

tetrahydrofuran. The reaction flask was placed in ice-water and 37 ml. (containing 0.015 mole) of the methyl-diphenylsilyllithium solution was added dropwise within 10 minutes. The dark color of the silyllithium compound was discharged immediately on addition to the solution of the chlorosilane. A slight deepening in color of the reaction mixture was noticed during the addition of the last few milliliters of silyllithium reagent. This was evidence for the slight excess of silyllithium present. Color Test I<sup>13</sup> was positive immediately after addition, but stirring for 1 hour gave a negative Color Test. The solution was allowed to stand for 16 hours and then poured into 100 ml. of 1.0 N hydrochloric acid. The aqueous layer was extracted with ether and the organic layers were combined and dried over magnesium sulfate. The solvents were removed and 25 ml. of petroleum ether (b.p. 60–70°) was added. A precipitate separated which on recrystallization from cyclohexane–petroleum ether (b.p. 60–70°; 1:1) yielded 1.5 g. (29%) of a white solid melting at 216–217°. Further recrystallization from a 2:1 mixture of acetone–chloroform gave a product melting at 222–223°. This solid was shown to be identical with the samples prepared in A and B above. The identity was established by the method of mixed melting points and superimposability of their infrared spectra.

Anal. Calcd. for C<sub>30</sub>H<sub>48</sub>Si<sub>4</sub>: C, 79.09; H, 6.11; Si, 14.8; hydrogen value, 89.0 (ml. at S.T.P./g. of compd.).

(13) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Found: C, 79.16, 79.11; H, 6.41, 6.24; Si, 14.85, 14.72; hydrogen value, 89.8, 88.5 (the hydrogen values given in the preliminary communication<sup>1</sup> were not corrected to S.T.P.).

**Preparation of Decaphenyltetrasilane.**—A solution of 0.02 mole of phenyllithium in 20 ml. of diethyl ether was added dropwise to 5.7 g. (0.0072 mole) of 1,4-dichlorooctaphenyltetrasilane suspended in 30 ml. of diethyl ether. The reaction mixture was stirred for 24 hours then hydrolyzed by addition to 300 ml. of 0.1 N hydrochloric acid. Ether was added and the insoluble material was filtered off to yield 2.8 g. (44%) of a product, m.p. 280–315°. After recrystallization from benzene–ethanol, ethyl acetate–ethanol, and benzene–petroleum ether (b.p. 60–70°) the product melted at 358–360°. A mixed melting point with an authentic sample of decaphenyltetrasilane<sup>9</sup> was not depressed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

## Organoboron Compounds. XIII. Steric Inhibition of Disproportionation and Isomerization Mechanism Studies on Unsymmetrical Trialkylboranes<sup>1,2</sup>

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Steric inhibition of disproportionation by *t*-butyl groups in unsymmetrical trialkylboranes is shown to be general while isobutyl groups do not inhibit disproportionation. Thermal isomerization of *t*-butyl to isobutyl groups is followed by rapid disproportionation. Isolation of isobutylene from the reaction of *t*-butylmagnesium chloride with boron fluoride and the effect of excess foreign olefin on the reaction indicate that isomerization occurs as an essential feature of the Grignard alkylation. Alkylation isomerization appears to proceed through reduction by the Grignard reagent and recombination of the olefin and alkyl boron hydride formed. Thermal isomerization may follow a different course. Two *t*-butyl groups survive alkylation isomerization when the third group is a normal alkyl group. When the third group is  $\beta$ -branched only one *t*-butyl group is retained, the second being isomerized to isobutyl. Excess olefin has no effect on the reaction of isobutylmagnesium bromide with boron fluoride. A trialkylborane with one *t*-butyl group exchanges alkyl groups with a Grignard reagent; when two *t*-butyl groups are present no exchange occurs.

The first reported attempt<sup>3</sup> to prepare an unsymmetrical triorganoborane resulted in the isolation of the symmetrical compounds only. In other more recent reports<sup>4–6</sup> the preparation of a number of unsymmetrical trialkylboranes has been described, but the compounds apparently were not subjected to efficient fractional distillation. When careful fractional distillation of the unsymmetrical trialkylboranes was attempted,<sup>7</sup> complete disproportionation to the symmetrical compounds took place.

