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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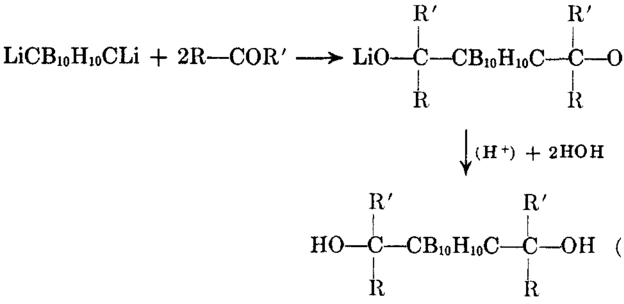
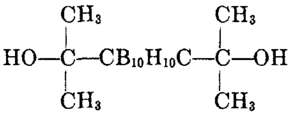
Preparations of primary and secondary diols of *o*-carborane[1] have been reported,[2] as well as that of a primary diol of *m*-carborane.[3] These were prepared as difunctional monomers for further reaction to polymeric products. We wish to report at this time the preparation of several tertiary diols 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.



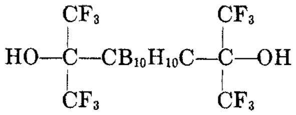
$$\mathrm{LiCB_{10}H_{10}CLi} + 2\mathrm{R{-}COR'} \longrightarrow \mathrm{LiO{-}\overset{R'}{\underset{R}{C}}{-}CB_{10}H_{10}C{-}\overset{R'}{\underset{R}{C}}{-}OLi} \xrightarrow{(H^+) + 2HOH} \mathrm{HO{-}\overset{R'}{\underset{R}{C}}{-}CB_{10}H_{10}C{-}\overset{R'}{\underset{R}{C}}{-}OH} \quad (1)$$

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).



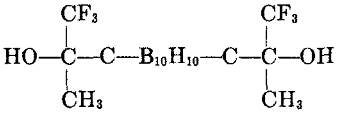
$$\mathrm{HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH}$$

I



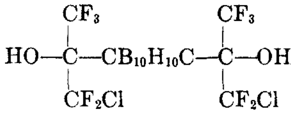
$$\mathrm{HO{-}\overset{CF_3}{\underset{CF_3}{C}}{-}CB_{10}H_{10}C{-}\overset{CF_3}{\underset{CF_3}{C}}{-}OH}$$

III



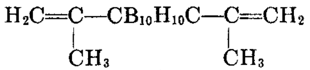
$$\mathrm{HO{-}\overset{CF_3}{\underset{CH_3}{C}}{-}C{-}B_{10}H_{10}{-}C{-}\overset{CF_3}{\underset{CH_3}{C}}{-}OH}$$

II



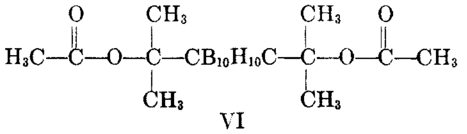
$$\mathrm{HO{-}\overset{CF_3}{\underset{CF_2Cl}{C}}{-}CB_{10}H_{10}C{-}\overset{CF_3}{\underset{CF_2Cl}{C}}{-}OH}$$

IV



$$\mathrm{H_2C{=}\underset{CH_3}{C}{-}CB_{10}H_{10}C{-}\underset{CH_3}{C}{=}CH_2}$$

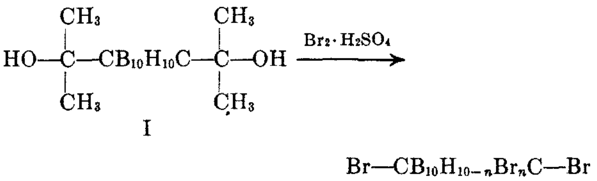
V



$$\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

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]



$$\mathrm{HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH} \ (\mathrm{I}) \xrightarrow{\mathrm{Br_2 \cdot H_2SO_4}} \mathrm{Br{-}CB_{10}H_{10-n}Br_nC{-}Br} \quad (2)$$

VII, $n = 1, 2$

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.

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(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).

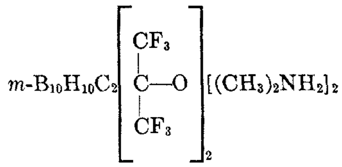
(2) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

(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).

