of the disproportionation reaction is not clear. The alkyldichloroboranes can be distilled up to about 180° with no sign of disproportionation, but in the presence of trialkylborane are rapidly converted to dialkylchloroboranes. Dialkylchloroboranes are apparently not converted to alkyldichloroboranes in the presence of excess boron chloride in this temperature range. The most stable molecule in this case appears to be the one with one atom of chlorine per boron rather than two or none. It would appear that this stability is fundamental in nature and that the formation of the dialkylchloroborane rather than the other products is not a result of a favorable route to reaction.

The factors which make for great stability in the dialkylchloroboranes apparently are not effective for the corresponding fluorine compounds. While the alkyldifluoroboranes have been shown to be stable to disproportionation,[9] less is known about the disproportionation tendencies of dialkylfluoroboranes. Only one such compound, dimethylfluoroborane, has been reported.[10] Although this compound has been reported to be stable to disproportionation at room temperature, it has been suggested[11] that in the presence of certain reaction products it may have disproportionated. Preliminary[12] work in these laboratories has indicated that the higher dialkylfluoroboranes are not readily obtainable from the reaction of boron fluoride with the anhydrides of dialkylborinic acids. They can be obtained by the fluorination of dialkylchloroboranes but appear to be much more readily disproportionated to alkyldifluoroboranes and trialkylborane than the corresponding chloro compounds.

The dibutylchloroborane produced in the reaction of boron chloride with the tributylborane from *t*-butylmagnesium chloride has the same physical constants and infrared spectrum as the product from triisobutylborane. This constitutes further evidence of the identity of the two tributylboranes. If one tertiary alkyl group was present in the starting tributylborane, it apparently isomerized during the reaction.

The results obtained from the reaction of boron chloride with the trialkylborane obtained from isopropylmagnesium bromide and distilled at atmospheric pressure at 153–155° are consistent with the assumption that the trialkylborane consisted of a mixture of tri-*n*-propylborane and tri-isopropylborane. A product boiling over a ten degree range was collected in three approximately equal fractions. Each fraction had, within the limits of experimental error, the same chlorine content. A mixture of di-*n*-propylchloroborane and diisopropylchloroborane would show exactly this behavior.

The isolation of di-*sec*-butylchloroborane from the reaction of tri-*sec*-butylborane with boron chloride shows that the reaction may take place without isomerization of the dialkylchloroborane formed. During the high temperature disproportionation reaction, however, the trialkylborane formed does undergo isomerization. It appears that two α-branched alkyl groups may be retained on a boron atom at moderately elevated temperatures, but when three such groups are present isomerization occurs more readily.

The expected reduced electrophilic character of the boron in dialkylchloroboranes, as compared to alkyldichloroboranes, results in easy separation of dialkylchloroboranes from ether in contrast to the cleavage which results from attempts to separate alkyldichloroboranes from ether.

Notre Dame, Indiana

---

[9] P. A. McCusker and L. J. Glunz, This Journal, **77**, 4253 (1955).

[10] A. Burg, *ibid.*, **62**, 2228 (1940).

[11] A. Burg and J. Banus, *ibid.*, **76**, 9303 (1954).

[12] P. A. McClusker, G. F. Hennion and A. J. Rutkowski, unpublished work.

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

Organoboron Compounds. VIII. The Reaction of Triorganoboranes with Boric Oxide[1]

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

Received February 11, 1957

Trialkylboroxines, $(RBO)_3$, containing primary alkyl groups, tricyclohexylboroxine and triphenylboroxine, are easily prepared by the reaction of triorganoboranes with anhydrous boric oxide. Reaction occurs slowly at atmospheric pressure and reflux temperature and affords yields of 70% and higher. α-Branched trialkylboranes are isomerized in the process and give the corresponding primary alkylboroxines. Thus tri-*n*-butylboroxine is produced in this way with both tri-*n*-butylborane and tri-*sec*-butylborane.

Discussion

Previous papers[3] in this series included brief discussions of the mechanism of disproportionation and rearrangement reactions of triorganoboranes. Specifically, it was proposed that the vacant p-orbital of one boron atom may overlap σ-orbitals of another boron atom (or σ-orbitals of other types) leading to bridged-dimers which cleave to yield products which are (usually) thermodynamically more stable. This notion, while not amenable to rigid proof, suggests that triorganoboranes should undergo a considerable variety of reactions with substances which are sterically and electronically capable of such interaction. A number of such reactions are now being studied in this Laboratory. In this paper we report the reaction of tri-

---

[1] Previous paper, This Journal, **79**, 5192 (1957).

