

474. *Peroxides of Elements other than Carbon. Part II.*¹ *The Formation of Boron Peroxides by Nucleophilic Substitution.*

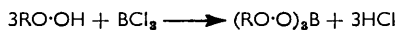
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Boron trichloride with *tert.*- and with *n*-butyl hydroperoxide forms the corresponding tri(alkylperoxy)boron compounds, (RO·O)₃B. Tetra-acetyl diborate gives the di(alkylperoxy)boron hydroxide (RO·O)₂B·OH; *o*-nitrophenyl dichloroboronite Cl₂B·OAr and di(*o*-nitrophenyl) chloroboronate ClB(OAr)₂ yield the alkylperoxy-aryloxy-compounds (RO·O)₂B·OAr and RO·OB(OAr)₂ respectively.

Alkylboronic acids R·B(OH)₂ and their derivatives reduce alkyl hydroperoxides and liberate the alcohol (or phenol) ROH. This reaction, carried out with an ¹⁸O-labelled boronic acid, and with an optically active alkyl hydroperoxide, proceeds consistently with a mechanism involving nucleophilic migration of the group R from boron to oxygen in the framework R-B-O-O-R'.

IN Part I¹ we described silicon peroxides which were prepared by the nucleophilic attack of peroxides on, in particular, chlorosilanes. This paper reports the organoperoxyboron compounds which are prepared by analogous reactions.

Derivatives of Boric Acid.—Boron trichloride with *tert.*- and with *n*-butyl hydroperoxide gives the corresponding tri(alkylperoxy)boron compounds in good yield:



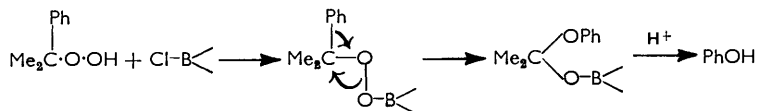
The products are colourless liquids, stable for some months at room temperature or for short periods at 100°, but initiating the slow polymerisation of styrene at 45°, presumably by O-O homolysis.

Both compounds reacted with water or ethanol rapidly and completely, liberating the corresponding hydroperoxide, and (cf. the peroxy-silanes¹) we were not able to prepare the pure organoperoxyboron compounds by treating boric acid or boric esters with hydroperoxides. Tri-(*tert.*-butylperoxy)boron, but not the *n*-butyl compound, when treated

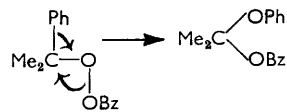
¹ Part I, Buncel and Davies, *J.*, 1958, 1550.

with ammonia, pyridine, or diethylamine in pentane, gave insoluble but rather unstable complexes.

The reaction between boron trichloride and 1-methyl-1-phenylethyl hydroperoxide was vigorous and phenol was isolated; similarly phenol was liberated exothermically from a mixture of *n*-propyl borate and the hydroperoxide at 70°. The reaction probably proceeds by O-O heterolysis accompanied by nucleophilic migration of the phenyl group from carbon to oxygen:



This is similar to the lability of 1-methyl-1-phenylethyl peroxybenzoate² and contrasts with the relative stability¹ of its silicon derivative $\text{Ph}\cdot\text{CMe}_2\cdot\text{O}\cdot\text{O}\cdot\text{SiMe}_3$.



Criegee³ has shown that the lability of peresters $\text{RO}\cdot\text{OX}$ is related to the electron-attraction by the group $-\text{OX}$. In the boron derivatives this electron-attraction might arise by overlap of the occupied $2p$ -orbitals of the oxygen atom with the vacant $2p$ -orbitals of the boron atom ($\overset{\curvearrowright}{\text{O}}-\text{B}<$ cf. $\overset{\curvearrowright}{\text{O}}-\text{C}-$).

The organoperoxy-derivatives of aluminium⁴ and of cadmium⁵ apparently exhibit a similar instability, which again may be associated with the presence of unfilled orbitals of low energy on the metal atom.

