Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.18; H, 8.22.

1-Ethyl-*cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (X) was obtained in a similar manner (50% yield). The m.p. after three recrystallizations from methanol was 82–83°.

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.59; H, 8.13.

3-Ethylpentan-3-yl *p*-nitrobenzoate (XIX) was prepared from the alcohol in 59% yield, m.p. 42.5–43.5° after three recrystallizations from methanol.

Anal. Calcd. for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22. Found: C, 63.64; H, 7.45.

General Kinetic Procedure.—The rates of saponification were determined as previously described[3] with the exceptions that 80% acetone was used as the solvent and brom cresol purple as the indicator.

In cases where the saponification proceeded very slowly (*i.e.*, for esters IX, X, XV and XIX) drift in the rate constants toward progressively greater consumption of alkali was observed. This was not due to solvolysis since solutions of the esters in the solvent remained neutral after five days at room temperature. An alkaline solution of 80% acetone, however, very slowly lost basic strength through some side reaction with the solvent. Corrections were therefore applied in those cases where drift was observed, to account for this side reaction. The corrections were satisfactory in all cases except for IX where the rate values then drifted in the opposite direction. This value is therefore approximate.

Notre Dame, Indiana

Organoboron Compounds. IX. Preparation and Properties of Diisobutyl-*t*-butylborane[1]

By G. F. Hennion, P. A. McCusker and A. J. Rutkowski[2]

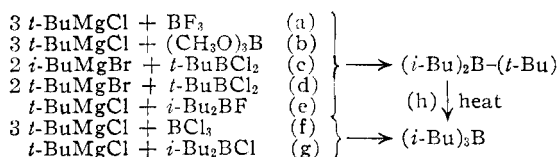Diisobutyl-*t*-butylborane, $((CH_3)_2CHCH_2)_2B-C(CH_3)_3$, *stable to disproportionation and to rearrangement when distilled in vacuo* (below *ca.* 60°), has been prepared in five ways. Distillation at atmospheric pressure causes rearrangement to triisobutylborane. All attempts to prepare tri-*t*-butylborane failed.

Discussion

It was reported in a previous paper[3] in this series that tri-*t*-butylborane was not obtainable from the reaction of *t*-butylmagnesium chloride with boron chloride or with boron fluoride and that distillation of all such reaction products at atmospheric pressure gave triisobutylborane in good yield. Since it has been demonstrated conclusively that one *t*-butyl group can be attached to boron to form *t*-butylboron oxide and *t*-butylboron dichloride,[4] attempts have been made to prepare mixed *t*-butyl-alkylboranes and hence to determine, *inter alia*, whether tri-*t*-butylborane can be made by disproportionation.

We wish to report now concerning the preparation and properties of diisobutyl-*t*-butylborane, $((CH_3)_2CHCH_2)_2B-C(CH_3)_3$. As shown below this compound has been prepared in five ways, (a) to (e). Reactions f and g gave only triisobutylborane.

$$
\begin{array}{ll}
3\ t\text{-BuMgCl} + BF_3 & (a) \\
3\ t\text{-BuMgCl} + (CH_3O)_3B & (b) \\
2\ i\text{-BuMgBr} + t\text{-BuBCl}_2 & (c) \\
2\ t\text{-BuMgBr} + t\text{-BuBCl}_2 & (d) \\
t\text{-BuMgCl} + i\text{-Bu}_2BF & (e) \\
3\ t\text{-BuMgCl} + BCl_3 & (f) \\
t\text{-BuMgCl} + i\text{-Bu}_2BCl & (g)
\end{array}
$$

$\longrightarrow (i\text{-Bu})_2B-(t\text{-Bu})$

(h) $\downarrow$ heat

$\longrightarrow (i\text{-Bu})_3B$

The properties of triisobutylborane and diisobutyl-*t*-butylborane are compared in Table I.

