analytical sample was obtained by recrystallization from a mixture of acetone and petroleum ether (bp 60–110°), mp 114–116°.

Anal. Calcd for $C_{15}H_{13}F_3SO_3$: C, 54.54; H, 3.97; S, 9.71. Found: C, 54.77; H, 4.13; S, 9.73.

B. From 1-Phenyl-2,2,2-trifluorodiazoethane and *p*-Toluenesulfonic Acid.—To a mixture of an excess of *p*-toluenesulfonic acid monohydrate in ether was added dropwise with stirring an ether solution of 1.24 g (0.0067 mole) of 1-phenyl-2,2,2-trifluorodiazoethane which had been isolated as described above. There was an immediate gas evolution and loss of color. When the addition was complete, the reaction mixture was stirred with water and the layers were separated. The organic phase was washed with aqueous $NaHCO_3$. Evaporation of the solvent left a residue, weighing 1.90 g (86%) of the desired ester which, when recrystallized from acetone and petroleum ether (bp 60–110°), was identical in melting point and infrared spectrum with a sample prepared as described in A above.

Attempted Reaction of 1-Phenyl-2,2,2-trifluorodiazoethane with Benzoic Acid.—To a solution of 1.3 g (0.011 mole) of benzoic acid in 30 ml of ether was added dropwise with stirring a solution of the diazo compound prepared by the oxidation of 2.0 g (0.011 mole) of α,α,α-trifluoroacetophenone hydrazone. No gas evolution or loss of color was noted, even after standing at room temperature for 3 days. The reaction mixture was washed with Na_2CO_3 solution. No ester could be obtained from the organic phase. Acidification of the Na_2CO_3 wash solution yielded 0.95 g (73%) of recovered benzoic acid.

Registry No.—1, 13652-07-8; 1-phenyl-2,2,2-trifluoroethanol, 340-04-5; 1-phenyl-2,2,2-trifluoroethylamine hydrochloride, 13652-09-0; N-(1-phenyl-2,2,2-trifluoroethyl)benzamide, 13652-10-3; α,α,α-trifluoroacetophenone *p*-toluenesulfonylhydrazone, 13652-11-4; α,α,α-trifluoroacetophenone hydrazone, 13652-12-5; 1-phenyl-2,2,2-trifluoroethyl *p*-toluenesulfonate, 13652-13-6.

Optically Active *sec*-Butylamine *via* Hydroboration

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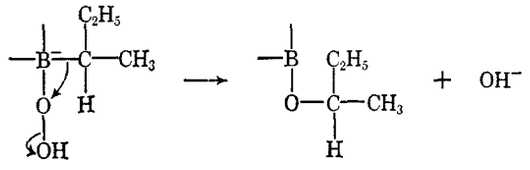
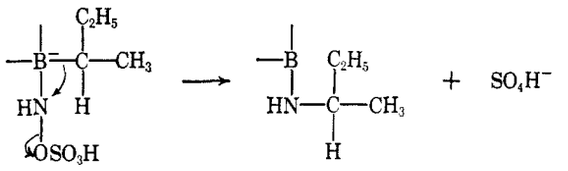
Brown's proposed mechanism for the hydroboration reaction involves a four-center transition state.[1] Treatment of the organoborane intermediate with alkaline hydrogen peroxide affords as product the corresponding alcohol in which the boron atom has been replaced stereospecifically by a hydroxyl group.[2] This step, illustrated for the case of *cis*-2-butene, presumably involves coordination of OOH^- to the boron followed by a 1,2 shift. Decomposition of the ensuing borate ester with water liberates the alcohol.



A test of the stereospecificity of the product-determining step for noncyclic systems would be of interest in obtaining information on the mechanism of the hydroboration reaction. One such experiment would be to change the migration terminus from oxygen to nitrogen. Then, utilizing the asymmetric hydroboration reaction[3] and the same olefin substrate one would examine the *optical purity* of the products in both cases to determine whether the observed stereospecificity was similar or markedly different.

Accordingly, we divided the optically active organoborane obtained from the hydroboration of *cis*-2-butene into two portions. One portion was oxidized with alkaline hydrogen peroxide to yield (*R*)-(−)-*sec*-butyl alcohol with an optical purity of 76%.[4] The second portion was treated with hydroxylamine-O-sulfonic acid.[5] Decomposition of the amine–borane complex



afforded (*R*)-(−)-*sec*-butylamine possessing an optical purity of *ca.* 75% (see Experimental Section).

