Transfer Reactions Involving Boron. XVI. The Hydroboration of 3- and 4-Heterosubstituted Cyclohexenes[1]

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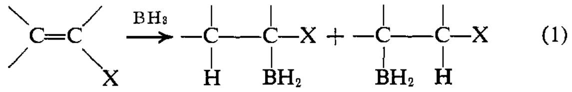
Abstract: A detailed study of the hydroboration of 3-chloro- and 3- and 4-methoxycyclohexenes is described. The hydroboration of 3-chlorocyclohexene produces 10.2% *cis*-2-, 84.7% *trans*-2-, 1.5% *cis*-3-, and 3.6% *trans*-3-chlorocyclohexylboranes. In tetrahydrofuran solution the *trans*-2 derivative undergoes a rapid elimination to produce cyclohexene, whereas in diethyl ether the *trans*-2 derivative is stable at room temperature. The *cis*-2-, *cis*-3-, and *trans*-3-chlorocyclohexylboranes were stable in both tetrahydrofuran and diethyl ether. The hydroboration of 3-methoxycyclohexene produces 9.9% *cis*-2-, 80.8% *trans*-2-, 3.2% *cis*-3-, and 6.0% *trans*-3-methoxycyclohexylboranes. The *cis*-2 derivative undergoes a relatively rapid elimination giving cyclohexene. The *trans*-2-methoxycyclohexylborane undergoes a slow β transfer reaction, with inversion of stereochemistry at carbon, to give ultimately cyclohexanol. The *cis*- and *trans*-3 derivatives are stable. The hydroboration of 4-methoxycyclohexene produces 22.2% *cis*-3-, 33.6% *trans*-3-, 19.1% *cis*-4-, and 25.1% *trans*-4-methoxycyclohexylboranes. All four intermediates were stable in tetrahydrofuran solution. The stereochemistry of attack and the direction of addition of borane to the 3- and 4-substituted cyclohexenes are discussed in terms of inductive and steric factors.

The chemistry of heterosubstituted organoboranes, derived from the hydroboration of appropriately substituted olefins (eq 1), has been extensively studied



$$\mathrm{>C{=}C<_{X}} \xrightarrow{\mathrm{BH_3}} -\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{\mathrm{BH_2}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{X} + -\underset{\mathrm{BH_2}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{X} \qquad (1)$$

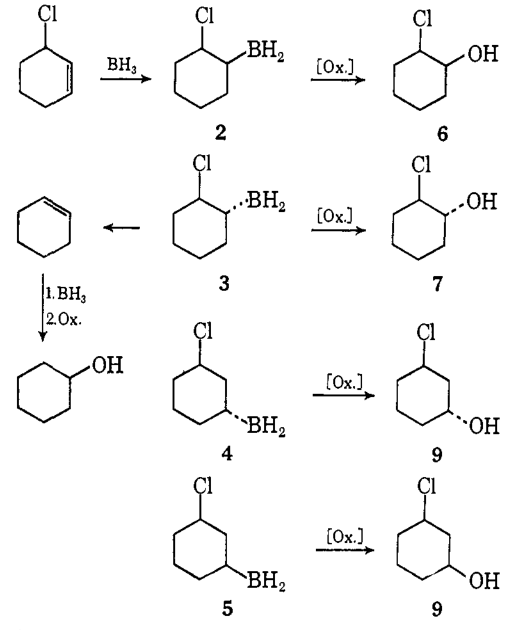
in a variety of acyclic systems.[4-9] However, relatively few substituted cyclic systems have been studied. It is of interest to compare the chemistry of such substituted cyclic organoboranes with the acyclic derivatives and to study the role of the heterofunctional groups in determining the stereochemistry of attack (*cis* or *trans* to the functional group) and the direction of addition of borane to the double bond.[10]

Binger and Koster[11] have reported that the hydroboration of 3-chlorocyclohexene produces, as the only alcoholic product, cyclohexanol. The cyclohexanol was believed to be formed by the elimination of an intermediate β-chloroorganoborane, the stereochemistry of which was not specified. Klein and Dunkelblum[12] reported that the hydroboration of isophorone produced a single diol assigned as the *trans* diol **1**.[13]

Results and Discussion

Hydroboration of 3-Chlorocyclohexene. The hydroboration of 3-chlorocyclohexene is expected to give rise to a mixture of the four isomeric chlorocyclohexylboranes **2**, **3**, **4**, and **5**, and in turn on oxidation the four isomeric chlorohydrins **6**, **7**, **8**, and **9** (see Scheme I).

