Anal. Calcd. for $C_{12}H_6BF_{21}O_3$ (608.0): C, 23.70; H, 0.99; F, 65.63. Found: C, 24.29, 24.48; H, 1.18, 1.19; F, 64.50, 64.33.

Tris(pentafluoropropyl) borate (II). The procedure given for III was followed exactly except treating 58 g. of 1,1-dihydropentafluoropropanol suspended in 60 ml. of petroleum ether with 17 g. of boron trichloride in 150 ml. of petroleum ether; yield of II, 39 g. (66%); b.p. 110° (200 mm.); n_D^{23} 1.2940.

Anal. Calcd. for $C_9H_6BF_{15}O_3$ (458.0): C, 23.60; H, 1.32; B, 2.36; F, 62.63. Found: C, 23.63, 23.89; H, 1.98, 2.18; B, 2.06, 1.96; F, 63.53, 63.89.

Tris(trifluoroethyl) borate (I) was obtained in analogy to the procedure given for III in 60% yield; b.p. 77° (200 mm.); n_D^{23} 1.2975.

Anal. Calcd. for $C_6H_6BF_9O_3$ (307.9): C, 23.40; H, 1.96. Found: C, 23.32, 23.19; H, 2.34, 2.55.

The following procedure is typical of the experiments performed.

Chlorination of tris(1,1-dihydrotrifluoroethyl) borate (I). Gaseous chlorine was passed slowly into 13.1 g. of I exposed to an ultraviolet lamp. When after 25 hr. the contents of the flask began to diminish, the reaction mixture was distilled at 200 mm. and 12.0 g. of products was obtained. Repeated fractional distillation gave 3.5 g. of IV and 3.0 g. of VII.

The *chlorination of 16 g. of tris(1,1-dihydropentafluoropropyl) borate* (II) afforded 14 g. of reaction products. Repeated fractional distillation yielded 5.5 g. of V and 1.5 g. of VIII.

The *chlorination of 15 g. of tris(1,1-dihydroheptafluorobutyl) borate* (III) gave 6 g. of VI and 2 g. of a mixture of IX and XI. Separation by distillation yielded 0.5 g. of IX.

Tris(trifluoromonochloroethyl) borate (IV) boiled at 100° (200 mm.); n_D^{25} 1.3405.

Anal. Calcd. for $C_6H_3BCl_3F_9O_3$ (411.3): C, 17.50; H, 0.73; B, 2.62; Cl, 25.87. Found: C, 16.87, 16.62; H, 0.93, 1.09; B, 2.87, 3.06; Cl, 25.93, 26.12.

Tris(pentafluoromonochloropropyl) borate (V) boiled at 117° (200 mm.); n_D^{25} 1.3262.

Anal. Calcd. for $C_9H_3BCl_3F_{15}O_3$ (561.3): Cl, 18.95. Found: Cl, 17.95.

Tris(heptafluoromonochlorobutyl) borate (VI) boiled at 150° (200 mm.); n_D^{25} 1.3250.

Anal. Calcd. for $C_{12}H_3BCl_3F_{21}O_3$ (711.3): C, 20.11; H, 0.42; B, 1.52; Cl, 15.00; F, 56.00. Found: C, 19.87, 19.80; H, 0.82, 0.91; B, 1.75, 1.86; Cl, 14.68, 14.52; F, 55.35, 55.14.

Bis(trifluoromonochloroethyl) chloroboronate (VII) boiled at 77° (200 mm.); n_D^{25} 1.3490. It is extremely sensitive to moisture, and fumes heavily in the open air.

Anal. Calcd. for $C_4H_2BCl_3F_6O_2$ (313.3): C, 15.34; H, 0.64; B, 3.45; Cl, 34.00. Found: C, 15.42, 15.28; H, 0.77, 0.96; B, 4.27, 4.40; Cl, 34.24, 34.49.

Bis(pentafluoromonochloropropyl) chloroboronate (VIII) is extremely sensitive to moisture; n_D^{25} 1.3330.

Anal. Calcd. for $C_6H_2BCl_3F_{10}O_2$ (413.3): Cl, 25.80. Found: Cl, 25.47, 25.25.

Bis(heptafluoromonochlorobutyl) chloroboronate (IX) is extremely sensitive to moisture; n_D^{20} 1.3360.

Anal. Calcd. for $C_8H_2BCl_3F_{14}O_2$ (513.3): C, 18.70; H, 0.39; B, 2.10. Found: C, 17.92, 17.80; H, 0.45, 0.49; B, 2.09, 1.96.

