

The occurrence of the sulfonic acid group in a hexose molecule suggests function of sulfo-carbohydrate metabolism in Nature. The sulfolipid<sup>6</sup> itself is unique among known lipids in possessing a readily metabolizable but chemically stable sulfonate radical which gives the lipid its strongly surfactant properties.

(6) The term sulfolipid denotes the sulfonic acid group. Those lipids such as cerebroside sulfuric ester have similar physical properties but must be classified as sulfatides because of their sulfate ester structure. Other neutral sulfur-containing lipids such as those in yeast and in lesser quantities in plants may be classified as thiolipids.

(7) Organisch Chemisches Institut der Technischen Hochschule, Munich.

DEPARTMENT OF AGRICULTURAL  
AND BIOLOGICAL CHEMISTRY  
THE PENNSYLVANIA STATE UNIVERSITY  
UNIVERSITY PARK, PENNSYLVANIA

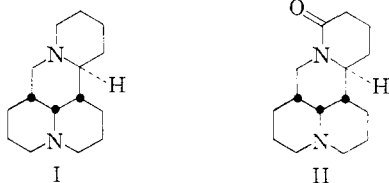
H. DANIEL<sup>7</sup>  
M. MIYANO  
R. O. MUMMA  
T. YAGI  
M. LEPAGE  
I. SHIBUYA  
A. A. BENSON

RECEIVED FEBRUARY 17, 1961

### THE SYNTHESIS OF *dl*-MATRIDINE

Sir:

We wish to report the synthesis of *dl*-matridine, I, a reduction product of matrine,<sup>1</sup> II, the principal alkaloid of *Sophora flavescens* Ait.<sup>2</sup> The relative stereochemistry as represented in I and II has been established by several groups of workers<sup>1,2,3,4</sup>



and is confirmed by the synthetic route herein reported. This route is an extension of the method we reported earlier<sup>5</sup> for the synthesis of hexahydrojulolidine which utilizes as an important step the bis alkylation of enamines with acrylonitrile after the method of Stork.<sup>6</sup>

Thus the pyrrolidine enamine<sup>7</sup> of 3-oxaquinolizidine,<sup>8</sup> III, was treated with one mole of acrylonitrile in ethanol to give, IV, b.p. 123° (0.2 mm.), picrate m.p. 179° (infrared spectrum shows nitrile at 2250 cm.<sup>-1</sup> and carbonyl at 1715 cm.<sup>-1</sup>) which was further treated with pyrrolidine and thence a second mole of acrylonitrile in ethanol-dimethylformamide solution (1:1) and refluxed for 30 hr. After hydrolysis V was obtained as a thick yellow liquid, b.p. 145° (0.15 mm.), picrate m.p. 189–191° with decomposition (infrared shows intense nitrile band at 2250 cm.<sup>-1</sup> and carbonyl at 1715 cm.<sup>-1</sup>).

(1) F. Bohlman, W. Weise, D. Rahtze and C. Arndt, *Ber.*, **91**, 2167 (1958).

(2) F. Bohlman, W. Weise, D. Rahtze and C. Arndt, *ibid.*, **91**, 2177 (1958).

(3) K. Tsuda, *et al.*, *Ber.*, **69**, 429 (1936); *J. Org. Chem.*, **21**, 1481 (1956).

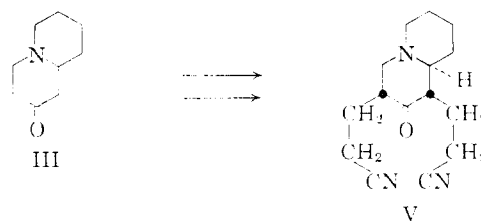
(4) E. Ochai, S. Okuda and H. Minato, *J. Pharm. Soc. Japan*, **72**, 781 (1952).

(5) K. P. Singh and L. Mandell, Abs. A.C.S. meeting, Sept., 1960, p. 62.

(6) G. Stork, Abs. of the 16th National Organic Chemistry Symposium, June, 1959, pp. 44–52.

(7) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5130 (1956).

(8) G. R. Clemo, T. P. Metcalfe and R. Raper, *J. Chem. Soc.*, 1429 (1936).



Compound V was hydrogenated in ethanol with W-5 Raney nickel catalyst at 1500 p.s.i. and 100° for 8 hr. The solvent was removed and the ether-soluble portion chromatographed on neutral alumina affording *dl*-matridine, I, m.p. (recrystallized from ethanol/acetone) 48–49°, picrate m.p. 229–232° with decomposition. The infrared spectrum was identical in every respect with *d*-matridine obtained by lithium aluminum hydride reduction of matrine. It was noted that no other di-tertiary amines were isolated from the reduction. In addition to the resolution of *dl*-matridine we are now extending this approach to the synthesis of *dl*-matrine.

**Acknowledgment.**—The authors express their thanks to McNeil Laboratories, Incorporated, Philadelphia, and the National Institutes of Health (Research Grant A-2397) for their financial aid in this project.

DEPARTMENT OF CHEMISTRY  
EMORY UNIVERSITY  
ATLANTA 22, GEORGIA

LEON MANDELL  
K. P. SINGH

RECEIVED DECEMBER 22, 1960

### THE PREPARATION OF DIBORON TETRACHLORIDE FROM BORON MONOXIDE<sup>1</sup>

Sir:

Although boron monoxide has been known for several years,<sup>2</sup> there have been few investigations of its chemistry. We wish to report a new reaction of boron monoxide which also constitutes a unique and useful synthesis of diboron tetrachloride, B<sub>2</sub>Cl<sub>4</sub>. Stock<sup>3</sup> originally prepared diboron tetrachloride, B<sub>2</sub>Cl<sub>4</sub>, in small quantities by a discharge reaction in which the electrodes were immersed in liquid boron trichloride. Schlesinger and co-workers<sup>4</sup> have obtained diboron tetrachloride in higher yields by passing gaseous boron trichloride through a glow discharge between mercury electrodes at 1–2 mm. pressure. Subsequent modifications of this general discharge method utilizing gaseous boron trichloride have not resulted in significantly higher yields.<sup>5,6,7</sup>

Diboron tetrachloride now has been prepared conveniently by the reaction of boron trichloride with boron monoxide, (BO)<sub>n</sub>, which was obtained by the vacuum dehydration of tetrahydroxydiboron as described previously.<sup>8</sup> Tetrahydroxydiboron

(1) The research reported in this document was supported by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contract AF 33(616)-5931.

(2) E. Zintl, W. Morawietz and E. Gastinger, *Z. anorg. allgem. Chem.*, **245**, 8 (1940).

(3) A. Stock, A. Brandt and H. Fischer, *Ber.*, **58B**, 643 (1925).

(4) T. Wartik, R. E. Moore and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5293 (1954).

(5) J. Frazer and R. Holzmann, *ibid.*, **80**, 2907 (1958).

(6) A. Holliday and A. Massey, *ibid.*, **80**, 4744 (1958).

(7) A. Holliday and A. Massey, *J. Chem. Soc.*, 43 (1960).

(8) T. Wartik and E. F. Apple, *J. Am. Chem. Soc.*, **77**, 6400 (1955).