Hydroboration of Prochiral Olefins with Chiral Lewis Base–Borane Complexes: Relationship to the Mechanism of Hydroboration

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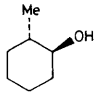
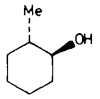
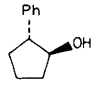
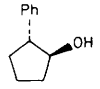
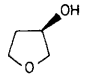
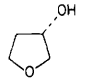
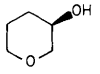
Alcohols with up to 19% enantiomeric excess were obtained on hydroboration/oxidation of representative prochiral olefins using *N*-isobornyl-*N*-methylaniline–borane or *N*-benzyl-*N*-isopropyl-α-methylbenzylamine–borane indicating that the Lewis base is present in the hydroboration transition state.

The discovery of the hydroboration reaction and the reactions of the resulting organoboranes have added many new important synthetic methods in organic chemistry.[1,2] However, the mechanism of hydroboration is still not clearly understood and differences of opinion exist.[3—8] We report here a simple tool for examining this problem, utilizing chiral amine–borane complexes for the hydroboration of prochiral olefins.

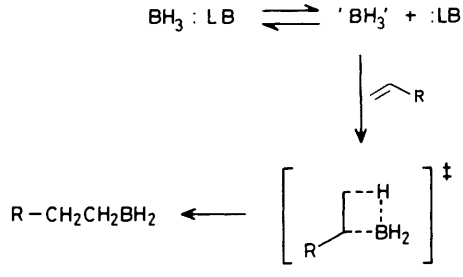
It remains to be established whether the addition of the borane moiety to the olefin takes place after dissociation of the borane–Lewis base complex into 'free' BH_3 (S_N1-like mechanism) or the olefin directly attacks the borane–Lewis base complex (S_N2-like mechanism), as outlined in Scheme 1. It has been suggested that in the S_N2-like mechanism the Lewis base does not completely leave the boron at any stage.[7]

Table 1. Hydroboration of prochiral alkenes using chiral amine-borane complexes[a].

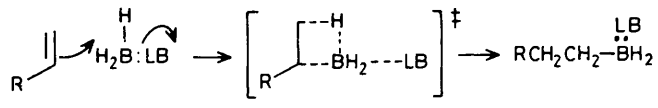
Olefin	Amine–Borane	Reaction time (h)[b]	Product[c]	Yield (%)[d]	$[\alpha]_D^{20}$/° (*c*, solvent)	% e.e.[i]
	(**1**)·BH_3	24		70	−1.66 ± 0.33 (*c* 3, CMeOH)[e]	3.9 ± 0.8
	(**2**)·BH_3	24		62	−1.5 ± 0.3 (*c* 3.3, MeOH)	3.4 ± 0.7
	(**1**)·BH_3	48		63	−0.22 ± 0.11 (*c* 9, EtOH)[f]	0.3 ± 0.2
	(**2**)·BH_3	48		60	−0.84 ± 0.12 (*c* 8.3, EtOH)	1.2 ± 0.2
	(**1**)·BH_3	4		76	−3.3 ± 0.4 (*c* 2.4, MeOH)[g]	19.2 ± 2.4
	(**2**)·BH_3	12		69	+2 ± 0.4 (*c* 2.5, MeOH)	11.6 ± 2.3
	(**1**)·BH_3	4		68	−1.25 ± 0.25 (*c* 4, MeOH)[h]	

[a] Reactions were carried out at room temperature with 10 mmol of amine–borane and 10 mmol of olefin in benzene (40 ml). The experiments were run at least twice in each case. [b] For hydroboration. [c] Product obtained after oxidation with H_2O_2/NaOH. Products were identified by analysis of spectral data (i.r. and ^{13}C n.m.r.) and comparison with reported data. Optical rotations were measured with an Autopol II automatic polarimeter. [d] Yields are of isolated and distilled products. [e] Based on the maximum $[\alpha]_D^{25}$ +43.1° (*c* 1, MeOH) (ref. 12). [f] Based on the maximum $[\alpha]_D^{25}$ +71.1° (*c* 11.9, EtOH) (ref. 13). [g] Based on the maximum $[\alpha]_D^{25}$ −17.3 (*c* 2.4, MeOH) (ref. 14). [h] Maximum reported value for this product α_D^{25} −11.8 (neat) (ref. 15). [i] Enantiomeric excess.

S_N1 - like mechanism



S_N2 - like mechanism

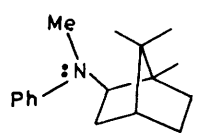


Scheme 1

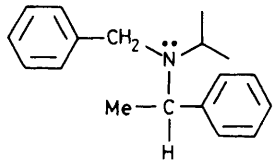
Accordingly, the difference between the two mechanisms is the presence or the absence of the Lewis base in the transition state. It occurred to us that this could be examined by performing the hydroboration of prochiral olefins with chiral Lewis base–borane complexes. We prepared the tertiary amines (**1**) and (**2**) from commercially available optically active starting materials by modifications of literature procedures.†

The borane complexes of (**1**) and (**2**) were prepared in benzene by generating B_2H_6 with I_2/$NaBH_4$.[11] The complex obtained from the amine (10 mmol) in benzene (40 ml) by bubbling an excess of B_2H_6 (20 mmol) [from I_2 (20 mmol) and $NaBH_4$ (40 mmol)] on treatment with Ph_3P gave PPh_3·BH_3 in essentially quantitative yield, thus confirming stoicheiometry. The olefin (10 mmol) was injected into the amine–borane complex (10 mmol) in benzene (40 ml) at 0 °C (bath temperature) and the mixture was stirred at room temperature under nitrogen for the time indicated in Table 1. Tetrahydrofuran (THF) (20 ml) was added, followed carefully by water (1 ml) and 6M-HCl (1 ml). After oxidation with H_2O_2/NaOH and workup, the alcohol was distilled out under reduced pressure from the amine residue and chromatographed on a silica gel

† The amine (**1**), $[\alpha]_D^{20}$ −22° (*c* 6, EtOH) was prepared from (+)-camphor, $[\alpha]_D^{20}$ +43.5 ± 1° (*c* 10, EtOH), *via* the known isobornylaniline,[9] methylated with butyl-lithium and MeI. The amine (**2**), $[\alpha]_D^{20}$ +17.29° (*c* 3.92, $CHCl_3$) was prepared from (+)-(*R*) α-methylbenzylamine, $[\alpha]_D^{20}$ +30 ± 2° (*c* 10, EtOH), by two successive alkylations with isopropyl iodide and benzyl bromide in the presence of powdered KOH.[10]



(1)



(2)

column (hexane/ether as eluant). The alcohol was once again distilled under reduced pressure and the optical rotations were measured (Table 1).

The enantiomeric excess (12—19%) observed in the hydroboration/oxidation of 2,3-dihydrofuran indicates the presence of the chiral Lewis base in the transition state. These results, along with the lower asymmetric inductions observed with 1-methylcyclohexene and 1-phenylcyclopentene, indicate the possibility of a spectrum of mechanisms for hydroboration.‡

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‡ A referee suggested that the results can be interpreted considering an 'early' transition state for the electron rich 2,3-dihydrofuran and 'late' transition states for the other olefinic substrates and the intermediacy of free BH_3 can be ruled out. However, we believe that there is a spectrum of mechanisms as there is evidence for the formation of an intermediate (free BH_3 or olefin–BH_3 π-complex) (refs. 2—8 and 16) in some cases. A full discussion, considering all the proposals and results, is reserved for the full paper.

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