Scheme I



Analysis of the chlorohydrin mixture by gas–liquid partition chromatography techniques (glpc) required the availability of the four isomeric 2- and 3-chlorocyclohexanols, as their trifluoroacetates, of which only the *cis*- and *trans*-2-chlorocyclohexanols were reported previously in the literature. A sample of *trans*-2-chlorocyclohexanol (**7**) was obtained from Aldrich Chemical Co.[14] A mixture of **6** and **7** was prepared

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(1) (a) Part XV: D. J. Pasto and S.-Z. Kang, *J. Am. Chem. Soc.*, **90**, 3797 (1968). Taken from the Ph.D. Thesis of J. H., University of Notre Dame, 1967. (b) The authors wish to thank Professor H. C. Brown for helpful discussions and for providing the results of a closely related investigation prior to publication (see H. C. Brown and E. F. Knights, *J. Am. Chem. Soc.*, **90**, 4439 (1968)).

(2) Alfred P. Sloan Foundation Fellow, 1967–1969.

(3) Reilly Research Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow (1-F1-GM-31,055-01A1), 1966–1967.

(4) D. J. Pasto and J. Miesel, *J. Am. Chem. Soc.*, **85**, 2118 (1963).

(5) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964).

(6) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).

(7) D. J. Pasto and R. Snyder, *ibid.*, **31**, 2777 (1966).

(8) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).

(9) D. J. Pasto, T.-C. Cheng, and J. Hickman, unpublished observations.

(10) Prior studies in our laboratories have been devoted to a study of the directive influences in the hydroboration of variously substituted alkylcyclohexenes (D. J. Pasto and F. Klein, *J. Org. Chem.*, **33**, 1468 (1968)). Klein and coworkers have also contributed to this area: J. Klein, E. Dunkelblum, and D. Aurahmi, *ibid.*, **32**, 935 (1967).

(11) P. Binger and R. Koster, *Tetrahedron Letters*, 156 (1961); R. Koster, G. Glasnow, W. Lorbig, and P. Binger, *Ann.*, **672**, 1 (1964).

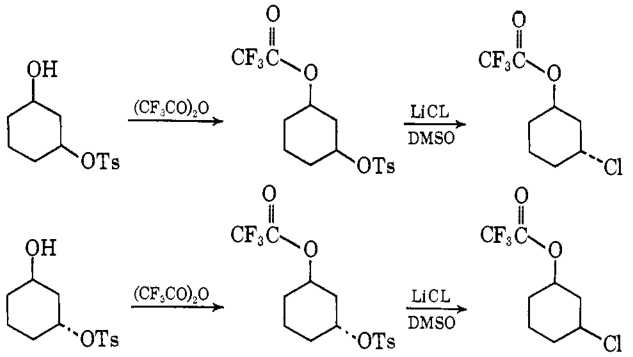
(12) J. Klein and E. Dunkelblum, *Tetrahedron Letters*, 6047 (1966).

(13) Brown and Gallivan have confirmed the formation of **1** as the predominant product formed in the hydroboration of **1** (H. C. Brown and R. M. Gallivan, Jr., *J. Am. Chem. Soc.*, **90**, 2906 (1968).

(14) Although advertised as a mixture of the *cis*- and *trans*-2 isomers, the sample was >99% *trans*.

by oxidation of **7** to 2-chlorocyclohexanone followed by reduction with sodium borohydride. Authentic *cis*-3-chlorocyclohexyl trifluoroacetate was prepared from *trans*-1,3-cyclohexanediol monotosylate (see Scheme II).

Scheme II



The monotosylate was converted to the *cis*-3-tosyloxycyclohexyl trifluoroacetate by treatment with trifluoroacetic anhydride followed by treatment with lithium chloride in dimethyl sulfoxide. *trans*-3-Chlorocyclohexyl trifluoroacetate was similarly prepared from *cis*-1,3-cyclohexanediol monotosylate (see Scheme II). (For spectral characterization of the 3-chlorocyclohexyl trifluoroacetates see the Experimental Section.)

