[Contribution from the Chemical Laboratories of the University of Notre Dame]

Organoboron Compounds. VI. Isomerization of Boranes Containing Secondary and Tertiary Alkyl Groups[1]

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All attempts to prepare tri-*t*-butylborane by the reaction of *t*-butylmagnesium chloride with boron chloride or with boron fluoride in ether have failed. The reaction with boron chloride yields only triisobutylborane identified by infrared spectrum, physical constants and oxidation to isobutyl alcohol. The product of the boron fluoride reaction, when distilled *in vacuo*, contains a preponderance of isobutyl groups as indicated by physical properties, infrared spectrum and oxidation to a mixture of isobutyl alcohol and *t*-butyl alcohol in which the former predominates. Redistillation of this material at atmospheric pressure completes the rearrangement and thus affords triisobutylborane in high purity. Tri-*sec*-butylborane, prepared in a similar manner from the *sec*-butyl Grignard reagent, could be distilled *in vacuo* without isomerization. Slow fractional distillation at atmospheric pressure resulted in rearrangement to tri-*n*-butylborane. A possible mechanism for these reactions is discussed.

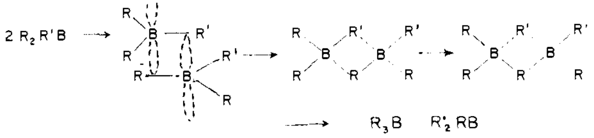
Discussion

Tri-*t*-butylborane[3] and triisobutylborane[4] are mentioned frequently in the literature. We have found that the tributylborane prepared from isobutyl bromide (*via* the Grignard reaction with boron halides) and the tributylborane made from *t*-butyl chloride in the same way are remarkably similar. The borane prepared from isobutyl bromide had the following physical properties: b.p. 188–188.5°, $n^{25}\text{D}$ 1.4203, d^{25} 0.735, and these values were reproducible. The borane prepared from *t*-butyl chloride had properties resembling the above, *e.g.*, in one instance, b.p. 64° at 7 mm., $n^{25}\text{D}$ 1.4215, d^{25} 0.7390, but these values were not reproducible. Considerable variation in refractive index and in density was noted in various preparations, depending on whether prepared from boron chloride or boron fluoride, whether distilled slowly or rapidly, at atmospheric pressure or *in vacuo*, etc. One sample prepared from boron fluoride distilled (once) at 54° (3.2 mm.), $n^{25}\text{D}$ 1.4247, gave by oxidation with alkaline hydrogen peroxide[5] *t*-butyl and isobutyl alcohols in approximately a 1:2 ratio indicating that the product may have been *t*-butyldiisobutylborane. Nevertheless, whenever a product obtained from *t*-butyl chloride was redistilled several times at atmospheric pressure, the physical properties changed and the later fractions had constants, including boiling point, in very good agreement with the values cited above for material prepared from isobutyl bromide. No matter how this material was prepared or handled, the infrared spectra were identical with the spectrum of the product from isobutyl bromide and in excellent agreement with the spectrum of triisobutylborane in the Sadtler file.[6,7]

That the product from *t*-butylmagnesium chloride is indeed chiefly or entirely triisobutylborane after distillation at atmospheric pressure is shown by other facts. Oxidation[5] of a 22-g. sample, b.p. 189.7–190°, $n^{25}\text{D}$ 1.4200, d^{25} 0.7328, gave isobutyl alcohol recovered by distillation in 92% yield. Reaction with boron chloride[8] at 150–160° gave diisobutylchloroborane in 90% yield. Thermal disproportionation of the latter yielded isobutyldichloroborane (identical with an authentic sample prepared from isobutylboron oxide and boron chloride) and triisobutylborane whose infrared spectrum was identical with the starting material. Reaction with boron oxide[9] gave isobutylboron oxide directly in 80% yield.

Experiments with tri-*sec*-butylborane indicate that this compound may be distilled *in vacuo* without isomerization while slow fractional distillation at atmospheric pressure results in conversion of tri-*n*-butylborane. Similar results have been noted with triisopropylborane. It is now clear that secondary and tertiary alkyl groups attached to boron isomerize thermally to the corresponding primary alkyl groups and that the *t*-butyl group is particularly sensitive to such rearrangement.