The authenticity of the product from the reactions a to e is indicated not only from these various

Table I

	B.p. °C.	Mm.	$n^{25}D$	d^{25}	MR_Dobs.
$(i\text{-}C_4H_9)_3B$	52–53	4	1.4203	0.7352	62.73
$(i\text{-}C_4H_9)_2B\text{-}t\text{-}C_4H_9$	48–49	2.7	1.4244	0.7428	62.62

modes of formation, but also from the fact that oxidation with alkaline hydrogen peroxide[3,5] gave isobutyl and *t*-butyl alcohols in exactly a 2:1 ratio. Surprisingly, diisobutyl-*t*-butylborane may be redistilled repeatedly *in vacuo*, if the boiling point does not exceed about 60°, without disproportionation or rearrangement.[6] At higher temperatures, as obtain during distillation at atmospheric pressure, rearrangement to triisobutylborane occurs smoothly. Disproportionation to tri-*t*-butyl- and triisobutylboranes has not been achieved. Furthermore, all attempts to prepare tri-*t*-butylborane *via* Grignard reactions (methods a, b, d and f) have met with failure under various experimental conditions, as have attempts to prepare di-*t*-butyl-isobutylborane.

Since the alkylation of a boron halide or ester with a Grignard reagent must proceed in a stepwise manner, *i.e.*, $BX_3 \rightarrow RBX_2 \rightarrow R_2BX \rightarrow R_3B$, it is not possible to determine unequivocally at what stage or how rearrangement occurs. It is believed that the reaction of *t*-BuMgX with boron fluoride (method a) produces initially *t*-BuBF₂ and that the subsequent alkylations proceed only with rearrangement. On the other hand, when boron chloride is used (method f), even the first butyl group attaches only with rearrangement.

(1) Previous paper, This Journal, **79**, 5190 (1957).

(2) Abstracted in part from the Ph.D. Dissertation of A. J. R. Presented at the New York Meeting of the American Chemical Society, September. 1957.

(3) G. F. Hennion, P. A. McCusker, *et al.*, This Journal, **79**, 5190 (1957).

(4) P. A. McCusker, *et al.*, *ibid.*, **79**, 5180, 5183 (1957).

(5) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956).

(6) To our knowledge this is the first recorded instance of a mixed trialkylborane completely stable to disproportionation at so high a temperature. This suggests that disproportionation of mixed boranes is subject to steric hindrance. Further work in this connection is under way.

When one t-butyl group is attached to boron, as by use of trimethyl borate (method b) or by use of preformed t-BuBCl$_2$ (method c), it survives and the subsequent alkylation steps involve rearrangement. It would appear from our results that the presence of even one chlorine atom on boron (as in method g) effectively prevents the attachment of a t-butyl group. This is not the case, however, when one fluorine atom is replaced (method e). The most likely interpretation of these observations is based on steric considerations since the major difference between chlorine and fluorine in these circumstances seems to be a matter of size.

The mechanism of the rearrangement reaction is not known. One suggestion offered in a previous paper[3] may apply to thermal rearrangement (method h) once a t-butyl group is attached to boron. This mechanism cannot explain, however, rearrangement prior to alkylation. It is now proposed, therefore, that the t-butyl group, as a carbanion, may act initially as a reducing agent to yield an intermediate hydroboron compound and isobutylene.

$$>B\text{-}Cl + (CH_3)_3C^- \longrightarrow >B\text{-}H + CH_2\text{=}C(CH_3)_2 + Cl^-$$
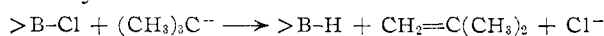
The isobutylene must then recombine rapidly with the hydroboron compound in the expected manner.[5,7]

$$>B\text{-}H + CH_2\text{:}C(CH_3)_2 \longrightarrow B\text{-}CH_2CH(CH_3)_2$$
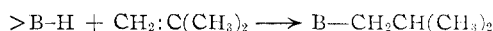
Experimental

t-Butyldichloroborane and diisobutylchloroborane were prepared as previously described. Measurements of physical constants and purification of products were also carried out according to previously described procedures.[4,8]

Diisobutylfluoroborane.—Anhydrous antimony trifluoride, 50.7 g. (0.28 mole), was treated dropwise with 45.7 g. (0.28 mole) of diisobutylchloroborane over a period of 20 minutes in an atmosphere of dry nitrogen. Reaction was immediate and exothermic and refluxing of the reaction mixture soon occurred. When addition of diisobutylchloroborane was complete a rapid distillation gave 50 ml. of distillate between 129 and 145° and 5 ml. of liquid collected in the cold trap (Dry Ice). The 50 ml. of liquid was redistilled *in vacuo* in a 60-cm., glass-helix packed column and gave 36 g. of product (yield 90%) boiling sharply at 49.0° at 52 mm., n^{25}D 1.3816, d^{25} 0.7662. Analysis for fluorine by the method of Booth and Martin[9] gave 13.05% F; calcd. 13.18%.