In this Laboratory<sup>8</sup> it has been observed that *t*-butyldiisobutylborane could be obtained and purified by thorough fractional distillation with no disproportionation. This result suggested that a *t*-butyl group attached to boron could offer steric interference to the disproportionation mechanism involving a bridged dimer.<sup>9,10</sup> Further studies bearing on the generality of steric inhibition of the disproportionation reaction have now been carried out.

Reaction of *t*-butylmagnesium chloride with boron compounds results in partial or complete isomerization of the *t*-butyl groups to isobutyl groups at low temperature. Results of some studies bearing on the mechanism previously proposed for low temperature isomerization during the preparative reaction are reported herein. Pre-

(1) Previous paper, P. A. McCusker and S. M. L. Kilzer, *J. Am. Chem. Soc.*, **82**, 372 (1960).

(2) Contribution from the Radiation Laboratory operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38. From the doctoral dissertation of Joseph V. Marra, 1959.

(3) E. Krause and P. Nobbe, *Ber.*, **64B**, 2112 (1931).

(4) R. W. Auten and C. W. Kraus, *J. Am. Chem. Soc.*, **74**, 3398 (1952).

(5) J. C. Perrine and R. N. Keller, *ibid.*, **80**, 1823 (1958).

(6) S. L. Clark and J. R. Jones, Abstracts 133rd Meeting, American Chemical Society, April, 1958, p. 34L.

(7) B. M. Mikhailov and T. A. Shchegoleva, *Doklady Akad. Nauk S.S.S.R.*, **108**, 481 (1956).

(8) G. F. Hennion, P. A. McCusker and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958).

(9) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

(10) T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **76**, 1714 (1954); **79**, 5091 (1957).

liminary reports<sup>11</sup> of some of this work have been given in previous communications.

### Experimental

Distillations and all manipulations were carried out in carefully dried equipment in an atmosphere of dry nitrogen. Organoboron compounds used as reagents were prepared and measurements made as described in previous papers of this series. The olefins used were obtained from Phillips Petroleum Co.

Analyses for boron were done according to a slight modification of the procedure described by Mikhailov and Shchegoleva.<sup>7</sup> Alkaline hydrogen peroxide oxidation<sup>12</sup> of the trialkylboranes in ether solution was used for alkyl group identification. The alcohols formed were either separated by fractional distillation and characterized or the composition of the alcohol mixture determined by vapor phase chromatography. Olefins were identified by conversion to their dibromides which were characterized by b.p., density and index of refraction. Molar refractions were calculated from Denbigh's values<sup>13</sup> and a boron-carbon value of 1.93.

**Preparation of *t*-Butyl-di-*n*-propylborane.**—To 1.7 moles of *n*-propylmagnesium bromide in 500 ml. of ether was added, during a period of 2 hours, 0.8 mole of *t*-butyldichloroborane in 350 ml. of ether. The mixture was refluxed for 3 hours, hydrolyzed and the aqueous layer extracted with ether. The ether solution was dried with calcium chloride and most of the ether distilled at atmospheric pressure. The last portions of the ether were removed under vacuum to keep the temperature of the mixture below 50°. The residue was fractionally distilled in a 1.3 × 60-cm. glass-helix packed column to give 93 g. (75% yield) of *t*-butyl-di-*n*-propylborane, b.p. 44.5–45.0° (6.2 mm.), *n*<sub>D</sub><sup>25</sup> 1.4187, *d*<sub>4</sub><sup>25</sup> 0.7285; *M*R<sub>D</sub> calcd. 53.45, obsd. 53.35. *Anal.* Calcd. for C<sub>10</sub>H<sub>22</sub>B: B 7.02. Found: B, 6.97. Oxidation produced *t*-butyl alcohol and *n*-propyl alcohol in a molar ratio of 2.1 to 1. Identity of the alcohols was confirmed by conversion in high yield to their 3,5-dinitrobenzoates.

**Stability of *t*-Butyl-di-*n*-propylborane.**—A sample of *t*-butyl-di-*n*-propylborane was allowed to stand in diffuse daylight for 6 months and redistilled. Efficient fractional distillation gave an 82% recovery of material with essentially the same physical constants as the original material.

