

The occurrence of the sulfonic acid group in a hexose molecule suggests function of sulfo-carbohydrate metabolism in Nature. The sulfolipid⁶ 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

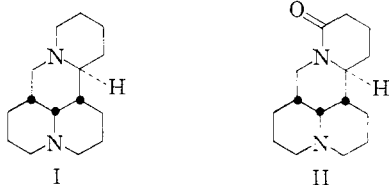
H. DANIEL⁷
M. MIYANO
R. O. MUMMA
T. YAGI
M. LEPAGE
I. SHIBUYA
A. A. BENSON

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THE SYNTHESIS OF *dl*-MATRIDINE

Sir:

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



and is confirmed by the synthetic route herein reported. This route is an extension of the method we reported earlier⁵ for the synthesis of hexahydrojulolidine which utilizes as an important step the bis alkylation of enamines with acrylonitrile after the method of Stork.⁶

Thus the pyrrolidine enamine⁷ of 3-oxaquinolizidine,⁸ 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.⁻¹ and carbonyl at 1715 cm.⁻¹) 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.⁻¹ and carbonyl at 1715 cm.⁻¹).

(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).

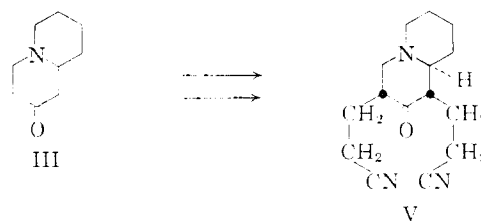
(4) E. Ochai, S. Okuda and H. Minato, *J. Pharm. Soc. Japan*, **72**, 781 (1952).

(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.

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DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
ATLANTA 22, GEORGIA

LEON MANDELL
K. P. SINGH

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THE PREPARATION OF DIBORON TETRACHLORIDE FROM BORON MONOXIDE¹

Sir:

Although boron monoxide has been known for several years,² 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, B₂Cl₄. Stock³ originally prepared diboron tetrachloride, B₂Cl₄, in small quantities by a discharge reaction in which the electrodes were immersed in liquid boron trichloride. Schlesinger and co-workers⁴ 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.^{5,6,7}

Diboron tetrachloride now has been prepared conveniently by the reaction of boron trichloride with boron monoxide, (BO)_n, which was obtained by the vacuum dehydration of tetrahydroxydiboron as described previously.⁸ 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).

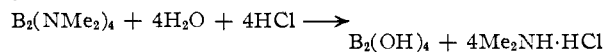
(5) J. Frazer and R. Holzmann, *ibid.*, **80**, 2907 (1958).

(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).

was prepared from tetra-(dimethylamino)-diboron in about 60% yield by low-temperature hydrolysis in hydrochloric acid solution as shown in the equation



Tetrahydroxydiboron prepared in this manner appears to be identical with that obtained by Wartik⁹ from diboron tetrachloride. Excess boron trichloride was passed over 80.6 mg. of boron monoxide at 200–236° at 450 mm. pressure. Fractionation of the boron trichloride stream gave 0.192 mmole (13% conversion of boron monoxide) of diboron tetrachloride which had vapor pressures of 2.3 and 6 mm. at –45 and –30°, respectively. The reported vapor pressures of diboron tetrachloride at these temperatures are 2.3 and 6.8 mm.⁴ The infrared spectrum of the material isolated was identical with that reported in the literature for diboron tetrachloride,¹⁰ and its elemental analyses were satisfactory for this compound.

(9) T. Wartik and E. F. Apple, *J. Am. Chem. Soc.*, **80**, 6155 (1958).

(10) M. J. Linevsky, *et al.*, *ibid.*, **75**, 3287 (1953); D. E. Mann and L. Fano, *J. Chem. Phys.*, **26**, 1665 (1957).

U. S. BORAS
RESEARCH CORPORATION
ANAHEIM, CALIFORNIA

A. L. McCLOSKEY
J. L. BOONE
R. J. BROTHERTON

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CESIUM FLUORIDE CATALYZED REARRANGEMENT OF PERFLUORODIENES TO PERFLUORODIALKYLACETYLENES

Sir:

We have found that reaction takes place between cesium fluoride and perfluorodienes at moderate temperatures in the absence of a solvent to yield perfluorodialkylacetylenes. We conclude that the reaction path consists of a series of $\text{SN}2'$ substitutions with fluoride ion as shown below with perfluoro-1,4-pentadiene. The greater stability indicated for the perfluoroalkylacetylenes as compared with the isomeric dienes is in contrast to the relative stabilities of corresponding hydrocarbons¹ and appears to be due to the presence of additional CF_3 - and $-\text{CF}_2$ - groupings. The ready conversion of terminal perfluoroolefins into internal olefins by fluoride ion supports this view.²

Perfluoro-1,3-butadiene, 4.4 g., and 6.0 g. of anhydrous cesium fluoride were heated in a sealed glass ampule at 150° for 0.5 hr. to yield 3.0 g., 68%, pure perfluoro-2-butyne, $\text{CF}_3\text{C}\equiv\text{CCF}_3$, as shown by gas chromatogram,³ infrared spectrum, and by chlorination to $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$, m. p. 82.7–83.5°, reported m. p. 83–84°.⁴ A similar reaction at 100° for 0.5 hr. yielded 83% $\text{CF}_3\text{C}\equiv\text{CCF}_3$ and 1% recovered $\text{CF}_2=\text{CFCF}=\text{CF}_2$. At room temperature after 100 days 76.4% pure $\text{CF}_3\text{C}\equiv\text{CCF}_3$ was isolated. At 200° with a 22 sec.