These results indicate that for open-chain systems, the product-determining 1,2 shift in both the olefin to amine and olefin to alcohol hydraborations proceeds with similar high degrees of stereospecificity. Since alcohol and amine of the same absolute configuration and degree of optical purity are obtained, the hydroboration reaction is of importance as a means of establishing configurational interrelationships of appropriate alcohols and amines.

Experimental Section[6]

(*R*)-(−)-*sec*-**Butylamine.**—Diisopinocampheylborane (0.3 mole) was prepared[4] from α-pinene ($[\alpha]^{27}D$ +34.62°, neat). A solution of *cis*-2-butene (Phillips Petroleum Co., 99 mole % pure; 16.5 g) in 50-ml of diglyme was added over a 10-min period. After 4 hr at 0° the white precipitate of diisopinocampheylborane had disappeared. Hydroxylamine-O-sulfonic acid (Allied Chemical Co., purified by repeated washings with tetrahydrofuran; 33.9 g) in 100 ml of diglyme then was slowly added to the mixture while the reaction temperature was kept below 20°. The mixture was then heated with stirring for 4 hr at 90° followed by a 4-hr reflux period. After being cooled to room temperature, the flask contents were acidified with 100 ml of 20% hydrochloric acid and then worked up in the usual manner. Fractionation of the crude product through a 10-cm column packed with stainless steel helices afforded 2.88 g (13%) of (*R*)-(−)-*sec*-butylamine, bp 62–63° (755 mm), $[\alpha]^{27}D$ −3.90° (neat). Vpc analysis indicated the presence of only one small impurity (<1%) which was shown to be neither α-pinene nor isopinocampheylamine. Significantly, this impurity was also present in the control runs in which diborane was used to yield inactive *sec*-butylamine. However, in order to ensure the absence of impurities, it was desirable to prepare a derivative of the amine which could be purified by crystallization, and from which the amine could subsequently be regenerated.

(*R*)-(−)-**N-(*sec*-Butyl)benzamide.**—This compound was prepared from the (−)-amine by the method of Vogel and Roberts.[7] Three recrystallizations from aqueous ethanol afforded white

(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).
(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 8.
(3) See ref 2, Chapter 14.
(4) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).
(5) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, **88**, 2870 (1966).
(6) Vpc analyses were carried out on an F & M Model 720 gas chromatograph using 0.25 in. × 6 ft Carbowax 20 M columns. Optical rotations were measured on a JASCO recording spectropolarimeter.
(7) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

needles of mp 88.4–89.6°. The benzamide was gas chromatographically pure and had $[\alpha]^{27}D$ −15.6° (95% ethanol).

Optical Purity Considerations.—The optically active amine was regenerated by treatment of the (−)-benzamide with polyphosphoric acid. Recovered (*R*)-(−)-*sec*-butylamine was pure by vpc and had $[\alpha]^{27}D$ −3.83° (neat). Since the α-pinene utilized in the hydroboration reaction had an optical purity of 68%,[8] correction of the specific rotation of the (−)-amine for optically pure α-pinene gives $[\alpha]^{27}D$ −5.63° (neat). The optical activity data, corrected in this manner, are summarized in Table I.

TABLE I
OPTICAL ROTATION AND OPTICAL PURITY DATA

	$[\alpha]D$, deg, optically pure material	*Via* hydroboration (present work), corrected for α-pinene, $[\alpha]D$, deg	% optical purity
sec-Butylamine	7.44[a]	−5.63	76
N-(*sec*-Butyl)benzamide	30.65[b]	−23.0	75
sec-Butyl alcohol	13.5[c]	−10.3	76

[a] L. G. Thome, *Ber.*, **36**, 582 (1903). [b] N. J. Leonard and E. W. Nommensen, *J. Am. Chem. Soc.*, **71**, 2808 (1949). [c] P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951).

Registry No.—(*R*)-(−)-*sec*-Butylamine, 13250-12-9; (*R*)-(−)-N-(*sec*-butyl)benzamide, 13250-13-0.

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(8) The highest reported rotation for α-pinene is $[\alpha]D$ 51.1°: F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1030 (1931).

