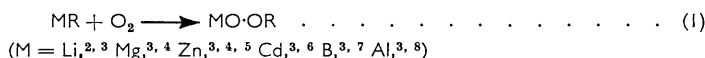


60. *Peroxides of Elements other than Carbon. Part VII.<sup>1</sup> The Relative Reactivity of the *t*-Butyl and the Isobutyl Group in the Autoxidation of Di-isobutyl-*t*-butylboron.*

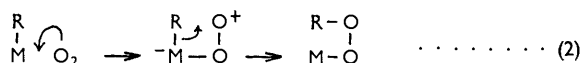
By ALWYN G. DAVIES, D. G. HARE, and R. F. M. WHITE.

The same order of reactivity of the alkyl groups,  $\text{Bu}^t > \text{Bu}^i$ , holds in the reaction of di-isobutyl-*t*-butylboron with hydrogen peroxide and with molecular oxygen. It is believed from other evidence that the former reaction involves a nucleophilic 1,2-rearrangement of an alkyl group from boron to oxygen, and it is suggested that these results are compatible with a mechanism for the reaction with oxygen involving now a nucleophilic 1,3-rearrangement from boron to oxygen.

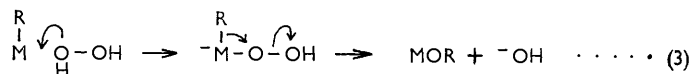
THE autoxidation of an organometallic compound gives initially an organoperoxymetallic compound:



From the change in reactivity as the organometallic compound was varied, and as other reagents were added, it was suggested that the reaction involved nucleophilic attack of oxygen upon the metal, accompanied or followed by a nucleophilic 1,3-rearrangement of the alkyl group from the metal to oxygen:<sup>3,7b</sup>



Further evidence has now been obtained by partial autoxidation of a mixed alkyl,  $\text{MRR}'$ , and analysis of the product for  $\text{RM}\cdot\text{O}\cdot\text{OR}'$  and  $\text{R}'\text{M}\cdot\text{O}\cdot\text{OR}$ ; the above mechanism might be expected to involve a similar order of relative mobility of the groups R and R' as in the oxidation of the same mixed alkyl with hydrogen peroxide, which involves a nucleophilic 1,2-rearrangement:<sup>7b,d,9,10</sup>



The choice of a compound for study is severely limited. Arylmetallic compounds cannot be used because the arylperoxy-structure is not stable, and the only known autoxidisable mixed alkylmetallic compounds that do not disproportionate are those of zinc or the very few of boron which contain a tertiary alkyl group. We have therefore used di-isobutyl-*t*-butylboron because it has been fully characterised<sup>7b,11</sup> and because we had had experience in the autoxidation of boron alkyls.<sup>7b,c,d</sup>

The possible products from the hydrogen peroxide oxidations would be  $\text{R}_2\text{B}\cdot\text{OH} + \text{ROH}$ , and then  $\text{R}\cdot\text{B}(\text{OH})_2 + 2\text{ROH}$ ; from the autoxidation one would expect  $\text{R}_2\text{B}\cdot\text{O}\cdot\text{OR}$

<sup>1</sup> Part VI, Davies and Hall, *J.*, 1959, 3835.

<sup>2</sup> Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

<sup>3</sup> Hock and Ernst, *Chem. Ber.*, 1959, **92**, 2716.

<sup>4</sup> Walling and Buckler, *J. Amer. Chem. Soc.*, 1953, **75**, 4372.

<sup>5</sup> Abraham, *Chem. and Ind.*, 1959, 750.

<sup>6</sup> Davies and Packer, *Chem. and Ind.*, 1958, 1177; *J.*, 1959, 3164.

<sup>7</sup> (a) Petry and Verhoek, *J. Amer. Chem. Soc.*, 1956, **78**, 6416; (b) Abraham and Davies, *Chem. and Ind.*, 1957, 1622; *J.*, 1959, 429; (c) Davies and Hare, *J.*, 1959, 438; (d) Davies, Hare, and White, *Chem. and Ind.*, 1959, 1315; *J.*, 1960, 1040.

