

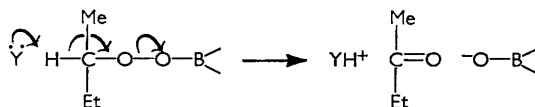
79. Peroxides of Elements other than Carbon. Part IV.¹ The Autoxidation of Tri-*sec.*-butylboron to *sec.*-Butyldi-(*sec.*-butylperoxy)boron.

By ALWYN G. DAVIES and D. G. HARE.

Tri-*sec.*-butylboron in dilute solution reacts readily with oxygen, giving *sec.*-butyldi-(*sec.*-butylperoxy)boron, $\text{Bu}^s\text{B}(\text{O}\cdot\text{OBu}^s)_2$, which has been isolated.

WE have shown¹ that the autoxidation of a mixed *iso*- and *tert.*-butylboron gave a similarly isomerically mixed diperoxide of the structure $\text{BuB}(\text{O}\cdot\text{OBu})_2$. For further investigations it was desirable to obtain a product of unambiguous structure. The autoxidation of tri-*sec.*-butylboron, which does not isomerise,² has therefore been investigated.

In dilute solution in ether or nitromethane the alkyl absorbed 2 mol. of oxygen, giving a product containing approximately 2 mol. of peroxide, and from the oxidation in ether, *sec.*-butyldi-(*sec.*-butylperoxy)boron, $\text{Bu}^s\text{B}(\text{O}\cdot\text{OBu}^s)_2$, was isolated as a colourless oil. It was readily hydrolysed, and *sec.*-butyl hydroperoxide, *sec.*-butyl alcohol, and a trace of butan-2-one were identified in the vapour-phase chromatogram of the products. The hydroperoxide is stable under the isolation procedure; hence the small amount of ketone is probably formed by a base-catalysed carbonyl-forming elimination of the alkylperoxyboron compound,³ where $p_\pi-p_\pi$ overlap from oxygen to boron assists heterolysis of the O-O bond (cf. the heterolysis of the O-O bond in 2-phenyl-2-propylperoxyboron compounds⁴):



The *sec.*-butyl alcohol probably arises from the nucleophilic migration of the *sec.*-butyl group from boron to oxygen, as described in Part III.¹ The loss in peroxide which is observed when *sec.*-butyldi-(*sec.*-butylperoxy)boron in ether is treated with tertiary amines probably follows principally this second type of mechanism. The reactivity of different bases is in the order pyridine < 2 : 6-lutidine < triethylamine, and in the presence of a large excess of pyridine the reaction appears to be of first order with respect to boron peroxide.

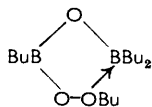
¹ Part III, Abraham and Davies, preceding paper.

² Hennion, McCusker, Ashby, and Rutkowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5190.

³ Kornblum and de la Mare, *ibid.*, 1951, **73**, 880.

⁴ Davies and Moodie, *J.*, 1958, 2372.

In aqueous suspension, tri-*sec.*-butylboron absorbed 1.52 mol. of oxygen, giving a product containing 0.98 mol. of peroxide, and probably consisting of the hydrolysis products of $\text{Bu}^s\text{B}(\text{O}^s\text{Bu})\text{O}^s\text{OBu}^s$. In pyridine solution the alkyl reacted relatively slowly, absorbing 1.33 mol. of oxygen, but giving a virtually non-peroxidic product; benzylamine completely inhibited the oxidation. This is consistent with the mechanism for the autoxidation suggested in Part III.¹



sec.-Butylboronous anhydride in ether absorbed only 1 mol. of oxygen, giving a monoperoxy-compound; in water 1.70 mol. were absorbed, producing 1.22 mol. of peroxide. A possible interpretation of this is that under anhydrous conditions the monoperoxide (inset) is intramolecularly associated, thereby inhibiting autoxidation at the second Bu^s_2B group.

