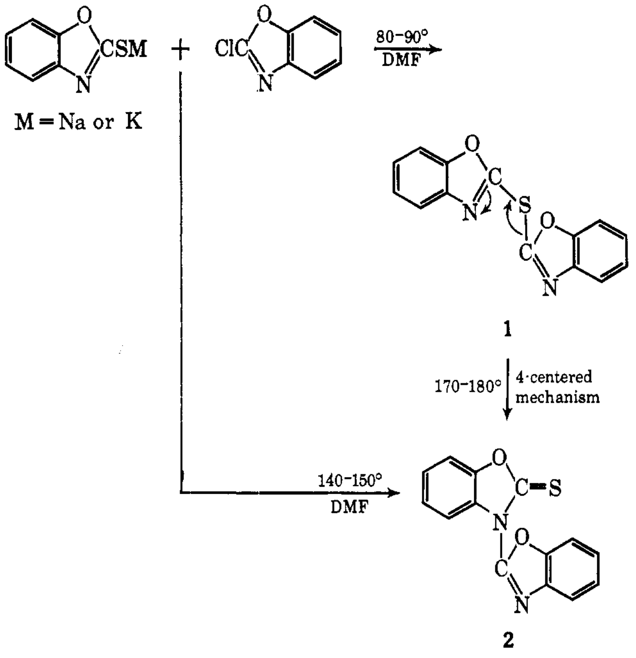
SCHEME I



3-methyl-2-benzoxazolinethione (4)[5] were determined in methanol. The absorption maxima and molar extinction coefficients follow: **1**, 283 mμ (ε 18,900) and 246 (18,100); **2**, 305 (17,800), 282 (24,000), and 245 (19,500); **3**, 285 (13,100), 278 (13,200), and 248 (13,200); **4**, 305 (13,600), 300 (13,600), and 258 (4900). The higher wavelength thioamide absorption band characteristic of intramolecular charge-transfer transition[6] is present in **2** and **4** and absent in **1** and **3**, as would be expected.

2,2′-Thiobis(benzoxazole) (1).—To a stirred solution of 0.20 mole of anhydrous potassium 2-mercaptobenzoxazole in 200 ml of dimethylformamide, 0.20 mole of 2-chlorobenzoxazole was added in one portion. The stirred reaction mixture was heated at 80–90° for 6 hr. After cooling to 25°, the reaction mixture was added to 800 g of ice water containing 32 g (0.2 mole) of 25% aqueous sodium hydroxide. After stirring at 0–10° for 1 hr, the precipitate was collected by filtration, washed with water until the washings were neutral to litmus, and air dried at 25–30°. The crude product (yield 93.2%, mp 127–132°) contained 92.0 and 6.5% of **1** and **2**, respectively. After recrystallization from heptane, it melted at 132–133° (99.5% **1**). The infrared spectrum of recrystallized sample was determined from 2 to 12 μ in chloroform and from 12 to 15 μ in dimethylformamide and contained bands at 3002 (w) (aromatic C–H st), 1506 (vs) and 1453 (s) (C=C and C=N stretching vibrations of the 2-thiobenzoxazole), 1239 (s), 1140 (vs), 1100 (m), 807 (m), 760 (s), and 750 (s) cm^{-1} (C–H out-of-plane deformation of phenyl ring).

Anal. Calcd for $C_{14}H_8N_2O_2S$: N, 10.44; S, 11.95; mol wt, 268.3. Found: N, 10.20; S, 11.74; mol wt, 265.

