

## Anodic Oxidation of n-Butylboronic Acid

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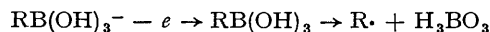
APPRECIATION of electrochemical synthetic methods in organic chemistry dates from Kolbe's study of the electrolysis of solutions of the alkali salts of aliphatic carboxylic acids.<sup>1</sup> Recent work on the chemical oxidation of boronic acids  $RB(OH)_2$ ,<sup>2</sup> has prompted us to investigate the electrochemical oxidation of these compounds.

Electrolysis of an aqueous solution of n-butylboronic acid in excess of alkali, *i.e.*, n-butylboronate anion,  $C_4H_9B(OH)_3^-$ , between smooth platinum electrodes, at a current density of 18 mA  $cm^{-2}$  produced boric acid (identified by paper chromatography using n-butanol as developing solvent and alcoholic curcumin for detection —  $R_f$  values: boric acid 0.54, n-butylboronic acid 0.89) and a mixture of hydrocarbons, consisting mainly of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene, in the ratios 3.3:1:1 (analysed by gas-liquid chromatography, using dimethylsulpholan as the stationary phase). Traces of n-butane were present, but no n-octane nor butanol was detected; the absence of the dimeric product n-octane, is consistent with observations on Kolbe's synthesis

using carboxylic acids, where dimeric products are favoured by higher current densities.

Using both n-butyl- and benzene-boronic acids, no anodic waves were observed when a polarographic investigation was carried out at a stationary platinum microelectrode. Benzeneboronic acid was recovered unchanged also when electrolysis was attempted under the conditions described above for n-butylboronic acid.

We are currently engaged in a more detailed study of the scope and mechanism of this new electrochemical process, but the results presented above are not inconsistent with a mechanism analogous to that suggested<sup>3</sup> for Kolbe's synthesis:



The primary butyl radical  $R\cdot$  could then lose a  $\beta$ -hydrogen, either directly, to give but-1-ene, or after rearrangement to the secondary butyl radical, forming the but-2-enes.

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<sup>1</sup> H. Kolbe, *Annalen*, 1849, **69**, 257; B. C. L. Weedon, *Quart. Rev.*, 1952, **6**, 380.

<sup>2</sup> H. Minato, J. C. Ware, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1963, **85**, 3024.

<sup>3</sup> A. C. Brown and J. Walker, *Annalen*, 1891, **261**, 107; C. L. Wilson and W. T. Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 4290.