EXPERIMENTAL

The general methods for the preparation of capsules, the autoxidations, and the analyses are described in Part III.¹

Tri-sec.-butylboron.—The reaction between *sec.*-butylmagnesium chloride and boron trifluoride in ether gave tri-*sec.*-butylboron (40% yield), b. p. 80—81°/12 mm., which was sealed under nitrogen in capsules (Found: B, 5.99. Calc. for $\text{C}_{12}\text{H}_{27}\text{B}$: B, 5.90%).²

sec.-Butylboronous Anhydride.—The reaction of *sec.*-butylmagnesium bromide and *n*-butyl ethylene borate in ether at -70° gave the ethylene ester of *sec.*-butylboronous acid; this was hydrolysed to the acid and dehydrated by fractional distillation with toluene, giving *sec.-butylboronous anhydride*, b. p. 113°/4 mm. (Found: B, 8.35. $\text{C}_{16}\text{H}_{36}\text{OB}_2$ requires B, 8.15%).

sec.-Butyl Hydroperoxide.—The "inverse" oxidation of *sec.*-butylmagnesium chloride in dilute ethereal solution at -75° gave *sec.*-butyl hydroperoxide,⁵ b. p. 29°/6 mm., n_D^{25} 1.4046. The infrared spectrum was identical with that described by Williams and Mosher.⁶ This material was used for comparative chromatography.

Autoxidation of sec.-Butylboron Compounds.—The results are shown in the Table.

Solvent	Volume (c.c.)	Boron alkyl (g.)	Time (min.)	O ₂ absorbed (mol.)	Peroxide formed (mol.)
<i>Tri-sec.-butylboron</i>					
Et ₂ O	50	0.1468	45	1.91	1.70
Et ₂ O	50	0.1310	330	<i>a</i>	1.90
H ₂ O	75	0.1765	10	1.52	0.98
Me·NO ₂	50	0.1951	60	1.90	1.82
C ₆ H ₅ N	50	0.1868	210	1.33	0.0
Ph·CH ₂ ·NH ₂	25	0.1896	180	0.0	0.0
<i>sec.-Butylboronous anhydride</i>					
Et ₂ O	50	0.1758	120	0.99	0.90
H ₂ O	50	0.7776	10	1.70	1.22

^a Oxygen was dispersed through a sintered-glass plate into the solution of the alkylboron. All the other experiments were carried out with the gas burette.

Isolation of sec.-Butyldi-(sec.-butylperoxy)boron.—A capsule of tri-*sec.*-butylboron (0.6936 g.) was broken in ether (200 c.c.) through which nitrogen was passed, to give a dilute solution of the alkyl before autoxidation commenced. Oxygen was then passed through the solution for 7 hr., giving a product containing 1.97 mol. of peroxide. Stringent precautions were taken throughout to exclude moisture. The resulting solution was filtered from broken glass in the dry box, and the ether removed under reduced pressure, leaving *sec.-butyldi-(sec.-butylperoxy)boron* as a clear oil [Found: C, 57.2 (uncorr.); H, 10.7; B, 4.40; peroxidic O, 24.6. Calc. for $\text{C}_{12}\text{H}_{27}\text{O}_4\text{B}$: C, 58.5; H, 11.1; B, 4.40; peroxidic O, 26.0%]. The peroxide was unreactive towards hydrogen and Raney nickel in ether at room temperature and pressure, and was not reduced by lithium aluminium hydride.

Hydrolysis of sec.-Butyldi-(sec.-butylperoxy)boron.—The peroxyboron compound was isolated

⁵ Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

⁶ Williams and Mosher, *Analyt. Chem.*, 1955, **27**, 517.

after autoxidation of the alkyl (0.6683 g.) as described above. The product was shaken with water (25 c.c.) for 2 hr.; 2N-sodium hydroxide (5 c.c.) was then added, and the solution shaken for 0.5 hr., then extracted with ether (3 × 20 c.c.). The extract was dried (MgSO₄), and the bulk of the ether removed. Vapour-phase chromatography of the product showed the presence of *sec.*-butyl hydroperoxide, *sec.*-butyl alcohol, and a trace of butan-2-one. The infrared spectrum showed a weak carbonyl-group absorption at 5.95 μ and a strong peak at 11.66 μ characteristic of the O–O stretching frequency of *sec.*-butyl hydroperoxide.

With respect to this and the preceding paper, we are indebted to Professors E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for their interest and encouragement, and to Mr. P. J. Chaffe for technical assistance. This work was carried out during the tenure of a D.S.I.R. Fellowship by D. G. H.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, July 1st, 1958.]