<sup>8</sup> Hall, Thesis, London, 1959; Davies and Hall, unpublished work.

<sup>9</sup> Kuivila and his co-workers, *J. Amer. Chem. Soc.*, 1957, **79**, 5659 and earlier papers.

<sup>10</sup> Davies and Moodie, *J.*, 1958, 2372.

<sup>11</sup> Hennion, McCusker, Ashby, and Rutkowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5190; Hennion, McCusker, and Rutkowski, *ibid.*, 1958, **80**, 617.

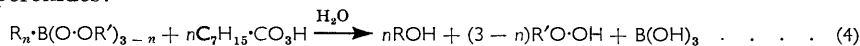
and then  $R \cdot B(O \cdot OR)_2$ . In the products of any one oxidation the three groups R would be composed of t-butyl and isobutyl groups in the ratio of 1 : 2, and it was necessary to determine the location of these groups. This has been done principally by vapour-phase chromatography of the fragments of oxidation by peroxyacid,<sup>7b,c,d,12</sup> by determining the proton magnetic resonance spectra of the organoboron compounds,<sup>7d</sup> and, where suitable, by isolating characteristic solid derivatives. These methods gave concordant results.

*Oxidation with Hydrogen Peroxide.*—Di-isobutyl-t-butylboron was treated with hydrogen peroxide (1 mol.) in ether, giving as the only products t-butyl alcohol (identified chromatographically) and isobutylboronous acid (identified by m. p. and by the proton magnetic resonance and infrared spectra of the anhydride). Therefore in the rearrangement generalised in equation (3), the t-butyl group migrates from boron to oxygen to the exclusion of the isobutyl group.

This order is reasonable in the light of our knowledge of the nucleophilic migration of alkyl groups from carbon to oxygen in the Baeyer-Villiger oxidation of ketones with peroxyacids. Although no experiments with isobutyl t-butyl ketone have been reported, it appears that in general t-alkyl groups are more mobile than primary alkyl groups. For example, in the oxidation of ketones, Ph·COR, with trifluoroperoxyacetic acid,<sup>13</sup> the mobilities of groups R compared with phenyl are: Et  $7 \times 10^{-2}$ ; Pr<sup>n</sup>  $7 \times 10^{-2}$ ; neopentyl  $1.1 \times 10^{-1}$ ; and Bu<sup>t</sup> 39; *i.e.*, Bu<sup>t</sup> : R<sup>p</sup> = 550—350 : 1.

*Oxidation with Molecular Oxygen.*—It was first shown that di-isobutyl-t-butylboron in dilute solution, like the other tributylborons which we have investigated,<sup>7b,c,d</sup> will absorb 2 mol. of oxygen to give a diperoxide, Bu·B(O·OBu)<sub>2</sub>. The reaction is exothermic and the first mol. of oxygen is taken up about twice as fast as the second. The oxidation is slowed by benzylamine and inhibited completely by a 100-fold molar excess.

Di-isobutyl-t-butylboron in ether was then allowed to absorb varying amounts of oxygen; peroxyoctanoic acid was immediately added to convert, after hydrolysis, alkyl groups into the corresponding alcohols and alkylperoxy-groups into the corresponding alkyl hydroperoxides:<sup>7b</sup>

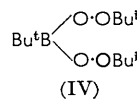
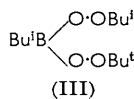
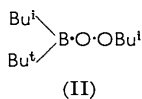
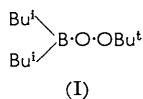


The mixture of iso- and t-butyl alcohol and hydroperoxides was then quantitatively analysed by vapour-phase chromatography. The results are shown in Table I.