3-(2-Benzoxazolyl)-2-benzoazolinethione (2).—The procedure was the same as described above except the stirred reaction mixture was heated at 140–150° for 6 hr. The crude product (yield 87.6%, mp 155–158°) contained 6.0 and 93.5% of **1** and **2**, respectively. After recrystallization from ethyl acetate, it melted 160° (100%). The infrared spectrum of recrystallized sample was determined from 2 to 12 μ in chloroform and from 12 to 15 μ in dimethylformamide and contained bands at 3002 (w) (aromatic C–H st), 1622 (m) (C=N st), 1570 (s), or 1480 (s) (N–C=S, thioureide), 1458 (m), 1410 (m), 1382 (m), 1325 (vs), or 1270 (s), (C=S st), 1240 (m), 1175 (w), 1089 (w), 1028 (m), 927 (w), 797 (w), 760 (s), and 752 (s) cm^{-1} (C–H out-of-plane of *ortho*-substituted phenyl ring).

Anal. Calcd for $C_{14}H_8N_2O_2S$; N, 10.44; S, 11.95; mol wt, 268.3. Found: N, 10.25; S, 11.92; mol wt, 272.

Registry No.—**1**, 4225-17-6; **2**, 2008-02-8; **3**, 13673-62-6; **4**, 13673-63-7.

Acknowledgment.—The authors wish to acknowledge their indebtedness to Drs. J. Gloede and H. Gross for their helpful suggestion during the course of this investigation.

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[5] B. Beilenson and F. M. Hamer, *J. Chem. Soc.*, 143 (1939).

[6] B. Ellis and P. J. F. Griffithe, *Spectrochimica Acta*, **22**, 2005 (1966).

Polyfluorodiazo Compounds. II. 1-Phenyl-2,2,2-trifluorodiazoethane[1]

ROBERT A. SHEPARD AND STANLEY E. WENTWORTH[2]

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

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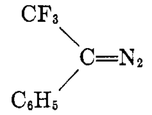
As part of a program of research into the syntheses and reactions of polyfluorodiazo compounds, it was of interest to prepare 1-phenyl-2,2,2-trifluorodiazoethane (I). We have prepared this compound by three different routes: diazotization of 1-phenyl-2,2,2-trifluoroethylamine hydrochloride, reaction of α,α,α-trifluoroacetophenone *p*-toluenesulfonylhydrazone with base,[3] and oxidation of α,α,α-trifluoroacetophenone hydrazone.



$(CF_3)(C_6H_5)C{=}N_2$

I

The previously unreported 1-phenyl-2,2,2-trifluoroethylamine used in the diazotization was prepared by the reduction of α,α,α-trifluoroacetophenone oxime[4] and was characterized as the benzoyl derivative. Diazotization was accomplished using the procedure of Gilman and Jones.[5] The yield of 1-phenyl-2,2,2-trifluorodiazoethane, estimated by reaction with *p*-toluenesulfonic acid and isolation of the resulting *p*-toluenesulfonate,[6] was 17%. This tosylate was also prepared from 1-phenyl-2,2,2-trifluoroethanol[7] and *p*-toluenesulfonyl chloride.

The *p*-toluenesulfonylhydrazone of α,α,α-trifluoroacetophenone, prepared by treating the ketone with *p*-toluenesulfonylhydrazine, gave the diazo compound in 32% yield when treated with sodium methoxide. The best route to the diazo compound (84%) was the oxidation of α,α,α-trifluoroacetophenone hydrazone with mercuric oxide.

1-Phenyl-2,2,2-trifluorodiazoethane has reasonable thermal stability. It could be heated to 100° for short periods of time with little apparent change. It also has relatively low reactivity as a diazo compound in that it does not react with benzoic acid, unlike both

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[1] R. A. Shepard and P. L. Sciaraffa, *J. Org. Chem.*, **31**, 964 (1966), may be considered part I in this series.

[2] NASA Predoctoral Trainee.

[3] D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

[4] E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

[5] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

[6] Since reaction of isolated 1-phenyl-2,2,2-trifluorodiazoethane (see Experimental Section) with excess *p*-toluenesulfonic acid gave an 86% yield of 1-phenyl-2,2,2-trifluoroethyl *p*-toluenesulfonate, yields of diazo compound estimated by this technique may be considered as minima and are significant primarily as a measure of the relative efficacy of the various preparative methods.

