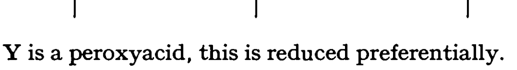
78. *Peroxides of Elements other than Carbon. Part III.* The Formation of Boron Peroxides by Autoxidation.*

By M. H. Abraham and Alwyn G. Davies.

The autoxidation of tri-*n*-butylboron and of a mixed *tert.*- and *iso*-butylboron has been investigated. It is shown that the primary reaction is represented by $R-B\!<\; + O_2 \longrightarrow R\cdot O\cdot O\cdot B\!<$, and from the latter the product $BuB(OBu)_2$ has been isolated.

If the oxygen supply is restricted, excess of the trialkylboron reduces the peroxy-group, and the boronic ester $RB(OR)_2$ is the ultimate product.

Nucleophilic attack by water or by pyridine at the boron atom in compounds containing the structure $R\overset{|}{B}\cdot O\cdot OR$ induces nucleophilic rearrangement with displacement of the alkyl group from boron to oxygen:



If the reagent Y is a peroxyacid, this is reduced preferentially.

It is suggested that the autoxidation of the alkylboron compounds proceeds through a mechanism involving co-ordination of molecular oxygen to the boron atom, and a shift of the alkyl group from boron to oxygen.

In Part I [1] it was pointed out that the peroxide group could be introduced into an organic molecule by the nucleophilic reaction of a peroxidic reagent, or by a reaction involving

---

* Part II, *J.*, 1958, 2372. A preliminary account of the present work has appeared in *Chem. and Ind.*, 1957, 1622.

[1] Buncel and Davies, *J.*, 1958, 1550.

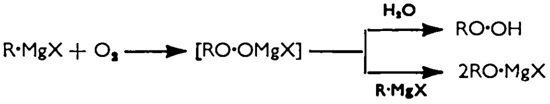
molecular oxygen, and we have described an extension of the former reaction to the preparation of organoperoxy-silicon [1] and -boron [2] compounds. This paper is the first of a number which will describe the preparation of peroxides of elements other than carbon by autoxidation.

Autoxidation of Organometallic Compounds.—Many metal and metalloid alkyls react with molecular oxygen, frequently with inflammation. For reaction to occur readily, the element must apparently have an unoccupied orbital of low energy and, within any one Sub-group, the reactivity can be correlated with the Pauling-scale electronegativity of the element (except possibly for the zinc and cadmium alkyls).[3]

It might be expected that the initial product of the autoxidation of an organo-element compound would generally retain intact a single O–O bond,[4] as it does in the autoxidation of a purely organic compound. However, the organometallic and organometalloid compounds are frequently strong reducing agents and under the usual conditions of autoxidation they might reduce the initial peroxides to non-peroxidic compounds:

$$\mathrm{RM} + \mathrm{O_2} \longrightarrow \mathrm{RMO_2} \xrightarrow{\mathrm{RM}} 2\mathrm{RMO}$$

The literature supports this: whereas non-peroxidic products have usually been isolated, the presence of traces of oxidising material has frequently been reported.[5] Walling and Buckler recently [6] showed that adding an ethereal solution of a Grignard reagent to oxygen-saturated ether at −80° gives high yields of the corresponding peroxides. Excess of the Grignard reagent reduces these peroxides to the alkoxides:



$$\mathrm{R{\cdot}MgX} + \mathrm{O_2} \longrightarrow [\mathrm{RO{\cdot}OMgX}] \begin{cases} \xrightarrow{\mathrm{H_2O}} \mathrm{RO{\cdot}OH} \\ \xrightarrow[\mathrm{R{\cdot}MgX}]{} 2\mathrm{RO{\cdot}MgX} \end{cases}$$

Autoxidation of Alkylboron Compounds.—In this field we have investigated first the autoxidation of the alkylboron compounds because we have already prepared a number of organo-peroxyboron compounds from alkyl hydroperoxides.[2]

Trialkylborons are rapidly autoxidised and the lower members inflame in the air. From the controlled oxidation, dialkyl alkylboronates have been obtained, and this reaction has been used to prepare several boronic acids:

$$\mathrm{R_3B} + \mathrm{O_2} \longrightarrow \mathrm{RB(OR)_2} \xrightarrow{\mathrm{H_2O}} \mathrm{RB(OH)_2} + 2\mathrm{ROH}$$

$$(\mathrm{R} = \mathrm{Et},^{7}\ \mathrm{Pr},^{8}\ \mathrm{Pr^i},^{9}\ \mathrm{Bu},^{10}\ \mathrm{Bu^i},^{8}\ \mathrm{Bu^t},^{9}\ \mathrm{CH_2Bu^i}\,^{8})$$

This formation of boronic esters was confirmed by Johnson and van Campen [10] who showed that tri-*n*-butylboron took up one mol. of oxygen to give the boronate, $\mathrm{BuB(OBu)_2}$. In the presence of water, however, only 0·5 mol. of oxygen was absorbed and the boronite, $\mathrm{Bu_2B(OBu)}$, was reported to be formed.

