the neighborhood of 13–14 kcal/mol can be ascribed to amide torsional barriers. Our results, however, are in striking contrast with those reported for the analagous compound in which the methoxy groups are replaced by fluorine atoms.[2b] Unless accidental equivalence is responsible for the differences in the two systems, it would appear that replacement of fluorine by methoxy both raises the amide barrier and lowers the barrier to nitrogen inversion[2b] (or ring reversal[2c]).

Experimental Section

N,N'-Biscarboethoxy-3,3,4,4-tetramethoxy-1,2-diazetidene was prepared as previously reported.[6]

The nmr spectra were measured on a Varian A-60A spectrometer equipped with a Varian variable-temperature probe using *ca.* 10% solutions. Temperatures were determined using methanol spectra as described in the Varian Manual. Rate constants and equilibrium constants were determined by matching experimental spectra with theoretical spectra. The theoretical spectra were generated using Saunder's Many Site NMR Lineshape Program.[7] This program allows the calculation of nmr spectra involving exchange between n sites ($2 \leq n \leq 25$) which must be uncoupled, but need not have the same population. The two "out" methoxy groups of **1b** which are diastereotopic with respect to the "in" methoxy groups were treated as two separate isomers. Exchange was assumed to be possible between **1a** and both sites in **1b** and between **1c** and both sites in **1b**, but not directly between **1a** and **1c**, nor between the "in" and "out" sites of **1b**. The chemical shift differences and the relative populations were temperature dependent and were determined by iterating to obtain the best fit.

Registry No.—**1**, 10200-65-4.

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(6) R. W. Hoffmann and H. Hauser, *Angew. Chem.*, **76**, 346 (1964).
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The Stereochemistry of the Hydroboration Reaction

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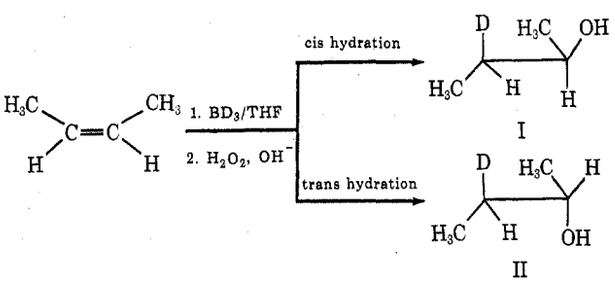
In the course of our efforts to elucidate the stereochemistry of various organoborane reactions, we had reason to deuterioborate *cis*- and *trans*-2-butene, respectively, and oxidize the resultant organoboranes. Nmr analysis of the resultant 2-butanol-*3-d* from the respective reaction mixtures demonstrates conclusively that the hydroboration–oxidation sequence is a stereospecific cis-hydration reaction.

The hydroboration–oxidation sequence is generally accepted as a method to achieve cis-hydration of alkenes. Evidence to that effect has been accumulating for a number of years.[1–5] However, essentially all of the studies have been carried out on cyclic systems. In general the products observed were the thermodynamically most stable ones. In one instance, it was demonstrated that isomeric acyclic alkenes could be hydroborated and then oxidized to produce different diastereomeric alcohols.[5] However, the configurations of the starting alkenes[6] and the product alcohols[7] were assigned by analogy to a related system.

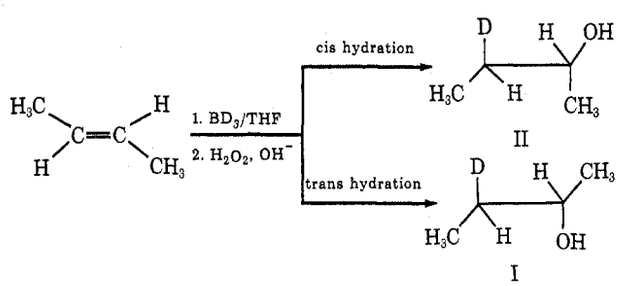
Results and Discussion

The 2-butene system would seem to be an ideal choice for the study of the stereochemistry of the hydroboration–oxidation sequence. The molecule contains a plane of symmetry with two stereoequivalent trigonal carbon atoms. Unlike cyclic or conjugated systems, free rotation of the tetrahedral addition or oxidation intermediates is possible, and if such rotation were to occur, there should be limited steric bias to affect the product distribution.

One could then visualize two possible products from the deuterioboration–oxidation sequence for *cis*-2-butene. The *erythro*-2-butanol-*3-d* (I) would arise from overall cis-hydration, whereas a trans-hydration would produce the *threo*-2-butanol-*3-d* (II).



The stereochemistry of the resultant products would, of course, be reversed in the case of *trans*-2-butene. The *threo*-2-butanol-*3-d* (II) would arise from overall cis-hydration, whereas a trans-hydration would produce the *erythro*-2-butanol-*3-d* (I).



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(6) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1949).
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It has been demonstrated that the two possible products (*erythro*- and *threo*-2-butanol-*3-d*) can be readily differentiated *via* nmr spectroscopy.[8] The differentiation is based on the fact that the methylene protons in 2-butanol are magnetically nonequivalent.