Hydroboration of 3-chlorocyclohexene in tetrahydrofuran, followed by basic oxidation and trifluoroacetoxylation, produced a mixture of *cis*-2-, *trans*-3-, and *cis*-3-chlorocyclohexyl trifluoroacetates and a considerable quantity of cyclohexyl trifluoroacetate (see Table I, column 2). (It should be noted that the yield of cyclohexyl trifluoroacetate is comparable to the yield of cyclohexanol cited by Binger and Koster.[11]) Previous studies in our laboratories have demonstrated that *trans*-β-chlorocyclohexylorganoboranes undergo a base-catalyzed (solvent) elimination, thus providing a rationalization for the formation of the cyclohexyl trifluoroacetate *via* elimination of *trans*-2-chlorocyclohexyborane followed by rehydroboration. In order to avoid this complication, the hydroboration of 3-chlorocyclohexene was carried out in diethyl ether[6] followed by oxidation with *m*-chloroperbenzoic acid[15] (see Table I, column 3). The isomer distributions observed in diethyl ether and tetrahydrofuran are within experimental error of each other.

Table I. Products Formed in the Hydroboration of 3-Chlorocyclohexene[a]

Product	Solvent THF	Solvent Diethyl ether	3-Methylcyclohexene[b]
cis-2	9.9	10.2	15.3
trans-2	0	84.7	34.2
cis-3	0.8	1.5	18.2
trans-3	3.1	3.6	32.2
Cyclohexanol	86.2	0	...
% *cis* addition	10.8	11.7	33.5
% 2 addition	96.7	94.9	49.5

[a] Yields are normalized to 100%. Absolute yields average 80–85%. [b] See ref 10.

Analysis of the results in Table I reveals that approximately 88–89% of the borane is introduced *trans* to the chloro group. This value is considerably greater than the corresponding percentage of *trans* addition to the 3-methylcyclohexene system. This observation is rationalized on the basis of a steric inhibition to attack *cis* to the 3-chloro group in the pseudoaxial conformation which must contribute substantially to the over-all structural compositions of 3-chlorocyclohexene.[16] Attack by borane *cis* with respect to the 3-chloro group is undoubtedly sterically impeded,[17] thus favoring attack *trans* to this group.[18]

Further analysis of the results tabulated in Table I reveals that approximately 95% of the boron is introduced at the 2 position.[19] The corresponding figure for the 3-methylcyclohexene system is 49.5%. The increased amount of boron introduced at the 2 position may be rationalized on the basis of the strong $-I$ effect of the chloro group.

Previous studies[7] involving β-chloroorganoboranes did not allow assessment of the possibility of the occurrence of a *cis* elimination. It is obvious that intermediate **2** does not undergo an uncatalyzed *cis* elimnation. This is consistent with our earlier observations[7] that β-alkyl- and -arylthioorganoboranes do not undergo a *cis* elimination under the conditions of the hydroboration reaction employed here.

Hydroboration of 3-Methoxycyclohexene. The hydroboration of 3-methoxycyclohexene is expected to produce the four isomeric methoxycyclohexylboranes **10, 11, 12,** and **13,** which in turn on oxidation will produce the *cis*- and *trans*-2- and 3-methoxycyclohexanols **14, 15, 16,** and **17** (see Scheme III). A mixture of **14, 15, 16,** and **17** was amenable to direct analysis by glpc.

The chemistry of the intermediates **10–13** derived from the hydroboration of 3-methoxycyclohexene differs in certain respects from intermediates **2–5** formed in the hydroboration of 3-chlorocyclohexene, although

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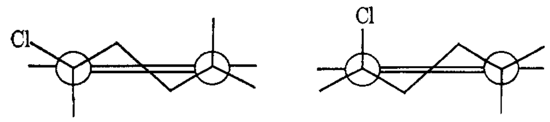
(15) Normal oxidation with aqueous base and hydrogen peroxide results in the elimination of the β-chlorocyclohexylborane (D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, 87, 1526 (1965). This complication may be avoided by employing *m*-chloroperbenzoic acid as the oxidizing agent (S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, 87, 2870 (1965)).

(16) The conformational free energy value for chlorine in a cyclohexene is not known. However a reasonable guess may be advanced as to its value. E. R. Talaty and G. A. Russell *ibid.*, 87, 4867 (1965)) have shown that $-\Delta G$ for the methyl group in cyclohexenesemidione radical anion is 0.49 kcal/mol. The corresponding value in the cyclohexyl system is 1.7 kcal/mol (E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 236). If we apportion similarly the $-\Delta G$ value of chlorine in the cyclohexyl system we arrive at a value of $-\Delta G$ for chlorine in the cyclohexene system of approximately 0.1–0.2 kcal/mol, indicating the presence of 40–45% of the pseudoaxial conformer ii.