In the vapour state trimethylboron reacts with one volume of oxygen to give one

---

[2] Davies and Moodie, *J.*, 1958, 2372.

[3] Frankland, *J.*, 1861, **13**, 177; M. H. Abraham, Thesis, London, 1957; see also Sanderson, *J. Amer. Chem. Soc.*, 1955, **77**, 4531; Gilman and Jones, *ibid.*, 1940, **62**, 2353.

[4] Gilman, Yablunky, and Svigoon, *ibid.*, 1939, **61**, 1170; Egerton and Rudrakanchana, *Proc. Roy. Soc.*, 1954, *A*, **225**, 427.

[5] *E.g.*, Frankland, *Annalen*, 1855, **95**, 46; Meyer and Demuth, *Ber.*, 1890, **23**, 394; Engler and Wild, *ibid.*, 1897, **30**, 1669; Engler and Weissberg, *ibid.*, 1898, **31**, 3055.

[6] Walling and Buckler, *J. Amer. Chem. Soc.*, 1953, **75**, 4372; 1955, **77**, 6032.

[7] Meerwein and Sönke, *J. prakt. Chem.*, 1936, **147**, 251; Frankland, *J.*, 1862, **15**, 363; *Annalen*, 1862, **124**, 129.

[8] Krause and Nitsche, *Ber.*, 1921, **54**, 2784.

[9] Krause and Nobbe, *Ber.*, 1931, **64**, 2112.

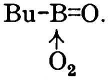
[10] Johnson and van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 121.

volume of product which was assigned the probable structure $MeB(OMe)_2$. Tri*iso*propylboron reacts similarly, but the boronate may undergo further slow oxidation to the borate.[11] While the present work was being carried out, Petry and Verhoek [12] described the oxidation of trimethylboron with a two-fold excess of oxygen in a flow system with a contact time of 2—3 min. at room temperature and 10—15 mm. Largely on the basis of physical evidence they assign their product the structure $Me_2B{\cdot}O{\cdot}OMe$.

Most dialkylboron compounds such as Bu_2BCl and $Bu_2B{\cdot}O{\cdot}BBu_2$ are also rapidly oxidised by air.[13] The controlled autoxidation of the spontaneously inflammable diethylboronous acid and ethyl diethylboronite has been reported to proceed as follows: [14]

$$Et_2B{\cdot}OH + \tfrac{1}{2}O_2 \longrightarrow Et{\cdot}B(OH){\cdot}OEt$$
$$Et_2B{\cdot}OEt + \tfrac{1}{2}O_2 \longrightarrow Et{\cdot}B(OEt)_2$$

Monoalkylboron compounds are much more stable towards oxygen.[15] Except for the tertiary and secondary alkylboron difluorides, which may ignite in the air, the alkylboron dihalides are unaffected by oxygen. Boronic esters are also stable, but the boronic acids are susceptible to oxidation. Secondary and especially tertiary alkylboronic acids are rapidly autoxidised, but water completely inhibits the reaction of the primary and secondary compounds.[16] The trimeric boronic anhydrides, $(RBO)_3$, are oxidised quantitatively to the metaborates—tertiary ones very rapidly and primary ones only slowly. Evidence was found for a peroxidic intermediate which liberated iodine from potassium iodide and initiated the polymerisation of styrene,[17] and was thought to be



$\text{Bu-}\underset{\underset{\textstyle O_2}{\uparrow}}{\text{B}}\text{=O.}$

The alkenyl- and aryl-boron compounds are relatively much more stable. Triphenylboron in 1-bromonaphthalene reacts with ½ mol. of oxygen fairly rapidly at room temperature to give presumably the phenylboronite. Under the same conditions tri-1-naphthylboron is much less reactive, and trimesitylboron is inert.[18] Trivinylboron similarly shows no reactivity at room temperature, but methyldivinylboron is more reactive.[19]

Diarylboron compounds have been reported to become brown on exposure to air,[20] but monoarylboron compounds are stable.[21]

Formation of Alkylperoxyboron Compounds by Autoxidation.—(i) *From tri*-n-*butylboron.* The autoxidation of tri-*n*-butylboron was studied first because this had been most extensively investigated.[10] In the gas burette in the absence of a solvent, tri-*n*-butylboron absorbed 1·01 mol. of oxygen, giving a product with properties corresponding to those of dibutyl butylboronate, but containing a trace (0·02 mol.) of a peroxidic compound (iodometrically).

