that a significant

(1) For leading references, see: (a) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic: New York, 1988. (b) Brown, H. C. *Hydroboration*; W. A. Benjamin: New York, 1962.

(2) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249−5255.

(3) For overviews of the chemistry of catecholborane, including synthetic applications of *B*-alkylboronic esters, see: (a) Lane, C. F.; Kabalka, G. W. *Tetrahedron* **1976**, *32*, 981−990. (b) Kabalka, G. W. *Org. Prep. Proc. Int.* **1977**, *9*, 131−147. (c) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 5080−5082. (d) VanNieuwenhze, M. S. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995.

(4) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878−879.

(5) For reviews, see: (a) Fu, G. C.; Evans, D. A.; Muci, A. R. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI: Greenwich, CT, 1995; Vol. 1, pp 95−121. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179−1191.

(6) A notable exception to this generalization is the observation by Arase that the presence of 10 mol % lithium borohydride facilitates the hydroboration of olefins with catecholborane: Arase, A.; Nunokawa, Y.; Masuda, Y.; Hoshi, M. *J. Chem. Soc., Chem. Commun.* **1991**, 205−206. The structure of the preoxidation product of the olefin hydroboration reaction (e.g., *B*-alkylboronic ester or trialkylborane) was not determined (no mechanistic studies of this system have been described). The regioselectivities reported by Arase for the hydroboration of 1-hexene and of styrene (94:6 and 85:15 (primary:secondary), respectively) are similar to those reported for BH_3−THF (94:6 and 80:20 (primary:secondary), respectively (ref 1)). We have found that treatment of 0.1 equiv of $LiBH_4$ with catecholborane (THF, room temperature, 5 min) results in the complete consumption of $LiBH_4$ and in the clean formation of BH_3−THF and $Li(B(C_6H_4O_2)_2)$ in a 2:1 ratio (cf. Männig, D.; Nöth, H. *J. Chem. Soc., Dalton Trans.* **1985**, 1689−1692). Subsequent addition of 1-dodecene leads to the generation of tri(*n*-dodecyl)borane.

(7) For early work, see: (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178−5179. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426−3428.

(8) Representative experimental procedure (Table 1, entry 1): 1-Dodecene (228 μL, 1.03 mmol), *N,N*-dimethylacetamide (9.4 μL, 0.10 mmol), and CH_2Cl_2 (0.68 mL) were added sequentially to a reaction vessel. The resulting solution was cooled to 0 °C, and catecholborane (220 μL, 2.06 mmol) was added dropwise (bubbling observed). Following completion of the addition of catecholborane, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. It was then cooled to 0 °C, and 1:1 THF:EtOH (2 mL), 2 N NaOH (2 mL), and 30% H_2O_2 (2 mL) were added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. It was then extracted (Et_2O/1 N NaOH), the organic layer was dried, and the solvent was removed in vacuo. Flash chromatography afforded 0.184 g (96%) of 1- and 2-dodecanol in a 94:6 ratio (GC).

(9) All reactions were conducted under an inert atmosphere with purified reagents (see the supporting information). However, in preliminary experiments we have found that the hydroboration of 1-dodecene proceeds equally smoothly when the reaction is run open to the air with unpurified reagents.

(10) Control experiments for each reaction establish that <10% conversion is observed in the absence of *N,N*-dimethylacetamide under otherwise identical conditions.

(11) Although we have not yet conducted a comprehensive screening of common Lewis-basic functional groups, we have determined that the hydroboration of olefins with catecholborane is facilitated by secondary amides and tertiary amines, but not by simple ethers. We suspect in general that extremely weak and extremely strong Lewis bases will not accelerate the hydroboration of olefins with catecholborane. In the context of a report that secondary amides direct iridium-catalyzed hydroboration reactions with catecholborane (Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 4042−4043), it is important to note that we have found that the hydroboration of 4-(*N*-(phenylmethyl)-carboxamido)cyclohexene is *not* directed by the amide in the absence of $[Ir(cod)(PCy_3)(py)]PF_6$.

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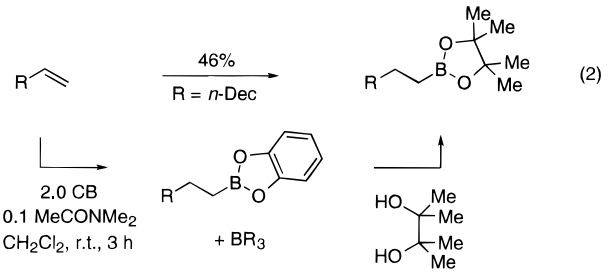
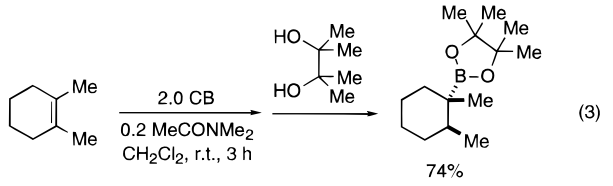
quantity of tridodecylborane is formed in the reaction of 1-dodecene (eq 2; vide infra).