Preparation of Diisobutyl-t-butylborane (1) from t-Butyl Chloride, Boron Fluoride and Magnesium.—To 97 g. (4 moles) of magnesium covered with anhydrous ether was added with stirring, during a period of seven hours, a mixture of 370 g. (4 moles) of t-butyl chloride and 68 g. (1 mole) of boron fluoride in one liter of ether. After further refluxing for 1 hour, the reaction mixture was hydrolyzed and the aqueous layer extracted with two 300-ml. portions of ether. The ether solution was dried over calcium chloride and the ether removed by distillation. During the reaction and removal of the ether the temperature never exceeded 40°. After removal of the ether the residue was fractionally distilled through a 60-cm., glass-helix packed column at a pressure of 3.3 mm. Ten grams of a forerun boiling between 37 and 49° at 3.3 mm. was collected as well as 12 g. of liquid in a cold trap. Eleven fractions totaling 127 g. (69% yield) were collected at 50–51° at 3.3 mm. Refractive indexes

were measured for each fraction and the densities determined for a number of combined fractions. The refractive indexes varied from 1.4238 to 1.4244 with 4 middle fractions, constituting 60% of the collected material, having n^{25}D 1.4244. These combined middle fractions had d^{25} 0.7428. The corresponding constants for triisobutylborane are n^{25}D 1.4203 and d^{25} 0.7352. The infrared spectrum of diisobutyl-t-butylborane resembled quite closely the spectrum for triisobutylborane but differed in two absorption peaks in the 7 to 9 μ region. Diisobutyl-t-butylborane shows absorption peaks at 8.0 and 8.95 μ while triisobutylborane has absorption peaks at 7.83 and 8.8 μ.

Preparation of Diisobutyl-t-butylborane (2) from t-Butylmagnesium Chloride and Methyl Borate.—To t-butylmagnesium chloride, formed from 4 moles of magnesium and 4 moles of t-butyl chloride in 1500 ml. of ether, was added 0.9 mole of methyl borate during a period of 12 hours. Refluxing was carried out for an additional 12 hours. Following essentially the same procedure as in preparation 1, 26 g. (24% yield) of product boiling at 35–36° at 1 mm., n^{25}D 1.4244, d^{25} 0.7430, was obtained. The infrared spectrum of this product was identical to that from preparation 1.

Preparation of Diisobutyl-t-butylborane (3) from Isobutylmagnesium Bromide and t-Butyldichloroborane.—To 0.9 mole of isobutylmagnesium bromide in 500 ml. of ether was added during a period of five hours 0.5 mole of t-butyldichloroborane. Following procedures described above there was obtained 41 g. (80% yield) of product, b.p. 48.5–49.1° at 2.7 mm., n^{25}D 1.4237, d^{25} 0.7436. The infrared spectrum was identical with that of previous preparations.

Preparation of Diisobutyl-t-butylborane (4) from t-Butylmagnesium Bromide and t-Butyldichloroborane.—To t-butylmagnesium bromide, prepared from 1.1 moles of t-butyl bromide and 1.1 moles of magnesium, in 500 ml. of ether was added during a period of five hours 0.5 mole of t-butyldichloroborane in 300 ml. of ether. There was obtained 47.6 g. (52% yield) of product, b.p. 49.8–51.2° at 3.3 mm., n^{25}D 1.4245, d^{25} 0.7426, and with the same infrared spectrum as for previous preparations.

Preparation of Diisobutyl-t-butylborane (5) from t-Butylmagnesium Chloride and Diisobutylfluoroborane.—From 0.4 mole of t-butylmagnesium chloride and 0.24 mole of diisobutylfluoroborane, in a total volume of 600 ml. of ether, there was obtained a 73% yield of product, b.p. 51–51.2° at 3.2 mm., n^{25}D 1.4240, d^{25} 0.7428, with infrared spectrum the same as for previous preparations.

