by Wood, Sweeney and Derbes are in good agreement with the above equation when the heat of transition is taken to be 1.55 kcal./mole. This value may be compared with data from the literature for the heat of transition of cesium chloride. Wagner and Lippert estimated the heat of transition to be 1.8 kcal./mole from lattice energies.[3] Cooling curves by Zemczuzny and Rambach give an estimated heat of transition equal to 1.2 kcal./mole.[4] It therefore seems reasonable to believe that the correct value for the heat of transition is close to 1.5 kcal./mole, with the cations statistically distributed over all cation positions in the solid solution.

NOTE ADDED IN PROOF.—After this paper was written, a calorimetric measurement of ΔH_{tr} equal to 0.581 kcal./mole has been published.[5] If the heat content equations given in that work are considered, one obtains $\Delta H_{tr} = 0.76$ kcal./mole, one half the value suggested in this paper. A pairing of the rubidium atoms in the solid solution thus seems to be indicated, if there is no solid solution of rubidium chloride in low cesium chloride.

(3) S. Zemczuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 403 (1910).
(4) G. Wagner and L. Lippert, *Z. physik. Chem.*, **B31**, 263 (1936).
(5) C. E. Kaylor, G. E. Walden and D. F. Smith, *J. Phys. Chem.*, **64**, 276 (1960).

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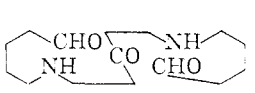
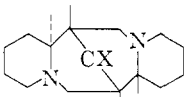
THE BIOGENETIC-TYPE SYNTHESIS OF *dl*-SPARTEINE

Sir:

An integral step in the proposed[1] biosynthesis of the alkaloid sparteine (II, X = H_2) is the formation of 8-ketosparteine (II, X = O) by cyclization of the diaminoketodialdehyde I, presumed to arise in nature by decarboxylation, deamination



I



II

and coupling of γ-keto-α,α′-diaminopimelic acid and two molecules of lysine.[2] In a laboratory synthesis designed to proceed through I, or a similar structure, the tetracyclic system of sparteine with the correct orientation of the four asymmetric centers, can be constructed in two simple operations starting from acetone, formaldehyde and piperidine.[3]

β,β′-Di-(N-piperidino)-diethyl ketone (III)[4] was prepared from the aforementioned starting materials by a Mannich reaction carried out in acetic acid.[5] Mercuric acetate dehydrogenation[6] of III to give I[7] (or the monocyclization product) is followed by stereoselective ring closure *in situ* to II (X = O), m.p. 71–72.5° (Found: C, 72.55; H, 9.79; N, 11.08). The constitution of this intermediate was proved by Wolff–Kishner reduction to *dl*-sparteine,[8] which was identified by comparison, through melting points of salts, with authentic *dl*-sparteine,[9] as well as by infrared spectral identity (chloroform solution) with *l*-sparteine free base.[10]

Biogenetic and mechanistic facets of this synthesis will be examined in a full publication.

(1) R. Robinson, "The Structural Relations of Natural Products," Oxford University Press, London, 1955, p. 75.
(2) The recent discovery (personal communication from Prof. M. Carmack, University of Indiana) of 8-oxygenated tetracyclic lupin alkaloids lends further credence to this biogenetic scheme.
(3) A reported physiological-type synthesis of 8-ketosparteine involving Δ¹-piperideine, formaldehyde and acetonedicarboxylic acid (E. Anet, G. K. Hughes and E. Ritchie, *Nature*, **165**, 35 (1950), has been discredited (C. Schöpf, G. Benz, F. Braun, H. Hinkel and R. Rokohl, *Angew. Chem.*, **65**, 161 (1953)). For utilization of the abnormal spiro compound actually produced, see abstract of lecture, C. Schöpf, GDCh-Ortsverband Frankfurt/M., *ibid.*, **69**, 69 (1957).
(4) First prepared by another method by S. M. McElvain and W. B. Thomas, THIS JOURNAL, **56**, 1806 (1934).
(5) See F. F. Blicke and F. J. McCarty, *J. Org. Chem.*, **24**, 1376 (1959).
(6) N. J. Leonard and F. P. Hauck, Jr., THIS JOURNAL, **79**, 5279 (1957).
(7) The aminoaldehyde, alkanolamine, enamine and iminium salt are regarded as equivalent structures for the present purpose.
(8) For prior syntheses of sparteine, see the references cited by N. J. Leonard in Manske and Holmes, "The Alkaloids," Vol. III, Academic Press, Inc., New York, N. Y., p. 163–166.
(9) N. J. Leonard and R. E. Beyler, THIS JOURNAL, **71**, 757 (1949); **72**, 1316 (1950).
(10) This investigation was supported by RG-3892, National Institutes of Health.

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CHLORODIFLUOROAMINE[1]

Sir:

The anticipated behavior of difluoroamine,[2,3] HNF_2, as a Lewis base prompted an investigation of its interaction with boron trichloride. Equimolar quantities of the two gases condensed *in vacuo* at −130° to form a white solid, stable at −80°. Warming toward room temperature resulted in decomposition to hydrogen chloride, chlorine, a non-volatile solid, and the new compound chlorodifluoroamine, NF_2Cl. Purification was accomplished by vacuum fractionation through traps maintained at −142° and −196°. The −196° fraction was passed through an Ascarite tower to remove hydrogen chloride and refractionated. The yield of chlorodifluoroamine after purification was 50%.

Chlorodifluoroamine is a colorless, air-stable gas. Its vapor pressure curve is given by the equation

$$\log P_{mm.} = -(950/T) + 7.478$$

The extrapolated boiling point is −67°. The heat of vaporization calculated from the above equation is 4350 cal./mole with a Trouton constant of 21.0. The melting point of chlorodifluoroamine was not obtained but lies between −183° and −196°. A molecular weight determination by the vapor density method gave a value of 87.8 (theoretical 87.5).

The mass spectrum of chlorodifluoroamine, obtained on a Consolidated Electrodynamics Model 620 Mass Spectrometer, is given in Table I. Peaks attributed to Cl_2^+ may result from partial disproportionation of the sample to Cl_2 and N_2F_4 in the metal inlet system of the mass spectrometer.

(1) This work was conducted under Army Ordnance Contract, DA-01-021-ORD 5135.
(2) A. Kennedy and C. B. Colburn, THIS JOURNAL, **81**, 2906 (1959).
(3) E. A. Lawton and J. Q. Weber, *ibid.*, **81**, 4755 (1959).