COMMUNICATIONS TO THE EDITOR

THE X-RAY STUDY OF INDIUM AND THE INDIUM-SILVER SYSTEM

Sir:

Debye–Scherrer–Hull patterns of 99.91% pure indium have been taken at different temperatures ranging from −25 to 141°. The finely divided indium powder mixed with chemically pure sodium chloride was kept at a constant temperature for periods of about two to six days. Only the known face-centered tetragonal modification was detected. Precision determinations of the cell dimensions of indium at 22° gave a = 4.588 Å. and c = 4.938 Å. Moreover, the two linear coefficients of expansion of indium were determined $\alpha_a = 1/a\cdot(da/dT)_P = 5.6 \times 10^{-5}$ and $\alpha_c = 1.3 \times 10^{-5}$.

With regard to the alloy system, seven indium–silver alloys were prepared in a vacuum quartz furnace. Mixtures of sodium chloride and alloy were used in powdered form, and excellent x-ray diffraction data were obtained for the alloys. In connection with the x-ray examination, microdensity determinations of the alloys were made. Five phases were encountered: (1) a face-centered tetragonal solid solution of silver in indium, (2) a complex phase which gave a pseudo-hexagonal close-packed arrangement of atoms, (3) a face-centered cubic phase very rich in indium, (4) a hexagonal phase with an axial ratio of c/a = 1.588 and (5) a face-centered cubic solid solution of indium in silver.

Further work on the indium–silver alloy system is contemplated and a detailed report will appear soon.

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Emil Ott

Received December 5, 1934

THE OD+ BANDS

Sir:

The writers have recently photographed the OD^+ bands in the electrodeless discharge in heavy water. These bands correspond to the OH^+ bands discovered by Rodebush and Wahl [This Journal, **55**, 1742 (1933)] which have recently been analyzed by Loomis and Brandt [*Phys. Rev.*, **46**, 79 (1934)]. The intensities appear to be the same, and the isotopic displacement, at least in the O—O band, is about that to be expected. The analysis of these bands is likely to be difficult as was the case with the OH^+ bands.

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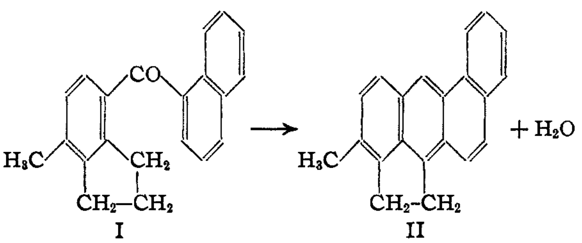
Received December 12, 1934

THE SYNTHESIS OF METHYLCHOLANTHRENE

Sir:

Wieland and Dane's isolation of methylcholanthrene (II) as a degradation product of desoxycholic acid [*Z. physiol. Chem.*, **219**, 240 (1933)] constitutes an important link in the evidence supporting the formulas currently accepted for the bile acids and for the various other natural products related to them. Although the conversion of the hydrocarbon by Cook and Haslewood [*J. Chem. Soc.*, 428 (1934)] into an anthraquinone of established structure leaves little doubt as to the structure of methylcholanthrene, the point in question is of such importance that confirmation by synthesis is desirable. In undertaking such a synthesis we have had in view the further objective of rendering more readily available for animal experimentation the only hydrocarbon of demonstrated carcinogenic activity (Cook and Haslewood) which has been obtained from substances normally present in the body.

The pyrolysis of the ketone I appeared to offer a possible route to methylcholanthrene and in order to determine whether the Elbs condensation can be accomplished when the usual methyl group is replaced by the methylene group of an alicyclic ring, we first investigated the following similarly constituted but more readily available ketones: ar-α-tetralyl α-naphthyl ketone (m. p. 107°) and ar-α-tetralyl β-naphthyl ketone (m. p. 183°).



