

labeled compound, or for transfer to a gas activity measuring device such as an ionization chamber or gas counter, it has been common practice to drop either concentrated phosphoric or sulfuric acid on the BaCO_3 .³ This procedure often involves the use of a stopcock in contact with concentrated acid, does not permit the ready attainment of high vacuum and may entail the formation of a crust of insoluble barium sulfate or phosphate around the active barium carbonate. In practice a still more disconcerting factor has been the spattering of the dry powder on contact with acid with the consequent sweeping of a portion of the sample out of the reaction vessel by the evolving gas. The direct thermal evolution of the C^*O_2 from BaC^*O_3 by roasting the dry salt in a quartz tube has also been used⁴ but the temperature necessary is inconveniently high.

These difficulties may be surmounted by using a thermal reaction between dry solids to evolve the carbon dioxide. Acids such as potassium bisulfate are unsuitable as the reaction will produce water as well as carbon dioxide. Inorganic acid anhydrides such as boric oxide and the pyro salts melt at too high a temperature to be used in Pyrex apparatus. Organic anhydrides sublime under vacuum. A convenient reaction, however, is a metathetic one producing a thermally unstable carbonate such as the reaction between barium carbonate and lead chloride. Lead chloride was used because it can be readily obtained in an anhydrous state, and has a low melting point and vapor pressure. Silver chloride can also be used.

To obtain the total carbon dioxide from a barium carbonate sample, two procedures have been worked out. In the micro-procedure the weighed barium carbonate, from 5 to 200 mg., is dropped into a Pyrex test-tube with attached ground joint.

(3) (a) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947); (b) J. T. Kummer, *THIS JOURNAL*, **69**, 2239 (1947); (c) J. L. Huston and T. H. Norris, *ibid.*, **70**, 1968 (1948).

(4) M. G. Inghram, Atomic Energy Commission, MDDC 60, June, 1946.

Over this is layered 5 to 10 times its weight of dry powdered lead chloride, and then a wad of glass wool is pushed down on top. After attaching the tube to the vacuum system and pumping at 100° , the carbon dioxide is released by carefully melting the lead chloride with a micro burner. The reaction is known to be at least 98% complete from gas buret and activity measurements. The fusion temperature may be lowered by using a 50-50 mixture of PbCl_2 - AgCl instead of pure lead chloride. The melt should not fill a full diameter of the reaction vessel or the latter may crack on cooling. For macro-quantities we have employed the following procedure. The two solids, one part by weight of barium carbonate and six parts by weight of lead chloride, were intimately mixed and ground together before placing the mixture in a reaction tube. The latter was connected to a standard vacuum system by means of a stopcock and a standard taper ground glass joint. The reaction mixture was pumped overnight at room temperature to a pressure of 10^{-5} mm. A tubular woven glass heating mantle was used as a heat source and the temperature was controlled by a Variac. Evolution of gas began at about 180° and each increment of temperature caused a more rapid evolution of gas which gradually decreased with time. It was found that the most convenient procedure was to raise the temperature to 400° as rapidly as possible (about twenty-five minutes) and maintain the reaction mixture at this temperature. The evolution of carbon dioxide was 65% complete in one hour from the start of heating, 80% in two hours and 96% complete in four hours. 3-9 g. of barium carbonate was employed in these experiments. Thus this reaction has been found to proceed at temperatures well below the fusion temperature and the system may therefore be used as a convenient, clean, "virtual" source of active carbon dioxide.

BROOKHAVEN NATIONAL LABORATORY

UPTON, NEW YORK

RECEIVED AUGUST 16, 1948

COMMUNICATIONS TO THE EDITOR

METALLIC ALUMINUM IN SOLUTION IN LIQUID AMMONIA

Sir:

It has long been generally accepted that the alkali metals, in dissolving in liquid ammonia, dissociate into alkali metal cations and free (solvated) electrons,¹ and that the latter impart the characteristic blue color to such solutions. The alkaline earth metals are known to dissolve simi-

larly, although to a smaller extent.² Makishima³ included the dissolution of electrons among electrode reactions which may occur at a cathode in liquid ammonia solutions, and Laitinen and Nyman⁴ have very recently pointed out that, theoretically, all metals should be in some degree soluble in liquid ammonia. According to the hypothesis

(2) Kraus, *ibid.*, **30**, 660 (1908).

