

liquid chromatographic pyrolysis temperatures of 200–275° were employed and yields of 10–25% (based on II) were obtained. Products were identified by molecular weight determinations and comparisons (infrared spectra and g.l.c. behavior) with authentic samples.^{13–16}

Except in the cases of Va and Vb, the only hydrocarbon by-products observed were traces of the starting diene arising from incomplete reduction of II. The pyrolysis of IIIb at 210° leads to the formation of Vb (60%) and hexadiene-1,5 (35%); at higher pyrolysis temperatures, the diene becomes the major constituent. The ready thermal conversion of Vb to the isomeric diene has been observed previously.^{8,13} In no case was fragmentation of the intermediate diradical to produce two olefins observed; such fragmentation has been commonly observed in the decomposition of tetrahydropyridazines^{6–8} and is pronounced in cases such as IVf.^{6,7}

Further efforts to extend this preparative method to substituted fused cyclobutane systems and to improve the reduction of II are in progress.

Acknowledgment.—This study was supported in part by a grant (RG-6811) from the Division of General Medical Sciences, Public Health Service. We are indebted to Professor R. Criegee for providing a generous sample of Va and to Drs. J. P. Chesick and M. L. Halberstadt for information regarding the g.l.c. analysis of Va.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH 13, PENNSYLVANIA
MELLON INSTITUTE
PITTSBURGH 13, PENNSYLVANIA

C. E. GRIFFIN
N. F. HEFFINGER

B. L. SHAPIRO

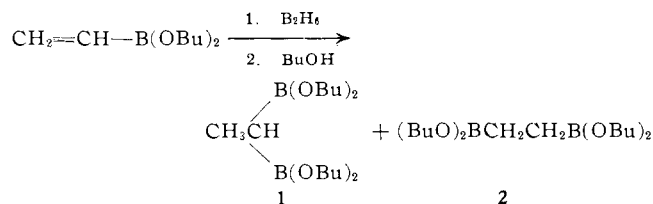
RECEIVED AUGUST 2, 1963

Ethane-1,1-diboronic Acid

Sir:

Stable, crystalline ethane-1,1-diboronic acid is easily prepared *via* the hydroboration of dibutyl ethyleneboronate. Mercuric oxide replaces both boron atoms with mercury. Only scattered examples of such *gem*-dimetallic compounds have been accessible.¹

Dibutyl ethyleneboronate² (54 g., 0.27 mole) was added in 4 hr. to a solution of 0.15 mole of distilled diborane in 300 ml. of tetrahydrofuran³ at 0° under nitrogen, then allowed to stand overnight. Addition of 50 g. of oxygen-free butanol in 4 hr. and stirring 6 hr. longer followed by vacuum distillation yielded 40 g. (44%) of tetrabutyl ethane-1,1-diboronic acid (1) mixed with some of its 1,2- isomer (2), b.p. 78–90° (0.05 mm.). *Anal.* Calcd. for C₁₈H₄₀B₂O₄: C, 63.18; H, 11.78; B, 6.32. Found: C, 63.50; H, 11.84; B, 6.57. This ester oxidized rapidly in air and was handled under nitrogen.



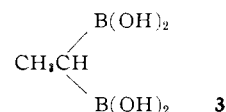
(1) Solutions containing *gem*-diboron compounds: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961); a 1,3,5-triboracyclohexane derivative: R. Köster and G. Benedikt, *Angew. Chem.*, **75**, 346 (1963); methylenedilithium and methylenemagnesium: K. Ziegler, K. Nagel, and M. Patheiger, *Z. anorg. allgem. Chem.*, **282**, 345 (1955); several α -metalloalkylsilicon compounds: P. D. George, M. Prober, and J. R. Elliot, *Chem. Rev.*, **56**, 1065 (1956).

(2) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

(3) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

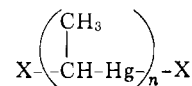
Addition of 1.6 g. of the ester mixture (1 and 2) to 0.5 ml. of water in 6 ml. of tetrahydrofuran followed by addition of 8 ml. of methylene chloride precipitated 0.08 g. of pure ethane-1,2-diboronic acid, (HO)₂BCH₂-CH₂B(OH)₂, m.p. 180–190° dec., lit.⁴ m.p. 130° dec. *Anal.* Calcd. for C₂H₈B₂O₄: C, 20.40; H, 6.85; B, 18.38. Found: C, 20.61; H, 6.84; B, 18.12. This acid yielded no aldehyde on treatment with hydrogen peroxide. It was only slightly soluble in water.

Treatment of the mother liquor with an additional 8–12 ml. of methylene chloride precipitated 0.37 g. (67%) of ethane-1,1-diboronic acid (3), m.p. 142–150° dec., analyzed without further purification. *Anal.* Found: C, 20.57; H, 6.78; B, 18.30. This moderately



water-soluble acid appeared to be free of 1,2- isomer on infrared examination. Treatment with hydrogen peroxide and 2,4-dinitrophenylhydrazine² yielded 67% of acetaldehyde 2,4-dinitrophenylhydrazone.

Dialkylmercuries have been prepared from boranes, freshly precipitated mercuric oxide, and alkali.⁵ Under nitrogen, a solution of 0.6 g. (5 mmoles) of ethane-1,1-diboronic acid (3) in 18 ml. of water was added in 1.5 hr. to a stirred slurry of mercuric oxide from 0.4 g. of sodium hydroxide and 1.35 g. (5 mmoles) of mercuric chloride, then stirred 3 hr. longer. The solid was collected, rinsed with water, and dried. For recrystallization, it was mostly dissolved by refluxing 3 hr. in 200 ml. of dry tetrahydrofuran. The solution was filtered and concentrated to 165 ml. Addition of 35 ml. of water precipitated 0.6 g., m.p. 173°; recrystallized, m.p. 195° dec. *Anal.* Found: C, 8.91; H, 2.37; Cl, 5.33; Hg, 79.35. We postulate the structure 4, polyethylidene-mercury, in which *n* may average about 3 and the groups X are partly -HgCl and partly oxygen-containing functions, based on the composition. Although the hydrogen content is high, the infrared spectrum did not reveal any -OH.



The structure 4 was confirmed by refluxing 0.20 g. of polyethylidene-mercury and 0.36 g. of iodine in 5 ml. of tetrahydrofuran 2 hr. to yield 0.4 g. of crude mercuric iodide and 0.08 g. (34%) of purified ethylidene iodide, identical with an authentic sample⁶ by infrared. Polyethylidene-mercury was shown to be crystalline by its X-ray powder pattern, but the material decomposed to metallic mercury under irradiation. It also decomposed to mercury on grinding with potassium bromide in air. Its solutions in dimethyl sulfoxide decompose in a few hours. However, it has considerable thermal stability, surviving heating at 150° under vacuum 1 hr. with sublimation of only a small part of the material and no change in the infrared spectrum.

Acknowledgment.—We thank Dr. R. D. Willett and Mr. J. M. Williams for the X-ray data and the National Institutes of Health (PHS Grant CA-05513) and the National Science Foundation (NSF G-19906) for financial support.

(4) A. K. Holliday and A. G. Massey, *J. Chem. Soc.*, 43 (1960).

(5) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **82**, 3051 (1960).

(6) R. L. Letsinger and C. W. Hammeyer, *ibid.*, **73**, 4476 (1951).

DEPARTMENT OF CHEMISTRY
WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON

DONALD S. MATTESON
JOSÉ G. SHDO

RECEIVED JULY 8, 1963