**Preparation of *t*-Butyl-di-*n*-amylborane.**—This compound was prepared by a modification of the procedure used for the preparation of *t*-butyl-di-*n*-propylborane. An excess of *t*-butyldichloroborane and a lower temperature, -70°, were employed to determine whether the partially alkylated compound, *t*-butyl-*n*-amylchloroborane, could be obtained. After the slow addition of 0.44 mole of *n*-amylmagnesium bromide in 275 ml. of ether to 0.43 mole of *t*-butyldichloroborane in 300 ml. of ether, the mixture was allowed to come to room temperature and stirred for an additional 20 hours. The reaction mixture was filtered from precipitated salts in an atmosphere of nitrogen. A rapid vacuum distillation of the ether solution was carried out to separate the ether solution from dissolved magnesium salts. Fractional distillation resulted in the recovery of a low boiling fraction, at 43.5–44.0° (55 mm.), *n*<sub>D</sub><sup>25</sup> 1.3970, *d*<sub>4</sub><sup>25</sup> 0.8748, identified as *t*-butylethoxychloroborane; *M*R<sub>D</sub> calcd. 40.74, obsd. 40.86. *Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>BClO: Cl, 23.8. Found: Cl, 23.6. The major fraction of the distillation, *t*-butyl-di-*n*-amylborane, 33.1 g. (72% yield), was collected at 47.5° (0.14 mm.), *n*<sub>D</sub><sup>25</sup> 1.4333, *d*<sub>4</sub><sup>25</sup> 0.7585; *M*R<sub>D</sub> calcd. 71.93, obsd. 72.06. *Anal.* Calcd. for C<sub>14</sub>H<sub>31</sub>B: B, 5.15. Found: B, 5.26.

**Preparation of *t*-Butylisobutyl-*n*-amylborane. I. From *n*-Amyldifluoroborane.**—To 1.3 moles of *t*-butylmagnesium chloride in 700 ml. of ether was added, over a 3-hr. period, 0.56 mole of *n*-amylidifluoroborane in 600 ml. of ether. The reaction mixture was cooled so that the temperature never exceeded 30°. Refluxing and stirring was continued for 18 hr. The reaction mixture was then hydrolyzed and worked up as in previous preparations. Fractional distillation yielded 53.9 g. of product, 49% yield, b.p. 44.0° (0.6 mm.), *n*<sub>D</sub><sup>25</sup> 1.4296, *d*<sub>4</sub><sup>25</sup> 0.7506; *M*R<sub>D</sub> calcd. 67.30,

obsd. 67.48. *Anal.* Calcd. for C<sub>13</sub>H<sub>29</sub>B: B, 5.52. Found: B, 5.56. Oxidation gave *t*-butyl alcohol, isobutyl alcohol and *n*-amyl alcohol in a 1.0:1.1:1.0 ratio.

**II. From *t*-Butyl-di-*n*-amylborane and Isobutylmagnesium Bromide.**—To 0.12 mole of isobutylmagnesium bromide in 130 ml. of ether was added 0.1 mole of *t*-butyl-di-*n*-amylborane. The solution was refluxed for 4 hr., worked up as above and distilled through a 0.7 × 33.0-cm. Heligrid-packed column. A 12% yield of product, b.p. 44.0° (0.5 mm.), *n*<sub>D</sub><sup>25</sup> 1.4291, *d*<sub>4</sub><sup>25</sup> 0.7497, was obtained. The physical constants were found to be in substantial agreement with those of *t*-butylisobutyl-*n*-amylborane, prepared as described above, and the infrared spectra of the two products were practically identical.

**Attempts to Isolate Diisobutyl-*n*-amylborane and Diisobutyl-*n*-hexylborane.**—Under exactly the same conditions as used for the preparation and isolation of unsymmetrical trialkylboranes containing *t*-butyl groups, the reaction of diisobutylchloroborane and *n*-amylmagnesium bromide gave two close boiling fractions consisting of triisobutylborane and tri-*n*-amylborane with a small wide-boiling intermediate fraction. A similar reaction using diisobutylchloroborane and *n*-hexylmagnesium chloride also gave only the symmetrical trialkylboranes.

**Evidence for Olefin Intermediate in the Reaction of *t*-Butyl Grignard with Boron Fluoride.**—To 3.4 moles of *t*-butylmagnesium chloride in 1800 ml. of ether was added 1.03 moles of boron fluoride in 400 ml. of ether. During the addition 19.0 g. of liquid was condensed in a cold trap. From the trap material 11.0 g. was volatilized and absorbed in bromine to yield 15.3 g. of isobutylene dibromide. This represents 0.07 mole of isobutylene and corresponds to 2.5% of the amount of *t*-butylmagnesium chloride originally present.

