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, Bergstrom[5] 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.

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ARTHUR W. DAVIDSON
JACOB KLEINBERG
WILLIAM E. BENNETT
ALBERT D. MCELROY

RECEIVED DECEMBER 10, 1948

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

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

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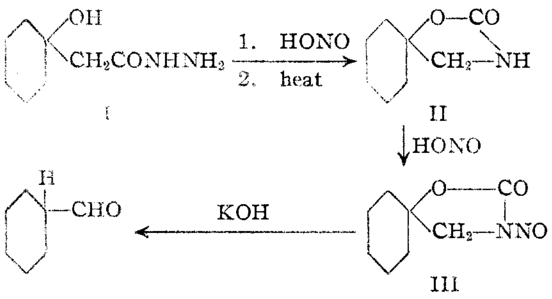
## A NOVEL REACTION IN ORGANIC CHEMISTRY

*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-Cyclohexanolacetic 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 urethan,[4] II, was isolated in 82% yield as colorless crystals, m. p. 101.0–102.4°.

*Anal.* Calcd. for $C_8H_{13}O_2N$: 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 $C_8H_{12}O_3N_2$: 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-

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(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°.

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RECEIVED DECEMBER 13, 1948

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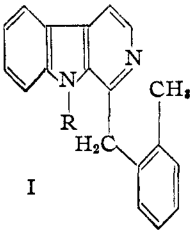
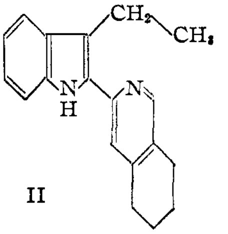
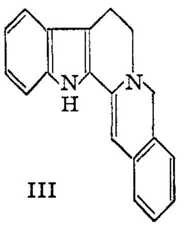
## THE STRUCTURE OF SEMPERVIRINE

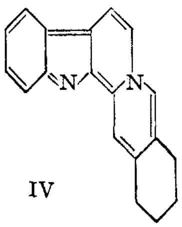
*Sir:*

The alkaloid sempervirine, $C_{19}H_{16}N_2$, from *Gelsemium sempervirens*, Ait., is remarkable for its color and its high degree of unsaturation. In a recent elegant investigation, Prelog[1] 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.

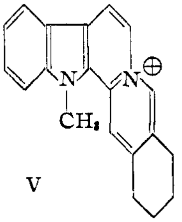

I

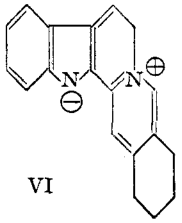

II


III


IV

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 $2.9\ \mu$; (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-methylyobyrine (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 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 $\longleftrightarrow$ VI) of a virtual (substituted) $\gamma$-picolinium system.


V


VI

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

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RECEIVED MAY 17, 1948

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[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.

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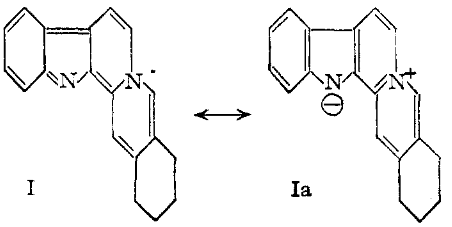
## THE SYNTHESIS OF SEMPERVIRINE METHOCHLORIDE

*Sir:*

It has been suggested on the basis of analytical and degradative evidence that the alkaloid sempervirine possesses the remarkable structure I $\longleftrightarrow$ 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.


I Ia

In model experiments, the lithium derivative of $\alpha$-picoline was condensed with isopropoxymethylene cyclohexanone[2] (II) [b. p. 64–65° (0.2 mm.), $n^{26}\text{D}$ 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-

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[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)).