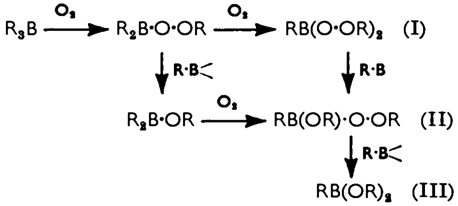
However, a solution of tri-*n*-butylboron in *cyclo*hexane absorbed much more than 1 mol. of oxygen, producing just over 1 mol. of oxidising agent. The product was diamagnetic and in solution did not lose its oxidising properties to an appreciable extent during some days. Tributylboron, if added at the end of the autoxidation or if in excess during the autoxidation, reduced the oxidising product to dibutyl butylboronate.

A reasonable interpretation of this behaviour might be that autoxidation of R_3B gives initially $R_2B{\cdot}O{\cdot}OR$ which can be reduced by an R–B group giving $R_2B{\cdot}OR$, or can be

---

[11] Bamford and Newitt, *J.*, 1946, 695.
[12] Petry and Verhoek, *J. Amer. Chem. Soc.*, 1956, **78**, 6416.
[13] Johnson, Snyder, and van Campen, *ibid.*, 1938, **60**, 115.
[14] Frankland, *Proc. Roy. Soc.*, 1877, **25**, 165.
[15] McCusker and Glunz, *J. Amer. Chem. Soc.*, 1955, **77**, 4253.
[16] Snyder, Kuck, and Johnson, *ibid.*, 1938, **60**, 105; Johnson, van Campen, and Grummitt, *ibid.*, p. 111.
[17] Grummitt, *ibid.*, 1942, **64**, 1811.
[18] Brown and Dodson, *ibid.*, 1957, **79**, 2302.
[19] Parsons, Silverman, and Ritter, *ibid.*, p. 5091.
[20] Torssell, *Acta Chem. Scand.*, 1955, **9**, 239.
[21] *Idem, ibid.*, 1954, **8**, 1779.

further oxidised by oxygen to $RB(O{\cdot}OR)_2$. The final product might therefore be (I), (II), or (III), depending on the conditions:



In the present case the combination of these reactions has given a product consisting largely of (II; R = Bu). Hydrolysis of this (see below) might liberate *n*-butyl hydroperoxide but, as this forms no convenient crystalline derivatives, we have also investigated the autoxidation of the *tert.*-butylboron group because *tert.*-butyl hydroperoxide is relatively stable and forms familiar crystalline derivatives.

(ii) *From* " tert.*-butylboron.*" Tri-*tert.*-butylboron (if indeed it exists) is unstable and partial rearrangement occurs to the *iso*butyl structure.[22] Oxidation of our product with hydrogen peroxide followed by estimation of the *iso*- and *tert.*-butyl alcohol formed showed our alkyl to contain an average of about 0·80 *iso*butyl group per molecule. We refer to this mixed alkyl as " *tert.*-butylboron." *

As in the case of the *n*-butyl compound, " *tert.*-butylboron " in concentrated *cyclo*hexane solution absorbed 1·01 mol. of oxygen giving a product containing only 0·04 mol. of peroxide. Hydrolysis gave a solid, m. p. 105°, which could be either *tert.*- or *iso*-butylboronic acid. (The structure of Krause and Nobbe's " *tert.*-butylboronic acid,"[9] is rendered unreliable by the above isomerisation.) Apart from the ambiguity of isomerisation, however, the oxidation can again be expressed as $R_3B + O_2 \longrightarrow RB(OR)_2$.

In dilute ethereal solution, however, the alkyl absorbed much more oxygen, giving highly peroxidic products. By bubbling oxygen through a very dilute ethereal solution, a product containing 1·94 mol. of peroxidic oxygen was obtained, and was isolated as a clear colourless oil, giving an analysis agreeing satisfactorily with the structure $BuB(O{\cdot}OBu)_2$. In a thin film the oil was hydrolysed very rapidly forming a white crust of boric acid and giving a characteristic peroxidic odour.

Hydrolysis of the Autoxidation Products.—Initial experiments to detect *n*-butyl hydroperoxide in the hydrolysate of the compound $Bu^nB(OBu^n){\cdot}O{\cdot}OBu^n$ were not successful, and under conditions under which the hydroperoxide and *n*-butylboronic acid are stable only *n*-butyl alcohol and boric acid could be recovered.

Similar loss of peroxide occurred during the hydrolysis of the oxidation products of " *tert.*-butylboron," but was incomplete when the initial peroxide content was greater than 1 mol. In the hydrolysate, *tert.*-butyl hydroperoxide was identified on the vapour-phase chromatogram, and isolated as its triphenylmethyl derivative. This therefore confirms that the autoxidation can be expressed by the reaction, $R_3B + 2O_2 \longrightarrow RB(O{\cdot}OR)_2$.

