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SELECTIVE REDUCTION OF ALDEHYDES WITH 8-OXYQUINOLINE DIHYDROBORONITE IN THE PRESENCE OF BORON TRIFLUORIDE ETHERATE

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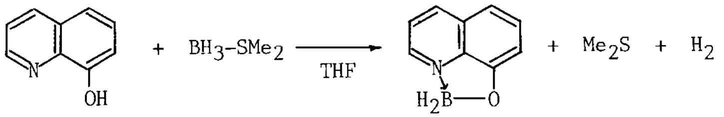
Summary: Aldehydes are selectively reduced to the alcohols in the presence of ketones with 8-oxyquinoline dihydroboronite and boron trifluoride etherate as a catalyst.

Chemoselective reduction of aldehydes in the presence of ketones is very useful reaction in organic synthesis and continues to attract considerable interest in recent years.[1]

In connection with our studies directed toward development of new hydride reducing agents,[2] we wish to report the use of a new complex hydride reducing agent, 8-oxyquinoline dihydroboronite, for selective reduction of aldehydes into the corresponding alcohols in the presence of ketones. The reagent was conveniently prepared by mixing equimolar amounts of 8-hydroxyquinoline and borane-dimethyl sulfide complex in tetrahydrofuran at room temperature and can be stored under nitrogen for several weeks in a refrigerator without any decomposition of hydride. The reagent was rapidly hydrolyzed in water with evolution of hydrogen gas. The reagent exhibited a ^{11}BNMR spectrum with a triplet at + 1.7 ppm (J_{BH} 125 Hz) with reference to BF_3-Et_2O and a strong IR absorption, due to the boron-hydrogen bond, at 2390 cm^{-1}. Thus, the structure of the reagent was assigned to 8-oxyquinoline dihydroboronite, containing a relatively rigid five membered ring system as shown below.



As we expected from the results in the literature,[3] this reagent containing pyridine moiety exhibited weak reducing ability in the absence of Lewis acid. Thus, nonyl aldehyde, 4-methylcyclohexanone, and acetophenone were reduced to the corresponding alcohols in 10%, 5%, and 1%, respectively with the reagent in tetrahydrofuran at room temperature in 7 h. Among various Lewis acids tested, it was found that BF_3-Et_2O is the best additive to promote the reduction with the reagent as reported by Jones[3a] and Suda[3b]. Not only was the rate of the reduction drastically increased, but also the ability to distinguish between aldehydes and ketones was found. The best condition found to the highest selectivity between aldehydes and ketones was to employ 1 molar equiv of the reagent and 0.1 molar equiv of BF_3-Et_2O for each mole of the substrate.

Several examples of selective reduction of aldehydes in the presence of ketones are presented in Table 1. A competition between nonyl aldehyde and 3-pentanone resulted in a 99% reduction of the aldehyde with no detectable reduction of the ketone. Similar high selectivity was observed in the reduction of aldehydes such as nonyl aldehyde, benzaldehyde, and croton-

Table 1. Selective Reduction of Aldehydes with 8-Oxyquinoline Dihydroboronite in the Presence of BF_3-Et_2O in THF at Room Temperature for 7 h.[a]

No.	Starting mixture	% Reduction[b]	No.	Starting mixture	% Reduction[b]
1	Nonyl aldehyde	99	6	Benzaldehyde	99
	3-Pentanone	<1		3-Pentanone	<1
2	Nonyl aldehyde	94	7	Benzaldehyde	99
	Cyclopentanone	1		Acetophenone	0
3	Nonyl aldehyde	98	8	Crotonaldehyde	95
	Cycloheptanone	1		Isophorone	0
4	Nonyl aldehyde	95	9	Nonyl aldehyde	90
	2-Octanone	0		4-Methylcyclohexanone	28
5	Nonyl aldehyde	97	10	4-Methylcyclohexanone	71
	Carvone	<1		3-Pentanone	<1

[a] Reduction was carried out with 1:1:2:0.2 molar ratio of the aldehyde, the ketone, the reagent, and BF_3-Et_2O, respectively. [b] Determined by GLC using an internal standard.

aldehyde in the presence of ketones such as 3-pentanone, cyclopentanone, and isophorone. However, the reagent reaches a limit with relatively reactive cyclohexanone derivatives. For example, reduction of an equimolar mixture of nonyl aldehyde and 4-methylcyclohexanone gave a 90:28 mixture of nonyl alcohol and 4-methylcyclohexanol under the same condition. Furthermore, it was found that reactive 4-methylcyclohexanone was selectively reduced to 4-methylcyclohexanol without no detectable reduction of 3-pentanone under the same condition.

We also examined two ketoaldehydes and in each case the hydroxyketone was obtained in high yield without detectable reduction of the ketone as shown below.[5]

$CH_3(CH_2)_4CO(CH_2)_7CH_2OH$	p-Br-$C_6H_4COCH_2OCO(CH_2)_4CH_2OH$
93% isolated yield	90% isolated yield

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References and Notes

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