Reaction of t-Butyl Chloride, Boron Chloride and Magnesium.—By a procedure paralleling that used for the reaction with boron fluoride, t-butyl chloride, boron chloride and magnesium gave a 38% yield of product, b.p. 37–38° at 0.5 mm., n^{25}D 1.4211, d^{25} 0.7340. These constants are close to those for triisobutylborane and very different from the values obtained for diisobutyl-t-butylborane. The infrared spectrum of the product from the boron chloride reaction was identical with that of an authentic sample of triisobutylborane.

Reaction of t-Butylmagnesium Chloride and Diisobutylchloroborane.—The reaction of t-butylmagnesium chloride from 0.9 mole of t-butyl chloride and 0.9 mole of magnesium in 350 ml. of ether with 0.26 mole of diisobutylchloroborane in 500 ml. of ether was carried out in the same manner as for the corresponding reaction using diisobutylfluoroborane. An 83% yield of product, b.p. 52–53° at 3.4 mm., n^{25}D 1.4218, d^{25} 0.7360, and with infrared spectrum identical with that of triisobutylborane, was obtained.

Thermal Isomerization of Diisobutyl-t-butylborane to Triisobutylborane.—Diisobutyl-t-butylborane (36.2 g.) was distilled slowly at atmospheric pressure through a 75-cm., glass-helix packed column and a series of fractions collected. The boiling point rose rapidly to 188° and held constant at that temperature; n^{25}D of the fractions ranged from 1.4200 to 1.4205 and d^{25} was 0.7333. A similar rapid distillation in a simple distilling flask gave a constant boiling fraction at 189°, n^{25}D 1.4213 and d^{25} 0.7384. These constants are close to those of pure triisobutylborane and quite different from those of diisobutyl-t-butylborane.

Oxidation of Diisobutyl-t-butylborane.—A sample from a close boiling fraction of diisobutyl-t-butylborane, prepared from t-butyldichloroborane and isobutylmagnesium bromide, was subjected to a hydrogen peroxide oxidation[5] as follows. A mixture of 19.5 g. (0.107 mole) of diisobutyl-t-butylborane, 6.42 g. (0.16 mole) of sodium hydroxide and 100 ml. of anhydrous ether was treated at ice-bath tempera-

(7) Considerable support for this mechanism is provided by the fact that when the reaction of t-butylmagnesium chloride with boron chloride is carried out in the presence of 1-pentene in excess, isobutylene is evolved with formation of considerable tri-n-amylborane. Experiments by Mr. Joseph Marra; further work in progress.

(8) P. A. McCusker, G. F. Hennion and E. C. Ashby, This Journal, **79**, 5193 (1957).

(9) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 245.

ture with 0.39 mole of hydrogen peroxide, as a 40% solution added slowly over a two-hour period. At the end of the addition period a small amount of solid appeared in the flask and the amount of solid increased during a subsequent four-hour period of vigorous stirring. The ether solution was decanted from the solid and the solid extracted with 60 ml. of ether. There was no apparent water layer. The combined ether solutions were dried over anhydrous potassium carbonate and stored over fresh potassium carbonate for eight hours. Ether was removed through a packed column until the solution was concentrated to 50 ml. The column was then washed down with 10 ml. of ether and the combined residue and wash ether were carefully fractionated through a 7 × 600 mm., stainless steel-coil packed, partial reflux, total take-off electrically heated column. t-Butyl alcohol (7 g.) was collected at 79 to 82°, and identified by its conversion in 87% yield to its 3,5-dinitrobenzoate ester, m.p. 139–140° (lit.[10] 141°). Isobutyl alcohol, 14.5 g., was

collected at 106° and identified by its conversion in 90% yield to its 3,5-dinitrobenzoate ester, m.p. 85–86° (lit.[10] 86°). The total weight of alcohol recovered represents a 90% yield from the oxidation. Isobutyl and t-butyl alcohols were obtained in a molar ratio very close to 2:1.

Samples of diisobutyl-t-butylborane from each of the other four methods of preparation were subjected to the same oxidation procedure and gave in each case isobutyl alcohol and t-butyl alcohol in good yield and in a ratio very close to 2:1.

