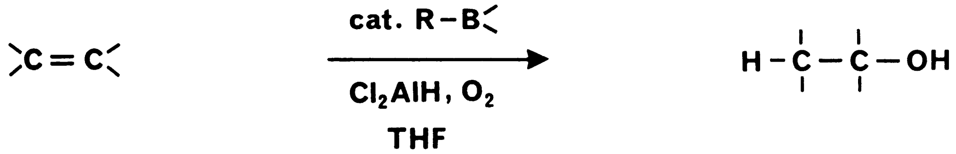
CHEMISTRY LETTERS, pp. 73-76, 1987.

Organoborane-Catalyzed anti-Markownikoff Hydration of Olefins#

Keiji MARUOKA, Hiromi SANO, Kiyotaka SHINODA, and Hisashi YAMAMOTO*
Department of Applied Chemistry, Faculty of Engineering,
Nagoya University, Chikusa, Nagoya 464

A new, catalytic procedure for the anti-Markownikoff hydration of olefins in the presence of organoborane catalyst and dichloroaluminum hydride under dry air has been described.

The hydration of olefins is an essential operation in organic synthesis and a variety of methodologies have been elaborated for this purpose.[1)] The industrially important, acid-catalyzed hydration and oxymercuration-reduction procedures gave rise to alcohols in a Markownikoff orientation. In contrast, hydroboration-oxidation sequence of olefins provides an anti-Markownikoff alcohols.[2)] In addition to these existing procedures, we wish to report herein a highly efficient anti-Markownikoff hydration of olefins which involves the combining use of catalytic organoborane and dichloroaluminum hydride (Cl_2AlH) in THF under dry air.[3)] Selected data are presented in Table 1.



Treatment of 1-dodecene with 5 mol% $PhB(OH)_2$ and Cl_2AlH (4 equiv.; prepared from $LiAlH_4$ and $AlCl_3$)[4)] in anhydrous THF under dry air at room temperature for 7 h furnished 1-dodecanol in 75% yield (entry 1). Similarly, terminal methylene

---

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

Table 1. Organoborane-Catalyzed Hydration of Olefins[a)]

Entry	Olefin	Catalyst (equiv.)	Yield/%[b)]
1	1-Dodecene	$PhB(OH)_2$ (0.05)	75
2	2-Methyl-1-undecene	$PhB(OH)_2$ (0.05)	78
3		$PhB(OH)_2$ (0.1)	92
4	4-_t_-Butyl-1-methylenecyclohexane	$PhB(OH)_2$ (0.05)	80
5		$PhB(OH)_2$ (0.1)	98
6	Cyclooctene	$PhB(OH)_2$ (0.05)	48
7		$PhB(OH)_2$ (0.2)	69
8		Et_3B (0.1)	81
9		Et_3B (0.2)	94
10	_trans_-3-Hexane	Et_3B (0.2)	78
11	Norbornene	Et_3B (0.2)	78[c)]
12	Cyclododecene	Et_3B (0.2)	76
13		$PhB(OH)_2$ (0.2)	47
14		$BuB(OH)_2$ (0.2)	48
15		$BF_3 \cdot OEt_2$ (0.2)	48
16		$B(OH)_3$ (0.2)	42
17		$B(OMe)_3$ (0.2)	39
18	Citronellol	Et_3B (0.2)	45
19		Et_3B (0.3)	65
20	1-Methylcyclohexene	Et_3B (0.2)	30
21		Et_3B (0.3)	48[d)]
22	(-)-α-Pinene	Et_3B (0.3)	44[e),f)]
23	(-)-β-Pinene	Et_3B (0.2)	92[f)], 87[g)]

a) Hydration of olefin was performed using organoborane catalyst and Cl_2AlH (4 equiv) in THF at room temperature for 7 h to furnish the anti-Markownikoff alcohol. b) Isolated yield. c) Ratio of endo/exo = 1:3. d) Cis/trans = 1:2. e) Use of large excess Cl_2AlH (10 equiv.). f) The products were identified with authentic samples which can be prepared by the hydroboration-oxidation sequence of the starting olefins. g) Yield in large-scale preparation (50 mmol scale).

