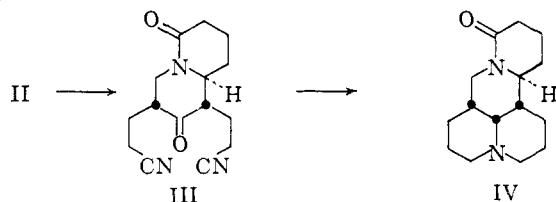


162–165° (0.05 mm.), infrared maxima at 5.78 and 6.13 μ (C, 58.35; H, 8.20; N, 5.02). Diekmann cyclization with sodium hydride in refluxing benzene gave a crystalline keto ester which was decarboxylated by refluxing 6 hr. in glacial acetic acid to the ketone II (55% over-all yield), b.p. 122°–124° (0.1 mm.), m.p. 34–35°, infrared maxima at 5.78 and 6.02 μ , DNP m.p. 215–215.5° (C, 51.45; H, 5.27; N, 20.55).



8-Oxo-2-quinolizidone II was biscyanoethylated *via* a modification of the Stork⁷ enamine procedure with acrylonitrile to give the impure dinitrile III.⁸ Reduction of III with 5% palladium on charcoal in acetic acid solution at room temperature and 50 p.s.i. gave a product which yielded *d,l*-matrine (0.5 g. from 1.5 g. of impure III) upon chromatography over alumina. The *d,l*-matrine had an infrared spectrum identical with that of natural *d*-matrine, but resisted attempts at crystallization. It gave a crystalline picrate (92% yield), m.p. 167–169°, which analyzed correctly for the picrate of matrine (C, 52.67; H, 5.61; N, 14.62). Attempts to regenerate crystalline *d,l*-matrine from the picrate failed.

Acknowledgment.—We wish to acknowledge the support of this research by the National Institutes of Health through Research Grant RG-7902.

(7) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(8) This material was a mixture of mono- and dinitriles and resisted purification. It was converted to a product suitable for catalytic hydrogenation by molecular distillation.

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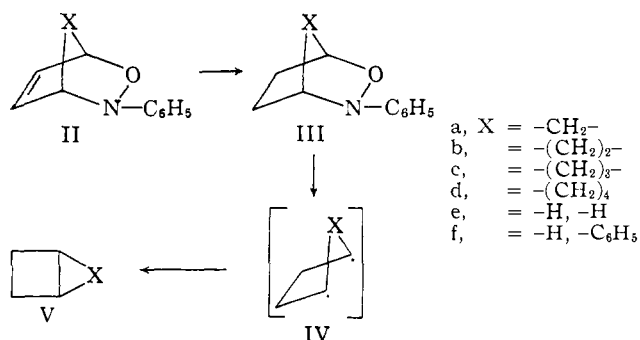
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RECEIVED JUNE 3, 1963

The Pyrolysis of 2-Phenyltetrahydro-1,2-oxazines as a Simple Preparative Entry to Cyclobutanes

Sir:

The dienophilic activity of nitrosobenzene (I) has been demonstrated¹ and the products from I and simple dienes have been shown to possess typical Diels–Alder adduct structures II^{2,3}; in a number of instances, the adducts have been shown to be thermally unstable, re-



(1) R. L. McKee in "The Chemistry of Heterocyclic Compounds," R. H. Wiley, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 332.

(2) G. Kresze and G. Schulz, *Tetrahedron*, **12**, 7 (1961); G. Kresze, G. Schulz, and F. Firl, *Angew. Chem. Intern. Ed. Engl.*, **2**, 263 (1963).

(3) N. F. Hepfinger, Ph.D. Thesis, University of Pittsburgh, 1963; C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, unpublished results.

generating starting materials.^{2,3} We now wish to report that the reduced forms of these adducts, 2-phenyltetrahydro-1,2-oxazines (III), undergo a pseudo Diels–Alder reversal with the formation of I and the cyclobutane V derived from the original diene. The conversion of dienes to the corresponding cyclobutanes has been achieved previously by the thermal and catalytic decomposition of tetrahydropyridazines^{4–8}; the decomposition of III is analogous and probably proceeds through a similar diradical intermediate IV.^{4,6} The ease of the over-all reaction (diene \rightarrow V) and the ready availability of starting materials indicate that the process constitutes a useful entry into simple and fused cyclobutane systems. Additionally, fragmentation and rearrangement of the diradical IV to olefinic products appear to be less prevalent than in tetrahydropyridazine decompositions.^{7,8}

