

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 C₁₆H₂₁O₂N*: 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 C₉H₁₅Br*: Br, 39.4. Found: Br, 39.1]. 1-Bromononyn-3 did not arise when heptynylmagnesium bromide was treated in ether solution with β -bromoethyl-*p*-toluene sulfonate [b. p. 203° (5 mm.). *Anal. Calcd. for C₉H₁₁O₃SBr*: Br, 28.7. Found: Br, 28.5]. It should be mentioned that the above sulfonic acid ester has an exceedingly bitter taste.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

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 CH₃D, CH₂D₂, 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.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

HUGH S. TAYLOR
K. MORIKAWA
W. S. BENEDICT

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 C₆H₁₁O₂N·HAuCl₄*: 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