compounds gave rise to the corresponding primary alcohols regioselectively in 78-80% yields (entries 2 and 4). However, this catalytic system was not effective for the hydration of internal olefins (entry 6). Accordingly, we have first examined various boron catalysts for effecting the hydration of cyclododecene with Cl_2AlH. As revealed in Table 1, triethylborane was found to be superior to $RB(OH)_2$ (R = Bu and Ph) (entries 12-14).[5] Inorganic boron catalysts such as $B(OH)_3$, $B(OMe)_3$, and $BF_3 \cdot OEt_2$ were less satisfactory (entries 15-17). The effect of hydride source was also studied in the hydration of cyclododecene with catalytic $PhB(OH)_2$ (0.2 equiv.) in THF under dry air. The yield of cyclododecanol follows: Cl_2AlH (44%); i-Bu_2AlH (23%); Et_2AlH (21%); AlH_3 (15%); $LiAlH_4$ (2%). Use of the pure oxygen gas lowered the yield of the reaction. A ready accessibility of less expensive, relatively air-stable Cl_2AlH coupled with organoborane catalyst enables a large-scale preparation in an open system under dry air, thereby providing a highly useful tool in the practical hydration of olefinic compounds, especially optically active terpenes such as (-)-α- and (-)-β-pinene (entries 22 and 23).

The following experimental procedure is representative. To a stirred solution of anhydrous aluminum chloride ($AlCl_3$) (400 mg, 3 mmol) in THF (2 mL) under argon was added at 0 °C lithium aluminum hydride ($LiAlH_4$) (38 mg, 1 mmol). The resulting solution was stirred at 0 °C for 30 min and treated successively with a 1 M hexane solution of triethylborane (Et_3B) (0.1 mL, 0.1 mmol) and cyclooctene (110 mg, 1 mmol) at 0 °C. The reaction flask was then fitted with a silica gel (blue) drying tube in order to replace argon by dry air. The mixture was allowed to warm to room temperature, stirred under dry air for 7 h, and quenched by addition of diluted HCl. Extractive workup with ether followed by column chromatography on silica gel (ether-hexane = 1:1 as eluant) afforded cyclooctanol as an oil (104 mg, 81% yield).

This work was supported by a Grant from Toyo Stauffer Chemical Co., Ltd.

References

1) J. F. Stoddart, "Comprehensive Organic Chemistry," Pergamon Press, New York (1979), Vol. 1, pp. 145, 592. See also: H. Kroph, Angew. Chem., Int. Ed. Engl., 5, 646 (1966); V. J. Nowlan and T. T. Tidwell, Acc. Chem. Res., 10, 252 (1977).

2) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, New York (1972); G. M. L. Cragg, "Organoboranes in Organic Synthesis," Dekker, New York (1973); H. C. Brown, "Organic Synthesis via Boranes," Wiley-Interscience, New York (1975); T. Onak, "Organoborane Chemistry," Academic Press, New York (1975).

3) For organoborane-catalyzed hydroalumination of olefins, see: K. Maruoka, H. Sano, K. Shinoda, S. Nakai, and H. Yamamoto, J. Am. Chem. Soc., in press.

4) E. L. Eliel, R. J. L. Martin, and D. Nasipuri, Org. Synth., Coll. Vol. V, 175 (1973).

5) Although the precise reaction mechanism of the present catalytic reaction has not been elucidated, it might be interpreted with some speculation as follows. The use of organoborane as initiator of the reaction allows this compound serving as the chain carrier of the catalytic cycle involving hydroboration. Initial reaction of boron compound (X-B<) with Cl_2AlH generates the reactive H-B< species which hydroborates olefin cleanly to furnish alkylboron intermediate. Oxidation with oxygen gave the alkylperoxy boron compound⁶⁾ which in the presence of Cl_2AlH was reduced in situ to furnish the anti-Markownikoff alcohol with regeneration of the >B-H species for further use in the catalytic cycle of the reaction. The direct exchange reaction of alkylboron intermediate with Cl_2AlH followed by oxidation of the resulting alkylaluminum compound seems to be unlikely, since the extent of such exchange reaction in ethereal solvents was already reported to be significantly diminished.³⁾

6) H. C. Brown, M. M. Midland, and G. W. Kabalka, J. Am. Chem. Soc., 93, 1024 (1971); H. C. Brown and M. M. Midland, ibid., 93, 4078 (1971); M. M. Midland and H. C. Brown, ibid., 95, 4069 (1973).

(Received September 18, 1986)