The formation of bicyclo[2.1.0]pentane (Va) is typical of the process. The adduct IIa^{2,3} of cyclopentadiene and I was reduced in ethanol at 0° according to the method of Brown and Brown.⁹ IIIa was isolated by elution from Florisil with hexane and further purified by Celite chromatography and recrystallization (-70°) from pentane; IIIa [Found: C, 75.67; H, 7.82; N, 7.80] melted at 40–41° and the absence of unsaturation was confirmed by its infrared spectrum. The pyrolytic behavior of IIIa was determined by g.l.c.¹⁰ Use of an inlet temperature of 225° led to the detection and identification of a trace amount of cyclopentadiene, I and products arising from its decomposition at 225°, and a major peak (*ca.* 70%) identified as Va. The identity of Va was established by infrared and p.m.r. and g.l.c. behavior comparisons with an authentic sample.⁵ At higher injection port temperatures, a mixture of Va and its isomer, cyclopentene, were formed; at temperatures in excess of 300°, only the olefin could be detected.¹¹ Larger scale pyrolyses¹² of IIIa also resulted in the formation of Va. In a typical run, 1.2 g. of IIIa led to the isolation of Va (55%), cyclopentene (30%), and cyclopentadiene (trace). Over-all yields of 10–18% of Va from cyclopentadiene have been obtained routinely.

In like manner, bicyclo[2.2.0]hexane¹³ (Vb), bicyclo[3.2.0]heptane¹⁴ (Vc), bicyclo[4.2.0]octane¹⁴ (Vd), cyclobutane¹⁵ (Ve), and phenylcyclobutane¹⁶ (Vf) have been prepared from the adducts II of I and cyclohexadiene, cycloheptatriene, cyclooctadiene-1,3, butadiene, and 1-phenylcyclobutadiene, respectively. Because of their limited stability, the tetrahydrooxazines III were pyrolyzed without extensive purification; isolations were achieved by column chromatography. Gas-

(4) G. C. Overberger, N. R. Byrd, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

(5) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(6) S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *J. Am. Chem. Soc.*, **79**, 4400 (1957).

(7) R. Ya. Levina, Yu. S. Shabarov, M. G. Kuz'min, N. I. Vasil'ev, S. I. Pokraka, and E. G. Treshchova, *J. Gen. Chem. USSR*, **29**, 3504 (1959).

(8) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(9) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493, 1494 (1962).

(10) All g.l.c. analyses were carried out with an F & M Model 720 gas chromatograph using a coupled column of 15 in. of 30% silver nitrate-ethylene glycol on firebrick and 4.5 ft. of silicone oil on firebrick with a helium flow rate of 40 ml./min. Column temperatures of 25–100° were employed. We are indebted to M. L. Halberstadt for supplying the details of this chromatographic separation procedure.

(11) The thermal isomerization of Va to cyclopentene has been extensively studied, *cf.* M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962), and ref. 5.

(12) Pyrolyses have been carried out by the use of a free flame with the sample contained in a tube of large surface area attached to a vacuum system; pyrolysis products were collected in liquid nitrogen traps.

(13) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, **No. 21**, 24 (1960).

(14) A. T. Blomquist and J. Kwiatek, *J. Am. Chem. Soc.*, **73**, 2098 (1951).

(15) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

(16) F. H. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934).

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.

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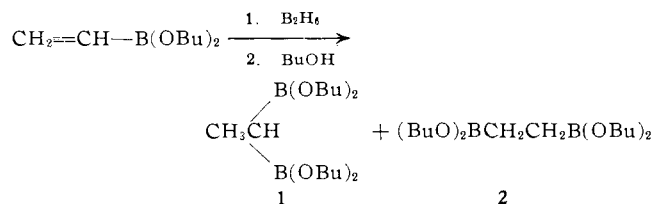
RECEIVED AUGUST 2, 1963

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.



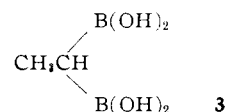
(1) Solutions containing *gem*-diboron compounds: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961); a 1,3,5-triboracyclohexane derivative: R. Köster and G. Benedikt, *Angew. Chem.*, **75**, 346 (1963); methylenedilithium and methylenemagnesium: K. Ziegler, K. Nagel, and M. Patheiger,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

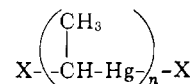
Addition of 1.6 g. of the ester mixture (1 and 2) to 0.5 ml. of water in 6 ml. of tetrahydrofuran followed by addition of 8 ml. of methylene chloride precipitated 0.08 g. of pure ethane-1,2-diboronic acid, (HO)₂BCH₂-CH₂B(OH)₂, m.p. 180–190° dec., lit.⁴ m.p. 130° dec. *Anal.* Calcd. for C₂H₈B₂O₄: C, 20.40; 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.

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

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