While there is no evidence at present bearing on the mechanisms of these rearrangements, comment may be in order if only to stimulate work in this field. It should be mentioned at the outset that unsymmetrical trialkylboranes are very sensitive to disproportionation, presumably *via* a bridge-bonded dimer.[10] We propose that such dimers form by way of a transition state which involves the overlap of vacant p-orbitals of the boron atoms with σ-orbitals of C–B bonds as



If the alkyl groups are bulky, there must be steric interference to the formation of the transition state

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[1] Presented at the Atlantic City Meeting of the American Chemical Society, September, 1956. Previous paper, This Journal, **79**, 5188 (1957).

[2] Abstracted in part from the Ph.D. Dissertations of E. C. A. and A. J. R.

[3] E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931); H. C. Brown, This Journal, **67**, 374 (1945); D. T. Hurd, *ibid.*, **70**, 2053 (1948).

[4] E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921); D. T. Hurd, This Journal, **70**, 2053 (1948).

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

[6] Samuel P. Sadtler and Son, Inc., Philadelphia, Pa.

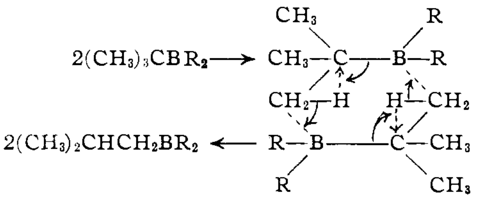
[7] Since many samples of triisobutylborane made from *t*-butylmagnesium chloride were admittedly not pure after one distillation, it must be concluded that infrared absorption (neat, Baird double beam instrument, NaCl optics) may not be capable of detecting a small percentage of *t*-butyl groups in this material.

[8] This reaction is discussed further in the subsequent paper in this series, This Journal, **79**, 5192 (1957).

[9] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **267**, 1 (1951), reported that the reaction of trimethylborane with anhydrous boric oxide at 300–330° under pressure yields methylboron oxide in quantitative yield. We have observed that the higher trialkylboranes react in the same way at reflux temperature without pressure.

[10] T. D. Parsons and D. M. Ritter, This Journal, **76**, 1710 (1954).

as pictured, permitting overlap of p-orbitals of boron with σ-C–H orbitals on the β-carbon atoms



It is imagined that a concerted mechanism permits detachment of a *t*-butyl group from a boron atom while isomerization and bonding to another boron atom occur within a quasi-six-membered ring as shown. Further work is in progress.

Experimental

All manipulations, including distillations, were carried out in carefully dried equipment and in an atmosphere of dry nitrogen.

Preparation of Triisobutylborane.—Yields of 60–70% were obtained from isobutyl bromide, magnesium turnings and either boron fluoride or boron chloride, using procedures substantially as described in the literature.[4,11] Fractional distillation through a 60-cm. glass-helix-packed column gave product, b.p. 68° at 7 mm., 188–188.5° at 745–750 mm.; $n^{25}\mathrm{D}$ 1.4203; d^{25} 0.7352. The $n^{25}\mathrm{D}$, d^{25} and infrared spectrum were not changed by redistillation.

Reaction of *t*-Butylmagnesium Chloride with Boron Fluoride.—The Grignard reagent was prepared from 495 g. (5.3 moles) of *t*-butyl chloride and 130 g. (5.3 moles) of magnesium turnings in one liter of ether. A solution of 87.1 g. (1.3 moles) of boron fluoride in 325 ml. of ether was then added dropwise with stirring (8 hr.). Excess Grignard reagent was decomposed and the inorganic salts dissolved by addition of 2 liters of 2% HCl. The aqueous layer was extracted with two 500-ml. portions of ether, and the combined ethereal layers were dried and distilled. The first distillation through a 60-cm. packed column gave three fractions (not weighed in this instance), b.p. 42–43° at 1 mm., $n^{25}\mathrm{D}$ 1.4231. Redistillation at 0.7 mm. did not change the refractive index appreciably as shown by the fact that seven fractions were collected, $n^{25}\mathrm{D}$ ranging from 1.4230 to 1.4236. The seventh fraction had d^{25} 0.7386. The pressure was then changed to 7 mm. and distillation was continued. Three additional fractions were collected at 65.8–66.1° (7 mm.), $n^{25}\mathrm{D}$ 1.4230–1.4235. Since redistillation *in vacuo* changed the physical constants only slightly, a final distillation was carried out at atmospheric pressure and gave three fractions, b.p. 189.2–190°, $n^{25}\mathrm{D}$ 1.4192–1.4203, d^{25} (third fraction) 0.7328. The infrared spectrum was identical with the spectrum of triisobutylborane.[6]