TABLE I. *Products of partial autoxidation of di-isobutyl-t-butylboron.*

O <sub>2</sub> absd. (mol.)	Bu <sup>t</sup> O <sub>2</sub> H (mol.)	Bu <sup>i</sup> O <sub>2</sub> H (mol.)	Bu <sup>t</sup> OH (mol.)	Bu <sup>i</sup> OH (mol.)	ΣBu <sup>i</sup> /ΣBu <sup>t</sup> (mol.)
0.00	0.00	0.00	1.00	2.00	2.00
0.36	0.25	0.11	0.75	1.89	2.00
1.08	0.75	0.33	0.28	1.64	1.91
1.10	0.75	0.35	0.27	1.63	1.94
1.98	0.99	0.99	0.02	1.01	1.98

During the uptake of the first mol. of oxygen the relative mobilities of the t-butyl and isobutyl groups are about 4.5 : 1, giving a product equivalent to 69% of compound (I) and 31% of compound (II). The selectivity during the uptake of the second mol. of oxygen is some ten times as great, and the ultimate product consists of about 99% of compound (III) and 1% of compound (IV).

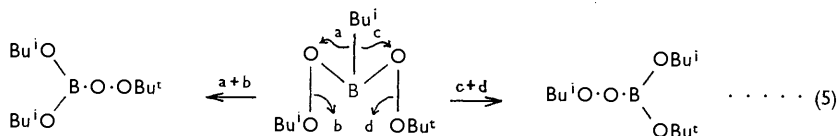


The ether was rapidly removed from a solution which had absorbed 2 mol. of oxygen, giving essentially pure isobutyl-isobutylperoxy-t-butylperoxyboron (III) as a colourless

<sup>12</sup> Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, **17**, 499.

<sup>13</sup> Hawthorne, Emmons, and McCallum, *J. Amer. Chem. Soc.*, 1958, **80**, 6393.

oil. The proton magnetic resonance spectrum of freshly prepared material, shown in the Figure (a), is compatible with this structure. At room temperature the doublet of the methyleneoxy-group and the singlet of the t-butoxy-group rapidly developed. We believe that this decomposition proceeds by the redox rearrangement of the peroxide (reaction 5); the relative size of the peaks then indicates that, as might be expected on



the basis of this mechanism, the isobutylperoxy-group is reduced (shifts a and b) more readily than the t-butylperoxy-group (shifts c and d).

A similar rearrangement is probably involved in the reduction which accompanies the hydrolysis of the peroxide.<sup>7b</sup> Chromatography of the alcohols and hydroperoxides which are formed showed that the isobutylperoxy-group is again reduced more readily (by a factor of about 5) than the t-butylperoxy-group.

The same order of reactivity,  $Bu^t > Bu^i$ , therefore holds in the reaction of di-isobutyl-t-butylboron with hydrogen peroxide and with oxygen. The mechanism of the first reaction is reasonably well established as nucleophilic 1,2-rearrangement of alkyl from boron to oxygen (reaction 3).<sup>\*</sup> These results therefore appear compatible with the mechanism proposed for the autoxidation reactions, involving a nucleophilic 1,3-rearrangement from boron to oxygen (reaction 2).

Autoxidation of the pure boron alkyl to a boronic ester,  $Bu^t \cdot B(OBu)_2$ , involves successively both these types of rearrangement, in both of which the  $Bu^t B$  group is the more reactive. As expected, the proton magnetic resonance spectrum of the product [Fig. (c)] showed it to have the structure  $Bu^i \cdot B(OBu^t) \cdot OBu^t$ ; hydrolysis gave isobutylboronic acid, m. p. 112°, identified by the proton magnetic resonance spectrum of its anhydride and by the preparation of its crystalline diethanolamine ester.<sup>†</sup>

Two further experiments were carried out. First, we tried to confirm the composition of the product after only one mol. of oxygen was absorbed by the boron alkyl in carbon tetrachloride. The proton magnetic resonance of the solution, however, showed that the product was the compound  $Bu^t B(OBu^t)(OBu^i)$ , and t-butyl chloride and carbonyl chloride were detected. These products could be accounted for if it were supposed that the autoxidation of the boron alkyl induces oxidation of the carbon tetrachloride to carbonyl chloride and chlorine, and that the chlorine (cf. hydrogen peroxide, above) reacts preferentially with the  $Bu^t B$  group to give t-butyl chloride. An analogous situation is encountered in the autoxidation of benzaldehyde in carbon tetrachloride, where carbonyl chloride is also formed.<sup>17</sup> A solution of the pure diperoxide,  $R \cdot B(O \cdot OR)_2$ , in carbon tetrachloride also liberated carbonyl chloride but apparently somewhat more slowly than it was formed during the above autoxidation. This might be taken to indicate, contrary to our conclusions above, that the autoxidation of the boron alkyl follows a homolytic mechanism.