An attempt to prepare a triacylperoxyboron compound by reaction between boron trichloride and peroxyoctanoic acid apparently resulted in the oxidation of the chloride to molecular chlorine.

The reactivity of ethers towards boron trichloride, giving alkyl chloride and alkyl borate,⁶ suggested that dialkyl peroxides might react similarly to form alkyl chlorides and alkylperoxy-compounds. The reaction between *tert.*-butyl peroxide and boron trichloride is vigorous at room temperature: *tert.*-butyl chloride and the corresponding olefin and hydrogen chloride are formed, together with an involatile boron compound with a low peroxidic content. The reaction is apparently analogous to that of ethers but does not constitute a useful preparative method.

Treatment of tetra-acetyl diborate $(\text{AcO})_2\text{BOB}(\text{OAc})_2$ with *tert.*-butyl hydroperoxide gave di(*tert.*-butylperoxy)boron hydroxide $(\text{Bu}^t\text{O}\cdot\text{O})_2\text{B}\cdot\text{OH}$. Whereas the tri(alkylperoxy)borons were unimolecular in boiling benzene, the dialkylperoxy-compound showed an anomalously high molecular weight indicating some molecular association. All three compounds absorbed strongly in the infrared region at about 1345 cm^{-1} , which has been attributed to the B-O stretching frequency.^{7*}

Many mixed alkoxides of silicon are known, and we isolated (*tert.*-butylperoxy)triethoxysilane on reaction of *tert.*-butyl hydroperoxide with triethoxychlorosilane.¹ On the

* This frequency is absent in the spectrum of tetra-acetyl diborate because the B-O bond multiplicity is lowered by intramolecular association between the boron atom and a carbonyl-oxygen atom; the case of the diethanolamine esters of boronic acids is similar.

² Hock and Kropf, *Chem. Ber.*, 1955, **88**, 1544.

³ Criegee, *Annalen*, 1948, **560**, 127.

⁴ Davies and Hall, unpublished work.

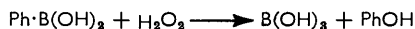
⁵ Davies and Packer, unpublished work.

⁶ Gerrard and Lappert, *J.*, 1952, 1486.

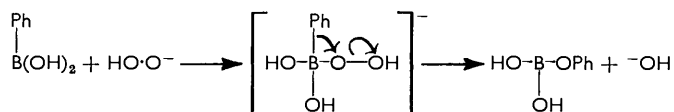
⁷ Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355; 1956, **9**, 137.

other hand, mixed alkoxides of boron readily disproportionate to the symmetrical compounds, and no simple examples have apparently yet been described. Mixed ethoxy-*o*-nitrophenoxyboron compounds, however, have recently been shown to be stable, probably because of intramolecular association between the nitro-group and boron atom.⁸ Likewise the di-(*tert.*-butylperoxy)-*o*-nitrophenoxyboron and *tert.*-butylperoxydi-*o*-nitrophenoxyboron were isolated as red oils from the reaction of *tert.*-butyl hydroperoxide with *o*-nitrophenyl dichloroboronite $\text{Cl}_2\text{B}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and di-*o*-nitrophenyl chloroboronate $\text{ClB}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ respectively.

Derivatives of Boronic Acids.—Oxidative dealkylation of phenylboronic acid was demonstrated in 1930,⁹ and the reaction was subsequently extended to alkylboron compounds:



Kuivila and his co-workers¹⁰ presented kinetic evidence that reaction of arylboronic acids with hydrogen peroxide proceeds by a nucleophilic shift of the aryl group from boron to oxygen in a four-covalent intermediate:

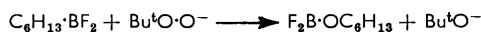


We have repeated this reaction with phenyl[¹⁸O]boronic acid in [¹⁸O]water containing isotopically normal hydrogen peroxide. The phenol which was formed was of normal isotopic composition, and must therefore derive its oxygen from the hydrogen peroxide, as is required by Kuivila's mechanism.