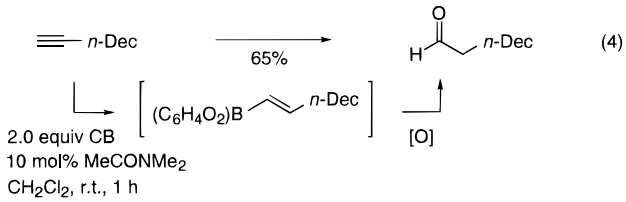


(2)



(3)

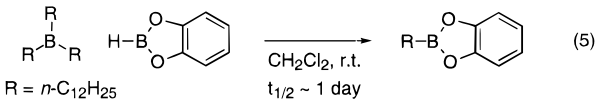
N,*N*-Dimethylacetamide (10 mol %) also facilitates the addition of catecholborane to alkynes (eq 4).[14] Less than 10% conversion is observed in the absence of amide under otherwise identical conditions.



(4)

We have begun to explore the mechanism by which *N*,*N*-dimethylacetamide facilitates olefin hydroboration with catecholborane. Baker, Marder, Burgess, and others have observed that certain transition metal complexes and phosphines react with catecholborane to generate $B_2(O_2C_6H_4)_3$ and BH_3-derived adducts.[15,16] In light of these reports, we have investigated the reactivity of catecholborane toward *N*,*N*-dimethylacetamide. Examination of the ^{11}B NMR spectrum obtained upon treatment of catecholborane with 0.05 equiv of *N*,*N*-dimethylacetamide for 3 min at room temperature reveals catecholborane to be the major species present, along with small amounts (3−6% each) of BH_3−(*N*,*N*-dimethylacetamide),[17] $B_2(O_2C_6H_4)_3$, and one as yet unidentified compound.

As indicated in eq 2, both *B*-alkylcatecholborane and BR_3 are generated in the amide-promoted hydroboration of 1-dodecene. Ligand exchange between BR_3 and catecholborane is one mechanism by which *B*-alkylcatecholborane might be formed in this process.[18−20] We have found that treatment of tri-*n*-dodecylborane with catecholborane at room temperature does indeed afford the *B*-alkylcatecholborane (eq 5), but at a rate that is too slow



(5)

($t_{1/2} \sim 1$ day) to account for the formation of *B*-alkylcatecholborane in the reaction of 1-dodecene (eq 2).[21] Clearly, additional mechanistic studies are warranted in order to elucidate the mechanism of this intriguing new amide-promoted hydroboration process.

In conclusion, we have discovered that 10−20 mol % of a tertiary amide (*N*,*N*-dimethylacetamide) efficiently promotes the hydroboration of olefins with catecholborane at room temperature. This work thus reveals unexpected reactivity for catecholborane in the presence of a common organic functional group. We have also established that catecholborane and a trialkylborane react at room temperature, in the absence of an additive, to generate a *B*-alkylcatecholborane.[21] Further studies are underway.

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Supporting Information Available: Experimental procedures and compound characterization data (10 pages).

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(12) This reaction also proceeds to completion in the presence of 1 mol % *N*,*N*-dimethylacetamide.

(13) *B*-Alkylpinacolboranes are more stable to chromatography than are *B*-alkylcatecholboranes. For a recent discussion, see: Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482−3485.

(14) For the catalyzed addition of catecholborane to alkynes, see: (a) BH_3−(*N*,*N*-diethylaniline): Suseela, Y.; Prasad, A. S. B.; Periasamy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 446−447. Suseela, Y.; Periasamy, M. *J. Organomet. Chem.* **1993**, *450*, 47−52. Periasamy noted that BH_3−(*N*,*N*-diethylaniline) does not promote the addition of catecholborane to alkenes and that BH_3−THF promotes the addition of catecholborane to alkynes. (b) Dialkylborane: Arase, A.; Hoshi, M.; Mijin, A.; Nishi, K. *Synth. Commun.* **1995**, *25*, 1957−1962.

(15) Transition metal complexes: (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863−8869. (b) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350−9359. (c) Burgess, K.; Jaspars, M. *Tetrahedron Lett.* **1993**, *34*, 6813−6816. (d) Burgess, K.; Jaspars, M. *Organometallics* **1993**, *12*, 4197−4200. (e) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930−936. (f) Lindsley, C. W.; DiMare, M. *Tetrahedron Lett.* **1994**, *35*, 5141−5144. (g) Burgess, K.; van der Donk, W. A. *Organometallics* **1994**, *13*, 3616−3620. (h) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.: A* **1995**, *95*, 121−128. (i) Reference 5a.

(16) Phosphines: Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175−2182.

(17) BH_3−*N*,*N*-dimethylacetamide was prepared independently by treatment of BH_3−THF with *N*,*N*-dimethylacetamide.

(18) Burgess has reported that, in the presence of catalytic Ti(O-*i*-Pr)$_4$, monoalkylboranes react with catecholborane to form *B*-alkylcatecholboranes (ref 15g).

(19) Periasamy has suggested that reaction of a *B*-alkenylborane and catecholborane to generate *B*-alkenylcatecholborane and a new boron hydride is responsible for turnover in the BH_3−(*N*,*N*-diethylaniline)-catalyzed hydroboration of alkynes with catecholborane (ref 14a).

(20) For a related observation, see: Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1816−1818.

(21) In earlier mechanistic and synthetic studies of metal-catalyzed hydroboration reactions, the observation that a *B*-alkylcatecholborane is formed has been put forward as evidence that the product results from a metal-catalyzed reaction manifold, rather than from catecholborane degradation products such as BH_3. Our observation (eq 5) suggests that in certain instances such conclusions should be drawn cautiously. This point has been made previously by Burgess in the context of a Ti(O-*i*-Pr)$_4$-catalyzed variant of eq 5 (ref 15g).