Secondly, an attempt was made to see if the autoxidation would initiate polymerisation

<sup>\*</sup> We have shown<sup>14</sup> that, as this mechanism requires, neopentylboron compounds are oxidised to neopentyl alcohol and no t-pentyl alcohol is formed.

<sup>†</sup> This confirms the view that the boronic acid, m. p. 113°, which Krause and Nobbe<sup>15</sup> obtained by the autoxidation of what was then thought to be tri-t-butylboron, was in fact isobutyl- rather than t-butyl-boronic acid.<sup>16</sup>

<sup>14</sup> Hare, Thesis, London, 1960.

<sup>15</sup> Krause and Nobbe, *Ber.*, 1931, **64**, 2112.

<sup>16</sup> See ref. 7b, p. 431.

<sup>17</sup> Jorissen and van der Beek, *Rec. Trav. chim.*, 1927, **46**, 44.

of an olefin. Acrylonitrile which is stable towards boron alkyls under nitrogen,<sup>18</sup> is polymerised rapidly if oxygen is admitted, but is equally rapidly polymerised in the presence of di(isobutylperoxy)isobutylboron (Table 3). This experiment is thus inconclusive as to the mechanism of the autoxidation. It seems reasonable to suggest that the peroxide,  $R\cdot B(O\cdot OR)_2$ , and the monomer form a complex<sup>19</sup> which undergoes O-O homolysis and induces polymerisation.<sup>20</sup> The situation differs, however, from that described by Bawn, Margerison, and Richardson<sup>20</sup> for polymerisation of methyl methacrylate in that no molecule of trialkylboron is involved.

### EXPERIMENTAL

The interconversion of the esters, acids, and anhydrides of boronous and boronic acids, and the determination and interpretation of the proton magnetic resonance spectra, have been described previously.<sup>7d</sup> Vapour-phase chromatography was carried out by comparison with standard mixtures through a column usually of glycerol on "Celite" at  $>80^\circ$ .<sup>12</sup> This gives better separation of alcohols and hydroperoxides than does dinonyl phthalate. The use of a fire-brick support is not recommended because it can induce decomposition of the hydroperoxides, perhaps because of the presence of metal ions such as  $Fe^{2+}$ .

*Di-isobutyl-t-butylboron.*—Di-isobutyl-t-butylboron, b. p.  $49^\circ/2.7$  mm.,  $n_D^{25}$  1.4240, was prepared by treating the boron trifluoride-ether complex with t-butylmagnesium chloride.<sup>7d</sup> The infrared spectrum was similar to that described in the literature;<sup>11</sup> the structure was checked as follows.

96% Hydrogen peroxide (0.4821 g., 3 mol.) in dry ether (2 c.c.) was added during 1 hr. to a stirred solution of the alkyl (0.7967 g., 1 mol.) in ether (5 c.c.) containing powdered sodium hydroxide at  $0^\circ$ . After a further 4 hr. the mixture was filtered and dried (KOH). The vapour-phase chromatogram (dinonyl phthalate) showed the presence of t-butyl alcohol and isobutyl alcohol in the molar ratio of 1.0 : 2.0. A similar result was obtained by oxidation with peroxyoctanoic acid (see below).

*Autoxidation of Di-isobutyl-t-butylboron.*—Autoxidations were carried out at the gas-burette as described previously;<sup>7b</sup> the results are given in Table 2.

