Two methyl doublets (J = 6.0 cps each) appeared in the pmr spectrum at τ 8.16 and 8.21 (vinyl and allylic methyls, respectively), while the vinyl and allylic protons each gave rise to a quartet (J = 6.0 cps) at 3.81 and 5.21, respectively. Compound **2** was also prepared by heating **1** at 160° for 1 hr. The material boiling at 87–90° (25 mm) was found to contain about 15% **1**. In this case **2** was purified by preparative glpc on a 20 ft × $^3/_8$ in. 20% DEGS column at 150°, helium flow of 200 ml/min, and trapped at liquid nitrogen temperatures. The retention time of **2** was 16 min.

Kinetic Study.—Kerosene solvent was purified by dilute acid wash, distillation, and drying over anhydrous sodium sulfate. A series of standards of **1** and **2** (glpc pure) in this solvent was prepared and the 1000–833-cm^{-1} region recorded four times for each concentration (constant base-line adjustment) in 0.46-mm matched cells, kerosene reference. The absorbance maxima at 933 and 905 cm^{-1} were employed for analysis with a base point at 870 cm^{-1}. Linear calibration curves (base-point method) for each component at each wavelength were obtained and converted to analytical expressions which reduced to

$$C_1 = 97A_{933} - 8A_{905}$$

where C_1 is the concentration (mg/ml) of **1** and A_{933} and A_{905} are net absorbance values at the respective wavelengths.

Kinetic runs at 145, 155, 160, and 165° were made in a constant-temperature oil bath. A 10% solution (w/v) of **1** in kerosene was introduced rapidly into a preheated reaction flask at desired temperature, the initial time was taken, and from eight to ten aliquots (1–2 ml) were withdrawn at irregular intervals until about 80–90% of **1** had rearranged. Aliquots were chilled and stored at 0° until the run was complete. Infrared analysis was done then after centrifugation and twofold dilution with solvent. The instrument was adjusted each time to a constant base-point absorbance equal to the initial sample value. All samples were included in computing the rate constants and mean deviations.

Selective Borane Reduction of a Trifluoroacetamide Substituent in the Presence of a Carbamate

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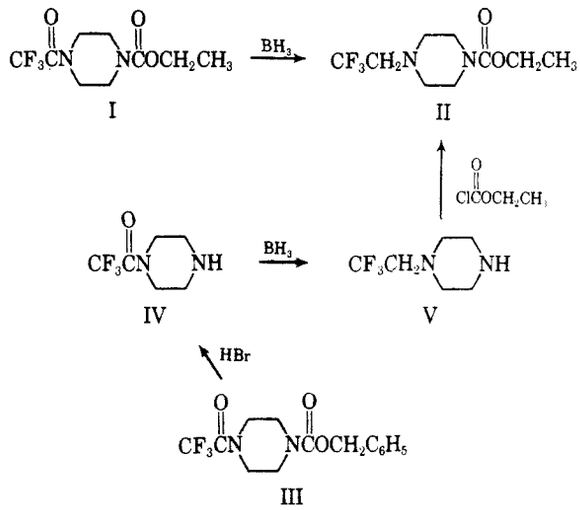
A number of selective reductions utilizing borane and metal borohydrides have been described recently.[1] In a similar manner we have found that borane will reduce the carbonyl of a trifluoroacetamido group[2] without affecting the carbonyl of a carbamate[3] moiety present in the same molecule.[4]

Ethyl 4-trifluoroacetylpiperazine-1-carboxylate (I) was prepared by the reaction between ethyl piperazine-1-carboxylate and ethyl trifluoroacetate. Compound I was treated with refluxing borane in tetrahydrofuran[5] to afford ethyl 4-trifluoroethylpiperazine-1-carboxylate[6] (II) in an 80% yield.