(1) D. D. Wagman, C. W. Beckett, J. E. Kilpatrick, K. S. Pitzer, E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **35**, 467 (1945); **42**, 225 (1949).

(2) W. T. Miller, Jr., J. H. Fried and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(3) Gas chromatographic separations and analyses were carried out with dioctyl phthalate on Chromosorb-W at room temperature.

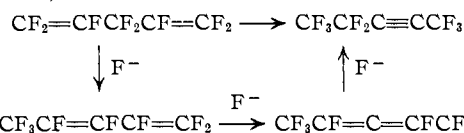
(4) A. L. Henne, J. B. Hinkamp and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **67**, 1906 (1945).

contact time over CsF 22% $\text{CF}_3\text{C}\equiv\text{CCF}_3$ and 40% $\text{CF}_2=\text{CFCF}=\text{CF}_2$ were recovered.

Recently, Christie, Tlumac, Dresdner and Young reported the preparation of perfluorobicyclopentane, b.p. 3.3–3.6°,⁷ from perfluoro-1,4-pentadiene by passing the diene over cesium fluoride at 250°.⁵ On repeating this reaction we find that the product, obtained in about 95% yield and purity with a 40 sec. contact time, is, in fact, perfluoro-2-pentyne, a result suggested to us by the rearrangement of perfluoro-1,3-butadiene described above.^{6,8}

After purification,³ $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$ was characterized by: b.p. 3–4°, weak λ_{max} at 4.27, 4.38, 4.92 μ , strong Raman λ_{max} 2300 cm^{-1} ¹¹; reported b.p. 7.5° with weak λ_{max} at 4.9 μ .¹² Chlorination gave $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_2\text{CF}_3$, b.p. 150°, n_{D}^{20} 1.3861 d_{4}^{20} 1.853 (Cl, calcd. 40.1; found 40.0%); reported b.p. 145–147°, n_{D}^{24} 1.3838, $d_{\text{4}}^{28.5}$ 1.8238.¹²

Reaction takes place very easily between liquid perfluoro-1,4-pentadiene and cesium fluoride. From 3.35 g. of $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$ ¹³ and 6.0 g. of CsF heated at 80° for 0.5 hr. were recovered 2.3 g., 68%, $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$ and 0.20 g., 6%, mixed pentadienes. The intermediate dienes were isolated³ from a reaction at 45° for 8 hr. and shown to have properties consistent with the structures and reaction sequence given below. From 5.6 g. of $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$ and 4.0 g. of CsF were recovered 0.27 g., 4.8%, of $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$; 0.47 g., 8.4%, $\text{CF}_3\text{CF}=\text{C}=\text{CFCF}_3$, b.p. 17°, λ_{max} 4.94 μ , tetrachloride, b.p. 151–152°, n_{D}^{20} 1.3853; 1.22 g., 21.7%, $\text{CF}_3\text{CF}=\text{CFCF}=\text{CF}_2$, b.p. 28.4°, λ_{max} 5.60 and 5.78 μ , tetrachloride, b.p. 151–152°, n_{D}^{20} 1.3798.



Perfluoro-1,5-hexadiene, b.p. 59.6°,⁹ on treatment with CsF also yields an acetylenic product, b.p. 27–28°, consisting of two compounds, presumably $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_2\text{CF}_3$ and $\text{CF}_3\text{CF}_2\text{C}\equiv\text{CCF}_3$

(5) W. H. Christie, F. N. Tlumac, R. D. Dresdner and J. A. Young, Abstracts of Papers, 138th Meeting, Amer. Chem. Soc., New York, N. Y., Sept. 1960, p. 18-M.

(6) The above workers have confirmed our conclusion regarding the formation of $\text{CF}_3\text{C}\equiv\text{CCF}_2\text{CF}_3$. We are grateful to them for details of their experiments and for a comparison sample of their product.⁷

(7) Private communications from R. D. Dresdner and J. A. Young.

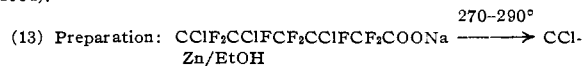
(8) Attempts to prepare perfluorobicyclopentane by thermal cyclization of perfluoro-1,4-pentadiene, following the procedure utilized by Fainberg and Miller to prepare perfluorobicyclo[2.2.0]hexane from perfluoro-1,5-hexadiene,⁹ have yielded perfluorocyclopentane as the major and thermally stable product.¹⁰ This reaction requires shift of a fluorine atom and probably takes place with the intermediate formation of perfluorobicyclopentane.

(9) A. H. Fainberg and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **79**, 4170 (1957).

(10) P. R. Resnick, Ph.D. Thesis, Cornell University, February, 1961.

(11) We are indebted to R. E. Hester for the Raman spectra.

(12) A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, **76**, 810 (1954).



(725 mm.), n_{D}^{20} 1.2911, d_{4}^{20} 1.5184. Chlorination yielded $\text{CClF}_2\text{CClFCF}_2\text{CClFCClF}_2$, b.p. 153.7° (742 mm.), n_{D}^{20} 1.3744, d_{4}^{20} 1.7902.