TABLE 2. *Autoxidation of di-isobutyl-t-butylboron.*

Solvent	Volume (c.c.)	$R_3B$ (g.)	Time (min.)	$O_2$ absd. (mol.)	Peroxide formed <sup>a</sup> (mol.)
$Et_2O$ .....	70	0.3325	60	1.90	1.88
$Et_2O$ .....	200	0.8204	180	<i>b</i>	1.94
$MeNO_2$ .....	50	0.3273	120	1.96	1.84
$C_6H_6$ .....	50	0.3200	90	1.85	1.69
PhOMe .....	50	0.3247	90	1.89	1.75

<sup>a</sup> Determined iodometrically. We now believe that these values are inclined to be low; quantitative hydrogenolysis (see below) gives slightly higher and more accurate values. <sup>b</sup> Oxygen was dispersed through a sintered-glass plate into the solution; the reaction is probably complete in 30 min.

*Diethanolamine Esters of Boronic Acids.*—The diethanolamine esters are very resistant to hydrolysis and autoxidation and are convenient crystalline derivatives of boronic compounds. They are readily prepared by warming together the boronic compound and diethanolamine, alone or in a solvent. Thus di-n-butyl s-butylboronate and diethanolamine gave the *diethanolamine ester*, m. p.  $156^\circ$  (from acetonitrile) (Found: C, 56.4; H, 10.8.  $C_8H_{17}BNO_2$  requires C, 56.2; H, 10.6%) (experiment by Dr. R. B. MOODIE).

Di-n-butyl isobutylboronate similarly gave the corresponding *derivative*, needles (from acetonitrile), m. p.  $155^\circ$  (Found: C, 56.0; H, 10.7%), and t-butylboronic anhydride gave the *derivative*, needles (from acetonitrile), m. p.  $248^\circ$  (Found: C, 56.3; H, 10.5%).

*Peroxy-acid Oxidation of Alkylperoxyboron Compounds.*—The alkyl and alkylperoxy-groups in compounds of the structure  $R_n\cdot B(O\cdot OR)_{3-n}$  were analysed by quantitative oxidation by

<sup>18</sup> Kolesnikov and Klimentova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1957, 652.

<sup>19</sup> Lyle, DeWitt, and Pattison, *J. Org. Chem.*, 1956, **21**, 61.

<sup>20</sup> Bawn, Margerison, and Richardson, *Proc. Chem. Soc.*, 1959, 397.

reaction (4). The alcohols and hydroperoxides were then determined by vapour-phase chromatography. Peroxyoctanoic acid, which is readily obtained pure,<sup>21</sup> is more convenient than peroxybenzoic acid which we used previously.<sup>7b</sup>

The boron compound (*ca.* 0.2—0.4 g.) in ether (5 c.c.) under nitrogen was treated dropwise with the calculated amount of peroxyoctanoic acid in ether. The mixture was stirred for 1 hr. and the bulk of the ether removed under reduced pressure. (The vapour-phase chromatogram confirmed that no oxidation products were removed at this stage.) Water (3 mol.) was added and the mixture was stirred for 1—3 hr. at room temperature to hydrolyse the borate. All volatile material was then removed into a trap at  $-75^{\circ}/1$  mm. and analysed chromatographically.

The procedure was checked by the recovery of mixtures of known composition, and by the analysis of di-isobutyl-*t*-butylboron and of isobutylisobutylperoxy-*t*-butylperoxyboron, for which there was independent evidence of structure.

*Hydrogenolysis of Alkylperoxyboron Compounds.*—Although alkylperoxyboron compounds are stable to hydrogen in the presence of Raney nickel, they are readily reduced over platinum oxide at room temperature and pressure; this reduction may take place directly on the boron peroxide, or indirectly on the hydroperoxide formed by hydrolysis by water derived from the platinum oxide. The following procedure was convenient for the hydrogenolysis *in situ* of peroxides formed by autoxidation at the gas-burette.

The burette was filled with hydrogen and a capsule of platinum oxide (0.02—0.04 g./g. of peroxide) under nitrogen was broken under the solvent. The solution was stirred magnetically until the uptake of hydrogen was complete (*ca.* 90 min.). A correction was made for the amount of hydrogen absorbed in the reduction of the platinum oxide.