The structure of compound II was firmly established by a four-step synthetic sequence involving (1) trifluoroacetylation of benzyl piperazine-1-carboxylate to give III; (2) decarbobenzoxylation of III to 1-trifluoroacetylpiperazine (IV); (3) borane reduction to N-trifluoroethylpiperazine (V); followed by (4) reaction of V with ethyl chloroformate to afford II.

Experimental Section

All distillations were carried out using a Nester–Faust spinning-band column.

1-Trifluoroacetylpiperazine Hydrobromide (IV).—Benzyl 4-trifluoroacetylpiperazine-1-carboxylate[7] (40.9 g, 0.13 mole) was dissolved in 160 ml of freshly prepared saturated hydrogen bromide in acetic acid and allowed to stand at room temperature for 1.0 hr. The reaction mixture was diluted with 800 ml of anhydrous ether and chilled to give a solid product, yield 23.9 g, (70%), mp 158–162°. For analyses a small portion of the compound was recrystallized from ethanol–ether, mp 160–165°.

Anal. Calcd for $C_6H_9F_3N_2O \cdot HBr$ (mol wt, 263): C, 27.4; H, 3.8; Br, 30.4; F, 21.7; N, 10.6. Found: C, 27.1; H, 4.3; Br, 30.5; F, 21.6; N, 10.4.

1-Trifluoroethylpiperazine (V).—1-Trifluoroacetylpiperazine hydrobromide (26.5 g, 0.10 mole) was dissolved in 25 ml of water, covered with 100 ml of ether, and cooled in an ice bath. The mixture was saturated with sodium bicarbonate and extracted with ten 100-ml portions of ether and four 100-ml aliquots of chloroform. The combined extracts were dried over $MgSO_4$ and evaporated to give 16.5 g of the free base. This product was dissolved in 100 ml of dry tetrahydrofuran and added dropwise to 150 ml of 1.0 M borane–tetrahydrofuran in an ice bath with good stirring in a nitrogen atmosphere. The mixture was refluxed for 1.0 hr, then cooled, and decomposed carefully with 25 ml of 6.0 N hyrochloric acid. The mixture was filtered and the filtrate was evaporated to dryness. The residue was diluted with 25 ml of water, made strongly basic by adding solid sodium hydroxide, and then extracted with four 40-ml portions of ether. The combined ether extracts were dried over magnesium sulfate and evaporated, and the residue was distilled, yield 4.3 g, bp 151–152°, n^{24}D 1.4079.

One gram of this product was dissolved in 25 ml of anhydrous ether and saturated with anhydrous hydrogen chloride to give a white, crystalline dihydrochloride, yield 1.4 g. The compound

(1) See (a) H. C. Brown, *J. Chem. Educ.*, **38**, 173 (1961); (b) H. C. Brown and P. M. Weissman, *J. Am. Chem. Soc.*, **87**, 5614 (1965), and previous articles in that series.

(2) (a) E. R. Bissell and M. Finger [*J. Org. Chem.*, **24**, 1256 (1959)] have prepared trifluoroethylamines by reduction of trifluoroacetamides using sodium borohydride–aluminum chloride, or sodium borohydride–boron trifluoride mixtures. Borane is known to be the active reducing agent in both cases. (b) Z. B. Papanastassiou and R. J. Bruni [*ibid.*, **29**, 2870 (1964)] have also reported the reduction of monofluoroacetamides using borane.

(3) N. G. Gaylord ["Reduction with Complex Metal Halides," Interscience Publishers, Inc., New York, N. Y., 1956, p 636] reports the reduction of carbamates to methylamines with $LiAlH_4$.

(4) Since H. C. Brown and P. Heim [*J. Am. Chem. Soc.*, **86**, 3566 (1964)] have described the borane reduction of a number of simple aliphatic and aromatic amides to amines under conditions similar to those used by us, it would seem likely that the selective reduction of amides in the presence of carbamates may be quite general.

(5) This solution is commercially available from Metal Hydrides Inc., Beverly, Mass. The preliminary data sheet on this product indicates that the borane forms a 1:1 molar complex with tetrahydrofuran.