Acknowledgment.—The work reported in this and previous papers of the series was made possible through the support of the Olin Mathieson Chemical Corporation, Niagara Falls, N. Y.

(10) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.
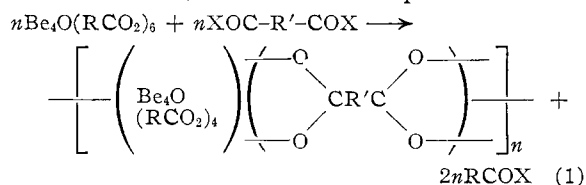
NOTRE DAME, IND.

Polymeric Basic Beryllium Carboxylates[1a]

BY C. S. MARVEL AND MICHAEL M. MARTIN[1b]

Low molecular weight polymers of basic beryllium carboxylates and dibasic acids have been prepared and their properties studied. Also polymers have been prepared by the vinyl polymerization of acrylate-containing basic beryllium carboxylates.

The basic beryllium carboxylates, $Be_4O(RCO_2)_6$, comprise a class of covalent compounds which exhibit remarkable thermal stability, being stable to distillation at atmospheric pressure well above 300°. It was the goal of this research to prepare polymeric materials which contain the basic beryllium carboxylate structure, both as a part of the polymer chain and as a substituent on a polymethylene chain, and to study the thermal and mechanical properties of such polymers. The structure of basic beryllium acetate was assigned by Bragg and Morgan[2] in 1923 as a result of X-ray studies. The structure is made up of a tetrahedron with a beryllium atom at each of the vertices bonded to an oxygen atom at the center. The six edges are occupied by acetate groups. To prepare a linear condensation polymer containing the basic carboxylate structure, it is necessary to replace two of the monobasic carboxyl groups by carboxyl groups of dibasic acids, as illustrated in equation 1.

$$nBe_4O(RCO_2)_6 + nXOC\text{-}R'\text{-}COX \longrightarrow$$

$$2nRCOX \quad (1)$$

The feasibility of this type of condensation polymerization was indicated by Bragg and Morgan[2] and Tanatar and Kurowski,[3] who reported that

if basic beryllium propionate were treated with excess acetyl chloride, carboxyl exchange took place to give basic beryllium triacetate tripropionate, and also that basic beryllium tetrabutyrate diacetate was the exclusive product of a similar reaction involving basic beryllium butyrate and acetyl chloride. These results could not be duplicated since the reaction gave mixtures of the various possible products of carboxyl exchange, but it was verified that carboxyl exchange occurs readily. The original claims that these reactions led to single products seem to rest on insecure evidence, since the structures of such products were assigned solely on the basis of beryllium analysis. The preparation of polymeric basic beryllium carboxylates is not without precedent, since polymeric materials were prepared, though not recognized as such, by Tanatar and Kurowski[3] and Meyer and Mantel,[4] who attempted to prepare basic beryllium succinate, $Be_4O(O_2CCH_2CH_2CO_2)_3$. This material was described as a hard, infusible glass. It seems probable that it was the three dimensional basic succinate polymer rather than the monomeric substance.

With this background in mind, efforts were directed toward developing a method for replacing two carboxylate groups with dibasic acid groups, resulting in the formation of a linear condensation polymer. Polymers so prepared were tested for solubility, viscosity and stability.

Condensation Polymerization.—Polymers were prepared from various combinations of basic beryllium acetate, propionate and benzoate, and the acid chlorides of adipic, sebacic, β-ethyladipic, terephthalic and isophthalic acids. The analytical and viscosity data for these materials appear in Table II in the Experimental part. The general

(1) (a) The work discussed herein was initiated as part of the synthetic rubber research project sponsored by the National Science Foundation and completed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright–Patterson Air Force Base, Ohio; Lt. L. E. Coleman, project engineer. (b) National Science Foundation Fellow 1955–1956.

(2) L. W. Bragg and G. Morgan, *Proc. Roy. Soc. (London)*, **104A**, 437 (1923).

(3) S. Tanatar and E. Kurowski, *J. Rus. Phys. Chem. Soc.*, **39**, 936 (1907); *Chem. Zentr.*, **79I**, 102 (1908).

(4) J. Meyer and E. Mantel, *Z. anorg. u. allgem. Chem.*, **123**, 43 (1922).