

56, 2790 (1934)] confirmed the preparation and properties of some of the compounds reported by Faucounau, and in addition gave the properties of another member of this series of alcohols. Apparently all of the above authors have overlooked the fact that this type of reaction was first reported by Iotsitch [*J. Russ. Phys.-Chem. Soc.*, **39**, 652 (1907); *cf. Bull. soc. chim.*, [iv] **6**, 98 (1909)] who used it to prepare 3-pentyn-1-ol.

Some time ago (1929) the writer also studied this reaction and prepared 3-nonyn-1-ol in 52% yields. Faucounau reports a boiling point of 103–130.5° at 19 mm. for this substance. This is doubtless a typographical error and should in all probability have been 130–130.5° at 19 mm., which corresponds to the boiling point as found by the author. The urethan was prepared and found to melt at 64.5° [*Anal.* Calcd. for  $C_{16}H_{21}O_2N$ : N, 5.41. Found: N, 5.44].

The above alcohol was converted into 1-bromononyn-3 by the action of phosphorus tribromide in benzene. This bromo hydrocarbon boiled at 95° at 9 mm. [*Anal.* Calcd. for  $C_9H_{16}Br$ : Br, 39.4. Found: Br, 39.1]. 1-Bromononyn-3 did not arise when heptynylmagnesium bromide was treated in ether solution with  $\beta$ -bromoethyl-*p*-toluene sulfonate [b. p. 203° (5 mm.). *Anal.* Calcd. for  $C_9H_{11}O_3SBr$ : Br, 28.7. Found: Br, 28.5]. It should be mentioned that the above sulfonic acid ester has an exceedingly bitter taste.

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G. BRYANT BACHMAN

RECEIVED JANUARY 5, 1935

#### EXCHANGE REACTIONS OF DEUTERIUM AND METHANE UNDER THE INFLUENCE OF EXCITED MERCURY

Sir:

Experiments of Taylor and Hill [THIS JOURNAL, **51**, 2922 (1929)] indicated that mixtures of methane and hydrogen in presence of mercury vapor were unchanged on prolonged exposure to high intensities of mercury resonance radiation. Other data of Bonhoeffer, Harteck and Geib [*Z. physik. Chem.*, **139A**, 64 (1928); *ibid.*, **170A**, 1 (1934)] indicated that methane is not attacked by atomic hydrogen even up to temperatures of 184°. Important conclusions with respect to the stability of methane and methyl radicals and to the bonding energies of these substances are de-

pendent on the accuracy of the above observations. Accordingly we have reexamined the matter making use of methane-deuterium mixtures in presence of mercury vapor and illuminated by resonance radiation. Examination of the products of illumination by the methods of infra-red spectroscopy reveals that considerable interaction occurs at all temperatures investigated from 40–300°. The deuteromethanes  $CH_3D$ ,  $CH_2D_2$ , etc., are always produced in amounts dependent on the time and temperature of illumination. This points to an energetic interaction between atomic deuterium and methane molecules, since the latter were screened from photo-decomposition by an acetic acid filter. Preliminary data on the activation energy of the process indicate that this is low, of the order of 5 kilo-cal., in marked contrast to the value of 17 kilo-cal., recently estimated by Geib and Harteck (*loc. cit.*). More accurate experiments now in progress will serve to give quantitative data on these hitherto unsuspected reactions of atomic deuterium (or hydrogen) with methane. Our observations have also been checked with the aid of Raman spectra as well as by the measurements of infra-red absorption. These also will be reported later. We wish to acknowledge our indebtedness to Dr. R. B. Barnes for his courtesy in permitting the use of his infra-red spectrometer.

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RECEIVED JANUARY 22, 1935

#### THE STRUCTURE OF THE ERGOT ALKALOIDS

Sir:

A communication, now in press and which will shortly appear in the *Journal of Biological Chemistry*, describes the results of an investigation of the products which result on the reductive cleavage of ergotinine with sodium and butyl alcohol. Our more recent work has now given a clue to the nature of the basic cleavage products therein described. We have since succeeded in identifying an additional basic cleavage product through its gold salt as the methyl ester of proline [*Anal.* Calcd. for  $C_6H_{11}O_2N \cdot HAuCl_4$ : C, 15.35; H, 2.58; Au, 42.03. Found: C, 15.60; H, 2.70; Au, 42.21]. We have also obtained a gold salt corresponding in properties to that of proline methyl ester from a fraction of the cleavage products resulting from the action of methyl alcoholic hydrochloric acid on

ergotinine. This at once supports the suggestion made by us in this article that certain fragments of the alkaloid molecule may have as their precursors amino acids or substances related to them. The precursor in the molecule responsible for the so-called Base VI, a phenylpropanolamine, may be phenylalanine. Base VI we have shown yields *p*-nitrobenzoic acid on oxidation with nitric acid as in the case of the ergot alkaloids.