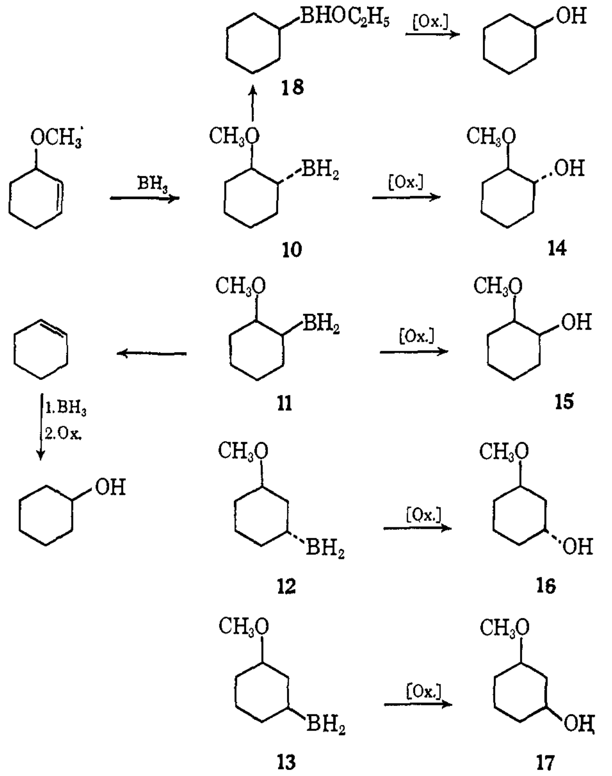
i ii

(17) The $-\Delta G$ value for chlorine is not a valid measurement of its steric interference in an intermolecular attack on the cyclohexene system. $-\Delta G$ values give an indication of intramolecular interactions only, the effective bulk of the functional in an intermolecular reaction being a function of its van der Waals radius and solvation sphere.

(18) The relative rates of attack by borane *cis* and *trans* to the chloro functional group in i and ii cannot be evaluated, and thus the full contribution of i and ii to the observed stereochemistry of attack cannot be evaluated.

(19) This value is quite close to the estimated percentage of boron introduced at the 2 position in the hydroboration of 1-chloro-2-butene; see Brown and Gallivan, ref 13.

Scheme III



the over-all directive effects are very similar (see Table II).

Table II. Products Formed in the Hydroboration of 3-Methoxycyclohexene[a]

	Length of reaction time		
Product	20 min	2 days	30 days
cis-2	4.9	0	0
trans-2	80.8	66.1	54.8
cis-2	3.2	5.0	4.2
trans-3	6.0	7.9	6.3
Cyclohexanol	5.0	20.9	34.7
% *cis* addition	12.4[b]	. . .	. . .
% 2 addition	90.7	. . .	. . .

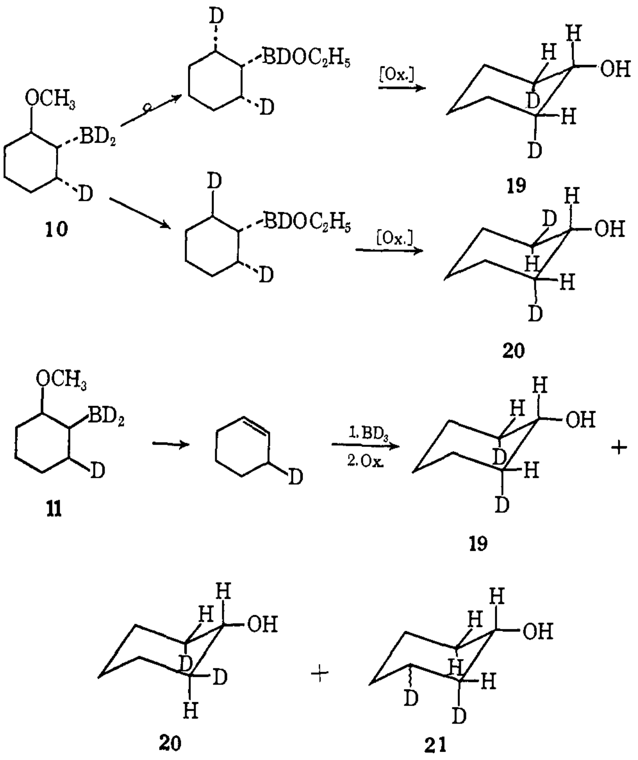
[a] Yields are normalized to 100%. Absolute yields averaged 80–85%. [b] Assuming that all of the cyclohexanol was derived from the *cis*-2 adduct **11**.