We have deuterioborated *cis*-2-butene and find that the oxidized product exhibits an nmr spectrum identical with the published spectrum of *erythro*-2-butanol-*3-d*.[8] There is no evidence for the presence of the threo isomer within the accuracy of our nmr analysis (approximately 1%). In addition we have deuterioborated *trans*-2-butene and find that the oxidized product exhibits an nmr spectrum identical with the published spectrum of *threo*-2-butanol-*3-d*[8] with no evidence for the presence of the erythro isomer.

Consequently, we conclude that the hydroboration–oxidation sequence achieves, exclusively, the stereospecific cis-hydration of simple, acyclic alkenes.

Experimental Section

Spectra.—The spectra were run on a Varian HA-100 spectrometer.

Materials.—Lithium deuteride (Merck Sharpe and Dohme), *cis*-2-butene (Matheson), and *trans*-2-butene (Matheson) were used as received. Diglyme (Ansul) and tetrahydrofuran (Fisher) were distilled from lithium aluminum hydride prior to use. Boron trifluoride etherate (Fisher) was distilled from calcium hydride prior to use.

Borane-d_3 in tetrahydrofuran was prepared according to standard procedures.[9,10]

Preparation of *erythro*-2-Butanol-*3-d*.—*cis*-2-Butene (4.1 ml, 50 mmol) was condensed at −78° and then introduced (as a gas) to a stirred solution of borane-d_3 (8.3 mmol) in THF which was maintained at 0°. The introduction of the *cis*-2-butene is readily accomplished by attaching the flask containing the condensed alkene to the reaction flask *via* a section of Tygon tubing and then allowing the alkene to warm to room temperature. This affords a slow addition of the 2-butene to the borane-d_3 solution.

The reaction mixture was stirred at 0° for 30 min and then allowed to warm to room temperature. The resultant tri-*sec*-butylborane was oxidized at 50° (water bath) by the addition of 3 ml of 3 *N* sodium hydroxide followed by 3 ml of 30% hydrogen peroxide. The reaction mixture was stirred at 50° for 1 hr and then was saturated with potassium carbonate. The THF layer was separated and the water layer was extracted with 2 × 30 ml of ethyl ether. The ether layers were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Gc analysis of the product at this point (utilizing decane as an internal standard) indicated a 96% yield of pure 2-butanol-*3-d*. The product was isolated by preparative gc (10% Carbowax on Chromosorb W, 20 ft).

Preparation of *threo*-2-Butanol-*3-d*.—The synthesis was carried out exactly as described above for the *erythro*-*3-d* except that *trans*-2-butene (4.1 ml, 50 mmol) was utilized rather than *cis*-2-butene.

Gc analysis of the resultant 2-butanol-*3-d* (decane as internal standard) indicated a 92% yield of pure alcohol. The product was isolated by preparative gc (10% Carbowax on Chromosorb W, 20 ft).

Registry No.—I, 10277-59-5; II, 10277-60-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

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The Configuration of the Thioindigo Anion Radical

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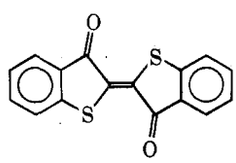
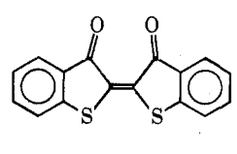
Although thioindigo was first reported in 1906,[2] the question of cis–trans isomerism does not appear to have been treated explicitly until 45 years later. Wyman and Brode established that the relative amounts of cis and trans isomers in solution were a function of temperature and irradiation.[3] Subsequently, Wyman studied the photochemical aspects of this system in greater detail.[4,5] We have recently elucidated the structure of the stilbene anion radical by ultraviolet and electron spin resonance spectroscopic techniques.[6] As part of a study to define the utility of this combined uv–esr procedure, we directed our attention to the thioindigo system (**1**).



trans-**1**



cis-**1**

From the visible spectrum of **1** in 1,2-dimethoxyethane (DME) it was determined that the cis:trans ratio was 15:85. These relative concentrations were estimated by computer simulation, based on the line shapes reported by Blanc and Ross.[7] When a small amount of thioindigo anion radical ($\mathbf{1}^-$) was generated by reduction with potassium, the visible spectrum of the solution was altered. The result was a complete shift to the trans isomer. The fact that no change in the spectrum was observed when the solution was quenched by exposure to air demonstrated that the anion radical concentration was very low. From these data it can be concluded that the anion radical does not affect the absorption curves but only serves to shift the relative concentrations toward the trans isomer; this behavior is the same as that observed in the stilbene system.[6] The isomerization can be considered to proceed *via* those species shown in Scheme I.[8] Simple molecular orbital calculations suggest that the conversion of **1** to $\mathbf{1}^-$ is accompanied by a decrease in the bond order of the central ethylenic linkage. Since the cis isomer is presumably less stable owing to repulsion between the carbonyl groups, the

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(7) J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2817 (1968).
(8) Only those contributing structures of the anion radical which seem pertinent to the isomerization are represented, although it is known from the esr spectrum that the unpaired electron is delocalized throughout both benzene rings.