(6) Attempts to prepare compound II by the direct alkylation of ethyl piperazine-1-carboxylate with trifluoroethyl iodide were not successful.

(7) H. P. Dalalian, L. N. Starker, and L. Goldman, U. S. Patent 2,909,524 (1959).

was recrystallized from ethanol–ether to afford 1.1 g, mp 198–205°.

Anal. Calcd for $C_6H_{11}F_3N_2 \cdot 2HCl$ (mol wt, 242): C, 29.8; H, 5.4; Cl, 29.3; F, 23.6; N, 11.6. Found: C, 30.5; H, 5.7; Cl, 28.7; F, 23.9; N, 11.4.

Ethyl 4-Trifluoroacetylpiperazine-1-carboxylate (I).—Ethyl trifluoroacetate (100 g, 0.707 mole) was added to ethyl piperazine-1-carboxylate (158 g, 1.0 mole) over a 1.5-hr period at room temprature with efficient stirring. The mixture was heated at total reflux in a Nester–Faust apparatus for 1.0 hr (bath temperature 150°) then the excess piperazine derivative was allowed to distill for the next 2.0 hr. The remainder was distilled and the fraction boiling at 86–95° (0.1–0.2 mm) was collected, yield 135.7 g (76%), $n^{25}D$ 1.4454.

Anal. Calcd for $C_9H_{13}F_3N_2O_3$ (mol wt, 254): C, 42.5; H, 5.2; F, 22.4; N, 11.0. Found: C, 42.2; H, 5.4; F, 22.4; N, 10.9.

Ethyl 4-Trifluoroethylpiperazine-1-carboxylate (II). Method A.—1-Trifluoroethylpiperazine (7.0 g, 0.042 mole) was dissolved in 25 ml of water and 1.0 ml (0.01 mole) of ethyl chloroformate, and 1.0 g of sodium acetate was added. The latter procedure was repeated four times at 15-min intervals. The reaction mixture was extracted with two 50-ml portions of ether then cooled in an ice bath and basified with 5.0 ml of 10 *N* sodium hydroxide. The mixture was again extracted with two 50-ml portions of ether. The ether extracts were all combined, dried over magnesium sulfate, and concentrated, and the residue was distilled. The fraction boiling at 66–67° (0.3–0.4 mm) was collected, yield 5.6 g, (56%), $n^{25}D$ 1.4255.

Method B.—Ethyl 4-trifluoroacetylpiperazine-1-carboxylate (50.0 g, 0.208 mole) in 200 ml of dry tetrahydrofuran was added slowly to 350 ml (0.35 mole) of 1.0 *M* borane in tetrahydrofuran while stirring under nitrogen in an ice bath. The mixture was refluxed for 2.0 hr then cooled again in an ice bath and treated carefully with 50 ml of 6 *N* hydrochloric acid. The tetrahydrofuran was evaporated in a hood and the residue was basified with solid sodium hydroxide, then extracted with three 200-ml portions of ether. The combined ether extracts were dried over magnesium sulfate and evaporated, and the residue was distilled, yield 39.5 g (80%), bp 62.5–65° (0.15 mm), $n^{24}D$ 1.4262. The infrared spectra of the products from methods A and B were identical.

Anal. Calcd for $C_9H_{15}N_2F_3O_2$ (mol wt, 240): C, 45.0; H, 6.3; F, 23.8; N, 11.7. Found: C, 45.4; H, 6.3; F, 23.5; N, 11.7.

Acknowledgment.—We are indebted to Mr. L. Brancone and staff for the microanalyses and to Mr. William Fulmor and staff for the infrared spectra.