Di-1,1-dihydroheptafluorobutyl ether (XII). A 10-g. sample of III was added to 25 g. of silver fluoride in a 50-ml. reaction flask immersed in an ice bath and provided with a reflux condenser. A vigorous reaction started immediately, then 5.5 g. of reaction product was distilled. It was added to 10 g. of silver fluoride and the reaction yielded 3.2 g. of products. This amount was added to 5 g. of silver fluoride, scarcely causing a reaction. Distillation at 200 mm. gave 2.3 g. of XII, b.p. 65° (200 mm.), n_D^{25} 1.2890.

Anal. Calcd. for $C_8H_4F_{14}O$ (382.1): C, 25.14; H, 1.05, F, 69.61. Found: C, 25.13, 25.22; H, 1.10, 1.30; F, 66.56, 66.41.

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Acylation and Alkylation of Aminoboronic Acids[1]

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The syntheses of organoboron compounds which we have carried out[2-4] have been based on their possible utilization in the therapy of brain tumors by neutron capture irradiation. The study in C_3H mice with subcutaneous brain tumors has shown[5,6] that organoboron compounds with hydrophilic groups offer the most promise for this type of treatment.

On this basis it seemed desirable to prepare boron compounds with carboxylic acid functions. Many with the carboxyl group attached directly to the aromatic ring[2,5,6] had been prepared and tested. Their utility prompted the synthesis of organoboron compounds containing an aliphatic carboxylic acid group.

Acylation and alkylation of a compound such as *m*-aminobenzeneboronic acid would permit the introduction of such a group. However, the stability of the boronic acid moiety in simple aromatic compounds has been shown[2,7-11] in a variety of systems to vary and to be dependent upon substituents. It was considered possible, therefore, that acylation and alkylation of aminobenzeneboronic acids might occur with loss of the borono group, even though acylations of such amines have been effected[9,12] in certain instances without cleavage of the carbon-boron linkage.

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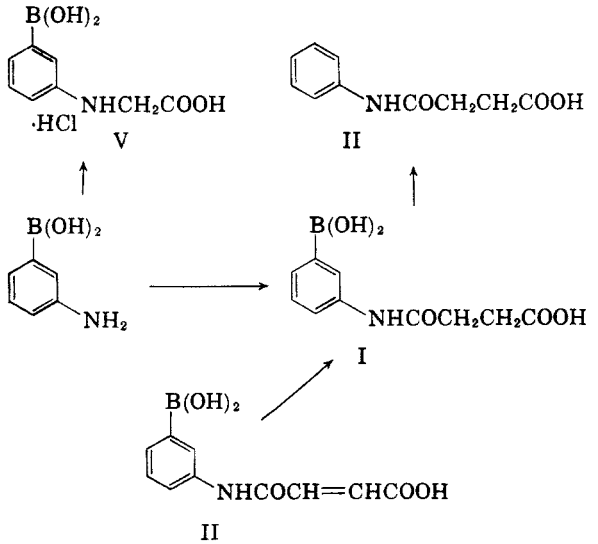
The reaction of 3-aminobenzeneboronic acid with succinic anhydride was carried out in refluxing ethylene glycol dimethyl ether to form 3-boronosuccinanilic acid (I). The product was characterized by deboronation with a silver salt[13] to succinanilic acid (II), identical in all respects with the compound which had been prepared from aniline and succinic anhydride. In a similar manner 3-amino-4-methylbenzeneboronic acid was converted to 2-methyl-5-boronosuccinanilic acid (III).

Maleic anhydride could replace succinic anhydride in this acylation reaction. In this way 3-boronomaleanilic acid (IV) was synthesized. This compound was characterized by analysis and by its absorption of one mole of hydrogen under catalytic reduction with platinum oxide to form 3-boronosuccinanilic acid. This was identical with the compound which was synthesized using succinic anhydride as the acylating agent.

The alkylation of 3-aminobenzeneboronic acid with chloroacetic acid occurred readily in an aqueous medium with sodium carbonate as a condensing agent. The product, 3-borono-*N*-phenylglycine (V), was very soluble and was isolated as the hydrochloride. In a similar manner 2-carboxy-5-borono-*N*-phenylglycine (VI) was synthesized from 2-amino-4-boronobenzoic acid. This compound was isolated as the free amino acid.

Screening of a variety of organoboron compounds resulted in attempts to prepare α-boronomalonic acid from ethoxymagnesium ethyl malonate. They were unsuccessful. However, it was possible to prepare *m*-trifluoromethylbenzeneboronic acid from *m*-bromo-α,α,α-trifluoromethylbenzene *via* the Grignard reagent.