Protonation Effects on Cyclic Amine Nucleophilicities. Piperazine[1a]

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The over-all hydrolysis of methyl *o*-formylbenzoate (MOFB) in aqueous solution, reported in detail by Bender and co-workers,[2] has been utilized in this study to observe the effect of protonation of a single amine group on the nucleophilicity of the cyclic diamine piperazine. In particular, we have studied the kinetics of the hydrolysis using hydroxide ion, piperazine, piperazinium ion, and, to a lesser extent, morpholine as nucleophiles. The last three contain the groups >NH, $>NH_2^+$, and –O–, respectively, γ to the site of nucleophilic activity.

For runs in aqueous piperazine solutions, the over-all reaction may be expressed by eq 1 where OFBA is *o*-formylbenzoic acid and P and PH^+ are piperazine and the piperazinium ion, respectively. (The equivalent expression for aqueous morpholine solutions involves $k_M[M]$ in place of $k_P[P]$; $k_{PH}[PH^+]$ does not appear.) The disappearance of MOFB is given by

$$\text{MOFB} \xrightarrow[k_P[P]]{k_{OH}[OH^-]} \text{OFBA} \qquad (1)$$

$$\frac{-d[MOFB]}{dt} = (k_{OH}[OH^-] + k_P[P] + k_{PH}[PH^+])[MOFB] \qquad (2)$$

Equation 2 reduces to eq 3 when piperazine is present

$$\frac{-d[MOFB]}{dt} = k_0[MOFB] \qquad (3)$$

in sufficient excess ([piperazine]/[MOFB]) > 5) so as to remain essentially constant during a run. In this case k_0 is given by eq 4 where k_{OH}, k_P, and k_{PH} are the second-order rate constants for catalysis by the subscript species and k_0 is the observed pseudo-first-order constant.

$$k_0 = k_{OH}[OH^-] + k_P[P] + k_{PH}[PH^+] \qquad (4)$$

The concentration of the three catalytic species will be dependent upon the pH of the solution and the total concentration of piperazine, $[P]_T$, given by eq 5.

$$[P]_T = [P] + [PH^+] + [PH_2^{2+}] \qquad (5)$$

Substitution of this quantity, along with K_w, the autoprotolysis constant for water, and the first and second ionization constants for piperazine, K_1 and K_2, into eq 4 yields

$$k_0 = \frac{k_{OH}K_w}{[H^+]} + \left[\frac{k_P}{f_P} + \frac{k_{PH}}{f_{PH}}\right][P]_T \qquad (6)$$

where

$$f_P = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2} \qquad (7)$$

and

$$f_{PH} = \frac{K_2}{[H^+]} + 1 + \frac{[H^+]}{K_1} \qquad (8)$$

Two types of data were obtained at each temperature, one set at constant pH and variable $[P]_T$ and the other at constant $[P]_T$ and variable pH. For the data at constant pH and variable $[P]_T$, plots of k_0 *vs.* $[P]_T$ gave good straight lines as required by eq 6 with slopes equal to $[(k_P/f_P) + (k_{PH}/f_{PH})]$ and intercepts of $k_{OH}K_w/[H^+]$. (The values of k_{OH} obtained from these intercepts were the same as those obtained from runs in which piperazine was absent.)

Simultaneous solution of eq 6, using the slopes of the above plots obtained at several pH's, gave the values of k_P and k_{PH} recorded in Table I. The factors f_P and f_{PH} were calculated from eq 7 and 8 using the pK_a values for piperazine of Paoletti, *et al.*[3] The data obtained at constant $[P]_T$ and variable pH were used to assess the error in the rate constants reported in Table I.

It was observed that the rate constants obtained in this fashion obey the relation $k_P/k_{PH} = K_1/K_2$ at all temperatures. An examination of eq 6 showed that this result is not unexpected since $f_P/f_{PH} = [H^+]/K_2$ and

(1) (a) Supported by Grant No. P-272 from the American Cancer Society. (b) To whom all correspondence should be addressed at the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

(2) (a) M. L. Bender and M. S. Silver, *J. Am. Chem. Soc.*, **84**, 4589 (1962); (b) M. L. Bender, J. A. Reinstein, M. S. Silver, and R. Mikulak, *ibid.*, **87**, 4545 (1965).

(3) P. Paoletti, M. Ciampolini, and A. Vacca, *J. Phys. Chem.*, **67**, 1065 (1963).