Some Tertiary Alcohols Derived from *m*-Carborane

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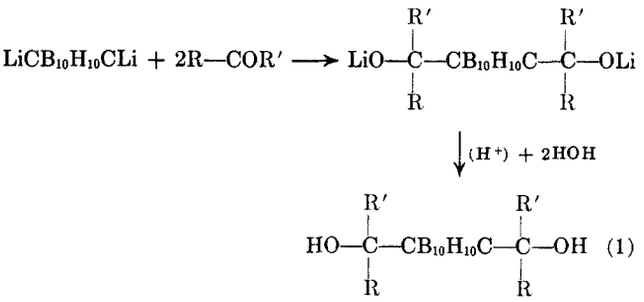
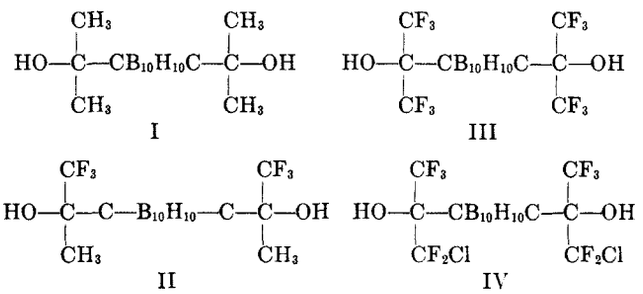
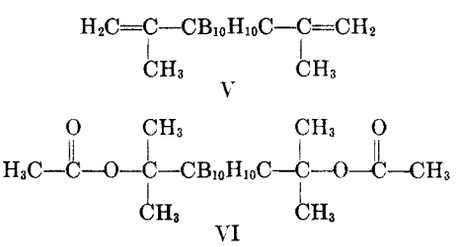
Preparations of primary and secondary diols of *o*-carborane[1] have been reported,[2] as well as that of a primary diol of *m*-carborane.[3] These were prepared as difunctional monomers for further reaction to polymeric products. We wish to report at this time the preparation of several tertiary diols of *m*-carborane,[1] such as $B_{10}H_{10}C_2[C(CH_3)_2OH]_2$ and their fluorinated derivatives such as $B_{10}H_{10}C_2[C(CF_3)_2OH]_2$. These were prepared by reaction of the dilithio salt of *m*-carborane with the appropriate ketone, according to eq 1.



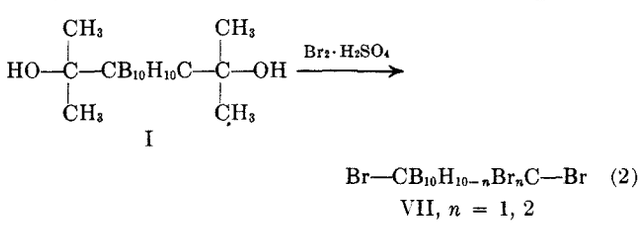
By this reaction we have prepared the compounds I–IV. Compound I failed to give a positive test with



Lucas reagent, even when heated. It did, however, react conventionally with aluminum chloride or sulfuric acid to yield the corresponding diisopropenylcarborane (V) and with acetic anhydride to yield the di(acetoxyisopropyl)carborane (VI).



The reaction with bromine–sulfuric acid was, however, unusual. This reaction involves cleavage of the



bond linking the carboranyl carbon atom with its neighbor, as well as substitution on the boron portion of the nucleus.[4]

The perhalogenated *m*-carborane diols behaved quite differently. The carborane nucleus itself is a very electronegative unit[5] and, especially in combination with perfluorinated groups such as CF_3, should render the hydrogen atoms of the hydroxyl group quite acidic. This proved to be the case, since reactions typical of an alcoholic hydroxyl, such as acylation, did not occur.

(1) We use the terms *o*- or *m*-carborane to refer to 1,2- and 1,7-dicarbaclovododecaborane, respectively. The basic nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

(2) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

(3) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(4) Its structure was proved by mass spectral, infrared and nmr analyses. See also H. D. Smith, T. A. Knowles, and H. A. Schroeder, *ibid.*, **4**, 107 (1965).

(5) M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 4746 (1965).