The method was developed by using di-(*s*-butylperoxy)-*s*-butylboron (Found, by hydrogenolysis: peroxidic O, 26.0. Calc. for  $C_{12}H_{22}BO_4$ : peroxidic O, 26.0%), and yielded crude *s*-butylboronic acid, m. p. 84—87°.

*Partial Oxidation of Di-isobutyl-*t*-butylboron with Hydrogen Peroxide.*—All operations were conducted under nitrogen. A capsule of the boron alkyl (0.8529 g., 1.0 mol.) was broken in dry ether (3.0 c.c.) at 0°. 100% Hydrogen peroxide (0.1595 g., 1.0 mol.) in ether (3.12 c.c.) was added dropwise during 0.75 hr. to the stirred solution. After a further 3 hr. at 0° the clear solution was warmed to room temperature and transferred to one limb of a molecular still of inverted Y design, and degassed.

Material volatile at 0.005 mm. was collected in the second limb at  $-75^{\circ}$ ; the vapour-phase chromatogram showed the presence of only *t*-butyl alcohol (and ether), and the absence of isobutyl alcohol.

The residual white solid showed the presence of a strong infrared band for the HO group. With the receiver at  $-180^{\circ}$  the compound sublimed, giving isobutylboronous acid, m. p. 93—95° with dehydration. This was dehydrated overnight over phosphoric oxide at 18 mm., giving isobutylboronous anhydride as a colourless oil (Found: B, 8.90. Calc. for  $C_{16}H_{36}B_2O$ : B, 8.15%). The proton magnetic resonance spectrum showed the presence of the isobutyl group and the absence of the *t*-butyl group. This spectrum, and the infrared spectrum, were identical with those of an authentic sample of isobutylboronous anhydride prepared by treating tri-isobutylboron (1 mol.) with hydrogen peroxide (1 mol.) by the above procedure.

*Partial Oxidation of Di-isobutyl-*t*-butylboron with Oxygen.*—A capsule of di-isobutyl-*t*-butylboron was broken in dry ether (100 c.c.) at the gas-burette and allowed to absorb a precalculated amount of oxygen. (The uptake could be measured only approximately at this stage because the reaction is fast and strongly exothermic, giving a rise in temperature of about 9°, and causing the vapour pressure of the ether to increase during the experiment. An accurate measure of the oxygen absorbed is given by the chromatographic analyses below.) The oxygen in the apparatus was then replaced with nitrogen (through the tap C, Fig. 2 of ref. 7b) and the peroxyoctanoic acid in slight excess was added to the stirred solution; these two operations were completed within 1 min. of the end of the autoxidation.

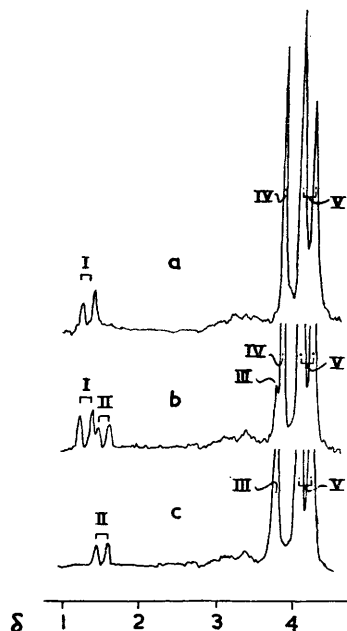
The mixture was stirred for 1 hr. and concentrated at the same time by evaporating most of the ether in a stream of nitrogen (a vapour-phase chromatogram showed that no alcohol or hydroperoxide was lost by this procedure). The product was hydrolysed with water (3 mol.) for 3 hr. All volatile material was collected in a trap at  $-75^{\circ}/1$  mm., and analysed chromatographically for *t*- and iso-butyl hydroperoxide and alcohols. No other product was present.

<sup>21</sup> Parker, Ricciuti, Ogg, and Swern, *J. Amer. Chem. Soc.*, 1955, **77**, 4037.

