The Reaction of Organoboranes with Neutral Hydrogen Peroxide

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WHILE the reaction of organoboranes with alkaline hydrogen peroxide leads to high yields of alcohol,[1] we have found that the reaction with neutral hydrogen peroxide follows a quite different course. At 0°, in tetrahydrofuran (THF) solution, the major products of reaction are dimeric hydrocarbons, as shown in the Table for tri-n-hexylborane prepared by the hydroboration of hex-1-ene. Similar yields are obtained by use of diglyme or methanol as solvent. The reaction is insensitive to temperature ($-20°$ to $+60°$) and to the concentration of organoborane (0·05—2·0M). One mole of hydrogen peroxide per mole of organoborane is sufficient to produce the maximum yield of hydrocarbons, and further hydrogen peroxide slowly produces only hexan-1-ol and a little hexan-2-ol. It therefore appears that only two of the three boron–carbon bonds of the organoborane are broken during the hydrocarbon-producing stages of the reaction. Addition of alkali and

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Percentage yields of products in the reaction of aqueous hydrogen peroxide (30% w/v) *with tri-n-hexylborane* (0·52M)

Product	THF solution,[a] 0°			CCl$_4$ solution,[b] 25°	THF–I$_2$ solution[c]
	3 hr. reaction	24 hr. reaction	24 hr. reaction followed by oxidation with excess NaOH–H$_2$O$_2$		
n-Hexane	—	6·5	6·5	3·1	—
Hex-1-ene	—	0·1	0·1	0·4	—
n-Dodecane	27·2	27·0	28·6	7·2	0·3
5-Methylundecane	8·1	8·1	8·1	2·4	0·1
n-Hexanol	5·6	5·4	39·6	24·0	20·5
Hexan-2-ol	—	0·1	2·3	—	—
1-Chlorohexane	—	—	—	27·3	—
1-Iodohexane	—	—	—	—	25·8

Molar ratios of reactants: [a]1·04 H$_2$O$_2$: 1·0 R$_3$B; [b] 2·72 H$_2$O$_2$: 1·0 R$_3$B; [c] 2·0 H$_2$O$_2$: 1·0 R$_3$B.

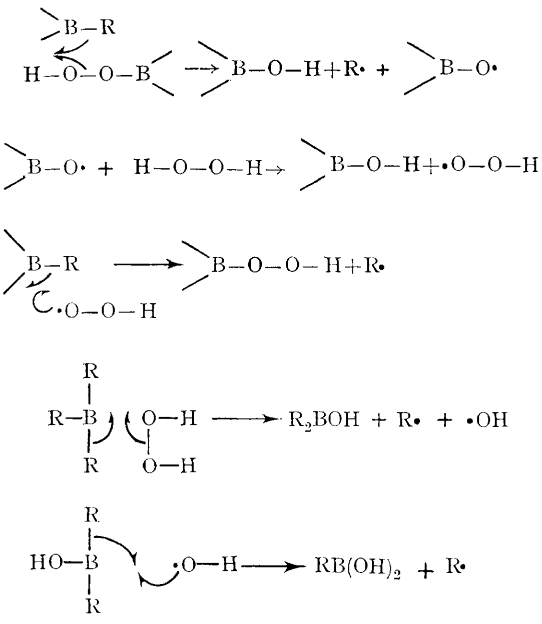
further hydrogen peroxide after 24 hr., under neutral conditions, released another mole of alcohol. Organoboranes containing t-alkyl groups react beyond the boronic acid stage, and less than 1 mole of alcohol is released on subsequent oxidation.

The dimeric products (see Table) suggest that a radical reaction is occurring, the products being similar to those obtained by Brown from the reaction of organoboranes with noble metal oxides.[2] In order to test this idea, we conducted the neutral peroxide reaction in well stirred solutions of CCl$_4$ and THF–iodine. The results are shown in the Table. The yield of dimers is considerably reduced, and the alkyl halides are produced in approximately corresponding yields. Hexachloroethane was produced in CCl$_4$ solution.

When tri-n-hexylborane (12·8 mmole) and tri-n-pentylborane (13·0 mmole), prepared separately and mixed at 0°, were together subjected to reaction with neutral hydrogen peroxide, n-decane, n-undecane, and n-dodecane were produced in a ratio of 1·03 : 2·0 : 0·96. These yields are very close to the statistical ratio, and are consistent with a radical mechanism in which the radicals readily penetrate their solvent cage.

Two reasonable mechanisms may be written for the neutral peroxidation reaction. Organoboranes react with organoperoxyboranes to give dimeric hydrocarbons,[3] and in the present case a chain reaction might be envisaged. Alternatively a molecular attack of H$_2$O$_2$ on the borane could precede the free radical displacement reaction on boron.[4]

Both mechanisms account for the stoicheiometry and products of the reaction, both in THF



and CCl$_4$ solutions. The diminished reactivity of the third boron–carbon bond will result from the weaker Lewis acidity of RB(OH)$_2$ and the consequently reduced co-ordination with a third oxygen atom.

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