A similar reaction takes place when organoboron compounds are treated with alkyl hydroperoxides. When phenyl[¹⁸O]boronic acid was treated with 1:2:3:4-tetrahydro-1-naphthyl hydroperoxide in [¹⁸O]aqueous dioxan, isotopically normal 1:2:3:4-tetrahydro-1-naphthol was obtained. The reaction therefore appears to be analogous to that described by Kuivila

Confirmation of this mechanism was obtained by carrying out the reaction with optically active 1-phenylethyl hydroperoxide under anhydrous conditions. Active 1-phenylethanol was isolated such that $\alpha(\text{Ph}\cdot\text{CHMe}\cdot\text{OH})/\alpha(\text{Ph}\cdot\text{CHMe}\cdot\text{O}_2\text{H}) = +0.34$. We have shown previously that this value probably indicates complete configurational retention in the 1-phenylethyl group,¹¹ which is compatible with the mechanism proposed.

This type of rearrangement has prevented our preparing the peroxy-analogues of boronic acids $\text{R}\cdot\text{B}(\text{O}\cdot\text{OR})_2$ or boronous acids $\text{R}_2\text{BO}\cdot\text{OR}$ by nucleophilic substitution. For example, hexylboron difluoride reacts vigorously with *tert.*-butyl hydroperoxide to give hexanol and *tert.*-butyl peroxide, the latter probably arising by acid-catalysed condensation of the hydroperoxide with *tert.*-butyl alcohol, or with itself:¹



In contrast, alkylperoxysilanes containing the structure $\text{R}-\overset{|}{\text{Si}}-\text{O}\cdot\text{OR}$ are stable, and only the acylperoxysilanes $\text{R}-\overset{|}{\text{Si}}-\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{R}$ rearranged.¹ We have, however, been able to isolate compounds containing the structure $\text{R}-\overset{|}{\text{B}}-\text{O}\cdot\text{OR}$ by autoxidation of boron alkyls¹² and to observe their rearrangement initiated by nucleophilic attack on boron.

⁸ Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

⁹ Ainsley and Challenger, *J.*, 1930, 2171.

¹⁰ Kuivila and Armour, *J. Amer. Chem. Soc.*, 1957, **79**, 5659, and earlier papers.

¹¹ Davies and Feld, *J.*, 1956, 665.

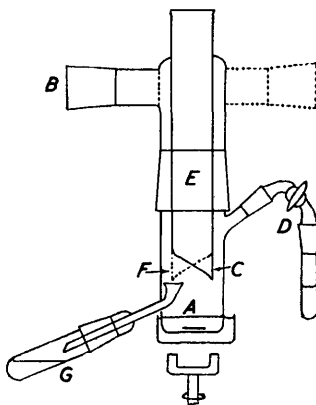
¹² Abraham and Davies, *Chem. and Ind.*, 1957, 1622; Davies and Hare, unpublished work.

EXPERIMENTAL

General.—The usual precautions were taken against explosion; no trouble was encountered.

Peroxidic oxygen was determined iodometrically and boron by titration as boric acid in the presence of mannitol.

To avoid the transference of easily hydrolysed and potentially hazardous material, the apparatus illustrated was used for preparing and purifying boron peroxides. When necessary, receivers were changed in a dry box. The use of the apparatus is described below.



Reaction between tert.-Butyl Hydroperoxide and Boron Trichloride—A solution of the hydroperoxide (8 g.) in an equal volume of pentane was placed in the apparatus at *A*, connected to the vacuum line at *B*. The cold-finger condenser, containing solid carbon dioxide–alcohol was arranged in position *C* for refluxing; boron trichloride (3.5 g.), cooled in the side-arm *D*, was then allowed to distil on warming into the hydroperoxide at *A*, cooled to 0°, and stirred magnetically.