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

[3] G. F. Hennion, P. A. McCusker, *et al.*, papers VI and VII, This Journal, **79**, 5190, 5192 (1957).

organoboranes with anhydrous boric oxide to produce triorganoboroxines $(RBO)_3$.[4]

$$R_3B + B_2O_3 \longrightarrow (RBO)_3$$

As was predicted, very nearly one mole of anhydrous boric oxide dissolved slowly in one mole of triorganoborane under dry nitrogen merely by heating to reflux temperatures (95° and higher, depending on the boiling point of R_3B). Distillation then gave the triorganoboroxines in yields of 70% and higher. It was observed that the low-boiling trialkylboranes, *e.g.*, triethyl- and tripropylborane, undergo the reaction more rapidly than do the higher boiling homologs. Since boric oxide is a polymer insoluble in R_3B (except by reaction), it was concluded that the desired reaction occurs only on the surface of B_2O_3 and is subject to steric hindrance in varying degrees, depending on R. It was therefore surprising to learn that Goubeau and Keller[5] reported a similar reaction with trimethylborane (no other examples) and stated that the reaction occurs only in a bomb at 300–330°.

Although the trimethylborane reaction was not reinvestigated due to handling difficulties (a gas, highly pyrophoric), triethylborane was easily employed without isolation. An ethereal solution was prepared in the usual way by the Grignard reaction[3] and, after drying, anhydrous boric oxide was added. The ether was then removed by distillation under nitrogen, and the residue was heated at reflux temperature for 24 hr. Distillation then gave triethylboroxine in good yield. The higher trialkylboranes, which are not so dangerously pyrophoric, usually were employed directly.

While this method appears to be the most convenient yet described for the preparation of trialkylboroxines, one important limitation must be mentioned, namely, that α-branched alkyl groups are isomerized in the process to the corresponding primary alkyl groups. Thus triisopropylborane and tri-*sec*-butylborane gave tri-*n*-propylboroxine and tri-*n*-butylboroxine, respectively. A tributylborane prepared from *t*-butylmagnesium chloride and believed to contain a mixed *t*-butyl-isobutylborane[6] gave only triisobutylboroxine. The α-branched isomers, which are accessible by another route,[7] isomerize thermally[8] to the primary alkyl compounds as do the α-branched trialkylboranes.[6] The latter may well be intermediates in the trialkylboroxine isomerizations, (2) being the irreversible step

$$(RBO)_3 \overset{200°}{\rightleftharpoons} R_3B + B_2O_3 \qquad (1)$$

$$R_3B \longrightarrow R'_3B \qquad (2)$$

$$R'_3B + B_2O_3 \rightleftharpoons (R'BO)_3 \qquad (3)$$

It should be recalled in this connection that alkyl group isomerization does not interfere in the trialkylborane–boron chloride reaction[1] probably because the latter proceeds much more rapidly and at a lower temperature.

All trialkylboroxines were stable to disproportionation below about 200° and thus were readily distillable below this temperature. Distillation at temperatures above 200° resulted in partial disproportionation, leaving a residue of boric oxide, as previously discussed.[7]

Experimental

Boric oxide, contained in a round-bottom flask immersed in an oil-bath and attached to a second flask containing phosphorus pentoxide, was dried by heating to 185° (oil-bath temp.) at 0.3–0.5 mm. for 24 hr.

The boric oxide–trialkylborane reactions were carried out in carefully dried apparatus under dry nitrogen.

Preparation of Tri-*n*-butylboroxine from Tri-*n*-butylborane.—Fifty grams (0.27 mole) of tri-*n*-butylborane was heated with 19.1 g. (0.27 mole) of boric oxide under total reflux for 40 hr. Distillation *in vacuo* gave a forerun fraction, 1.3 g., b.p. 110–133.5° at 16 mm., and then tri-*n*-butylboroxine in two fractions: (a) 34.8 g., b.p. 133.4–133.5° at 16 mm., $n^{25}D$ 1.4186, d^{25} 0.8698; (b) 12.9 g., b.p. 133.5–133.6° at 16 mm., yield 47.7 g. (69%). The distillation residue weighed 15.6 g. The physical constants and infrared spectrum of fraction a agreed well with material made by another method (lit.[7] b.p. 134° at 16 mm., $n^{25}D$ 1.4175, d^{25} 0.8718).

The experiment described above was repeated with 54.7 g. (0.3 mole) of tri-*sec*-butylborane and 20.8 g. (0.3 mole) of boric oxide. The product boiled at 105° at 3 mm., $n^{25}D$ 1.4189, d^{25} 0.8701, and the infrared spectrum was in very good agreement with the spectrum of authentic tri-*n*-butylboroxine.