**Preparation of Di-*t*-butyl-*n*-butylborane.**—To 1800 ml. of ether containing 3.36 moles of *t*-butylmagnesium chloride and 4.15 moles of 1-butene was added during 2 hr. 1.01 moles of boron fluoride in 450 ml. of ether. The temperature of the reaction mixture was maintained near 20°. During the course of the reaction low-boiling materials were condensed in a solid-carbon dioxide trap and periodically returned to the reaction flask. Stirring was continued for an additional 2-hour period and the mixture let stand overnight. Fractional distillation, as in previous preparations, gave 125 g. of di-*t*-butyl-*n*-butylborane (55% yield), b.p. 47.5–48.9° (1.7 mm.). A 30-g. portion of the distillate was treated with 10% sodium hydroxide for the removal of oxide impurities and redistilled to give a sample, b.p. 47.5° (1.7 mm.), *n*<sub>D</sub><sup>25</sup> 1.4373, *d*<sub>4</sub><sup>25</sup> 0.7608; *M*R<sub>D</sub> calcd. 62.67, obsd. 62.76. *Anal.* Calcd. for C<sub>12</sub>H<sub>27</sub>B: B, 5.94. Found: B, 6.08. Oxidation gave *t*-butyl alcohol and *n*-butyl alcohol in a ratio of 2:1.

**Preparation of Di-*t*-butyl-*n*-amylborane.**—To 1800 ml. of ether containing 3.16 moles of *t*-butylmagnesium chloride and 3.5 moles of 1-pentene was added over a period of 2 hr. 0.97 mole of boron fluoride etherate in 400 ml. of ether. The mixture was stirred for an additional 20 hr. During the course of the reaction 89 g. of liquid was condensed in the solid-carbon dioxide trap. The condensate was fractionally distilled and the portion distilling below room temperature was converted to its dibromide and thereby identified as isobutylene. The weight of dibromide obtained showed that 24 g. of isobutylene had been liberated. The reaction mixture was treated as in previous preparations and gave a 39% yield of di-*t*-butyl-*n*-amylborane, b.p. 44.8–45.0° (0.57 mm.), *n*<sub>D</sub><sup>25</sup> 1.4397, *d*<sub>4</sub><sup>25</sup> 0.7668; *M*R<sub>D</sub> calcd. 67.30, obsd. 67.38. *Anal.* Calcd. for C<sub>13</sub>H<sub>29</sub>B: B, 5.52. Found: B, 5.56. Oxidation of the product gave *t*-butyl alcohol and *n*-amyl alcohol in a ratio of 1.9 to 1.

**Reaction of *t*-Butylmagnesium Chloride with Boron Fluoride in the Presence of Excess Isobutylene.**—Into a solution containing 2.48 moles of *t*-butylmagnesium chloride in 1800 ml. of ether at 15°, was passed a rapid stream of isobutylene for a period of 1 hour with complete absorption of the isobutylene. With the temperature of the mixture held at 15°, 0.75 mole of boron fluoride in 350 ml. of ether was added slowly. When one-third of the boron fluoride had been added, the temperature of the reaction mixture was allowed to rise to 20° and large amounts of gas were evolved and collected in a cold trap. During the remainder of the reaction period low-boiling condensate was intermittently collected and returned to the reaction flask to maintain at all times a large excess of isobutylene. The reaction mix-

(11) G. F. Hennion, P. A. McCusker and J. V. Marra, *J. Am. Chem. Soc.*, **80**, 3481 (1958); **81**, 1768 (1959).

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

(13) G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

ture was stirred for 2.5 hr. at 5° after addition of boron fluoride was completed. On warming to 20°, 200 g. of isobutylene was evolved and collected in the cold trap. Hydrolysis resulted in an additional liberation of 140 g. of isobutylene. From the separated, dried ether layer there was obtained 73.7 g. (54% yield) of *t*-butyldiisobutylborane, identified by refractive index, density and infrared spectra in agreement with those of previously identified *t*-butyldiisobutylborane.<sup>8</sup> There was no trace of the possible lower boiling product di-*t*-butylisobutylborane.