The contents of *A* were allowed to warm to room temperature, hydrogen chloride being evolved. After 2 hours' stirring, the refrigerant in the cold-finger was removed, and the pentane and any residual hydroperoxide were taken off by successive reductions of pressure to 15 mm. and 1 mm. The condenser was then rotated about the axis of the B40 joint *E* to position *F* for distillation (broken lines), and the product distilled into the receiver *G* at 10⁻⁴ mm. from a bath at 40–70°.

The crude material, m. p. 12–15°, was recrystallised from pentane at –80° three times in the dry box, giving *tri*-(*tert*-butylperoxy)boron, m. p. 15–18° [Found: C, 50.8; H, 9.4; B, 4.4; peroxidic O, 34.7%; *M* (ebullioscopically in benzene), 280. C₁₂H₂₇O₆B requires C, 51.8; H, 9.8; B, 3.9; peroxidic O, 34.6%; *M*, 278].

Amine Complexes of Tri-(*tert*-butylperoxy)boron.—When pyridine, diethylamine, or ammonia was added to a solution of the peroxy-compound in pentane, the amine complexes were precipitated. Filtration in a dry atmosphere gave a solid which dissociated and liquified at room temperature. The *pyridine complex* was the most stable (Found, on a freshly prepared sample: peroxidic O, 25.9. C₅H₅N·C₁₂H₂₇O₆B requires peroxidic O, 26.9%).

Reaction between n-Butyl Hydroperoxide and Boron Trichloride.—*n*-Butyl hydroperoxide, b. p. 42°/7.5 mm., *n*_D²⁰ 1.4705, was prepared from *n*-butyl methanesulphonate in 20% yield by Williams and Mosher's method.¹³

The hydroperoxide (3.53 g.) in pentane (4 c.c.) was caused to react with boron trichloride (1.6 g.) by the above method, giving a good yield of *tri*-(*n*-butylperoxy)boron, b. p. 40–60° (bath)/10⁻³ mm., liquid at –80° (Found: C, 52.6; H, 9.75; B, 3.71; peroxidic O, 32.2%).

Reaction between 1-Methyl-1-phenylethyl Hydroperoxide and Boron Trichloride.—The reaction between the hydroperoxide (6.1 g.) in pentane (6 c.c.), and boron trichloride (2 g.), by the usual method was vigorous. Vacuum-sublimation of the brown liquid product gave phenol (2 g.) (tribromo-derivative, m. p. 93°).

¹³ Williams and Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 2984.

Hydrolysis and Alcoholysis of Tri-(tert.-butylperoxy)boron.—A solution of the peroxy-compound in acetic acid containing sulphuric acid and triphenylmethanol, gave, by the usual method,¹⁴ *tert.*-butyl triphenylmethyl peroxide, m. p. and mixed m. p. 72·5°.

Immediately after addition of dry ethanol (0·92 g.) to tri-(*tert.*-butylperoxy)boron (1·93 g.), no ethanol could be recovered at 30 mm. The product, presumably a mixture of ethyl borate and the hydroperoxide, distilled at 35—40°/16 mm.

Reaction between Hydroperoxides and Propyl Borate.—(i) In a preliminary experiment it was shown that propan-1-ol and *tert.*-butyl hydroperoxide can be separated by distillation at 60 mm. *tert.*-Butyl hydroperoxide (4·13 g.) and propyl borate (2·1 g.) were kept at 60°/60 mm. During 2 hr. a small volume of distillate was obtained (Found: peroxidic O, 20. Calc. for C₄H₉O₂H: peroxidic O, 35%). Unchanged hydroperoxide and alkyl borate were removed at 0·1 mm., leaving a residue (Found: peroxidic O, 21·5%).

(ii) No volatile material was obtained at 40 mm. when a mixture of 1-methyl-1-phenylethyl hydroperoxide (5·2 g.) and propyl borate (2·1 g.) was kept at room temperature for 3 hr. After a further 2 hr. at 70°/40 mm., a small amount of propanol was obtained; an exothermic reaction suddenly occurred and phenol was recovered from the product.

