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.

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[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).

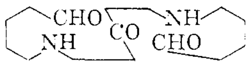
SVENSKA SILIKATFORSKNINGSINSTITUTET
GÖTEBORG, SWEDEN J. KROGH-MOE

RECEIVED FEBRUARY 22, 1960

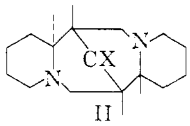
THE BIOGENETIC-TYPE SYNTHESIS OF *dl*-SPARTEINE

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 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]



I



II

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.

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[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 Δ^1-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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN EUGENE E. VAN TAMELEN
MADISON, WISCONSIN RODGER L. FOLTZ

RECEIVED MARCH 30, 1960

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.

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[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).

TABLE I

FRAGMENTATION PATTERN OF $ClNF_2$

m/e	Relation intensity	Ion
14	3.8	N^+
19	1.6	F^+
33	37.1	NF^+
35	21.9	Cl^+
37	6.5	
49	30.1	NCl^+
51	7.2	
52	100.	NF_2^+
68	26.2	$NFCl^+$
70	22.4	
72	8.5	Cl_2^+
74	1.3	
87	46.4	NF_2Cl^+
89	14.5	

Samples giving essentially the same cracking pattern were shown to contain less than 0.5% Cl_2 by ultraviolet spectrometry.

The infrared spectrum of chlorodifluoroamine consists of very strong bands centered at 10.8 (triplet), 11.7 (doublet) and 14.4μ (triplet); a doublet of medium intensity centered at 13.4μ and weak bands at 5.4, 5.7, 5.9 and 7.3μ.

The F^{19} n.m.r. spectrum of chlorodifluoroamine consists of a single broad band centered at 8685 cycles to the low field side of trifluoroacetic acid.

Chlorine and fluorine analyses were obtained by conversion to ammonium chloride by reaction with ammonia at 150°, and by conversion to sodium chloride and fluoride by reaction with sodium in liquid ammonia at $-50°$. Calcd. for NF_2Cl: F, 43.45: Cl, 40.54. Found: F, 42.35; Cl, 39.92.

Chlorodifluoroamine has been kept at ambient temperatures in Pyrex vessels for extended periods without decomposition. It is reactive toward mercury at room temperature (forming N_2F_4 and Hg_2Cl_2), necessitating the use of a spoon gauge or Kel-F oil-protected manometers for pressure measurements.

Caution should be exercised in handling chlorodifluoroamine since N-halogen compounds are known to exhibit explosive properties.

ROHM & HAAS COMPANY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA ROBERT C. PETRY

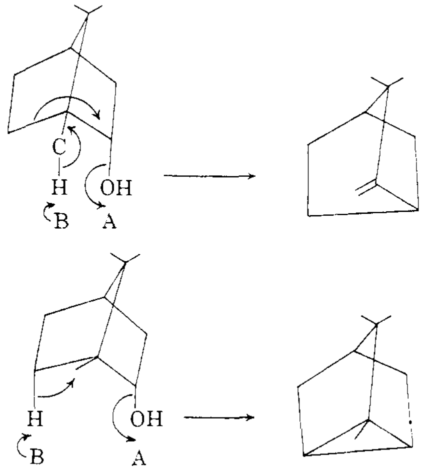
RECEIVED MARCH 18, 1960

DEHYDRATION OF ALCOHOLS OVER ALUMINA MODIFIED BY AMMONIA[1,2]

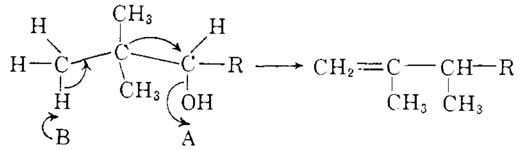
Sir:

We wish to report a new dehydration catalyst which was obtained by modifying alumina by ammonia. On the modified catalyst, *d*-borneol on dehydration forms 23% of tricyclene and 77% of *d*-camphene with 94% retention of configuration.[3] The main feature of the catalyst is the suppression of the carbonium ion character of dehydration. This is due to the preferential poisoning of the "strong acid sites" of alumina by ammonia.[4] In contrast to these results, borneol, over an unmodified alumina gave a mixture containing at least twelve hydrocarbons as shown by vapor-phase chromatography.

We suggest that the surface of the modified alumina has both acidic and basic sites and that the dehydration takes place by a concerted mechanism as shown below, A and B representing acidic and basic sites, respectively.



On the modified alumina catalyst, neopentyl alcohol yielded on dehydration 70% of 2-methyl-1-butene (I) and 30% of 2-methyl-2-butene, while pinacolyl alcohol formed 73% of 3,3-dimethyl-1-butene and 25% of 2,3-dimethyl-1-butene (II). On the unmodified alumina a complex mixture of olefinic hydrocarbons is obtained. The formation of I and II is in accordance with the postulated mechanism in which the participation of the γ-carbon atom occurs



Menthol was dehydrated over the modified alumina to form 2-menthene of 91% purity, while neomenthol gave a mixture of 2- and 3-menthene, the latter forming 75% of the total. These experiments demonstrate that when dehydration proceeds by a 1,2-elimination, the *trans* elimination is the preferred one. On the unmodified alumina dehydration is not selective.

The experimental technique involves passing a stream of ammonia along with the alcohol over the heated catalyst. Pure alumina, prepared by the hydrolysis of aluminum isopropoxide and modified by ammonia in this manner gave the best selectivity with the highest dehydration activity. The reactions were carried out in the temperature range of 240–340°.

The synthetic uses of the new catalyst are evident. 3,3-Dimethyl-1-butene could be prepared

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(1) Part V of the series, "Alumina: Catalyst and Support"; for paper IV, see H. Pines and C. T. Chen, THIS JOURNAL, in press.

(2) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

(3) The camphene and tricyclene could be separated from each other by chromatography over silica gel.

(4) H. Pines and W. Haag, THIS JOURNAL, **82**, May 20 (1960).