Preparation of Triisobutylboroxine from Triisobutylborane.—Triisobutylborane (71.4 g., 0.39 mole) and boric oxide (27.4 g., 0.39 mole) heated under total reflux for three days and then distilled *in vacuo* gave 81.2 g. (83% yield) of triisobutylboroxine in three fractions, b.p. 116–116.3° at 15 mm. The middle fraction had $n^{25}D$ 1.4130, d^{25} 0.8550 (lit.[7] b.p. 96° at 5 mm., $n^{25}D$ 1.4127, d^{25} 0.8540).

The experiment was repeated with 78.9 g. (0.43 mole) of impure triisobutylborane, b.p. 74.4–75° at 12 mm., prepared from *tert*-butylmagnesium chloride and boron chloride[6] using 30 g. (0.43 mole) of boric oxide. After heating for four days, distillation gave 81.5 g. of triisobutylboroxine, b.p. 89–101° at 7 mm. (75% yield). Redistillation gave 68.9 g. (63%), b.p. 95–96° at 7 mm. When distilled again the b.p. was 117° at 15 mm., $b^{25}D$ 1.4127, d^{25} 0.8552.

Preparation of Tri-*n*-propylboroxine.—When equimolar quantities of tri-*n*-propylborane and boric oxide were heated at reflux, the temperature (inside) rose from 156 to 204° within only 2 hr. Distillation then gave tri-*n*-propylboroxine in 52% yield. Due to foaming in the distilling flask, the distillation was discontinued prematurely; hence the low yield. Equimolar quantities of a tripropylborane (prepared from isopropylmagnesium bromide) and boric oxide gave, by distillation after refluxing for 5 days, an identical product in 76% yield.

Preparation of Triethylboroxine.—Triethylborane was prepared from 82 g. of magnesium turnings, 351 g. of ethyl bromide and 67.8 g. (1 mole) of boron fluoride in the usual way. The ethereal solution was concentrated by a distillation to a volume of *ca.* 250 ml., and 150 ml. of this solution estimated to contain about 0.4 mole of triethylborane) was treated with 28.5 g. (0.41 mole) of boric oxide. The ether was removed by distillation and the residue was heated at reflux for 24 hr. Distillation was resumed and yielded 15.3 g. of triethylboroxine, b.p. 156°, $n^{25}D$ 1.3954, d^{25} 0.8959 (lit.[7] b.p. 153°, $n^{25}D$ 1.3958, d^{25} 0.08963).

Preparation of Tricyclohexylboroxine.—Tricyclohexylborane (31 g., 0.12 mole) was refluxed for 48 hr. with 8.2 g. (0.12 mole) of boric oxide. Distillation of the reaction mixture in a simple distillation apparatus gave 33 g. of tricyclohexylboroxine, b.p. 210–211° at 8 mm., m.p. 91–92°. This represents a yield of 85%.

Preparation of Triphenylboroxine.—Triphenylborane (13.2 g., 0.05 mole) was heated at reflux with 3.8 g. (0.05 mole) of boric oxide for 48 hr. From the reaction mixture there was isolated by recrystallization from carbon tetrachloride 14.5 g. of triphenylboroxine, m.p. 208–209°. A

---

[4] Also known as triorganoboroxols, organoboron oxides and organoboronic acid anhydrides.

[5] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **267**, 1 (1951).

[6] G. F. Hennion, *et al.*, paper VI, THIS JOURNAL, **79**, 5190 (1957).

[7] P. A. McCusker, *et al.*, paper II, *ibid.*, **79**, 5179 (1957).

[8] Thermal isomerization frequently has been observed to be more rapid when accomplished by slow distillation at atmospheric pressure through a helix-packed fractionating column than by mere boiling under a reflux condenser.

mixed melting point determination with an authentic sample of triphenylboroxine showed no depression of melting point; yield of triphenylboroxine, 85%.

Isomerization of Tri-*sec*-butylboroxine.—Fifty grams (0.2 mole) of tri-*sec*-butylboroxine[7] was subjected to reflux under a 60-cm. column for 24 hr. Distillation gave only tri-*n*-butylboroxine, b.p. 242–243°, as shown by infrared spectrum.

Isomerization of Tri-*tert*-butylboroxine.—Fifty-three grams (0.21 mole) of tri-*tert*-butylboroxine,[7] m.p. 31°, treated substantially as described above, gave triisobutylboroxine. Three fractions boiled at 220–224°, $n^{25}\text{D}$ 1.4120–1.4123. The third fraction had d^{25} 0.8525 (lit.[7] $n^{25}\text{D}$ 1.4127, d^{25} 0.8540).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Colorless and Yellow Forms of N-Hydroxyphthalimide

BY WILLIAM R. RODERICK[1] AND WELDON G. BROWN

RECEIVED MAY 31, 1957

Contrary to a published report, the colorless and yellow forms of the compound known as "phthaloxime" have identical infrared spectra. Additional evidence is provided to show that the characteristic color and fluorescence of the yellow form is due to a trace impurity. The weight of evidence favors the N-hydroxyphthalimide structure.