[7] E. T. McBee, O. R. Pierce, and J. F. Higgins, *ibid.*, **74**, 1736 (1952).

1,1,1-trifluoro-2-diazopropane[1] and diphenyldiazomethane.[8] This behavior is not surprising in view of the known stabilizing influence of the phenyl[9a] and trifluoromethyl[9b] groups upon the diazo function.

Experimental Section

Melting points and boiling points are uncorrected; the infrared spectra were obtained on a Beckman IR-5 spectrophotometer. Preparative scale gas chromatography was performed on a Fisher Prep-Partitioner using four 20 in. × 1 in. columns packed with 20% Dow-Corning silicone fluid on Columnpak (Fisher Scientific Co.). Analytical gas chromatography was performed on an F & M 500 gas chromatograph using a 2 ft × 0.25 in. column packed with the same material. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

α,α,α-Trifluoroacetophenone was purchased from Pierce Chemical Co. or prepared as described in the literature.[10]

1-Phenyl-2,2,2-trifluoroethanol.—To a stirred suspension of 1.1 g (0.029 mole) of lithium aluminum hydride in 100 ml of ether was added 10.0 g (0.058 mole) of α,α,α-trifluoroacetophenone in 50 ml of ether. After standing overnight, 125 ml of 10% H_2SO_4 was added dropwise to the stirred, chilled reaction mixture. The layers were separated and the aqueous phase was extracted with three 50-ml portions of ether. The combined ether layers were dried over Na_2SO_4 and the ether was removed by distillation. The residue was vacuum distilled to yield 7.88 g (77%) of 1-phenyl-2,2,2-trifluoroethanol, bp 86–90° (15 mm) (lit.[7] bp 64–65° (5 mm)). Its phenylurethan melted at 100–102° (lit.[11] mp 103–104°).

α,α,α-Trifluoroacetophenone oxime was prepared as described in the literature.[4] Our material melted at 84–86° (lit.[4] mp 75°).

Anal. Calcd for $C_8H_6F_3NO$: C, 50.80; H, 3.20; N, 7.41. Found: C, 51.11; H, 3.24; N, 7.04.

1-Phenyl-2,2,2-trifluoroethylamine Hydrochloride.—To a stirred suspension of 1.62 g (0.043 mole) of lithium aluminum hydride in 100 ml of ether was added dropwise 5.0 g (0.026 mole) of α,α,α-trifluoroacetophenone oxime in 50 ml of ether. After stirring for 2 hr, the reaction mixture was treated dropwise with 15.0 g (0.37 mole) of NaOH in 30 ml of water. The layers were separated and the aqueous phase was extracted with two 50-ml portions of ether. The combined ether extracts were dried over Na_2SO_4.

Addition of dry gaseous hydrogen chloride gave a precipitate of 4.5 g (82%) of the amine hydrochloride. No melting point could be observed, even in a sealed capillary, up to 303°.

N-(1-Phenyl-2,2,2-trifluoroethyl)benzamide.—To a chilled (ice bath) solution of 1-phenyl-2,2,2-trifluoroethylamine in ether prepared by the lithium aluminum hydride reduction of 5.0 g (0.026 mole) of α,α,α-trifluoroacetophenone oxime as described above, was added dropwise with stirring 2.97 g (0.021 mole) of benzoyl chloride in 50 ml of ether. After removing the resulting precipitate (presumably amine hydrochloride), the filtrate was concentrated to yield 3.5 g (60%) of 1-phenyl-2,2,2-trifluoroethylbenzamide. Recrystallization from ethanol yielded an analytical sample, mp 160.5–163°.

Anal. Calcd for $C_{15}H_{12}F_3NO$: C, 64.51; H, 4.33; N, 5.02. Found: C, 64.73; H, 4.19; N, 5.20.