(3) Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, No. 3, 115 (1938).

(4) Laitinen and Nyman, *THIS JOURNAL*, **70**, 3002 (1948).

(1) Kraus, *THIS JOURNAL*, **30**, 1323 (1908).

of these latter authors, however, the solubility of metals less active than calcium should be exceedingly small.

On the basis of the reaction of metallic aluminum with solutions of alkali metal amides in liquid ammonia, Bergstrom⁵ postulated that aluminum must be soluble in this solvent to a slight extent. There is no record in the literature, however, of any actual observation of a blue solution of metallic aluminum in ammonia, although Booth and Merlub-Sobel,⁶ in a study of the electrolysis of aluminum iodide, reported the formation at the cathode of a transitory blue-black film which they suggested might be a subiodide or subnitride of aluminum.

In the course of an investigation, recently begun in this Laboratory, of the anodic oxidation of aluminum in solutions of various salts in liquid ammonia, we have carried out several electrolyses with aluminum iodide as electrolyte. In every such case, we have observed the appearance, in the immediate vicinity of the *cathode*, of a deep blue color. This color is at first impermanent, disappearing upon diffusion into the body of the solution with the concurrent formation of a white precipitate, and being regenerated at the cathode. On prolonged electrolysis, however, the rate of disappearance gradually decreases, and the entire solution eventually becomes dark blue. The most striking results were obtained in a solution containing 0.3 g. of aluminum iodide in 48 g. of ammonia, which was electrolyzed at -33° in an atmosphere of nitrogen between a bright platinum cathode and a chemically pure aluminum anode, at a cathode current density of about 0.01 amp. per sq. cm.

We are unable to account for these results in terms of any hypothesis other than the following. The cathode reaction appears to consist of the dissolution of electrons, which are able to exist in the presence of a considerable concentration of Al^{+++} ion. The blue solute, consisting therefore of ionized metallic aluminum, at first reacts rapidly with the solvent, liberating hydrogen and yielding an insoluble white derivative of aluminum amide; subsequently, however, the rate of this reaction decreases, so that an appreciable concentration of aluminum metal is able to persist in the solution for as much as fifteen minutes after the current is discontinued.

This phenomenon is being studied further, and will later be the subject of a more complete report.

ARTHUR W. DAVIDSON
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

JACOB KLEINBERG
WILLIAM E. BENNETT
ALBERT D. McELROY

RECEIVED DECEMBER 10, 1948

(5) Bergstrom, *THIS JOURNAL*, **45**, 2788 (1923); **46**, 1545 (1924); *f. Fernelius and Watt*, *Chem. Revs.*, **20**, 195 (1937).

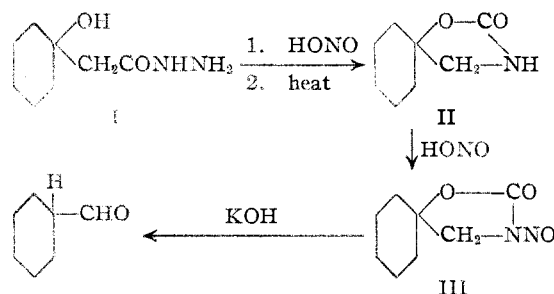
(6) Booth and Merlub-Sobel, *J. Phys. Chem.*, **35**, 3303 (1931)

A NOVEL REACTION IN ORGANIC CHEMISTRY

Sir:

In connection with studies designed to develop a new approach to ring enlargement of cyclic ketones, an interesting new reaction has been discovered. When 3-nitroso-1-oxa-3-azaspiro[4,5]-decan-2-one, III, is treated with alkali, nitrogen is evolved immediately and hexahydrobenzaldehyde is produced. This aldehyde has been isolated in over 50% yield as the semicarbazone,^{1,2} m. p. 172-173° after sintering at 166°.

The nitroso compound was prepared by the following series of reactions



Further studies as to the generality and mechanism of this reaction are under way in this Laboratory.

The author wishes to acknowledge a grant from the Research Corporation which has greatly assisted in this work.

Hydrazide of 1-Cyclohexanacetic Acid, I.—This compound, m. p.³ 102.2-104.4°, was prepared in 78% yield.