**Reaction of *t*-Butylmagnesium Chloride with Boron Fluoride in the Presence of Excess 2-Methyl-1-butene.**—Following the procedure described immediately above, 3.6 moles of *t*-butylmagnesium chloride was treated with 1.1 moles of boron fluoride in the presence of a large excess of 2-methyl-1-butene. During the addition of boron fluoride, 121 g. of condensate was collected in the cold trap. The condensate was found to contain about 50% isobutylene, representing slightly more than one mole of liberated olefin. The reaction mixture was let stand for 14 hr. and stirred for an additional 4 hr. Hydrolysis was carried out as described above and after removal of ether the residue was treated with 10% sodium hydroxide to remove oxide impurities. Fractional distillation yielded a series of fractions ranging in boiling point from 38° at 1 mm. to 63° at 3 mm. Recombination of two of the lower boiling fractions which might be expected to contain di-*t*-butylamylborane and redistillation did not give a sharp boiling fraction characteristic of a single compound. The infrared spectrum of this fraction was, however, very similar to that of *t*-butyldiisobutylborane and very different from the spectrum of di-*t*-butyl-*n*-butylborane. The boiling point, index of refraction and density were in good agreement with the values expected for a dibutylamylborane having only one *t*-butyl group. Oxidation with alkaline hydrogen peroxide gave an alcohol mixture having less than 33% *t*-butyl alcohol along with isobutyl alcohol and a higher alcohol assumed to be 2-methylbutanol-1.

**Attempted Reaction between Di-*t*-butyl-*n*-butylborane and Isobutylmagnesium Bromide.**—In a further attempt to prepare di-*t*-butylisobutylborane, there was added to 0.21 mole of isobutylmagnesium bromide in 200 ml. of ether 0.18 mole of di-*t*-butyl-*n*-butylborane. The mixture was refluxed for 6 hr. and let stand for an additional 46 hr.

When the mixture was hydrolyzed and treated as above no trace of di-*t*-butylisobutylborane was found. Unchanged di-*t*-butyl-*n*-butylborane was recovered in 81% yield.

**Reaction between Isobutylmagnesium Bromide and Boron Fluoride in the Presence of 1-Pentene.**—Following exactly the same procedure as used for the reaction of *t*-butylmagnesium chloride with boron fluoride in the presence of olefin, 0.95 mole of isobutylmagnesium bromide was treated with 0.30 mole of boron fluoride in the presence of 1.05 moles of 1-pentene. During the reaction 3.5 g. of liquid condensed in the cold trap and was shown to consist of ether and 1-pentene only. There was no trace of evolved isobutylene. From the reaction mixture there was obtained an 80% yield of triisobutylborane. No higher boiling fraction was observed. Thus there was no evidence of the presence of any product containing amyl groups attached to boron.

**Isomerization and Disproportionation of *t*-Butylisobutyl-*n*-amylborane and Di-*t*-Butyl-*n*-amylborane.**—A 6.5-g. sample of *t*-butylisobutyl-*n*-amylborane was heated at its reflux temperature, 205°, for 20 minutes, cooled rapidly to 25° and physical constants taken on the product. The density, refractive index and infrared spectrum were found to be significantly different from those of the original compound. A synthetic mixture containing tri-*n*-amylborane and triisobutylborane in a 1:2 molar ratio was found to have a refractive index and density very close to those of the product of the thermal treatment of *t*-butylisobutyl-*n*-amylborane. The infrared spectra of the synthetic mixture and the product of the thermal treatment were indistinguishable.

A 10.0-g. sample of di-*t*-butyl-*n*-amylborane was similarly heated at 205° for 15 minutes and again it was observed that significant changes had occurred in the refractive index, density and infrared spectrum. The density and refractive index of the product of the thermal treatment of di-*t*-butyl-*n*-amylborane were very similar to those of the synthetic mixture of tri-*n*-amylborane and triisobutylborane. The infrared spectra of the thermal product and the synthetic mixture were indistinguishable. Thermal isomerization of both unsymmetrical trialkylboranes evidently gives rise to the same mixture of symmetrical trialkylboranes.