α,α,α-Trifluoroacetophenone *p*-Toluenesulfonylhydrazone.—A mixture of 10.7 g (0.058 mole) of *p*-toluenesulfonylhydrazine and 10.0 g (0.058 mole) of α,α,α-trifluoroacetophenone in 35 ml of 95% ethanol was refluxed for 10 min. After cooling, the reaction mixture was poured into water to yield a precipitate of 12.0 g (61%) of crude α,α,α-trifluoroacetophenone *p*-toluenesulfonylhydrazone. This material was deemed sufficiently pure for further reaction. An analytical sample, mp 134.5–137.5°, was obtained by chromatography on acid-washed alumina, using benzene as the eluent.

Anal. Calcd for $C_{15}H_{13}F_3N_2O_2S$: C, 52.62; H, 3.83; S, 9.37. Found: C, 52.90; H, 3.98; S, 9.40.

α,α,α-Trifluoroacetophenone Hydrazone.—To a mixture of 36.6 g (0.349 mole) of hydrazine dihydrochloride, 67.2 g (0.820 mole) of sodium acetate, 30.0 g (0.172 mole) of α,α,α-trifluoroacetophenone, and 545 ml of water was added enough 95% ethanol to achieve homogeneity. The solution was stirred at room temperature for 6 days. Most of the ethanol was then removed by distillation (to a boiling point of 95°). The cooled aqueous residue was extracted with two 200-ml portions of ether. The combined ether extracts were washed with $NaHCO_3$ solution and dried over Na_2SO_4. Evaporation of the ether left a residue which was vacuum distilled. The fraction of bp 111–120° (22 mm) weighing 20.4 g (63%) was collected as α,α,α-trifluoroacetophenone hydrazone. Gas chromatography showed it to be pure enough for further reaction. An analytical sample was obtained by preparative gas chromatography.

Anal. Calcd for $C_8H_7F_3N_2$: C, 51.06; H, 3.75; N, 14.89. Found: C, 51.09; H, 3.62; N, 14.53.

1-Phenyl-2,2,2-trifluorodiazoethane. A. From 1-Phenyl-2,2,2-trifluoroethylamine Hydrochloride.—Following the general procedure of Gilman and Jones,[5] 3.0 g (0.014 mole) of 1-phenyl-2,2,2-trifluoroethylamine hydrochloride was dissolved in 15 ml of water. The solution was layered with 15 ml of ether and chilled in an ice bath. When cool, 1.08 g (0.016 mole) of $NaNO_2$ was added to the vigorously stirred solution. There was an immediate red-orange coloration of the ether layer. After 5 min, the layers were separated. A second layer acquired little additional color. The combined layers were washed with Na_2CO_3 solution and dried over $CaCl_2$. The infrared spectrum of the solution exhibited a strong band at 2210 cm^{-1} characteristic of the diazo group. The estimated yield was 17%.

B. From α,α,α-Trifluoroacetophenone *p*-Toluenesulfonylhydrazone.—The procedure used was that described by Farnum[3] in which the tosylhydrazone is dissolved in pyridine and treated with sodium methoxide. The infrared spectrum of the resulting solution showed the same strong band at 2210 cm^{-1}. The estimated yield was 32%.

C. From α,α,α-Trifluoroacetophenone Hydrazone.—To a chilled, rapidly stirred mixture of 7.8 g (0.036 mole) of yellow mercuric oxide, a catalytic amount of alcoholic KOH, and 75 ml of ether, was added dropwise 5.0 g (0.027 mole) of α,α,α-trifluoroacetophenone hydrazone in 25 ml of ether. Elemental mercury soon appeared and the supernatant solution became deep red-orange. The mixture was stirred for 15 min after the addition was complete. It was then filtered through a cotton plug. The bright red-orange filtrate was washed with water and dried over Na_2SO_4. Again the same strong band appeared in the infrared spectrum at 2210 cm^{-1}. The estimated yield was 84%. The estimated yields reported in parts A–C were determined by treating the respective solutions of 1-phenyl-2,2,2-trifluorodiazoethane with an excess of *p*-toluenesulfonic acid as described in part B below.