The loss of peroxide, and the accompanying formation of boric acid and alcohol during the hydrolysis of compounds containing the structure $R\overset{|}{B}{\cdot}O{\cdot}OR$, was surprising. Further investigation showed (Table 2) that the peroxide content decreased from $1 + n$ to n groups

---

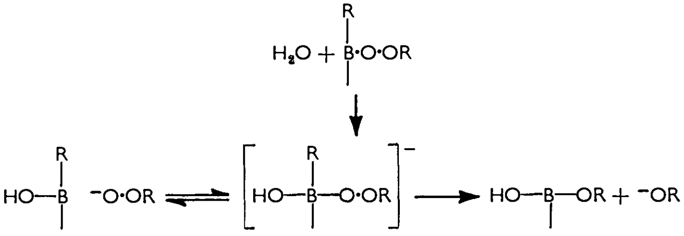
* In a recent thorough investigation,[23] Hennion, McCusker, and Rutkowski isolated only di*iso*butyl-*tert.*-butylboron by three different routes which might be expected to give tri-*tert.*-butylboron, including the one which we have followed. We would not exclude the possibility that our alkyl contained an average of more than one *iso*butyl group per molecule, although we think it is unlikely; our general argument, however, does not depend on this fact.

[22] Hennion, McCusker, Ashby, and Rutkowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5190.
[23] Hennion, McCusker, and Rutkowski, *ibid.*, 1958, **80**, 617.

per boron atom. This reaction is reminiscent of the oxidative dealkylation of organoboron compounds by hydrogen peroxide and by alkyl hydroperoxides. Kuivila has shown kinetically that this rearrangement proceeds through a four-covalent boron intermediate,[24] and our experiments[2] with phenyl[^{18}O]boronic acid and with optically active 1-phenylethyl hydroperoxide support his conclusions.

It therefore appears that the dealkylation and loss of peroxide content which we observe on hydrolysis result from a similar rearrangement in the intermediate (IV).

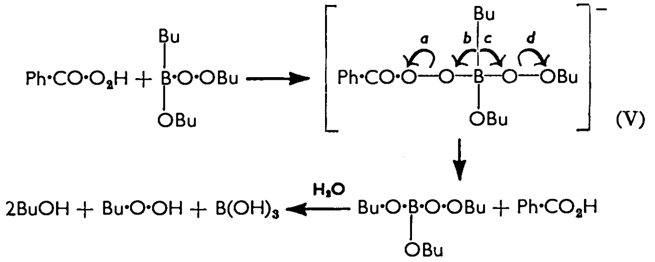
This type of rearrangement prevented the preparation of compounds of the type R$\overset{|}{\mathrm{B}}$·O·OR by the nucleophilic substitution of a hydroperoxide at a boron atom, a reaction which would also proceed through a four-covalent intermediate.[2]



(IV)

Similar oxidative dealkylation occurred when the organoperoxyboron compounds were treated with pyridine or piperidine. It appears that the reaction is now induced by nucleophilic attack of the amine upon boron.

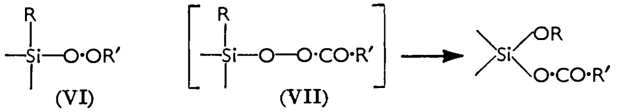
The reaction of the peroxide from tri-*n*-butylboron with peroxybenzoic acid supports this mechanism:



(V)

The alkyl group now can migrate in either of two directions, involving the electron shifts *a* and *b*, or *c* and *d* (structure V); the former is favoured by electron-attraction in the benzoyloxy-group. Rearrangement therefore leads to the formation of benzoic acid; hydrolysis liberated *n*-butyl hydroperoxide, identified by comparison with an authentic specimen on the vapour-phase chromatogram.

We have obtained a similar relative mobility in the acylperoxy- and alkylperoxy-derivatives of silicon.[1] Whereas no rearrangement could be induced in structures of the type (VI), the structure (VII) was too unstable to be isolated.



(VI) (VII)

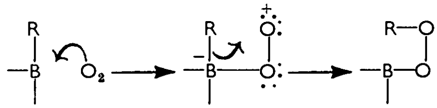
Nature of the Autoxidation Process.—The autoxidation of tri-*n*-butylboron was inhibited in propylamine solution. In aqueous emulsion "*tert.*-butylboron" absorbed 1·21 mol. of

---

[24] Kuivila, *J. Amer. Chem. Coc.*, 1954, **76**, 870; Kuivila and Armour, *ibid.*, 1957, **79**, 5659.

oxygen and gave (in a separate experiment) a product containing 0·33 mol. of peroxide. Quinol in small amount has no effect on the rate or overall uptake of oxygen.

A reasonable interpretation of these results, and those of previous workers quoted above, is that the autoxidation proceeds by co-ordination of molecular oxygen on to the boron atom, accompanied or followed by a 1 : 3-shift of the alkyl group from boron to oxygen:



Consonant with this, a general parallel can be traced between the ease of autoxidation of organoboron compounds and the readiness with which other reagents co-ordinate to the boron atom, modified by the migratory aptitude of the group R. Any group which can donate electrons inter- or intra-molecularly to the unfilled shell of the boron atom will by doing so render the compound less susceptible to attack by oxygen. For example the reactivity series

$$\text{Alkyl-B}\!<\; > \;\text{Vinyl-B}\!<\; \sim \;\text{Aryl-B}\!<$$

on this picture might arise from p_π–p_π overlap from the organic group to boron, and the series

$$R_3B > R_2B{\cdot}OR' > RB(OR)_2$$
$$R_2B{\cdot}OH > R_2B{\cdot}OR > R_2B{\cdot}O^-Na^+$$
$$R_3B > R_2BCl > RBCl_2$$

from a similar overlap from the oxygen or halogen atoms.