Anal. Calcd. for $C_8H_{16}O_2N_2$: C, 55.8; H, 9.4; N, 16.3. Found: C, 55.6, 55.8; H, 8.9, 8.7; N, 16.3, 16.4.

1-Oxa-3-azaspiro[4,5]decan-2-one, II.—The hydrazide, I, was dissolved in dilute hydrochloric acid and treated with a slight excess of sodium nitrite at 10-15°. The reaction mixture containing the resulting oily azide was slowly heated to 45° when decomposition began. Rapid stirring and temp. control near 50° are necessary to prevent violent decomposition. The cyclic urethane,⁴ II, was isolated in 82% yield as colorless crystals, m. p. 101.0-102.4°.

Anal. Calcd. for $C_8H_{15}O_2N$: C, 61.9; H, 8.4; N, 9.0. Found: C, 61.8; H, 8.2; N, 9.3.⁵

On alkaline hydrolysis 1-aminomethylcyclohexanol (m. p. of N-benzoate,⁶ 143-144°) was obtained.

3-Nitroso-1-oxo-3-azaspiro[4,5]decan-2-one, III.—II was converted into III, m. p. 82.8-83.2°, in 94% yield by nitrous acid.

Anal. Calcd. for $C_8H_{15}O_3N_2$: C, 52.2; H, 6.6; N, 15.2. Found: C, 52.3, 52.1; H, 6.3, 6.1; N, 15.5, 15.6.

Semicarbazide of Hexahydrobenzaldehyde.—To a solution of 1.84 g. of III in 15 cc. of alcohol was added drop-

(1) Melting points ranging from 167° to 176° for this derivative have been reported in Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, 1925, 4th ed., Vol. VII, p. 20.

(2) The author wishes to thank Mr. Abraham Kutner for preparing authentic samples.

(3) All melting points corrected.

(4) A similar cyclization has been reported [Schroeter, *Frdl.*, **10**, 1309 (1910-12)] but no details are mentioned and analyses for the products were not reported.

(5) This analysis by H. S. Clarke, Microanalytical Laboratories, Urbana, Illinois. Other analyses by Mrs. E. H. Klotz, O.S.U.

(6) M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943).

wise a slight excess of 50% potassium hydroxide. The evolution of nitrogen was quantitative. After warming to 60° the semicarbazone was prepared directly to yield 0.95 g. (56%) of semicarbazone, m. p. 172–173°, sintering at 166°.

CHEMISTRY LABORATORY OF
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

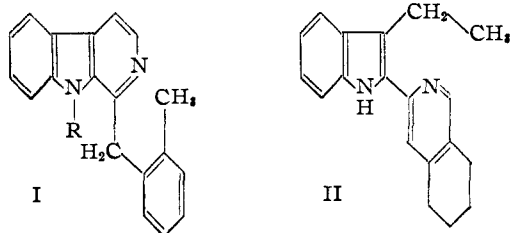
MELVIN S. NEWMAN

RECEIVED DECEMBER 13, 1948

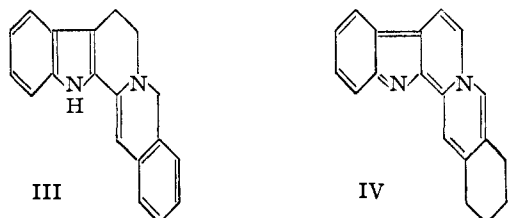
THE STRUCTURE OF SEMPERVIRINE

Sir:

The alkaloid sempervirine, $C_{19}H_{16}N_2$, from *Gel-semium sempervirens*, Ait., is remarkable for its color and its high degree of unsaturation. In a recent elegant investigation, Prelog¹ has shown that the substance is transformed to the isomeric yobyrine (I, R = H) when heated with selenium, and to tetrahydroisoyobyrine (II) on treatment



with Raney nickel. These results led to the proposal of structure (III) for sempervirine.