Isolation of 1-Phenyl-2,2,2-trifluorodiazoethane.—A pentane solution of 1-phenyl-2,2,2-trifluorodiazoethane was prepared using procedure B. The solution was concentrated on the rotary evaporator and the resulting deep red liquid was vacuum distilled. A fraction, bp 30–32° (2.5 mm), was collected as pure 1-phenyl-2,2,2-trifluorodiazoethane: d^{27} 1.26; $n^{27}\text{D}$ 1.4951.

Anal. Calcd for $C_8H_5F_3N_2$: C, 51.62; H, 2.71; N, 15.05. Found: C, 51.92; H, 2.71; N, 14.83.

In addition to the strong diazo band at 2210 cm^{-1}, the infrared spectrum of the neat compound showed bands at 1600 and 1500 cm^{-1} (aromatic) and a series of strong absorbances from 1400 to 1100 cm^{-1} ($-CF_3$). A sample prepared in this manner very slowly lost its color on standing in a Pyrex test tube for 4–5 months at room temperature.

1-Phenyl-2,2,2-trifluoroethyl-*p*-toluenesulfonate. A. From 1-Phenyl-2,2,2-trifluoroethanol and *p*-Toluenesulfonyl Chloride.—To a mixture of 5.43 g (0.028 mole) of *p*-toluenesulfonyl chloride and 5.0 g (0.028 mole) of 1-phenyl-2,2,2-trifluoroethanol in 30 ml of acetone was added 1.26 g (0.032 mole) of NaOH in 7 ml of water. After stirring at room temperature for 5 days, the acetone was removed by means of a rotary evaporator. The resulting semisolid was partitioned between ether and water. The layers were separated and the aqueous layer was extracted with two 50-ml portions of ether. The combined ether extracts were washed with concentrated NH_4OH. Evaporation of the ether left a residue of 1-phenyl-2,2,2-trifluoroethyl *p*-toluenesulfonate which, after trituration with petroleum ether (bp 30–60°), weighed 8.8 g (94%) and melted at 113–116°. An

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(8) L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 352.

(9) (a) C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, pp 42, 43; (b) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 3617 (1966).

(10) A. Sykes, J. C. Tatlow, and C. R. Thomas, *J. Chem. Soc.*, 835 (1956).

(11) R. Stewart and R. Vander Linden, *Can. J. Chem.* **38**, 399 (1960).

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

Lawrence Verbit and Peter J. Heffron

Department of Chemistry,
State University of New York at Binghamton,
Binghamton, New York

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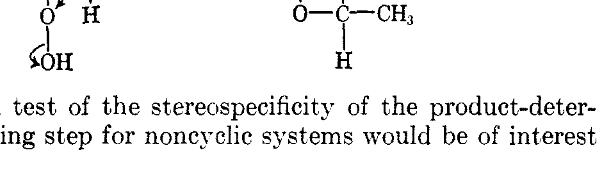
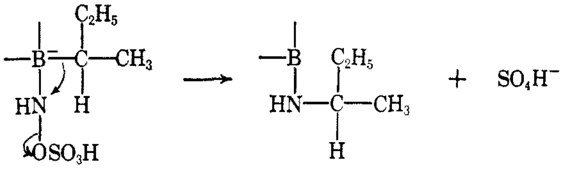
Brown's proposed mechanism for the hydroboration reaction involves a four-center transition state.[1] Treatment of the organoborane intermediate with alkaline hydrogen peroxide affords as product the corresponding alcohol in which the boron atom has been replaced stereospecifically by a hydroxyl group.[2] 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 ($[\alpha]^{27}\mathrm{D}$ +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), $[\alpha]^{27}\mathrm{D}$ −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

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(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).