The results are shown in Table 1, where the amount of oxygen absorbed is calculated from the ratio of total hydroperoxides to total alcohols. Some check on the analytical techniques is provided by the molar ratio of total isobutyl compounds to total t-butyl compounds ( $\sum \text{Bu}^i / \sum \text{Bu}^t$ ) which should be 2 : 1.

*Isolation and Identification of Isobutylisobutylperoxy-t-butylperoxyboron.*—*Isolation.* A capsule of di-isobutyl-t-butylboron (0.4824 g.) was broken under dry ether (50 c.c.) through which dry oxygen was passed. After 1.75 hr. the solution was filtered from glass in a dry box,

Proton magnetic resonance spectra.



(a)  $\text{Bu}^i\text{B}(\text{O}\cdot\text{OBu}^i)(\text{O}\cdot\text{OBu}^t)$ . (b)  $\text{Bu}^i\text{B}(\text{O}\cdot\text{OBu}^i)(\text{O}\cdot\text{OBu}^t)$  partially rearranged to  $\text{Bu}^i\text{O}\cdot\text{O}\cdot\text{B}(\text{OBu}^i)\cdot\text{OBu}^t$  and  $\text{Bu}^t\text{O}\cdot\text{O}\cdot\text{B}(\text{OBu}^i)_2$  (reaction 5) after 1.75 hr. at room temperature. (c)  $\text{Bu}^i\text{B}(\text{OBu}^i)(\text{OBu}^t)$ .

$\delta$  values <sup>2d</sup> are given in the annexed Table.

Structural assignments of resonances

Fig.	(i) $\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{OB}$	(ii) $\text{CH}\cdot\text{CH}_2\cdot\text{OB}$	(iii) $(\text{CH}_3)_3\text{C}\cdot\text{OB}$	(iv) $(\text{CH}_3)_3\text{C}\cdot\text{O}\cdot\text{OB}$	(v) $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2$
a	1.18    1.35	—	—	3.83	4.05    4.20
b	1.18    1.35	1.43    1.57	3.78	3.83	4.05    4.20
c	—	1.41    1.55	3.78	—	4.10    4.25

and the ether rapidly removed under reduced pressure, leaving *isobutylisobutylperoxy-t-butylperoxyboron* as a colourless oil [Found: peroxidic O, 21.0 (iodometrically).  $\text{C}_{12}\text{H}_{27}\text{BO}_4$  requires Peroxidic O, 26.0%. We now know this method of analysis to give low peroxide values].

*Proton magnetic resonance.* The proton magnetic resonance spectrum of the product is shown in the Figure (a) and shows clearly the presence of  $\text{Bu}^i\text{B}$ ,  $\text{Bu}^i\text{O}\cdot\text{O}$ , and  $\text{Bu}^t\text{O}\cdot\text{O}$  groups (see legend). This spectrum was obtained within 10 min. of the end of the autoxidation; if the operations were conducted more slowly, the spectrum showed that some redox rearrangement had occurred, giving the isobutoxy and t-butoxy groups, as in the Figure (b).

*Hydrogenolysis.* Hydrogenolysis of the peroxide gave isobutylboronic acid as white plates (from water), m. p. 112.5°. It was dehydrated to the anhydride; the proton magnetic resonance spectrum was identical with that of authentic isobutylboronic anhydride, and showed the absence of t-butyl groups.

*Hydrolysis.* A solution of the peroxide (*ca.* 0.25 g.) in ether (2 c.c.) was shaken with 5*N*-sodium hydroxide (5 c.c.) for 2 hr. and then extracted with ether. The extract was dried ( $\text{MgSO}_4$ ), the bulk of the ether removed, and the product analysed chromatographically. The only compounds present were (molar ratios, out of 3, in parentheses):  $\text{Bu}^t\text{OH}$  (0.158);  $\text{Bu}^i\text{OH}$  (1.80);  $\text{Bu}^t\text{O}_2\text{H}$  (0.845);  $\text{Bu}^i\text{O}_2\text{H}$  (0.192) (Found: Total peroxide/total alcohol, 0.53; calc., 0.50. Found: total *t*-butyl compounds/isobutyl compounds, 0.50; calc., 0.50).