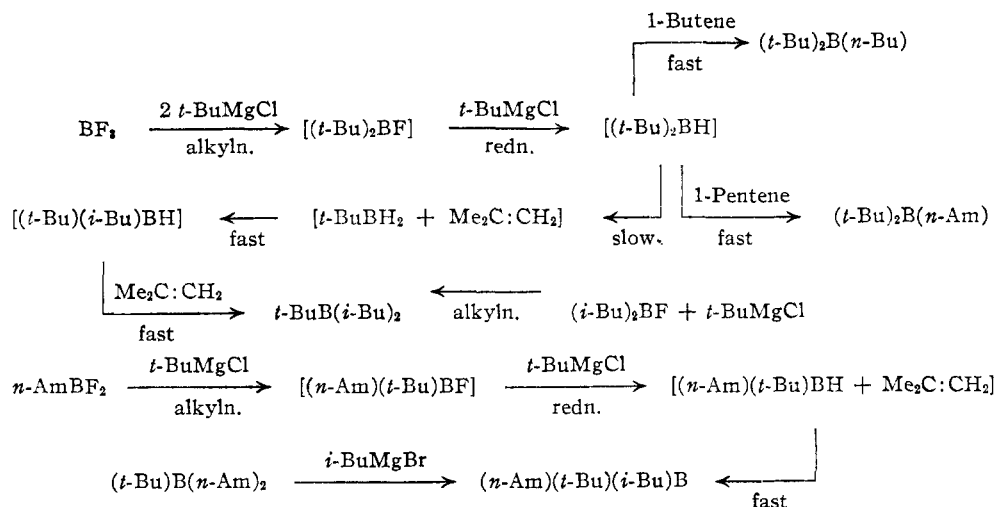
## Discussion

The complete resistance to disproportionation exhibited by *t*-butyldiisobutylborane, under conditions of efficient fractional distillation and at temperatures below which thermal isomerization of *t*-butyl groups occurs, was interpreted<sup>8</sup> as resulting from steric interference with the formation of the dimeric intermediate. Whether this interference was due solely to the *t*-butyl group, or was the combined effect of the *t*-butyl group and the two isobutyl groups, was not clear from the single example available. To obtain further information on this point the reactions of *t*-butyl-dichloroborane with *n*-propyl and *n*-butyl Grignard reagents were carried out and the resulting products subjected to fractional distillation *in vacuo* under the same conditions as used for *t*-butyldiisobutylborane. The *t*-butyldi-*n*-propylborane and *t*-butyldi-*n*-butylborane thus obtained proved to be completely resistant to disproportionation. It may be concluded that the presence of a single *t*-butyl group is sufficient to prevent disproportionation. The completeness of this steric interference with disproportionation is indicated by the fact that a sample of *t*-butyldi-*n*-propylborane after standing for 6 months at room temperature in diffuse daylight was recovered completely unchanged on redistillation.

That steric inhibition of disproportionation occurs when the alkyl group is  $\alpha$ -branched, but not when the alkyl group is  $\beta$ -branched, was shown by the reactions of diisobutylchloroborane with *n*-amylmagnesium bromide and with *n*-hexylmagnesium bromide. The immediate products of these reactions would be the unsymmetrical trialkylboranes, diisobutyl-*n*-amylborane and diisobutyl-*n*-hexylborane. When the products of these reactions were worked up under the same conditions as used for the isolation of di-*t*-butyl-*n*-alkylboranes, no unsymmetrical trialkylboranes were found. Instead high yields of the two symmetrical disproportionation products were obtained.

The formation of *t*-butyldiisobutylborane from the reaction of boron fluoride with *t*-butylmagnesium chloride requires that isomerization of two of the three *t*-butyl groups occur during the synthesis. Since it has been shown that reaction of diisobutylfluoroborane with *t*-butylmagnesium chloride also results in the formation of *t*-butyldiisobutylborane, it appears that alkylation by a *t*-butyl group is not interfered with by the presence of two primary alkyl groups in a dialkylfluoroborane while the presence of one *t*-butyl group induces isomerization of the second entering alkyl group. Accordingly the reaction of a *n*-alkyldifluoroborane with *t*-butylmagnesium chloride should result in the placement of one *t*-butyl on the boron atom, but the second alkylation step should occur with isomerization of the *t*-butyl to an isobutyl group. Thus the reaction of amylidifluoroborane with *t*-butylmagnesium chloride should produce *t*-butylisobutyl-*n*-amylborane. This completely unsymmetrical trialkylborane was obtained in this way in good yield and proved to be completely resistant to disproportionation.