On the other hand, ammonia, hydrazine, and aliphatic amines reacted to give salt-like compounds such as the following.



$$m\text{-}B_{10}H_{10}C_2\left[\begin{matrix}CF_3\\ |\\ C\text{—}O\\ |\\ CF_3\end{matrix}\right]_2[(CH_3)_2NH_2]_2$$

VIII

Experimental Section

m-Carboranyl-1,7-bis(dimethylcarbinol) (I).—m-Carborane (14.4 g 0.10 mole), was converted to its dilithio derivative as previously reported.[6] The washed material was slurried in 200 ml of diethyl ether, cooled to 0°, and stirred rapidly while acetone (12.8 g, 0.22 mole) was added dropwise over a period of 45 min. Stirring was continued for 1 additional hr at 0–5°; the mixture was then hydrolyzed by slow addition of dilute hydrochloric acid. The ether layer was separated and dried over anhydrous $MgSO_4$, and the ether was evaporated to give 23 g of white, solid residue. This was recrystallized from benzene to give 8 g of white crystals (mp 122–123°).

Anal.[7] Calcd for $B_{10}C_8H_{24}O_2$: B, 41.5; C, 36.9; H, 9.3. Found: B, 41.7; C, 36.9; H, 9.9.

m-Carboranyl-1,7-bis(methyltrifluoromethylcarbinol) (II).—The dilithio salt of m-carborane (10 g, 0.069 mole) was prepared as described above and then slurried in diethyl ether. Trifluoroacetone (17.1 g, 0.1526 mole) was slowly added to the slurry, keeping the reaction temperature at 0° by cooling. After addition, the mixture was stirred for 1 hr at 5–10°, then hydrolyzed, and the ether layer was dried and the solvent was evaporated to give 18 g of yellow liquid residue. This was distilled under vacuum (1–2 mm) to give 4.9 g of a light yellow oil (bp 120–124°), which slowly solidified on standing.

Anal. Calcd for $B_{10}C_8H_{18}F_6O_2$: B, 29.3; C, 26.1; H, 4.9; F, 31.0. Found: B, 29.4; C, 26.2; H, 5.2; F, 31.0.

m-Carboranyl-1,7-bis(ditrifluoromethylcarbinol) (III).—The dilithio salt of m-carborane (10 g, 0.069 mole) was prepared as above and slurried in diethyl ether. Hexafluoroacetone was passed into the stirred mixture through a dip tube until reaction appeared to be complete (1.5 hr at 0–5°). The mixture was then hydrolyzed, and the ether layer was dried and then evaporated to give 32.0 g of light yellow liquid residue; this crystallized after a few hours of standing. Recrystallization from petroleum ether (bp 30–60°) gave 5.8 g of white crystals (mp 80–81°).

Anal. Calcd for $B_{10}C_8H_{12}F_{12}O_2$: B, 22.7; C, 20.2; H, 2.5; F, 47.9. Found: B, 22.5; C, 20.2; H, 2.7; F, 47.7.

m-Carboranyl-1,7-bis(chlorodifluoromethyltrifluoromethylcarbinol) (IV).—This preparation was the same as described for III, using pentafluoromonochloroacetone instead of hexafluoroacetone. Hydrolysis and evaporation of the dried ether layer from the reaction gave 31.5 g of brown, oily residue. This was vacuum distilled (1–2 mm) to yield 13.0 g of light yellow liquid, bp 140–145°. This solidified after standing for several hours (mp 43–45°).

Anal. Calcd for $B_{10}C_8H_{12}Cl_2F_{10}O_2$: B, 21.2; C, 18.9; F, 37.4; H, 2.4. Found: B, 21.5; C, 18.9; F, 37.2; H, 2.7.

1,7-Bis(2′-isopropenyl)-m-carborane (V).—m-Carboranyl-1,7-bis(dimethylcarbinol) (I, 26.0 g, 0.10 mole) was dissolved in 500 ml of benzene. Aluminum chloride (13.3 g, 0.10 mole) was added and the mixture was stirred and heated at reflux for 16 hr. The cloudy mixture was filtered under nitrogen and the filtrate was evaporated under reduced pressure to give 23.6 g of liquid residue. This was distilled under vacuum (1 mm) to yield 10 g of liquid, bp 85–91°; this solidified in the receiver. Recrystallization from petroleum ether (bp 30–60°) gave 4.8 g of white crystals (mp 46–47°).

