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.

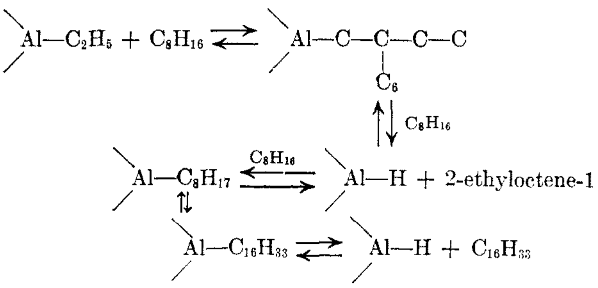
The complete distribution of products from the reaction between triethylaluminum and octene-1 is shown in Table I. The components which were determined as paraffins are expressed in the table arbitrarily as the corresponding pure organoaluminum compounds. While most of the products were identified by 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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1.2,[4] b) tritium oxide as 1.4–1.8,[5] c) phenol-*O-t* as 1.3,[6] and d) *tert*-butylcatechol-*O-t* as 3.0–3.5.[6] In the latter case, *n*-butyl ether was used as a solvent to prevent the formation of coordination compounds between the reactants, thus accounting for the greater isotope effect. The deuterium isotope effect between deuterium oxide and diethylzinc has been reported as 2.5.[7] In light of the above reports, the values reported herein are plausible. The higher tritium isotope effect found for methanol-*O-t* compared with isobutyl alcohol-*O-t* may result from the solubility of the reaction mixture in excess isobutyl alcohol and its insolubility in excess methanol.

EXPERIMENTAL

Materials. The materials used for these experiments included: Ethyl Corp. triethylaluminum (>95%), Phillips Pure grade octene-1 (>99%), argon, originally containing <20 ppm oxygen, <8 ppm water, dried further over Linde 5A molecular sieve, methanol (>99.85%), and isobutyl alcohol (98%). The tritiated alcohols were prepared by exchange with tritium oxide, followed by removal of water by distillation.

Reaction procedure and isotope effects. Triethylaluminum was mixed with octene-1 in a weight ratio of 1:3.5, corresponding to a ratio of 1.2 moles of octene-1 per ethyl group. The mixture was allowed to react under argon for 2 hr. at 145–160°. Then the temperature was raised to 195° in 1 hr. The reaction mixture was cooled to 25° and dropped slowly into a greater than ten-fold excess of either methanol-*O-t* or isobutyl alcohol-*O-t* at the same temperature. Inorganic products and excess alcohol were removed by extraction with dilute hydrochloric acid, dilute sodium hydroxide solutions, and distilled water. The paraffins in a portion of the product mixture were separated from the olefins using the fluorescent indicator adsorption technique.[8]

The average molecular weights of the saturated products were determined cryoscopically. The radioactivities of the reagent alcohols and the saturated reaction products were measured with a Packard Instrument Company Tri-Carb liquid scintillation counter, using a phosphor which consisted of 0.05 g./l. *p*-bis[2-(5-phenyloxazolyl)]benzene and 3.0 g./l. 2,5-diphenyloxazole dissolved in a xylene mixture.[9]

The tritium kinetic isotope effects (k_H/k_T), were calculated according to the equation:

$$\frac{k_H}{k_T} = \frac{A_a}{A_p} \cdot \frac{1}{M}$$

where A_a is the activity in counts per min. per mole for the alcohol, A_p is the activity in counts per min. per g. for the saturated products, and M is the cryoscopic average molecular weight.

A control determination to test the technique was carried out by adding the labeled alcohols slowly to part of the triethylaluminum and octene-1 reaction mixture held at 25°. Complete reaction was allowed to occur between incremental additions of alcohol. Separation and measurements of radioactivity and molecular weight were carried out as described above. An apparent isotope effect of unity for the control indicated that the reaction with alcohol was quantitative.

Analysis. The products which were recovered after treating the reaction mixture with alcohol were identified and determined quantitatively. Hexadecane and hexadecene were identified and determined directly by mass spectrometry; the distribution of C_{16} isomers was not determined. The other components were separated and measured quantitatively by gas chromatography at 80°, using a two-meter column packed with 20% *o*-xenyl-diphenyl phosphate on red Chromosorb. They were identified by infrared and mass spectra.

2-Ethyloctene-1. Several milliliters of pure 2-ethyloctene-1 were isolated from the product mixture using a large capacity gas chromatograph with a 14-foot, one-inch diameter column packed with the same substrate mentioned above. The isolated material, of high purity as determined by mass spectrometric analysis, was used for determination of physical constants. These were: n_D^{25}, 1.4231; d^{25}, 0.7438; b.p., 167.0–167.6°, surface tension at 25°, 22.9 dynes/cm.

Anal.[10]: Calcd. for $C_{10}H_{20}$: C, 85.71%; H, 14.29%; mol. wt., 140. Found: C, 85.81%, H, 14.55%, mol. wt., 138 ± 7.

The compound shows strong absorption in the infrared at 890, 1460, 2900 cm.$^{-1}$, medium bands at 730, 1380, 1650 cm.$^{-1}$, and weak bands at 775, 794, 962, 1060, 1120, 1780 cm^{-1}. A portion of the isolated material was hydrogenated, using a platinum dioxide catalyst, and the recovered hydrogenation product was identified through its infrared spectrum, which was identical with that of 3-methylnonane.[11]

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