EXPERIMENTAL

All melting points were determined in capillary tubes and are uncorrected.

m-Boronosuccinanilic acid (I). To a solution of 1.4 g. of *m*-aminobenzene-boronic acid[14] in 15 ml. of ethylene glycol dimethyl ether (Ansul Ether 121), was added 1.2 g. of succinic anhydride in 20 ml. of this ether. The solution was refluxed on a steam bath for 1 hr. and then concentrated to near dryness under reduced pressure. The solid residue was triturated with water, cooled and filtered. A 900-mg. sample of a brown solid was obtained, m.p. 185–189°. Successive recrystallizations from water, utilizing a decolorizing charcoal gave a white crystalline solid, m.p. 196–197°.

Anal. Calcd. for $C_{10}H_{12}BNO_5$: C, 50.66; H, 5.10. Found, C, 49.71; H, 5.17.

In 1.5 ml. of an ammoniacal silver nitrate solution[15] was added 100 mg. of *m*-boronosuccinanilic acid. The solution was warmed on a steam bath for 5 min. and allowed to remain at room temperature for 30 min. The mixture was acidified with 30% nitric acid and filtered. A 45-mg. sample of succinanilic acid (II) was obtained, m.p. 148–150°, which showed no melting point depression on admixture of succinanilic acid prepared from aniline. The melting point of a mixture of boronosuccinanilic acid with succinic acid was 174–178°, a lowering of the melting point of each by 15°.

2-Methyl-5-boronosuccinanilic acid (III). A 3.0-g. sample of 3-amino-4-methylbenzeneboronic acid[14] was dissolved in 25 ml. of ethylene glycol dimethyl ether. To this was added a solution of 2.2 g. of succinic anhydride in 40 ml. of the same solvent. The solution was refluxed on a steam bath for 35 min. Solid had already begun separating out of solution after 25 min. The mixture was cooled and filtered, yielding 1.6 g., m.p. 171–173°, of 2-methyl-5-boronosuccinanilic acid. The filtrate was refluxed an additional 35 min. After cooling, the solution was filtered and yielded a second amount, 1.9 g., of the product, m.p. 160–167°. The combined yield of crude boronic acid was 3.5 g. After successive recrystallizations from water a white crystalline product was obtained, m.p. 182–183°, which was analyzed.

Anal. Calcd. for $C_{11}H_{14}BNO_5$: C, 52.62; H, 5.62. Found: C, 52.90; H, 5.88.

m-Boronomaleanilic acid (IV). To a solution of 6.9 g. of 3-aminobenzeneboronic acid in 35 ml. of ethylene glycol dimethyl ether was added a solution of 30 ml. of this ether containing 4.9 g. of maleic anhydride. The solution was refluxed for 90 min. It was then concentrated to half its volume, cooled and filtered. A 4.5-g. sample of *m*-boronomaleanilic acid was obtained, m.p. 201–202°. From the filtrate a second crop of crystals were isolated, m.p. 201–202°. Successive recrystallizations from water gave pale yellow crystals, m.p. 209–211°.

Anal. Calcd. for $C_{10}H_{10}BNO_5 \cdot H_2O$: C, 47.46; H, 4.78. Found: C, 47.49; H, 5.11.

A solution of 1.0 g. of *m*-boronomaleanilic acid in 20 ml. of methanol was catalytically reduced in the presence of 10 mg. of platinum oxide. When the uptake of hydrogen was completed the solution was filtered, the catalyst was washed with water and the filtrate was concentrated to a small volume. On cooling, 850 mg. of a white precipitate settled out of solution. Its melting point, 190–192°, showed no depression on mixture with *m*-boronosuccinanilic acid but a definite lowering with *m*-boronomaleanilic acid.

3-Borono-N-phenylglycine (V). A mixture of 6.9 g. of *m*-aminobenzeneboronic acid, 11 g. of the monohydrate of sodium carbonate and 5 g. of chloroacetic acid in 100 ml. of water was heated on the steam bath for 3 hr. The solution was cooled and acidified carefully with concd. hydrochloric

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acid. After remaining overnight in the refrigerator the solution was filtered and washed with a small amount of ice water. A 2.5-g. sample of white needles was obtained, m.p. >350°. This is the hydrochloride of the amino acid. The high solubility in aqueous solution of the free amino acid prevented its isolation when acetic acid was used as the acidifying agent. The hydrochloride was recrystallized three times from small amounts of water and the final solid analyzed.