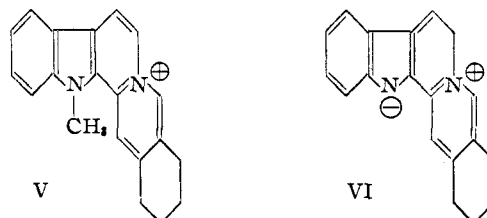


We wish to propose a new structure (IV) for the alkaloid. In our view, the new formula is better in accord with the color of sempervirine, and with the formation from it of tetrahydroisoyobyrine. Beyond that we have been able to marshal new facts which provide further strong support for (IV). Thus, (i) the infrared spectrum of sempervirine contains no band in the NH region, while by contrast, all N-unsubstituted indole derivatives are characterized by an intense sharp band at 2.9 μ ; (ii) when sempervirine methochloride is heated with selenium, a new base, m. p. 103° [hydrochloride, m. p. 229°, picrate, m. p. 235°, (calcd. for $C_{26}H_{21}O_7N_5$: C, 60.58; H, 4.11. Found: C, 60.38; H, 4.15)], is formed, which is clearly N-methyl-yobyrine (I, R = Me), since its ultraviolet spectrum is nearly identical with that of yobyrine, and its infrared spectrum possesses no NH band.² These observations support the

(1) Prelog, *Helv. Chim. Acta*, **31**, 588 (1948).

(2) More recently the nature of the base has been confirmed through direct comparison with a synthetic sample kindly supplied by Dr. Percy L. Julian.

view that the metho-salts of sempervirine contain the cation (V). The expression IV implies of



course an important contribution of the fully aromatic ionic structure (VI). Consideration of this fact makes understandable the formation of metho-salts of the structure (V), as well as the color of the alkaloid, and its high basicity (pK , 10.6). The formation from sempervirine of a mole of methane in the Zerewitinow determination can be attributed to the presence in (IV \leftrightarrow VI) of a virtual (substituted) γ -picolinium system.

We wish to thank M. Raymond-Hamet (Paris) and Professor M.-M. Janot for their gracious gifts of sempervirine.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

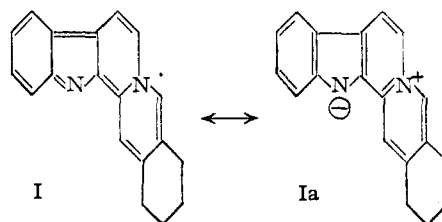
R. B. WOODWARD
BERNHARD WITKOP

RECEIVED MAY 17, 1948

THE SYNTHESIS OF SEMPERVIRINE METHOCHLORIDE

Sir:

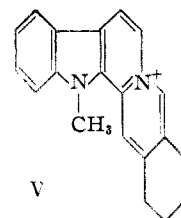
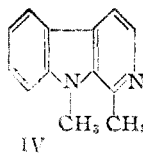
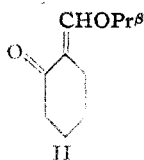
It has been suggested on the basis of analytical and degradative evidence that the alkaloid sempervirine possesses the remarkable structure I \leftrightarrow Ia.¹ We have now been able to provide conclusive evidence for the proposed structure through the synthesis of sempervirine metho-salts by an unambiguous route.



In model experiments, the lithium derivative of α -picoline was condensed with isopropoxy-methylene cyclohexanone² (II) [b. p. 64–65° (0.2 mm.), n_D^{20} 1.4980, calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.18; H, 9.40]. From the acid-treated reaction-mixture, salts of the dehydroquinolizinium cation (III) were readily obtained (picrate, m. p. 237–238°, calcd. for $C_{19}H_{16}O_7N_4$: C, 55.34; H, 3.91; N, 13.59. Found: C, 55.41; H, 4.17; N, 13.36; per-

(1) Woodward and Witkop, *THIS JOURNAL*, **71**, 379 (1949).

(2) Prepared from hydroxymethylene cyclohexanone by the method of Claisen, as reported by v. Auwers (*Ber.*, **71**, 2082 (1938)) and developed by Johnson and Posvic (*THIS JOURNAL*, **69**, 1361 (1947)).



chlorate, m. p. 187.1–187.8°, calcd. for $C_{13}H_{14}O_4 \cdot NCl$: C, 55.05; H, 4.97. Found: C, 55.12; H, 5.05).