Hydroboration of 3-methoxycyclohexene at 0° followed by immediate oxidation produces low yields of cyclohexanol. The formation of the cyclohexanol is believed to occur *via* a *cis* elimination involving intermediate **11**, consistent with earlier observations,[7] producing cyclohexene which on subsequent hydroboration and oxidation gives cyclohexanol. However, if one allows the hydroboration mixture to stand for longer periods of time at room temperature, intermediate **10** slowly disappears with the ultimate formation of cyclohexanol (see Table II). This observation is consistent with the proposal that **10** undergoes a slow β-transfer reaction to give **18** which on oxidation produces cyclohexanol.[5]

Substantiation of this proposal and the determination of the stereochemistry of this β-transfer reaction were obtained by hydroboration of 3-methoxycyclohexene with perdeuterioborane. Unfortunately, the formation of the cyclohexanol occurs *via* two independent pathways. However, one pathway is limited, *i.e.*, the product formed *via* the elimination of intermediate **11** is limited to a maximum of approximately 10% of cyclohexanol, whereas the total yield of cyclohexanol may reach as high as 90%, the main contribution being *via* a pathway **10** → **18** → cyclohexanol.

Consideration of these two pathways leads to the prediction of the products indicated in Scheme IV. Deuterioboration of 3-deuteriocyclohexene will produce 2.5% **19**, 2.5% **20**, and 5.0% **21** (based on the formation of 10% **11** and ignoring any isotope effect which may be present in the deuterioboration of 3-deuteriocyclohexene). A β transfer involving **10** with inversion will produce approximately 25% **19** (based on the amount of cyclohexanol which must be formed from **10** after 30 days), whereas a β transfer with retention will yield approximately 25% **20**. As the amount of specifically labeled cyclohexanol formed from **10** is considerably greater than that derived from **11**, distinction between the inversion and retention mechanisms for **10** should be possible.

Scheme IV



Identification of the predominant dideuterated cyclohexanol is possible by nuclear magnetic resonance. Compound **19** with two equatorial–axial couplings with the carbinol hydrogen will give rise to a triplet with $J = \sim 4$ Hz[20] (ignoring the coupling due to deuterium). Compound **20** will produce an nmr spectrum displaying a double doublet with J's = ~12 and 4 Hz.[20] The resonance signals for **19**, **20**, and **21** formed from **11** should not sufficiently obscure the resonance signal patterns for **19** and **20**. The nmr spectrum of the dideuterated cyclohexanol derived from the perdeuterioboration of 3-methoxycyclohexene displayed a clean triplet with $J = 3.7$ Hz (employing H–D heteronuclear decoupling to remove the deuterium coupling). This

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[20] J. L. Musher, *J. Chem. Phys.*, 34, 594 (1961).

observation is consistent only with a β-transfer reaction occurring with inversion.[21]

Hydroboration of 4-Methoxycyclohexene. The results of the hydroboration of 4-methoxycyclohexene are presented in Table III. These results are quite similar with the results of Klein, Dunkelblum, and Aurahmi[10] on the hydroboration of 4-methylcyclohexene. The slight preference for addition *trans* to methoxyl and methyl are undoubtedly due to steric effects imposed by the pseudoaxial groups in the pseudoaxial conformers. The inductive effect of the methoxyl is greatly attenuated compared to the 3-methoxycyclohexene systems resulting in only a slight preference for the attack of boron at C-2 of the olefin. All of the intermediate methoxycyclohexylboranes derived from 4-methoxycyclohexene are stable.

Table III. Products Formed in the Hydroboration of 4-Methoxycyclohexene and 4-Methylcyclohexene[a]

Product	4-Methoxy	4-Methyl
cis-3	22.2	28
trans-3	33.6	27
cis-4	19.1	20
trans-4	25.1	25
% *cis* addition	41.7	48
% 3 addition	55.8	55

[a] Yields are normalized to 100%. Absolute yields averaged 80–85%.

Summary

The results of the hydroboration of 3-chloro- and 3- and 4-methoxycyclohexenes are summarized in Table IV. The general trend in the stereochemistry and the direction of attack in the 3-cyclohexenyl systems studied here compares very favorably with the results of Brown and Knights[1b] obtained with the 3-pentenyl systems.