Anal. Calcd. for $C_8H_{10}BNO_4 \cdot HCl$: C, 41.51; H, 4.79. Found: C, 41.15; H, 4.91.

2-Carboxy-5-borono-N-phenylglycine (VI). To a mixture of 6.0 g. of 2-amino-4-boronobenzoic acid[12] and 8.2 g. of sodium carbonate monohydrate in 50 ml. of water was added 3.1 g. of chloroacetic acid. There was an immediate reaction and following this, the solution was heated on the steam bath for 4 hr. The mixture was cooled, acidified with acetic acid, and filtered. The product, 2.3 g., m.p. >350°, was washed with a small amount of water and dried. Successive recrystallizations from water gave an analytical sample.

Anal. Calcd. for $C_9H_{10}BNO_6$: C, 45.23; H, 4.17. Found: C, 45.63; H, 4.82.

3-α,α,α-Trifluoromethylbenzeneboronic acid anhydride. m-Bromo-α,α,α-trifluoromethylbenzene (25 g.) was converted in the usual manner[2] *via* the corresponding Grignard reagent to 7.3 g. of 3-α,α,α-trifluoromethylbenzeneboronic acid anhydride, m.p. 161–164°. Successive recrystallizations from water gave a white crystalline product, m.p. 165–167°.

Anal. Calcd. for $C_7H_4BF_3O$: C, 48.90; H, 2.34. Found: C, 49.32; H, 2.65.

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Observations on the Reaction between Triethylaluminum and Octene-1

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While attempting to measure the tritium isotope effects of the reactions between tritiated alcohols and organoaluminum compounds, the reaction between triethylaluminum and octene-1 was studied and the products identified. The products included 2-ethyloctene-1, a compound mentioned only briefly in the literature[1,2] and for which no reliable physical constants have been reported. Here we report briefly on the determination of the products of the reaction between triethylaluminum and octene-1, the measurement of some physical constants of 2-ethyloctene-1, and the determination of tritium kinetic isotope effects for methanol-*O-t* and isobutyl alcohol-*O-t* with the reaction mixture.

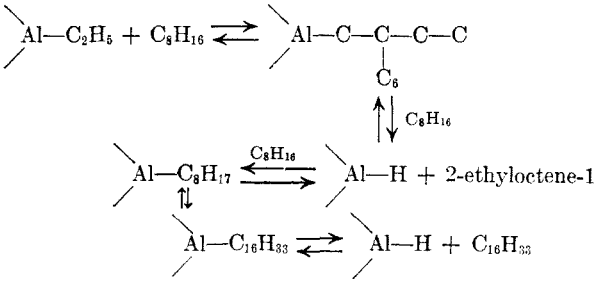
The complete distribution of products from the reaction between triethylaluminum and octene-1 is shown in Table I. The components which were determined as paraffins are expressed in the table arbitrarily as the corresponding pure organoaluminum compounds. While most of the products were identified by comparison with known infrared and mass spectra, no reference data were available for 2-ethyloctene-1. Carbon-hydrogen analysis and molecular weight measurements on this material indicated a composition of $C_{10}H_{20}$. The skeletal structure was determined by identification of its hydrogenation product as 3-methylnonane. Absorption bands at 890 cm.$^{-1}$ and 1650 cm.$^{-1}$, characteristic of vinylidene unsaturation, were observed in the infrared spectrum. For a molecule with the same skeletal structure as 3-methylnonane, vinylidene unsaturation is possible at only one position; therefore, 2-ethyloctene-1 was identified unambiguously.

TABLE I

COMPOSITION OF THE REACTION MIXTURE

Component	Mole Percent
Tri-*n*-octylaluminum	12.1
Octene-1	2.7
Tri-3-methylnonylaluminum	10.5
2-Ethyloctene-1	44.0
Trihexadecylaluminum	6.5
Hexadecene	24.3

The parachor calculated from measured physical constants, neglecting the vapor density, is 414 and compares well with that calculated from parachor equivalents,[3] 415. The components listed in Table I were the only ones formed in significant quantities as a result of the reaction between triethylaluminum and octene-1. One can deduce that the reaction proceeds as follows:



Other compounds, such as *n*-decene, *n*-decane, dodecanes, etc., which would have been expected from other reaction modes, were not found.

The tritium isotope effects (k_H/k_T), at 25° for isobutyl alcohol-*O-t* and methanol-*O-t*, with the organoaluminum compounds in the mixture shown in Table I, were 2.5 and 3.2, respectively.

Tritium isotope effects with Grignard reagents have been reported for a) methanol-*O-t* as 1.0–

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