Anal. Calcd for $B_{10}C_8H_{20}$: B, 48.3; C, 42.8; H, 8.9. Found: B, 48.4; C, 42.8; H, 9.1.

Diacetate of m-Carboranyl-1,7-bis(dimethylcarbinol) (VI).—The diol I (3.0 g, 0.015 mole) was dissolved in 50 ml of acetic anhydride. Three drops of concentrated sulfuric acid was added, and the mixture was stirred and warmed to 35° for 3 hr. After standing overnight at room temperature, the mixture was diluted with water and neutralized by slow addition of sodium bicarbonate. The mixture was then extracted with ether, the extract was dried, and the ether was evaporated to yield about 3 g of a yellow, crystalline solid. Recrystallization from petroleum ether (bp 30–60°) gave 1 g of white, crystalline product (mp 64.5–65.0°).

Anal. Calcd for $B_{10}C_{12}H_{28}O_4$: B, 31.4; C, 41.8; H, 8.2. Found: B, 31.5; C, 41.9; H, 8.4.

Dimethylammonium Salt of m-Carboranyl-1,7-bis(ditrifluoromethylcarbinol) (VIII).—Two grams (0.0042 mole) of diol III was dissolved in 25 ml of benzene, and 25 ml of petroleum ether (bp 30–60°) was added. Dimethylamine was then introduced through a glass dip tube until no further precipitate formed. The suspension was filtered, and the filter cake was washed with fresh petroleum ether and then dried under vacuum. The white solid weighed 2.2 g (mp 105–106°).

Anal. Calcd for $B_{10}C_{12}H_{26}F_{12}N_2O_2$: C, 25.4; H, 4.6; F, 40.3; N, 5.0. Found: C, 25.8; H, 4.7; F, 40.3; N, 4.9.

Acknowledgment.—The authors are grateful to Drs. N. S. Semenuk, H. A. Schroeder, and T. L. Heying for helpful discussions and wish to acknowledge the support of this work by the Office of Naval Research.

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[6] S. Papetti and T. L. Heying, *Inorg. Chem.*, **3**, 1448 (1964).

[7] All new carborane derivatives were also characterized by their infrared spectra, as well as by elemental analysis. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected.

Preparation and Dimerization of 4,5-Methano-3-keto Steroids[1]

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Received May 20, 1966

A continuing interest in modified steroids[2] led us to investigate the effect on the biological activity of the steroid system when the double bond of the 3-keto-Δ^4 grouping was replaced by a cyclopropane ring. Isomeric 4,5-methano-3-keto steroids were prepared stereospecifically[3] by allowing either a 3α- or a 3β-hydroxy-Δ^4 steroid to react with the Simmons–Smith reagent[4] (methylene iodide and zinc–copper couple) and the cyclopropane carbinols were, in turn, oxidized to the 3-keto compounds using the Jones reagent.[5]

The first material studied was 3β-hydroxy-Δ^4-cholestene (**1a**) and this compound reacted with the Simmons–Smith reagent to yield the desired 4β,5-methano derivative **2a**, at a rate about one-fifth that of the simple cyclic alcohols.[3] Upon oxidation **2a** gave the ketone **3a** in high yield. It was found that when the crude product from the Simmons–Smith reaction was allowed to stand, a dimer (**4**) was formed. This same material was obtained in 65% yield when a solution of the pure alcohol **2a** in methylene chloride containing a trace of iodine was allowed to stand for 12 hr at 0°. Thus, it seems reasonable to assume that, when the crude product was allowed to stand without solvent, iodine, formed from

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[1] This work was supported in part by Grant No. CY-04284, U. S. Public Health Service.

[2] For the previous paper in this series, see W. G. Dauben, G. A. Boswell, W. Templeton, and J. W. McFarland, *J. Am. Chem. Soc.*, **85**, 2302 (1963).

[3] W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

[4] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[5] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).