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These compounds yielded on pyrolysis isomeric hydrocarbons of the composition $C_{21}H_{16}$ (m. p. 119 and 270°, respectively), indicating that the method of synthesis is practical and that pyrolysis proceeds without migration of the aroyl group in the naphthalene nucleus. The ketone I was then synthesized as follows: *p*-bromotoluene was converted by the Blanc reaction into a mixture of the two chloromethyl derivatives; this was treated with sodium malonic ester and the product was hydrolyzed and decarboxylated. Ring closure through the acid chloride mixture gave an easily separated mixture of two methylbromohydrindones (m. p. 154 and 95°) which on reduction by the Clemmensen method yielded the same hydrindene (b. p. 265–267°). The Grignard reagent from this hydrindene on reaction with α-naphthoyl chloride gave the ketone I (liquid) and on pyrolysis of I there was obtained a yellow hydrocarbon (*Anal.* Calcd. for $C_{21}H_{16}$: C, 93.98; H, 6.02. Found: C, 94.11, 94.18; H, 6.26, 5.96) which when purified through the picrate formed yellow needles melting at 176.5–177.5°; picrate 180–181°. No depression in the melting points was observed on admixture with samples of methylcholanthrene (m. p. 176–177°) and its picrate (m. p. 178–179°) prepared from desoxycholic acid.

This synthesis of a bile acid degradation product having 21 of the 24 original carbon atoms and all four of the original rings serves to confirm the accepted structures and it opens the way to the preparation of other hydrocarbons of interest in the study of carcinogenic activity. Further work in this direction is in progress. Before reporting the details of the above synthesis we are attempting to establish the structures of the intermediates obtained in the preparation of the ketone I, although this is not essential to a knowledge of the structure of the latter compound.

CONVERSE MEMORIAL LABORATORY LOUIS F. FIESER
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RECEIVED DECEMBER 17, 1934

THE PREPARATION OF GLUCOSIDODIHYDROXYACETONE PENTAACETATE

Sir:

It has been pointed out by Evans and Hockett [THIS JOURNAL, **53,** 4384 (1931)] that in the alkaline degradation of gentiobiose (6-glucosidoglucose) to lactic acid, 3-glucosido-glyceric aldehyde is a theoretically possible intermediate compound. Under such alkaline conditions it is possible for this derivative of glyceric aldehyde to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give glucosidodihydroxyacetone. It was furthermore pointed out that the alkaline degradation of melibiose (6-galactosidoglucose) should yield 3-galactosido-glyceric aldehyde as an intermediate stage in the reaction.

Through the Koenig and Knorr reaction, with powdered "Drierite" as a desiccant in the chloroform, we have recently synthesized the glucosidodihydroxyacetone pentaacetate in good yields by the use of bromoacetoglucose tetraacetate and dihydroxyacetone monoacetate reported by Fischer, Baer and Feldmann [*Ber.*, **63,** 1732 (1930)]. This compound crystallized from ether, having m. p. 103° (corr.); $[\alpha]^{18}_{D}$ −25.2° ($CHCl_3$); an acetyl number equivalent to 10.81 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 10.82). Its *p*-nitrophenylhydrazone crystallizes from alcohol as a yellow derivative with m. p. 187° (corr.); $[\alpha]^{19}_{D}$ −129.8° ($CHCl_3$); an acetyl number equivalent to 8.37 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 8.37).

The study of the behavior of glucosidodihydroxyacetone pentaacetate toward deacetylation reagents as well as potassium hydroxide after the manner of Evans and Hockett (*loc. cit.*) is now in progress in this Laboratory. The syntheses of the corresponding galactosido compounds as well as the corresponding hexosido-glyceric aldehyde ones are also being studied.

DEPARTMENT OF CHEMISTRY L. C. KREIDER
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RECEIVED DECEMBER 20, 1934

STRUCTURE OF VITAMIN B

Sir:

On treatment with sulfite the vitamin is quantitatively split into $C_6H_9N_3SO_3$ (I) and C_6H_9NSO (II). (I) on the basis of ultraviolet absorption and chemical evidence is a 6-aminopyrimidine sulfonic acid. We provisionally allocate $—SO_3H$ to position 5 and $—C_2H_5$ to position 4.

The second cleavage product has been submitted to Dr. H. T. Clarke for examination. He has proposed a thiazole ring nucleus, which finding is confirmed by ultraviolet absorption studies. This base contains a free —OH group also present in the vitamin, gives a negative iodo-