Since *t*-butylisobutyl-*n*-amylborane is a new type of trialkylborane, confirmation of its identity was



sought through its preparation by a different type of reaction. The exchange reaction between a Grignard reagent and a trialkylborane, first reported by Clark and Jones,<sup>6</sup> was used. Isobutylmagnesium bromide was found to exchange one alkyl group with *t*-butyldi-*n*-amylborane resulting in the formation of *t*-butylisobutyl-*n*-amylborane in 12% yield. The exchange reaction also indicates that the presence of one *t*-butyl group on a trialkylborane does not interfere sterically in reaction of a Grignard reagent with a trialkylborane.

A mechanism previously suggested<sup>8</sup> for the isomerization of *t*-butyl to isobutyl groups during the reaction of *t*-butylmagnesium chloride with boron fluoride involves the reducing reaction of the sterically hindered Grignard reagent on the sterically hindered alkylfluoroborane, resulting in the formation of alkyl boron hydride and olefin. Recombination of the alkyl boron hydride and olefin occurs so as to form the isomerized product. Such reducing action is known to occur when sterically hindered ketones react with sterically hindered Grignards. In the more directly comparable case it has been shown that sterically hindered organosilicon halides, such as triphenylchlorosilane, react with *t*-butylmagnesium chloride to form triphenylsilane and the corresponding olefin.<sup>14</sup>

Support for the proposed mechanism for the isomerization of *t*-butyl groups during the alkylation reaction has been obtained from the observation that isobutylene was evolved in small amounts when *t*-butylmagnesium chloride and boron fluoride react. Further evidence for the mechanism was obtained from a study of the reactions of *t*-butylmagnesium chloride and boron fluoride in the presence of various olefins in excess. If, as proposed, the mechanism involves the formation of alkyl boron hydride and olefin followed by recombination, excess foreign olefin would be expected to enter into reaction displacing another olefin and forming an unsymmetrical trialkylborane. In the presence of excess foreign olefin, incorporation of the foreign olefin into the trialkylborane occurred readily and isobutylene was evolved in large quantity. In this manner several unsymmetrical

trialkylboranes were produced in high yield. The type of trialkylborane formed, however, was found to be different when a normal terminal olefin was used and when a branched olefin was used. In the case of the normal terminal olefins a hitherto unreported type of trialkylborane was formed in which two *t*-butyl groups were present on the boron. In this way di-*t*-butyl-*n*-butyl- and di-*t*-butyl-*n*-amylborane were obtained. When, however, the olefin used was branched, as in the case of isobutylene or 2-methyl-1-butene, only one *t*-butyl group survived the alkylation reaction while the second was isomerized to an isobutyl group. From the reaction of *t*-butylmagnesium chloride with boron fluoride in the presence of excess isobutylene the only product isolated was triisobutylborane. When 2-methyl-1-butene was used as the excess olefin, the products were triisobutylborane and a dibutylamylborane having one *t*-butyl group and one isobutyl group.

In the case of the reactions in the presence of normal terminal olefins, it must be assumed that the first two alkylation steps occur by simple replacement of fluorine by *t*-butyl groups to form di-*t*-butylfluoroborane. This sterically hindered intermediate must then react with *t*-butylmagnesium chloride by reduction and isobutylene elimination to form di-*t*-butylboron hydride. The normal terminal olefin present in excess and di-*t*-butylboron hydride then combine to form di-*t*-butyl-*n*-alkylborane. Steric interference with the normal alkylation reaction apparently does not occur until two *t*-butyl groups are present on the boron, and reduction occurs only at the third step in the reaction.

To reconcile the different results obtained with the two different types of olefins, it must be assumed that di-*t*-butylboron hydride is formed in each case but that it is able to add rapidly to a normal terminal olefin but can add only slowly or not at all to a branched olefin. In the absence of rapid addition to olefin, di-*t*-butyl boron hydride is believed to eliminate a molecule of isobutylene to form *t*-butyl boron hydride, *t*-C<sub>4</sub>H<sub>9</sub>BH<sub>2</sub>. Subsequent stepwise addition of two molecules of isobutylene results in the formation of *t*-butyldiisobutylborane. A similar sequence of steps is ade-

(14) M. C. Harvey, W. H. Nebergall and J. A. Peake, *J. Am. Chem. Soc.*, **79**, 2762 (1957).

quate to explain the results obtained with 2-methyl-1-butene as excess olefin. The various transformations and correlations bearing on the isomerization mechanisms are summarized in the equations which follow (Me = methyl, Pr = propyl, Bu = butyl and Am = amyl).