The inhibition of the autoxidation of tributylboron by propylamine, and of the less reactive boronic acids by water, can perhaps be ascribed to the successful competition of these reagents with oxygen for co-ordination to boron.

The mechanism of autoxidation discussed here differs from that proposed by Bamford and Newitt for the reaction of trimethyl- and tripropyl-boron in the vapour phase,[11] and by Coates for the reaction of organozinc compounds,[25] but is similar to Walling and Buckler's picture of the autoxidation of Grignard reagents.[6]

EXPERIMENTAL

Tri-n-*butylboron.*—The reaction between *n*-butylmagnesium bromide and boron trifluoride in ether gave tri-*n*-butylboron, b. p. 96—98°/12 mm., in 59% yield.

" tert.-*Butylboron.*"—This material, b. p. 66—68°/7 mm., was prepared similarly in 45% yield (on BF_3) from *tert.*-butylmagnesium chloride (Found: B, 5·91. Calc. for $C_{12}H_{27}B$: B, 5·90%). A solution of this material (4·55 g.) in *cyclo*hexane (4 c.c.) was shaken for 2 hr. with 30% hydrogen peroxide (10 c.c.), with ice-cooling. The mixture was kept overnight at room temperature, then treated with more hydrogen peroxide (5 c.c.), made alkaline with potassium hydroxide, and shaken for a further 1·5 hr. Potassium carbonate was added, the mixture extracted with ether, and the extract dried and concentrated through a Dufton column to 11·05 g. This extract was then treated as follows.

(i) On the vapour-phase chromatogram, comparison of the area of the *iso*butyl alcohol peak with those for *cyclo*hexane and for ether, both for the extract alone and for a mixture of the extract (0·1980 g.) and *iso*butyl alcohol (0·0452 g.), showed that 0·79 mol. of *iso*butyl alcohol had been isolated from the oxidation of " *tert.*-butylboron."

(ii) By a carefully controlled procedure, *iso*butyl 3 : 5-dinitrobenzoate (0·87 g.), m. p. and mixed m. p. 86·2°, was isolated from a portion of the extract (3·66 g.). By an identical procedure, *iso*butyl alcohol (0·50 g.) yielded the 3 : 5-dinitrobenzoate, m. p. 86° (0·87 g.); about 0·82 mol. of *iso*butyl alcohol had therefore been isolated from the oxidation.

Preparation of Capsules.—The boron alkyl was introduced under nitrogen through the B10 side-arm *A* (Fig. 1) which could be connected directly to the distillation apparatus. In a nitrogen-filled glove-box, the weighed, thin, glass capsules *B*, ending in a narrow capillary and filled

---

[25] Coates, " Organo-metallic Compounds," Methuen, London, 1956, p. 39.

with nitrogen, were inverted in the neck of the apparatus and the B29 cap *C* replaced. The pressure in the apparatus was reduced through *D*, and nitrogen readmitted through *E*. The capsules were removed in the wire stirrup *F* while they were still under reduced pressure so that the capillaries filled with nitrogen. The capsules were then sealed and reweighed.

Autoxidations.—Fig. 2 illustrates the apparatus found most convenient for carrying out the autoxidations. The capsule *A* was placed in the solvent *B* with the capillary neck in the arm of the tap *C* which enters the swan-neck adapter through a rubber sleeve. The adapter leads to the gas burette and the dimethyl phthalate bubbler through the three-way tap *D*.

Oxygen was passed in through *C* and out at *D*, and the mercury reservoir was lowered to fill the burette with oxygen. Taps *C* and *D* were then closed to the atmosphere, and when the apparatus had reached thermal equilibrium the capsule was crushed by depressing the tap *C*, the mixture being stirred magnetically. Further liquid reagents can be added if necessary through the tap *C*.

FIG. 1. *Apparatus for filling capsules.*

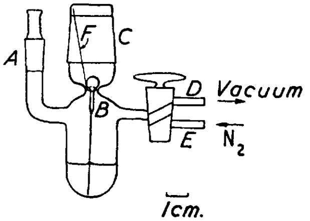
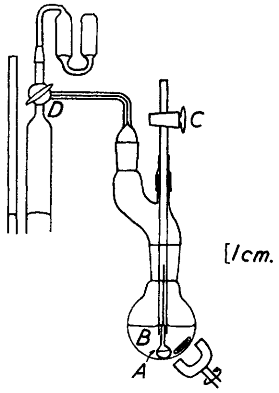


FIG. 2. *Apparatus for autoxidations.*



Determination of Boron.—The sample (0·1—0·2 g.) was added to 30% hydrogen peroxide (10 c.c.). After 2—3 hr., mannitol (1·0 g.) was added, and the solution was titrated with 0·1N-sodium hydroxide with phenolphthalein as indicator. A blank estimation was run concurrently. Use of Bromothymol Blue gives a better end-point and smaller blank estimations (Dr. M. F. Lappert, personal communication), and we used this in subsequent work.