Table IV. Summary of the Results of the Hydroboration of 3-Chloro- and 3- and 4-Methoxycyclohexenes

	Substituted cyclohexene		
Product	3-Chloro	3-Methoxy	4-Methoxy
cis-2	10	9.9	22.2 (*cis*-3)
trans-2	86	80.8	33.6 (*trans*-3)
cis-3	1	3.2	19.1 (*cis*-4)
trans-3	3	6.0	25.1 (*trans*-4)
% *cis* addition	11	12.4	41.7
% 2 addition	96	90.7	55.8 (% 3 addition)

Experimental Section

General. 3-Chlorocyclohexene was purchased from Frinton Laboratories and was purified by distillation. 3-Methoxycyclohexene was purchased from Sapon Laboratories and was purified by distillation. Pure samples of *trans*-2-, *cis*-3-, and *trans*-4-methoxycyclohexanol and mixtures of the *cis*-2- and *trans*-2- and *cis*-3- and *trans*-3-methoxycyclohexanols were obtained from Professor Ernest L. Eliel.

***trans*-2-Chlorocyclohexanol.** The *trans*-2-chlorocyclohexanol was prepared by the general procedure of Lapporte and Fesstandig;[22] bp 84.2–84.4° (12 mm) (lit.[22] 84.5–85.0°).

Mixture of *cis*- and *trans*-2-Chlorocyclohexanols. To a mixture of 3.6 g (0.027 mol) of *trans*-2-chlorohexanol in 12 ml of acetone was added over a period of 20 min a solution of 1.0 g (0.019 mol) of chromium trioxide in 3 ml of concentrated sulfuric acid and 10 ml of water. Approximately 5 g of sodium chloride was added to the reaction mixture and then extracted with ether. The ether extract was washed with two 5-ml portions of concentrated potassium carbonate solution and two 20-ml portions of saturated sodium chloride and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the product, 2-chlorocyclohexanone, was distilled at 53.5–56.0° (2 mm) (lit.[23] bp 90–91° (14–15 mm)).

To 0.76 g (0.020 mol) of sodium borohydride in 15 ml of methanol was added the 2-chlorocyclohexanone in 10 ml of methanol. The reaction mixture was stirred at room temperature for 3 hr and then hydrolyzed with 10 ml of water. The mixture was extracted with ether, and the ether extract was washed with two 15-ml portions of saturated sodium chloride and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, and the product was distilled at 83–86° (12 mm), yield 50%. Glpc analysis on a 20-ft 20% DEGS on acid-washed Chromosorb P column at 140° indicated the presence of 53.6% *trans*-2- and 46.4% *cis*-2-chlorocyclohexanols.

***trans*-2-Chlorocyclohexyl Trifluoroacetate.** The *trans*-2-chlorocyclohexyl trifluoroacetate was prepared by the general procedure of Cotter and coworkers.[24] To 1.0 g (7.5 mmol) of *trans*-2-chlorocyclohexanol was added 2.5 g (11.9 mmol) of trifluoroacetic anhydride. The reaction mixture was refluxed for 2 hr and then distilled giving *trans*-2-chlorocyclohexyl trifluoroacetate (94%) with bp 53.0–53.4° (2.4 mm) (lit.[24] bp 89° (24 mm)).

Mixture of *cis*- and *trans*-2-Chlorocyclohexyl Trifluoroacetates. The procedure outlined for the preparation of *trans*-2-chlorocyclohexyl trifluoroacetate was followed using 2.0 g (14.9 mmol) of the mixture of *cis*- and *trans*-2-chlorocyclohexanols and 5.0 g (23.8 mmol) of trifluoroacetic anhydride. The product (91%) was distilled at 53–55° (2.3 mm) (lit.[24] *cis:* 75–77° (5 mm); *trans:* 89° (24 mm)).

The distilled product was analyzed by glpc on a 20-ft 20% DEGS on acid-washed Chromosorb P column at 140° indicating the presence of 53.7% *trans*- and 46.3% *cis*-2-chlorocyclohexyl trifluoroacetates.

Cyclohexyl Trifluoroacetate. The procedure outlined in the preparation of *trans*-2-chlorocyclohexyl trifluoroacetate was followed using 0.5 g (5.0 mmol) of cyclohexanol and 1.5 g (7.11 mmol) of trifluoroacetic anhydride. The product (89%) was distilled at 40° (6 mm) (lit.[25] bp 150°).

