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$LiBH_4$-promoted Hydroboration of Alkenes with 1,3,2-Benzodioxaborole

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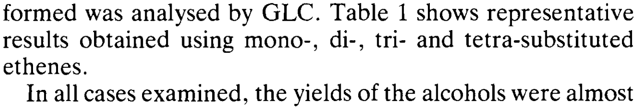
In the presence of a small amount of $LiBH_4$ mono-, di-, tri- and tetra-substituted ethenes were hydroborated almost quantitatively with 1,3,2-benzodioxaborole (catecholborane) under very mild conditions.

Hydroboration of alkenes and alkynes with catecholborane provides 2-alkyl- and 2-alkenyl-1,3,2-benzodioxaboroles, potentially useful synthetic intermediates.[1] However, catecholborane is a relatively unreactive hydroborating agent which requires rather drastic conditions to obtain satisfactory results. For example, the hydroboration of terminal alkenes needed to be carried out at 100 °C and that of terminal alkynes at 70 °C employing neat catecholborane.[2] Recently the presence of a small amount of $Rh(PPh_3)_3Cl$ was shown to increase greatly the rate of the hydroboration of relatively unhindered alkenes with catecholborane, enabling hydroboration to be carried out at low temperatures.[3] The regio- and stereo-selectivity of the hydroboration have been studied.[4] Enantioselective hydroboration using modified rhodium catalysts has also been studied.[5] The presence of *N,N*-dimethylaniline–borane complex has been reported to promote the hydroboration of alkynes with catecholborane,[6] but it did not promote the hydroboration of alkenes effectively.

We now report a new type of promotion of the hydroboration of alkenes with catecholborane where the reaction was carried out in the presence of a small amount of $LiBH_4$ (procedure *A*, Scheme 1). Thus, an alkene (10 mmol) and $LiBH_4$ (1 mmol) in tetrahydrofuran (THF) were added successively to catecholborane (10 mmol) in THF at 0 °C followed by stirring for 1 h at room temperature and then by oxidation with alkaline hydrogen peroxide. The alcohol formed was analysed by GLC. Table 1 shows representative results obtained using mono-, di-, tri- and tetra-substituted ethenes.

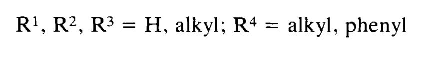
In all cases examined, the yields of the alcohols were almost quantative indicating that the present hydroboration procedure is applicable to a wide variety of alkenes. It is noteworthy that the reaction can be applied satisfactorily to trisubstituted ethenes whose hydroboration with catecholborane in the presence of $Rh(PPh_3)_3Cl$ is sluggish requiring 24 h at 25 °C to obtain 10% conversion.[4] Even tetrasubstituted ethenes, 2,3-dimethylbut-2-ene and 1,2-dimethylcyclohexene, were almost quantitatively hydroborated. Another notable fact is that the orientation of the boron atom in the hydroboration of styrene is quite different from that in the rhodium-catalysed hydroboration.[5b] Thus, in the presence of the rhodium catalyst the boron atom attached preferentially to the α-carbon atom of the double bond, while in the presence of $LiBH_4$ the boron attached predominantly to the β-carbon atom. The large difference in the orientation seems to suggest that the mechanism of the promotion is quite different in the two reactions.

Neat catecholborane may be obtained by the reaction of BH_3 in THF with catechol followed by distillation (79% yield); it must be handled carefully because it is moisture-sensitive. The low temperature hydroboration realized in the present study prompted us to examine a one-pot process starting from the reaction of catechol and BH_3 in THF to avoid the loss of catecholborane and to simplify the hydroboration procedure (procedure *B*, Scheme 2).



R^1, R^2, R^3 = H, alkyl; R^4 = alkyl, phenyl

Scheme 1



Scheme 2

Table 1 Alcohols derived from alkenes

Alkene	Alcohol	Ratio of isomer[a] A[b]	Ratio of isomer[a] B[c]	Total yield[a] (%) A[b]	Total yield[a] (%) B[c]
Hex-1-ene	Hexan-1-ol	94	94	100	100
	Hexan-2-ol	6	6	100	100
Styrene	1-Phenylethanol	15	14	95	100
	2-Phenylethanol	85	86		
Cyclohexene	Cyclohexanol			100	100
2-Methylbut-2-ene	3-Methylbutan-2-ol			99	99
1-Methylcyclohexene	2-Methylcyclohexanol[d]			98	95
2,3-Dimethylbut-2-ene	2,3-Dimethylbutan-2-ol			100	100
1,2-Dimethylcyclohexene	1,2-dimethylcyclohexanol[d]			95	96

[a] Determined by GLC. [b] Obtained by procedure *A*. [c] Obtained by procedure *B*. [d] Derived from *cis*-hydroboration.

Thus, to a THF solution of catechol (10 mmol) was added BH_3 (10 mmol) in THF at 0 °C. After quantitative evolution of hydrogen, an alkene (10 mmol) and $LiBH_4$ (1 mmol) in THF were successively added at the same temperature followed by stirring for 1 h at room temperature. After treatment of the mixture with alkaline hydrogen peroxide, the resulting alcohol was analysed by GLC. As shown in Table 1, both procedures, *A* and *B*, gave almost the same results indicating that the latter, more convenient, procedure could be applied to the hydrobration of alkenes.

$LiBEt_3H$ in THF and $NaBH_4$ in diglyme also showed a similar promoting effect though not so marked as $LiBH_4$.

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