This experiment was repeated many times with various modifications, and yields of 50–60% based on boron halide were obtained consistently.[12]

Preparation of Tri-*sec*-butylborane.—Using the procedure cited above tri-*sec*-butylborane was prepared from 97.2 g. (4 moles) of magnesium turnings, 548 g. (4 moles) of *sec*-butyl bromide and 70 g. (1.03 moles) of boron fluoride previously absorbed in 500 ml. of anhydrous ether. Two distillations through a 60-cm. column gave product, b.p. 59.7–60° at 2.5 mm., $n^{25}\mathrm{D}$ 1.4349, d^{25} 0.7658, weight 91 g. The infrared spectrum was in excellent agreement with the published spectrum.[6]

Isomerization of Tri-*sec*-butylborane.—Thirty-five ml. of tri-*sec*-butylborane, $n^{25}\mathrm{D}$ 1.4349, contained in a 50-ml. round-bottom flask equipped with a reflux condenser and provisions for maintaining a nitrogen atmosphere, was heated under total reflux. After 20 hr. of heating $n^{25}\mathrm{D}$ was 1.4301 and after 48 hr., 1.4298. The product was then distilled into three fractions: (1) b.p. 200–212°, $n^{25}\mathrm{D}$ 1.4248 (3 ml.); (2) b.p. 212–213°, $n^{25}\mathrm{D}$ 1.4259 (10 ml.); (3) b.p. 213–214°, $n^{25}\mathrm{D}$ 1.4262 (18 ml.). The physical constants and the infrared spectrum of fraction 3 were in excellent agreement with those for tri-*n*-butylborane prepared from *n*-butyl bromide.

Oxidation of Tributylborane Prepared from *tert*-Butylmagnesium Chloride.—Twenty-two grams (0.12 mole) of tributylborane (prepared from *tert*-butylmagnesium chloride and distilled twice at atmospheric pressure) was dissolved in 150 ml. of ethanol containing 14.4 g. (0.36 mole) of sodium hydroxide. Hydrogen peroxide (37.4 g. of 30% solution) was added dropwise with stirring. The mixture was extracted with 100 ml. of ether and then with two 20-ml. portions. The combined ethereal extract was dried over anhydrous potassium carbonate and then distilled through a 60-cm. column. Isobutyl alcohol, b.p. 106–107°, $n^{25}\mathrm{D}$ 1.3990, was recovered in 92% yield (24 g.). The 3,5-dinitrobenzoate had m.p. 85° (lit.[13] 86°).

The procedure described above was used for the oxidation of samples of tributylborane prepared from boron fluoride and *t*-butylmagnesium chloride and distilled only *in vacuo*. Isobutyl and *t*-butyl alcohols were recovered by precise fractional distillation and were identified through their 3,5-dinitrobenzoates. The *t*-butyl alcohol never exceeded one-third of the recovered alcohol mixture. The *t*-butyl alcohol was distilled as its water azeotrope, b.p. 79.9–80.0°. Its 3,5-dinitrobenzoate had m.p. 140–141° (lit.[13] 141°).

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[11] J. R. Johnson, *et al.*, THIS JOURNAL, **60**, 115 (1938).

[12] Since tri-*t*-butylborane (if capable of existence and amenable to distillation) should distil ahead of triisobutylborane, lower boiling fractions were always examined by infrared. In no instance could any material of narrow boiling range originating with boron chloride be obtained whose infrared spectrum differed significantly from that of triisobutylborane. It is recognized from consideration of physical constants and behavior on oxidation that mixed *t*-butylisobutylboranes may be formed in this reaction when boron fluoride is used and survive distillation *in vacuo*. Hence the 50–60% yields claimed do not refer specifically to triisobutylborane unless the product is distilled several times at atmospheric pressure.

[13] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 26.