A further attempt was made to produce di-*t*-butylisobutylborane by means of a Grignard exchange reaction. When, however, di-*t*-butyl-*n*-butylborane was treated with isobutylmagnesium bromide, under the same conditions as used for the exchange reaction with *t*-butyl-di-*n*-amylborane, no exchange occurred and di-*t*-butyl-*n*-amylborane was recovered unchanged. This indicates that while one *t*-butyl group on boron does not interfere with the Grignard exchange reaction, the presence of two *t*-butyl groups offers sufficient steric hindrance to prevent interaction.

That a  $\beta$ -branched alkyl group does not offer steric interference to normal alkylation is shown by the fact that reaction of isobutylmagnesium bro-

midate with boron fluoride in the presence of excess 1-pentene gave a product in which no trace of a trialkylborane containing amyl groups could be found. Triisobutylborane was the sole product of the reaction. This result is of significance in regard to the proposed mechanism since it eliminates the possibility that exchange between trialkylborane and olefin may have occurred directly and not through the reduction reaction. Such an exchange is known to occur<sup>15,16</sup> at temperatures above 120°.

Thermal isomerization of *t*-butyl to isobutyl groups occurs rapidly at 205° and is followed by rapid disproportionation of the unhindered trialkylboranes formed. In less than 30 minutes at 205° *t*-butylisobutyl-*n*-amylborane and di-*t*-butyl-*n*-amylborane were converted to the same mixture of symmetrical trialkylboranes.

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## The Photodecomposition of Diazonium Salt Solutions<sup>1</sup>

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The quantitative determination of the products of the photodecomposition of *p*- and *m*-nitrobenzenediazonium salts has been made for a variety of experiments using various solvents and added free radical traps. The results show that the dominant primary process in alcohol solution leads to nitrophenyl radical formation. In ethanol, nitrobenzene,  $\alpha$ - and  $\beta$ -arylethanol and butanediol are formed but no dinitrophenyl. In aqueous solution carbonium ion formation appears to follow the light absorption process exclusively. Photolysis in glasses at -196° suggest that the benzenediazonium salt photodecomposition proceeds through the intermediate formation of a long-lived triplet state which is stable at low temperatures. In view of our evidence it is suggested that the magnetic measurements of Boudreaux and Boulet on the irradiated aqueous solutions of benzenediazonium salt reflect the presence of this photoexcited state, rather than free radicals as they have suggested. Attractive photochemical synthetic methods for the preparation of aromatic iodo and bromo derivatives from diazonium salts are presented. A possible solution to the problem of synthesis of aromatic hydroperoxides is reported.

The mechanism of the photochemical decomposition of diazonium salts is not completely understood. The nature of the products formed is still uncertain. The thermal decomposition of diazonium salts has been studied by several investigators.<sup>3-8</sup> Recent results<sup>5-12</sup> have suggested that under proper conditions scission of the C-N bond can occur by two distinct processes. A heterolytic process results under acidic conditions

in aqueous media, or under the varied conditions used in the Schiemann reaction. A homolytic process may result under basic conditions, as in the Gomberg-Bachmann reaction, or in buffered alcoholic solutions. DeTar and Kosuge<sup>9</sup> have recently cited evidence for a hydride ion transfer mechanism in the decomposition of diazonium salts in alcohol.

The published research on the photochemical decomposition of diazonium salts also suggests that the two processes analogous to those of the thermal decomposition may occur. Previous workers<sup>10,11</sup> have reported that a phenol is formed when diazonium salts are photolyzed in water and an aryl ether results when an alcohol replaces water as the solvent. Horner and Stohr<sup>12</sup> report that a process analogous to reductive deamination in preference to ether formation results in alcohols. Recently Boudreaux and Boulet<sup>13</sup> have suggested the importance of free radical intermediates in the photodecomposition based on magnetic susceptibility measurements.

The quantum efficiency of nitrogen formation,

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