(iii) Pinane hydroperoxide (3·65 g.) and propyl borate (1·30 g.) were kept for 5 hr. at 80°/60 mm. Some propanol was collected. At 0·1 mm., much unchanged borate and hydroperoxide were recovered, leaving an oil which could not be distilled (Found: B, 2·2; peroxidic O, 14·7. Calc. for C₃₀H₅₁O₈B: B, 2·1; peroxidic O, 18·5%).

Reaction between Peroxyoctanoic Acid and Boron Trichloride.—Peroxyoctanoic acid (Found: peroxidic O, 20·1. Calc. for C₈H₁₆O₃: peroxidic O, 20·0%) was prepared by Swern and his co-workers' method¹⁵ in 70% yield. When boron trichloride (0·88 g.) was distilled into the peroxy-acid (2·9 g.) in pentane at 0°, heat was evolved and the mixture became yellow. Volatile material carrying with it the yellow colour was removed at 15 mm. into a cold trap; the colour was lost when the liquid was warmed, and was apparently due to chlorine. At 10⁻² mm. the pasty residue in the apparatus gave a sublimate of hexanoic acid on the cold-finger, leaving a residue of boric oxide.

Reaction between tert.-Butyl Peroxide and Boron Trichloride.—When a mixture of boron trichloride (2·35 g.) and *tert.*-butyl peroxide (7·8 g.) at -80° was allowed to warm to room temperature, a vigorous reaction took place. The volatile material contained hydrogen chloride (0·5 g.), olefin (0·3 g.), and *tert.*-butyl chloride (a trace, identified on the vapour-phase chromatogram¹⁶). Filtration of the residue gave boric acid, and hydrolysis of the mother-liquors liberated the hydroperoxide (0·2 g.).

Reaction between tert.-Butyl Hydroperoxide and Tetra-acetyl Diborate.—Tetra-acetyl diborate (Found: B, 7·75%; acid equiv., 46·0. Calc. for C₈H₁₂O₉B₂: B, 7·91%; acid equiv., 45·6) was prepared by reaction of boric acid with acetic anhydride.¹⁷ The hydroperoxide (4·01 g.) contained in a dropping funnel fitted to the apparatus illustrated at the side-arm *D* was added to the acetate (2·26 g.) at *A*. The mixture was stirred at room temperature and 5·5 mm. for 8 hr.; acetic acid, probably mixed with the anhydride, collected in the cold trap. The excess of hydroperoxide was removed at 1 mm. and the residue sublimed in a high vacuum, then recrystallised from pentane, yielding *di*-(*tert.*-butylperoxy)boron hydroxide, m. p. 38—42° (Found: B, 5·2; peroxidic O, 30·9. C₈H₁₆O₈B requires C, 5·25; peroxidic O, 31·1%).

Reaction of tert.-Butyl Hydroperoxide with o-Nitrophenyl Dichloroboronite.—*tert.*-Butyl hydroperoxide (3·336 g.) was added to the dichloroboronite⁸ (4·078 g.) in methylene chloride at -40°. Volatile material was removed at 0·1 mm., yielding *di*-(*tert.*-butylperoxy)-*o*-nitrophenoxyboron as a red liquid (Found: C, 50·9; H, 6·65; peroxidic O, 18·3. C₁₄H₂₂O₇NB requires C, 51·4; H, 6·78; peroxidic O, 19·6%).

Reaction of tert.-Butyl Hydroperoxide with Di-(o-nitrophenyl) Chloroboronate.—*o*-Nitrophenol (1·845 g.) in methylene chloride was added to the dichloroboronite (2·928 g.) in methylene chloride at -40°. After 1 hr. at room temperature, the hydroperoxide (1·195 g.) was added similarly, with cooling. Some *o*-nitrophenol was collected at 0·1 mm. on the cold-finger. The residue, a red liquid, m. p. ca. 15°, was *tert.*-butylperoxydi-(*o*-nitrophenoxy)boron (Found: C, 50·4; H, 4·5; peroxidic O, 8·35. C₁₆H₁₇O₈N₂B requires C, 51·1; H, 4·5; peroxidic O, 8·5%).