The product from the reaction of phthalic anhydride with hydroxylamine, commonly known as "phthaloxime," has been described[2] as existing in two forms, colorless and yellow, but substantially identical in all other physical and chemical characteristics and as furnishing two series of derivatives likewise different only in color. Brady[3] proposed the term "xanthoisomerism" to describe this and other known examples of similar behavior. More recently, Mathis[4] reported a finding of substantial differences in the infrared spectra of the two forms and has renewed earlier efforts to assign to them radically different structures. His observations constitute the only evidence not reconcilable with a simpler explanation of the color—namely, that it is due to a difficultly separable impurity—and consequently we have re-examined the spectra.

We have found that the two forms of "phthaloxime" exhibit identical infrared spectra throughout the rock-salt region and, moreover, that the corresponding derivatives (acetates, methyl and benzyl ethers) are also indistinguishable by this means. The spectra (Table I), compared with known pairs of isomers having the phthalimide and isophthalimide structures, clearly support the N-hydroxyphthalimide structure.[5]

TABLE I

INFRARED ABSORPTIONS IN THE REGION 1700–1800 CM.$^{-1}$

N-Hydroxyphthalimide	1710sb[a]	1740sb	1787m
N-Methoxyphthalimide	.....	1735sb	1788m
N-Benzyloxyphthalimide	.....	1728sb	1788m
Phthalimide	.....	1735sb	1772m
Phthalanil	1708sb	1735m	1777w
Isophthalanil	1705sb	....	1785sb 1795s,sh

[a] s = strong, m = medium, w = weak, b = very broad absorption; sh = shoulder.

Carpino,[6] having prepared an isomeric compound to which he assigns the isophthalimide type of structure on the basis of infrared comparisons and method of synthesis, likewise concludes that the compound under discussion here is N-hydroxyphthalimide.[7]

Our further observations relating to impurities in the yellow form are the following. Although the color could not be removed by crystallization procedures nor by means of ion-exchange chromatography, it could be partially removed by fractional vacuum sublimation or by solution in concentrated sulfuric acid followed by immediate precipitation by water. Complete removal was effected by chromatography of the acetate and by purification of the sodium or ammonium salts and regeneration of N-hydroxyphthalimide.[8]

Secondly, whereas the crude and initially colorless product from the reaction of phthalic anhydride with hydroxylamine can be converted to the yellow form, the purified product can no longer be converted by refluxing an acetic acid solution.[9] If, however, hydroxylamine is added to the purified product, the conversion to the yellow form is again possible. Finally, the N-methoxy- and N-benzyloxyphthalimides prepared from the yellow form became progressively less colored upon repeated crystallization; the N-benzyloxyphthalimide in particular was obtained in an essentially colorless form although it could still be differentiated from that derived from colorless N-hydroxyphthalimide by its ultraviolet-excited fluorescence. It is concluded that the reaction mixture contains a precursor, rather easily eliminated from the crude product by recrystallization, that is converted on heating to the persistent contaminant responsible for

---

[1] Monsanto Chemical Co. Fellow, 1956–1957.

[2] W. R. Orndorff and D. S. Pratt, *Am. Chem. J.*, **47**, 89 (1912).

[3] O. L. Brady, L. C. Baker, R. F. Goldstein and S. Harris, *J. Chem. Soc.*, 529 (1928).

[4] F. Mathis, *Bull. soc. chim. France*, [5] **20**, 797 (1953).

[5] D. E. Ames and T. F. Grey, [*J. Chem. Soc.*, 3518 (1955)], have reported the resemblance of the infrared spectrum of "phthaloxime" to that of N-ethylphthalimide and of the ultraviolet spectrum to that of phthalimide.

[6] L. A. Carpino, THIS JOURNAL, **79**, 98 (1957).

[7] Carpino's designation of the new isomer as "phthaloxime," while logically supportable, is likely to prove confusing in view of the extensive literature in which N-hydroxyphthalimide is referred to as phthaloxime. It seems preferable to drop the term "phthaloxime," the compounds under discussion being named as derivatives of phthalimide.

[8] Conversion of the yellow form to the colorless form has been effected by formation of the acetate, hydrolysis by aqueous ammonia and regeneration of N-hydroxyphthalimide from the ammonium salt.[2]

[9] The failure to confirm isolation of the yellow form, reported by L. Bauer and S. V. Miarka [THIS JOURNAL, **79**, 1983 (1957)] is consistent with this observation.