***trans*-3-Chlorocyclohexyl Trifluoroacetate.** To a solution of 2.0 g (0.018 mol) of *cis*-1,3-cyclohexanediol[26] in 7 ml of anhydrous pyridine at 0° was added 3.46 g (0.018 mol) of *p*-toluenesulfonyl chloride. The reaction mixture was allowed to stand at room temperature for 3 days and then 50 ml of chloroform was added. The reaction mixture was washed with two 100-ml portions of 4 *N* sulfuric acid and a 100-ml portion of saturated sodium chloride and was dried over anhydrous magnesium sulfate. The chloroform was removed under reduced pressure leaving an oil which was recrystallized from chloroform–Skellysolve B to give the *cis*-1,3-cyclohexanediol monotosylate, approximate mp 25° (ν_{OH} at 3280 cm^{-1} and ν_{SO} at 1178 and 1190 cm^{-1}).

To a solution of 1.8 g (0.0067 mol) of the *cis*-1,3-cyclohexanediol monotosylate in 15 ml of chloroform was added 3.0 g (0.014 mol) of trifluoroacetic anhydride. The reaction mixture was refluxed for 3 hr and, after cooling, the solvent and other low-boiling compounds were removed at 25° (10 mm) leaving a viscous oil ($\nu_{C=O}$ at 1786 cm^{-1} and ν_{SO} at 1178 and 1190 cm^{-1}).

To a solution of 1.8 g (0.004 mol) of *cis*-1,3-cyclohexanediol monotosylate monotrifluoroacetate in 30 ml of anhydrous dimethyl

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[21] The uncatalyzed α transfer reaction has been shown to occur with complete inversion of configuration.[8] The β transfer observed here cannot be rationalized on the basis of a strictly intramolecular rearrangement because of the geometry required in the transition state. It is therefore believed that the β transfer reaction observed with **10** involves an intermolecular reaction in which another molecule of organoborane acts as a Lewis acid in removing the ethoxyl group.

[22] S. J. Lapporte and L. L. Fesstandig, *J. Org. Chem.*, **26**, 3681 (1961).

[23] M. S. Newman, M. D. Farbman, and H. Hipsher, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1954, p 188.

[24] J. L. Cotter, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 793 (1962).

[25] E. J. Bourne, M. Stacey, J. C. Tatlow, and R. Worrell, *J. Chem. Soc.*, 3268 (1958).

[26] M. F. Clark and L. N. Owen, *ibid.*, 2103 (1950).

sulfoxide was added 0.18 g (0.004 mol) of anhydrous lithium chloride. The reaction mixture was stirred for 20 days and then 5 ml of water was added. The reaction mixture was extracted several times with ether, and the combined ether extract was dried over anhydrous magnesium sulfate. The ether was removed, and the product (10%) was purified by preparative glpc. The nmr spectrum displayed the following peaks for the methine hydrogens: −229 (*CH*Cl, width at half-peak height: 12 Hz) and −302 Hz (*CH*O-OCCF$_3$, width at half-peak height: 14 Hz).

Anal. Calcd for $C_8H_{10}ClF_3O_2$: C, 41.67; H, 4.37; Cl, 15.37. Found: C, 41.17; H, 4.54; Cl, 16.19.

***cis*-3-Chlorocyclohexyl Trifluoroacetate.** The procedure described above for the preparation of *trans*-3-chlorocyclohexyl trifluoroacetate was employed starting with 2.0 g (0.018 mol) of *trans*-1,3-cyclohexanediol.[26]

The *cis*-3-chlorocyclohexyl trifluoroacetate (~10%) was isolated by preparative glpc techniques. The nmr spectrum, determined in carbon disulfide at 25°, displayed the following peaks for the methine hydrogens: −227 (*CH*Cl, width at half-peak height: 19 Hz) and −294 Hz (*CH*OOCCF$_3$, width at half-peak height: 26 Hz).

Anal. Calcd for $C_8H_{10}ClF_3O_2$: C, 41.67; H, 4.37; Cl, 15.37. Found: C, 42.07; H, 4.51; Cl, 15.41.

Hydroboration of 3-Chlorocyclohexene in Tetrahydrofuran. To 17 ml of 1.47 *M* borane in tetrahydrofuran at 0°, under nitrogen, was added 1.5 g (0.013 mol) of 3-chlorocyclohexene in 7 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred at 0° for 30 min, then hydrolyzed with 3 ml of water and 1.5 ml of 20% sodium hydroxide solution, and oxidized with 1.2 ml of 30% hydrogen peroxide. The reaction mixture was extracted with several portions of ether. The combined ether extract was washed with water and dried over anhydrous magnesium sulfate.

