Mechanism of Asymmetric Induction in Hydroborations with Optically Active Tetraisopinocampheyldiborane

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H. C. BROWN and his collaborators have discussed[1] the course of asymmetric induction observed when olefins add to the reagent prepared from optically active α-pinene and diborane, which was represented as di-isopinocampheylborane rather than the dimer named in the title. It seems clear, however, *inter alia* from the work of the same authors, that the tetra- and tri-substituted dimers are the important actual hydroborating agents for *cis*- and *trans*-1,2-disubstituted olefins respectively, and the monomer-addition model (which consistently predicts the wrong chirality for the alcohol derived from *trans*-olefins) seems to have been intended as a useful *aide-memoire* rather than a description of the physical process, which we visualise as follows.

Part-representations of the apparently preferred conformation of (−)-tetraisopinocampheyldiborane, prepared from (+)-α-pinene, are shown in Figures 1 (elevation) and 2 (plan). A characteristic feature is the arrangement of alkyl groups—at the corners of a parallelogram—which exercise compressive interactions on the olefin undergoing addition. The corresponding parallelogram for the bottom face of the reagent is shown in Figure 2 by dotted lines. An olefin approaching as shown (straight arrow) in Figure 1 develops increasing bonding with the diborane by overlap of the olefinic π-orbital with the weakly B–B antibonding orbital illustrated. Replacement of this bonding interaction with those associated with the usual 4-centre type of activated complex is consequent on a reaction pathway for the olefin involving (i) a dip (arrow a) of the least hindered olefinic carbon, which will ultimately bond with boron, (ii) a swing (arrow b) ultimately through ~90°, clockwise because of the geometrical disposition of the hindering alkyl groups, and (iii) a rotation (arrow c), also ultimately through ~90°, maintaining the correct phase for the overlapping orbitals. The observed chiralities (*R*, *R*, and *S* respectively) are predicted for alcohols derived from acyclic *cis*-1,2-dialkyl olefins, and *cis*- and *trans*-1-deutero-1-hexene (Figure 1; $R^1 = {}^2H$, $R^3 = Bu^n$, $R^2 = R^4 = H$; and $R^2 = {}^2H$, $R^3 = Bu^n$, $R^1 = R^4 = H$, respectively); the same model can also serve for consideration of the addition of cyclic olefins and other substrates. The marked difference in optical purity between the alcohols prepared from the deuterated olefins (*cis*, 42%; *trans*, 86%) may be ascribed to the particularly strong compressions on hydrogen or deuterium, R^1, during the reaction pathway. This implied "steric" secondary isotope effect may, however, be enhanced by a primary effect associated with partial bonding of hydrogen or deuterium, R^2, to boron.

Reaction of olefins with (−)-tetraisopinocampheyldiborane.

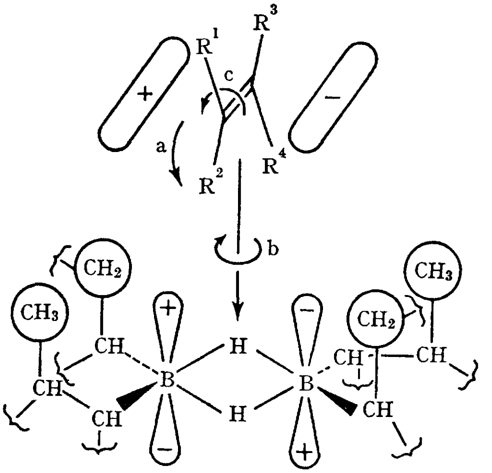

FIGURE 1. *Elevation, showing olefin approach and significant features of diborane conformation, as also illustrated in* FIGURE 2 (*plan*).

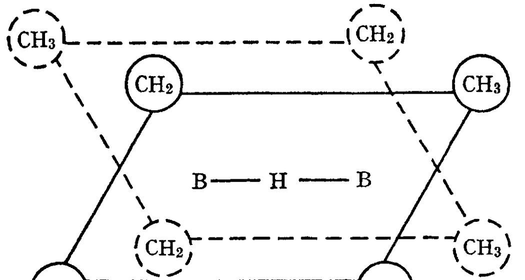

Figure* 1 *is somewhat schematic*: *bonds to encircled methyl and methylene groups are not strictly vertical, and the methyl groups lie rather higher than the methylenes.

trans-Olefins will evidently bond less well during the earlier stages of this reaction pathway, and may thus prefer to react with the trisubstituted dimer (formed by slow dissociation) in the more open immediate environment of which asymmetric induction will be less, as experimentally observed.[1] It does not at present seem useful to discuss this stereoselectivity qualitatively, and the same may be said of the low selectivities observed in additions of 1,1-disubstituted olefins,[3] where the differential effective bulk of the groups R^3 and R^4 (much less compressed than R^1, R^2) is the controlling factor, or of ketones.[4] Some of these reactions in any case appear to follow more than one overall mechanism.

If, as we think likely, kinetically important saddle-points on the reaction paths leading ultimately (after peroxide oxidation) to alcohols of opposite chirality arise somewhat in advance of the four-centre bonding stage (Figure 3) then we do not have to consider much deformation of the original conformation of the diborane in the competitive transition states. Such deformations, represented by the wavy line, would undoubtedly arise, however, at the stage represented in Figure 3, and here the indicated disposition of non-bonding interactions, which may be permissively (rather than compellingly) demonstrated on a molecular model, would also be consistent with the preferred direction of the most strongly developed asymmetric inductions. At neither stage (Figures 1 and 2;

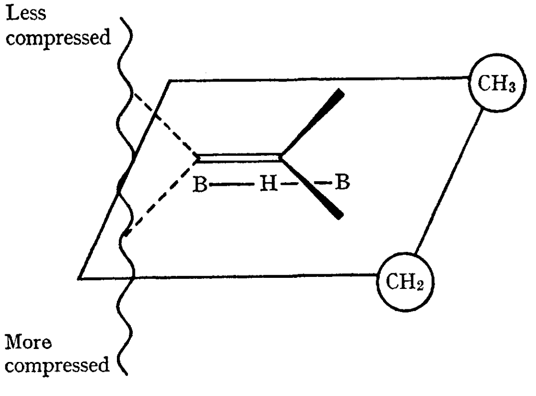

FIGURE 3. *Plan, showing possible steric interactions near the end of the reaction path.*

Figure 3) are interpretations or predictions particularly sensitive to valency geometry (how near to trigonal or tetrahedral?) at the olefinic carbon atoms.

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[1] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, 1964, **86**, 397, 1071, and earlier papers by H. C. Brown and his collaborators.

[2] H. Weber, P. Loew, and D. Arigoni, *Chimia* (*Switz.*), 1965, **19**, 595.

[3] G. Zweifel, N. R. Ayyangar, T. Munekata, and H. C. Brown, *J. Amer. Chem. Soc.*, 1964, **86**, 1076.

[4] H. C. Brown and D. B. Bigley, *J. Amer. Chem. Soc.*, 1961, **83**, 3166.