¹⁴ Davies, Foster, and White, *J.*, 1954, 2200.

¹⁵ Parker, Ricciuti, Ogg, and Swern, *J. Amer. Chem. Soc.*, 1955, 77, 4037.

¹⁶ Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, 17, 499.

¹⁷ Cook, Illet, Saunders, and Stacey, *J.*, 1950, 3125.

Reaction of Hydrogen Peroxide with Phenyl[¹⁸O]boronic Acid.—A mixture of butyl phenylboronate ¹⁸ (20 g.; b. p. 136—138°/8—10 mm.) and [¹⁸O]water (α 0.876) ¹⁹ was fractionally distilled; the water was recycled until all of the butanol had been collected (20 min.). The alcohol was isotopically normal. Cooling caused phenyl[¹⁸O]boronic acid (9.8 g.) to separate.

This labelled boronic acid (1 g.) was stirred with 20 c.c. of a 6% solution of 100% hydrogen peroxide in [¹⁸O]water. Heat was evolved as the solid dissolved in a few minutes. An ethereal extract yielded phenol which was isotopically normal.

Reaction of Hydroperoxides with Phenylboronic Acid.—(i) *tert.-Butyl hydroperoxide.* A solution of phenylboronic acid (1.35 g.) and *tert.*-butyl hydroperoxide (1 g.) in water (100 c.c.) was heated under reflux for 3 hr. An ethereal extract yielded phenol (tribromo-derivative, m. p. 93°).

(ii) 1 : 2 : 3 : 4-*Tetrahydro-1-naphthyl hydroperoxide.* A solution of the hydroperoxide (3.63 g.) and [¹⁸O]boronic acid (2.7 g.) in [¹⁸O]aqueous dioxan (4 : 1 by vol.) was kept at 25° for 72 hr. 1 : 2 : 3 : 4-*Tetrahydro-1-naphthol* (1.0 g.) of normal isotopic composition was isolated, having b. p. 255°, n_D^{25} 1.5625 (phenylurethane, m. p. and mixed m. p. 122°).

(iii) (–)-1-*Phenylethyl hydroperoxide.* The hydroperoxide ¹¹ (1.195 g.), $\alpha_D^{16.5}$ –1.94°, and phenylboronic acid (1.12 g.) were dissolved together in ether (20 c.c.). After 3 days the precipitated boric acid was removed by filtration; distillation yielded (–)-1-phenylethanol, b. p. 86°/15 mm., n_D^{25} 1.5279, α_D^{20} –0.66°.

Reaction between tert.-Butyl Hydroperoxide and Hexylboron Difluoride.—Hexylboron difluoride ²⁰ (2.37 g.) was distilled in dry nitrogen into a mixture of *tert.*-butyl hydroperoxide (3.51 g.) and pentane (5 c.c.) at 0° in the apparatus illustrated. Reaction was vigorous and the mixture became coloured. After removal of the pentane at 30 mm. liquid was collected at 0.5 mm. in the cold-trap. Redistillation of the liquid gave di-(*tert.*-butyl) peroxide, b. p. 112°, which was identified by vapour-phase chromatography.¹⁶ The residue in the still was hydrolysed and extracted with light petroleum. Treatment of the extract with α -naphthyl isocyanate gave *n*-hexyl α -naphthylurethane, m. p. and mixed m. p. 59°.

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¹⁸ Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415; Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.

¹⁹ Basse, Bunton, Davies, Lewis, and Llewellyn, *J.*, 1955, 2471.

²⁰ McCusker and Glunz, *J. Amer. Chem. Soc.*, 1955, **77**, 4253.