Vapour-phase Chromatographic Analysis.—The general method has already been described.[26] Preliminary identification of compounds was based on the retention times (*T*), relative to *tert.*-butyl peroxide, which are given in Table 1; this was followed by adding an authentic sample of the suspected component to the mixture, and redetermining the chromatogram.

Quantitative analysis was based on the measurement of the areas under curves, determined by weighing a cut-out replica. Values of *F* (*tert.*-butyl peroxide = 1), defined by the expression

$$\frac{\text{Area of A}}{\text{Area of B}} \times F\frac{\text{A}}{\text{B}} = \frac{\text{Wt. of A}}{\text{Wt. of B}}$$

are given in Table 1.

TABLE 1. *Vapour-phase chromatographic analysis.*

Packing: dinonyl phthalate on kieselguhr. Temp.: 80—85°. Carrier gas: N_2, 3·95 l./hr.

	H_2O	Et_2O	Me_2CO	$Bu^t\cdot OH$	$Pr^i\cdot CHO$	$Pr^n\cdot CHO$
T	0·18	0·22	0·31	0·46	0·46	0·68
F	—	—	—	0·199	—	0·135
	$Bu^t{}_2O_2$	$Bu^i\cdot OH$	$Bu^n\cdot OH$	$Bu^t\cdot O_2H$	$Bu^i\cdot O_2H$	$Bu^n\cdot O_2H$
T	1·00	1·16	1·170	2·77	4·82	6·50
F	1·00	0·158	0·135	1·53	0·272	0·303

*Autoxidation of Tri-*n*-butylboron.*—(i) *With no solvent.* Tri-*n*-butylboron (2·2762 g.) was allowed to absorb oxygen in the gas burette, the temperature being kept below 20—25° by

---

[26] Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, **17**, 499.

intermittent cooling. 1·01 Mol. of oxygen were absorbed, giving a product (2·647 g. Calc.: 2·676 g.) containing 0·02 mol. of peroxide, b. p. 119°/23 mm., n_D^{20} 1·4171, n_D^{25} 1·4150. Recorded data for di-*n*-butyl butylboronate are b. p. 108·5°/13 mm., n_D^{20} 1·4169.

Partial hydrolysis (of 1·626 g.) occurred with 6N-hydrochloric acid (5 c.c.) in 5 hr., giving boric acid (0·03 g.), m. p. and mixed m. p. 165—166°, and *n*-butyl alcohol (0·10 g.) (3 : 5-dinitrobenzoate, m. p. 58—59°, unchanged on admixture with authentic material, m. p. 64°).

(ii) In *cyclo*hexane. Tri-*n*-butylboron (0·4648 g.) in *cyclo*hexane (5 c.c.) absorbed 1·21 mol. of oxygen in 1 hr., giving a product containing 1·06 mol. of peroxide.

(iii) *Reduction of the product by the reactant.* Tri-*n*-butylboron (0·6340 g.) in *cyclo*hexane (7·0 c.c.) absorbed oxygen, giving a product (5·7842 g. in all) containing 0·71 mol. of peroxide. This solution (5·1383 g., containing 3·98 × 10^{-3} mole of peroxide) was mixed with a solution of the trialkyl (0·7263 g., 3·98 × 10^{-3} mole) in *cyclo*hexane (3·0 c.c.), heat being evolved. After being kept overnight under nitrogen, the solution was allowed to absorb oxygen, and gave a product containing 0·76 × 10^{-3} mole of peroxide. Di-*n*-butyl *n*-butylboronate (0·58 g.) was isolated, having b. p. 124—127°/26 mm., n_D^{25} 1·4148 [Found: C, 65·7 (uncorr.); H, 12·4. Calc. for $C_{12}H_{27}O_2B$: C, 67·4; H, 12·6%].

(iv) *Stability of the peroxide.* The trialkylboron (3·667 g.) in *cyclo*hexane (40 c.c.) was allowed to absorb oxygen. Next day the solution was diluted to 50 c.c. with *cyclo*hexane. Aliquot portions showed the following peroxide contents (in mol.): initially, 0·51; after 6 hr./35°, 0·47; after 6 hr./53°, 0·41; after 3 days/20°, 0·43.

(v) *Oxidation with a restricted oxygen supply.* The trialkylboron (0·6980 g.) in *cyclo*hexane (10 c.c.) was allowed to absorb 0·55 mol. of oxygen in a few minutes. The supply of oxygen was then interrupted at tap *D*. Next day the oxygen supply was restored. The final product contained 0·31 mol. of peroxide.