In a similar reaction, the use of the lithium derivative of N-methylharman⁸ (IV) led to the smooth synthesis of salts of the methylsempervirinium cation (V). Synthetic samples of sempervirine methopicate, m. p. 239–240°, and

(3) Cf. Späth and Lederer, *Ber.*, **63**, 2102 (1930). Our material was made from N-methyltryptophan, which was itself prepared very smoothly by a new synthesis analogous to that used by Warner and Moe (*THIS JOURNAL*, **70**, 2766 (1948)) for the preparation of tryptophan. Our melting point (285°) for N-methyltryptophan agrees with that (289°) of Wieland, Konz and Mittasch (*Ann.*, **513**, 23 (1934)) rather than that (225°) recently reported by Snyder and Eliel (*THIS JOURNAL*, **70**, 3855 (1948)).

sempervirine methochloride, m. p. 330–332°, showed no depression in melting point on admixture with the corresponding salts of identical melting points prepared from natural sempervirine. The identity was further confirmed through the reproduction by synthetic sempervirine methochloride of the very characteristic ultraviolet absorption behavior of the salt from the natural alkaloid [λ_{\max} . (log ϵ): 241 (4.56), ~250 (4.49), 292 (4.20), 330 (4.28), 395 (4.22); λ_{\min} . (log ϵ): 280 (4.14), 305 (4.09), 365 (4.10)].

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
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R. B. WOODWARD
W. M. McLAMORE

RECEIVED JANUARY 11, 1949

NEW BOOK

Microdiffusion Analysis and Volumetric Error. By EDWARD J. CONWAY, M.B., D.Sc., Professor of Biochemistry, University College, Dublin, and Member of the Royal Irish Academy. Crosby Lockwood and Son, Ltd., 20 Tudor Street, London, E. C. 4, England, 1947. xix + 357 pp. Illustrated. 14 × 22.5 cm. Price 21/- net.

Although the literature shows an ever-increasing application of the microdiffusion principle, the lack of a general description of the technique in books on methodology makes this detailed and carefully written book especially valuable.

Conway was the first to develop the microdiffusion technique to a point where full advantage is taken of the simplicity, accuracy and convenience inherent in this method. By eliminating distillation or aeration in the determination of volatile substances, labor, apparatus and time are saved particularly in serial analyses. It may surprise many that the diffusion time in the micro-ammonia procedure, for example, may be less than thirty minutes and that the accuracy is equal to that of the macro procedure.

The book is divided into three sections. The first deals with the design of the diffusion cell and the factors governing the rate of diffusion. The second section describes critically and in detail most of the published applications of the microdiffusion principle. The last section discusses the factors influencing variable error in volumetric analysis and establishes a rational basis for maintaining macro accuracy in micro procedure. This discussion should be of value to all analysts who wish to maintain given standards of accuracy in volumetric analysis.

JACOB W. DUBNOFF

BOOKS RECEIVED

November 10, 1948–December 10, 1948

- A. D. BOOTH. "Fourier Technique in X-Ray Organic Structure Analysis." Cambridge at the University Press. The Macmillan Company, 60 Fifth Ave., New York 11, N. Y. 1948. 106 pp. \$2.75.
- LI CH'IAO-P'ING, "The Chemical Arts of Old China." Chemical Education Publications, 2030 Northampton St., Easton, Pa. 1948. 215 pp. \$5.00.
- ALEXANDER FINDLAY. "A Hundred Years of Chemistry." The Macmillan Company, 60 Fifth Ave., New York 11, N. Y. 1948. 318 pp. \$4.50.
- R. W. HARMON AND C. B. POLLARD. "Bibliography of Animal Venoms." University of Florida Press, Law Building, Gainesville, Fla. 1948. 340 pp. \$8.00.
- JOSEPH H. KEENAN AND JOSEPH KAYE. "Gas Tables. (Thermodynamic Properties of Air Products of Combustion and Component Gases. Compressible Flow Functions.)" John Wiley and Sons, Inc., 440 West 44th St., New York 16, N. Y. 1948. 238 pp. \$5.00.
- HUGH C. MULDOON. "Organic Chemistry." Third Edition. The Blakiston Company, Philadelphia 5, Pa. 1948. 648 pp.
- R. T. SANDERSON. "Vacuum Manipulation of Volatile Compounds." John Wiley and Sons, Inc., 440 West 44th St., New York, N. Y. 1948. 162 pp. \$3.00.
- R. STOOPS, Editor. "Rapports et Discussions sur les Isotopes," 76-78 Coudenberg, Bruxelles. 411 pp.
- "Reports of the Biochemical Research Foundation of the Franklin Institute." Vol. IX. 1946-47. Dr. Ellice McDonald, Director. Biochemical Research Foundation, Newark, Del.