In this article other substances which are described are derivatives of a base  $C_{10}H_{20}N_2$  (Base IV), of a base  $C_{14}H_{20}N_2$  (Base II) and of a hydroxyamine  $C_8H_{13}ON$  (Base V). Base IV is probably a substituted piperazine  $C_{10}H_{18}N_2$  resulting from the reduction of proline anhydride. Similarly, Base II can be a piperazine resulting from the reduction of propylphenylalanine anhydride. The formula of Base V (a hydroxyamine) should now be revised to  $C_8H_{11}ON$  and can result from the reduction of proline or its ester to the carbinol,  $\alpha$ -pyrrolidylcarbinol. The procedure employed by us can well be responsible for the production of such bases.

Thus it would now appear that ergotinine and therefore ergotoxine are built up of lysergic acid ( $C_{16}H_{16}O_2N_2$ ) (or ergine,  $C_{16}H_{17}ON_2$ ), proline, phenylalanine and isobutyrylformic acid. When these components are added together with loss of three molecules of water, a substance  $C_{35}H_{39}O_6N_5$  would result which is the formula for ergotinine at present accepted. It is suggested that lysergic acid (ergine), the constituent perhaps responsible for the pharmacodynamic action of these alkaloids, is joined to a group consisting of a polypeptide composed of proline and phenylalanine. Lysergic acid may have a biogenetic relationship to tryptophan and isobutyrylformic acid to valine.

The details of this work as well as the results of its logical development will appear later. The alkaloids ergotamine and ergotaminine are also being included in our studies from this standpoint.

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## NEW BOOKS

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**Experimental Physical Chemistry.** Second Edition. By FARRINGTON DANIELS, J. HOWARD MATHEWS AND JOHN WARREN WILLIAMS, University of Wisconsin. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, 1934. xix + 499 pp. 140 figs. 14.5 × 21.5 cm. Price, \$3.50.

In this revision of their well-known laboratory text the authors have retained the original organization of material and the thought-provoking style in outlining procedures which characterized the former edition (reviewed in *THIS JOURNAL*, 52, 2585 (1930)). Part I (Laboratory Experiments) is unchanged in length, but 16 of the original 78 experiments have been dropped and 9 new ones added. It is safe to say that few users will find their favorites missing. The additions: molecular films on liquids, electrokinetic phenomena, distribution of particle size, reaction rate from dilatometric measurements, galvanic cells with and without transference, the glass electrode, dielectric capacity by heterodyne beat method, heavy hydrogen. Twelve of the exercises retained, notably those dealing with properties of gases and boiling points of solutions, require new or modified apparatus. In addition, so many minor changes have been introduced that the whole book has been reset. Most of the important changes obviously have been made in the interest of greater accuracy without

undue complexity of apparatus. Experience may well show that this aim has been realized.

Part II (Apparatus) is not greatly altered. Here and there new material has been added, particularly on high vacuum technique, on apparatus for measurements of capacitance, and on photochemical and photographic procedures. To Part III (Miscellaneous Operations) have been added short chapters on vacuum tubes and on errors of measurement. In spite of the addition of 24 pages to these sections the volume is less bulky than before, due to the use of thinner paper.

The book is recommended to the attention of teachers and students of physical chemistry.

ARTHUR F. BENTON

**Boiling Points of Ring and Chain Compounds.** By F. F. E. GERMANN and O. S. KNIGHT. Available from the Authors, Department of Chemistry, University of Colorado, Boulder, Colo. Two charts, \$2.00.

The authors have selected values from the literature for the vapor pressures of some 183 common and representative organic substances, and have plotted them in a novel and ingenious fashion using line coordinates. The compounds listed range from methyl ethyl ether to anthraquinone (boiling points 7.7 and 380°, respectively).