The ethereal solution was carefully concentrated by distillation of the ether, and the alcohol mixture was treated with 5.0 g (0.024 mol) of trifluoroacetic anhydride as described before for the conversion of chlorocyclohexanols to the corresponding trifluoroacetates. After refluxing for 2 hr, the low-boiling compounds were removed by distillation at 25° (10 mm). The resulting trifluoroacetate mixture was analyzed by glpc on a 20-ft 20% DEGS on acid-washed Chromosorb P column at 140°. The results are summarized in Table I.

Hydroboration of 3-Chlorocyclohexene in Diethyl Ether. 3-Chlorocyclohexene (1.5 g, 0.013 mol) was dissolved in 30 ml of anhydrous diethyl ether and was treated at 0° with an excess of diborane, generated externally from 25 g of boron trifluoride etherate and 5 g of sodium borohydride in 15 ml of anhydrous diglyme and transported in a stream of dry nitrogen to the reaction flask. The reaction mixture was allowed to stand at room temperature for 24 hr. Most of the ether and the excess diborane were removed by distillation under a nitrogen atmosphere. The residue was cooled at 0° and oxidized by the addition of 3.0 g (0.017 mol) of *m*-chloroperbenzoic acid in 30 ml of anhydrous chloroform. The oxidized reaction mixture was allowed to stand at room temperature for 4 days and was then extracted with five 50-ml portions of acidified ferrous ammonium sulfate. The chloroform layer was then washed with three 50-ml portions of 10% sodium bicarbonate solution and three 50-ml portions of water and then dried over anhydrous magnesium sulfate. To the chloroform solution was added trifluoroacetic anhydride. After refluxing for 2 hr, the low-boiling compounds were removed by distillation at 25° (10 mm). The resulting trifluoroacetate mixture was analyzed by glpc techniques on a 20-ft 20% DEGS on acid-washed Chromosorb P column at 140°. The results are summarized in Table I.

Hydroboration of 3-Methoxycyclohexene. To 6.0 ml of 1.47 *M* borane in tetrahydrofuran solution at 0° was added, under nitrogen, 0.5 g (4.6 mmol) of 3-methoxycyclohexene in 4 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred for 20 min at 0° and then hydrolyzed, oxidized, and worked up as described above. The product mixture was analyzed by glpc on a 20-ft 20% Carbowax 20M Chromosorb P column. The results are given in Table II.

Deuterioboration of 3-Methoxycyclohexene. The procedure outlined immediately above for the hydroboration of 3-methoxycyclohexene was followed using 0.5 g (4.5 mmol) of 3-methoxycyclohexene and 2.8 ml of 1.77 *M* borane-d_3 in tetrahydrofuran. The deuterioboration mixture was allowed, however, to stand at room temperature for 30 days before hydrolysis and oxidation. The oxidative work-up at 0° and the glpc analysis were carried out as described above. The results are summarized in Table II.

The cyclohexanol fraction was isolated by preparative glpc. The nmr spectrum of the sample, recorded in deuteriochloroform, displayed the following peaks: −92 (8 H, multiplet, ring hydrogens), −120.3 (1 H, singlet, OH), and −216.0 Hz (1 H, multiplet, *CH*OH). Heteronuclear spin decoupling caused the multiplet centered at −216.0 Hz to collapse to a broad triplet, $J = 3.7$ Hz.

4-Methoxycyclohexene. The 4-methoxycyclohexene was prepared by the procedure of Gogek and coworkers.[27]

Hydroboration of 4-Methoxycyclohexene. To 6.0 ml of 1.47 *M* borane in tetrahydrofuran at 0° was added slowly, under nitrogen, 0.5 g (4.5 mmol) of 4-methoxycyclohexene in 4 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred at 0° for 20 min and then hydrolyzed, oxidized, and worked up as described above. The product mixture was analyzed on a 20-ft 20% Carbowax 20M on Chromosorb P column leading to separation of the *cis*- and *trans*-3-methoxycyclohexanols from the 4-methoxycyclohexanol fraction. The 4-methoxycyclohexanol fraction was collected by preparative glpc techniques and analyzed on a 10-ft Tide column. The results are given in Table III.

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(27) C. J. Gogek, R. M. Moir, and C. B. Purves, *Can. J. Chem.*, **29**, 946 (1951).