(vi) " *Inverse oxidation.*" The trialkylboron (0·9702 g.) in *cyclo*hexane (50 c.c.) was added during 3·5 hr. to *cyclo*hexane (25 c.c.) stirred in dry oxygen. The product contained 0·783 mol. of peroxide.

Autoxidation of " tert.*-Butylboron.*"—(i) *In* cyclo*hexane.* The trialkyl (1·14 g.) in *cyclo*hexane (1·0 c.c.) absorbed 1·01 mol. of oxygen, giving a product containing 0·04 mol. of peroxide. Alkaline hydrolysis of the product under nitrogen gave a white solid (recrystallised from water), m. p. 105°.

(ii) *In ether.* The trialkylboron (0·1212 g.) in dry ether (3·3 c.c.) absorbed oxygen at room temperature during 3·5 hr., giving a product containing 1·79 mol. of peroxide. In a similar experiment at —70° for 9 hr., 1·26 mol. of peroxide were produced.

A solution of the trialkyl (6·30 g.) in dry ether (100 c.c.) was added slowly during 9 hr. to dry ether (250 c.c.) which was continuously saturated with dry oxygen and cooled in ice (" inverse oxidation "), giving a product containing 0·01 mol. of peroxide.

The ether was removed from 250 c.c. of the solution, leaving a clear liquid (1·21 g.), b. p. 38—40°/0·15 mm., n_D^{20} 1·4078, n_D^{25} 1·4056. This (1·0 g.) was shaken with 3N-sodium hydroxide (50 c.c.); *tert.*- and *iso*-butyl alcohol were identified in the ethereal extract of the steam-distillate.

The alkaline residue from the steam-distillate was concentrated and acidified under nitrogen, yielding a white solid (0·27 g.), m. p. 100° (after sublimation). Above the m. p. a liquid was evolved with an odour similar to that of *tert.*-butyl alcohol, leaving a residue of boric acid.

(iii) *Isolation of the product.* A capsule of the trialkyl (*ca.* 0·2 g.) was broken under dry ether (40 c.c.) through which oxygen was passed for 8 hr., and which was stirred magnetically. The combined products from five such reactions (total wt. of alkyl, 0·8204 g.) were filtered from glass in the dry box and shown to contain 1·94 mol. of peroxide.

The solvent was removed at the pump under anhydrous conditions, leaving *butyldi(butylperoxy)boron* as a clear colourless liquid (0·8501 g.) [Found: C, 55·9 (uncorr.); H, 11·0; B, 4·5; peroxidic O, 24·5. $C_4H_9B(O_2C_4H_9)_2$ requires C, 58·5; H, 11·1; B, 4·4; peroxidic O, 26·0%].

Hydrolysis of the Autoxidation Products.—n*-Butylperoxy-compounds.* An autoxidation product containing 1·14 mol. of peroxide in ether (250 c.c.) was hydrolysed as follows.

(i) *With acid.* A 100 c.c. aliquot part was concentrated and hydrolysed during 1 week with 6N-hydrochloric acid (10 c.c.), and the hydrolysis product (2·3580 g.) was collected in ether. The chromatogram showed the presence of *n*-butyl alcohol and a trace of *n*-butyraldehyde. Quantitative analyses by chromatography and by isolation of *n*-butyl 3 : 5-dinitrobenzoate

(m. p. 64°) were in good agreement, and showed that from the oxidation product containing 1·14 mol. of peroxide, 1·88 mol. of *n*-butyl alcohol had been isolated.

(ii) *With alkali.* A second 100 c.c. aliquot portion was similarly treated with 3N-sodium hydroxide (10 c.c.) for 5 hr. The clear liquid residue (1·8803 g.) from the ethereal extract contained 0·04 mol. of peroxide. Again the chromatogram showed the presence of only ether, *n*-butyl alcohol (2·38 mol.), and a trace of *n*-butyraldehyde.

(iii) *With peroxybenzoic acid.* A 12·5 c.c. sample of the solution was added to a solution of peroxybenzoic acid (1·0 g.) in dry ether (5 c.c.). Next day the mixture was shaken with water (0·5 c.c.) for 5 hr. and the material volatile at 0·1 mm. was collected in a trap at −80° as a clear liquid (0·445 g.). On the chromatogram peaks corresponding to *n*-butyl alcohol (2·09 ± 0·3 mol.), *n*-butyl hydroperoxide (0·57 ± 0·07 mol.), and *n*-butyraldehyde (0·44 ± 0·07 mol.) were identified. If it is assumed that the aldehyde is derived from the hydroperoxide, the combined yields of 1·01 mol., and that of the alcohol, *ca.* 2 mol., correspond satisfactorily with the peroxidic content, 1·14 mol. of the autoxidation product.