*Autoxidation of Undiluted Di-isobutyl-*t*-butylboron.*—The boron alkyl (5 g.) in a loosely stoppered bottle was allowed to absorb air slowly during 42 days in a dry box ( $\text{P}_2\text{O}_5$ ). The proton magnetic resonance spectrum [Figure (c)], showed the product to be isobutyl *t*-butyl isobutylboronate,  $\text{Bu}^i\text{B}(\text{OBu}^i)\text{OBu}^t$ . A specimen was converted into the diethanolamine ester of isobutylboronic acid, *m. p.* and mixed *m. p.* 155°. The rest was hydrolysed to the boronic acid, *m. p.* 112°, and dehydrated to the anhydride. The proton magnetic resonance spectrum was identical with that of the authentic material and showed the absence of the *t*-butyl group.

*Attempts to Isolate a Monoperoxide.*—The experiments summarised in Table 1 show that the reaction between di-isobutyl-*t*-butylboron and oxygen (1 mol.) gives a product equivalent to 69% of  $\text{Bu}^i_2\text{B}\cdot\text{O}\cdot\text{OBu}^t$  and 31% of  $\text{Bu}^i\text{B}(\text{Bu}^i)\text{O}\cdot\text{OBu}^t$ . An attempt was made to confirm this composition from the proton magnetic resonance spectrum of a sample prepared by autoxidation in carbon tetrachloride. This appeared to be an appropriate solvent because autoxidation of tri-isobutylboron was known to be slow in this medium, so that the reaction could be stopped at the appropriate stage, and because the absence of hydrogen atoms in the solvent would permit proton resonance spectra to be determined on solutions, perhaps avoiding the redox rearrangement which would occur if attempts were made to isolate the peroxide.

Di-isobutyl-*t*-butylboron (0.4592 g.) in carbon tetrachloride (55 c.c.) was allowed to absorb 1 mol. of oxygen at the gas-burette. One sample (A) was immediately removed; the bulk of the solvent was removed from the remainder (B) under reduced pressure. The proton magnetic resonance spectra of both samples were similar to that of isobutyl *t*-butyl isobutylboronate, showing that substantially no peroxide was present; however, sample A, and the carbon tetrachloride which had been removed from B, showed the presence of a new singlet at  $\delta$  3.28, in the correct position for *t*-butyl chloride. The carbon tetrachloride was therefore fractionally distilled, and the presence of *t*-butyl chloride confirmed in the chromatogram of the first fraction. Carbonyl chloride was also identified by smell, and by the formation of a precipitate of diphenylurea with aniline. Carbonyl chloride was also liberated, but apparently rather more slowly, by a solution of the di(alkylperoxy)boron compound in carbon tetrachloride.

*Polymerisation Experiments.*—A capsule of tri-*s*-butylboron (0.2745 g.) was broken under redistilled and outgassed acrylonitrile (15 c.c., 12 g.) under nitrogen (Specimen i). A portion (7 c.c.) was withdrawn into a test-tube open to the air (Specimen ii). Pure di(isobutylperoxy)-isobutylboron (0.1 g.) was added to redistilled and outgassed acrylonitrile (10 c.c., 8 g.) under

TABLE 3. *Polymerisation of acrylonitrile (data in min.).*

Specimen	Opalescent	Milky	Pasty	Solid
(i) $\text{Bu}^s_3\text{B}$ .....	60	180	—	—
(ii) $\text{Bu}^s_3\text{B} + \text{air}$ .....	0.5	4	15	21 *
(iii) $\text{Bu}^i\text{B}(\text{O}_2\text{Bu}^i)_2$ .....	0.5	3	10	20

\* The polymer gave a strong test for peroxide.

nitrogen (Specimen iii). The progress of the polymerisation is shown in Table 3. All three specimens were kept in a thermostat at 24°, but the polymerisation is exothermic: specimen (ii) reached a maximum internal temperature of 36° after 21 min., and specimen (iii) 60° in 10 min.

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