(iv) *With piperidine.* Tri-*n*-butylboron (0·9397 g.) in *cyclo*hexane (40 c.c.) was allowed to absorb oxygen for 6 hr., giving a product containing 0·50 mol. of peroxide. Piperidine (2·0 c.c.) was added, giving a slightly exothermic reaction. After 16 hr. at 40°, the solution gave a negative test for peroxide. To check that this was not due to base-catalysed decomposition of the primary alkyl peroxide, the solution was analysed for butyraldehyde as its 2 : 4-dinitrophenylhydrazone which was isolated by chromatography on alumina. The optical density of the product at 360 μ showed that a maximum of 4% of the *n*-butyl peroxide had been converted into the aldehyde.

tert.-*Butylperoxy-compounds.*—(i) *The products of hydrolysis.* An autoxidation product in ether containing 1·60 mol. of peroxide was shaken for 1 hr. with 6N-sodium hydroxide (5 c.c.) and then steam-distilled. The product was extracted into ether, and on the chromatogram showed the presence of *tert.*-butyl hydroperoxide, *iso*butyl alcohol, *tert.*-butyl alcohol, and a trace of acetone.

(ii) *Isolation of* tert.-*butyl triphenylmethyl peroxide.* "*tert.*-Butylboron" (0·2137 g.) in ether (6·0 c.c.) was allowed to absorb oxygen for 4 hr., giving a product containing 1·59 mol. of peroxide. The product was hydrolysed as above. Triphenylmethanol (0·08 g.) in glacial acetic acid (3·5 c.c.) containing sulphuric acid (2 drops) was added to the residue (0·5 c.c.). After 3 hr. the mixture was poured on ice, yielding *tert.*-butyl triphenylmethyl peroxide (0·045 g.), m. p. 71°, undepressed on admixture with authentic material,[27] m. p. 73°.

In a check experiment, a solution of *tert.*-butyl hydroperoxide (0·05 g.) in water (5·0 c.c.) by the same procedure yielded 0·06 g. of the triphenylmethyl derivative. About 0·36 mol. of hydroperoxide was therefore formed in the hydrolysis of the autoxidation product.

(iii) *Reaction with pyridine.* Four capsules of "*tert.*-butylboron" (in all, 0·4987 g.) were oxidised in ether, giving 100 c.c. of a solution of the product containing 1·94 mol. of peroxide. Dry pyridine (1 c.c.) was added. Next day the solvent was removed, leaving a compound containing 0·94 mol. of peroxide. After 3 weeks in contact with pyridine the peroxide content was 0·77 mol.

(iv) *Loss of peroxide during hydrolysis.* Various products from the autoxidation of "*tert.*-butylboron" were hydrolysed as described above, and the peroxide content was determined before and after hydrolysis. These results are recorded in Table 2. The values marked *s* were determined after steam-distillation and have been corrected for the loss of about 25% of peroxide which occurs during this process.

TABLE 2. *Loss of peroxide accompanying hydrolysis.*

Peroxide content (mol.)			Peroxide content (mol.)		
Before hydrolysis	After hydrolysis	Reagent	Before hydrolysis	After hydrolysis	Reagent
1·26	0·29	HCl	1·60	0·60	NaOH
1·50	0·55 ^{s}	NaOH	1·68	0·63 ^{s}	NaOH
1·59	0·48 ^{s}	NaOH	1·94	0·94	C_5H_5N

Effect of Reagents on the Autoxidation.—*Water.* "*tert.*-Butylboron" (0·0616 g.) in water (0·70 c.c.) absorbed 1·21 mol. of oxygen in 3 hr.

A vigorous stream of oxygen was passed through a suspension of "*tert.*-butylboron" in water (25 c.c.); after about 15 min. the mixture became homogeneous. After 7 hr. the aqueous solution and the contents of a subsequent trap at −70° were shown to contain 0·33 mol. of peroxide. *tert.*-Butyl hydroperoxide and *iso*- and *tert.*-butyl alcohol were identified on the chromatogram.

Propylamine. " *tert.*-Butylboron " (0·0431 g.) in *n*-propylamine (4·5 c.c.) was left in contact with oxygen overnight. No measurements of the volume absorbed were possible because of the high vapour pressure of the system. The residual alkyl was therefore estimated by treating it with an excess of *tert.*-butyl hydroperoxide and determining the excess of hydroperoxide in the usual way: 2·49 of the original 3 alkyl groups were still available for reduction.

Quinol. " *tert.*-Butylboron " (0·3305 g.) and quinol (0·10 g.) in di*iso*propyl ether (5 c.c.) absorbed 1·22 mol. of oxygen in 6 hr. The quinol was recovered and no benzoquinone could be detected. In a parallel experiment the alkyl (0·3644 g.) in di*iso*propyl ether (5 c.c.) absorbed 1·28 mol. of oxygen at the same rate.

We are indebted to Dr. J. Artozoul for preparing the tri-*n*-butylboron. This work was carried out during the tenure of a Nottinghamshire Major County Award (by M. H. A.).

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

[*Received, July* 1*st*, 1958.]