terest to ascertain whether the bufagins, on dehydrogenation with selenium, would yield methylcyclopentenophenanthrene. The formation of this hydrocarbon, $C_{18}H_{16}$, is generally considered a characteristic of the sterol ring system. Cinobufagin, $C_{25}H_{32}O_6$ [Jensen and Evans, *J. Biol. Chem.*, **104**, 307 (1934)] (the analytical data obtained for cinobufagin and certain of its derivatives would also agree with $C_{26}H_{34}O_6$ [Crowfoot, *Chem. and Ind.*, **54**, 568 (1935)]), was therefore subjected to dehydrogenation by the procedure of Diels [Diels, Gaedke and Koerding, *Ann.*, **459,** 1 (1927)]. As only a limited amount of material was available for this study, and losses were involved in the separation of compounds closely related chemically, the quantity of the hydrocarbon finally obtained was so small that a complete characterization was impossible. From the mixture of the reaction products about 10 mg. of a hydrocarbon fraction was secured which melted at 120–121°. This hydrocarbon is believed to be identical with methylcyclopentenophenanthrene. Its analytical data agree with the formula $C_{18}H_{16}$, and on mixing it with methylcyclopentenophenanthrene obtained by Elderfield and Jacobs [*J. Biol. Chem.*, **107**, 143 (1934)] by dehydrogenation of strophanthidin, no melting point depression was observed. It appears, therefore, that cinobufagin and probably also the various other bufagins contain the same ring system as the cardiac plant aglucones and the sterols. After completing this work, a paper by Ikawa [*J. Pharm. Soc. Japan*, **55**, 144 (German abstract), 748 (original Japanese) (1935)] appeared, in which he reports the isolation of the Diels hydrocarbon $C_{18}H_{16}$ from the dehydrogenation mixture of ψ-bufotaline. In this connection it might be mentioned that Wieland and Hesse [*Ann.*, **517** 22 (1935)] recently have obtained a hydrocarbon from the dehydrogenation mixture of bufotaline which they believe to be identical with chrysene. Investigations are now in progress to determine, in the bufagins, the exact nature of the side chain which contains the lactone ring.

Five grams of cinobufagin, dried at 110° *in vacuo*, was mixed with 6 g. of selenium and heated in a flask with a glass joint ascending tube for thirty-five hours at 310–320° and then for ten hours at 320–340°. The reaction mass was extracted with ether and the residue from evaporation of the solvent was subjected to fractional distillation at 12 mm. The fraction distilling at 200–230° was semi-crystalline and was fractionally recrystallized from alcohol according to the triangle scheme. After numerous crystallizations a hydrocarbon fraction was secured which melted at 120–121° and showed a m. p. of 121–122° when mixed with methylcyclopentenophenanthrene (m. p. 123–124°) prepared from strophanthidin (Elderfield and Jacobs). *Anal.* (by Dr. Ing. A. Schoeller, Berlin-Schmargendorf, Germany). Calcd. for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.81; H, 6.82.

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LABORATORY FOR ENDOCRINE RESEARCH H. JENSEN
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RECEIVED NOVEMBER 22, 1935

THE COLLAPSE OF MONOMOLECULAR FILMS OF PALMITIC ACID UPON ACID SOLUTIONS

Sir:

When monomolecular films of palmitic acid were compressed on very pure hydrochloric acid or phosphate buffer solutions contained in a Langmuir film-pressure trough, in the range 15–20°, it was noticed that after each increment of weight had been placed in the balance pan, and the barrier advanced to establish equilibrium, a slow shrinkage followed, the area, however, finally attaining a value which was reproducible to a high degree. When the compression was carried out in this manner, with an attempt to obtain "equilibrium areas" at every point of the force–area curve, the films collapsed at a pressure apparently connected with the hydrogen-ion concentration (*i. e.*, the films could be compressed without limit when a definite pressure was reached, the value of which has been called the "collapse pressure" in the literature). When the collapse pressure values were plotted against *p*H values of the substrate (which varied from *p*H 1 to *p*H 6) an S-shaped curve resulted, similar to the percentage neutralization curve in the case of a weak organic acid in water solution. However, the mid-point of this curve was about *p*H 3, as compared to *p*H 5, the mid-point of neutralization curves of fatty acids. Since the variation of collapse pressure with *p*H may be considered as related to neutralization, this appears to be evidence of increased activity of palmitic acid when oriented on a water surface.

The collapse pressure was specific for hydrogen ions alone, although increased spread at low pressures was noticed when calcium or magnesium ions were present in the hydrochloric acid solution. A specific effect, in causing what may be either collapse or solution of the film at room temperatures, has been noticed in the case of neutral potassium permanganate solutions. This was not noticed with hydrogen peroxide, potassium ferricyanide or potassium dichromate solutions.

In view of the work of Cary and Rideal [*Proc. Roy. Soc.* (London), **A109,** 301 (1925)] on the spreading of fatty acid crystals on acid solutions, which indicates that many of the films should be thermodynamically unstable above 8 dynes, in the neighborhood of 20°, work is now in progress on a repetition of the above studies, using mixtures of higher hydrocarbons, such as tetradecane, with palmitic and other acids, to determine whether this relation between collapse pressure and hydrogen-ion concentration holds for an interface where the acid film may collapse in a reversible manner. It is planned further to apply thermodynamic interpretation, such as Harkins' spreading coefficient to the collapse phenomena. The results with the monomolecular films alone will be reported more fully in the near future, together with those obtained with mixed films.

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ROBERT J. MYERS

RECEIVED OCTOBER 17, 1935

THE ACTIVATION OF SPECIFIC BONDS IN COMPLEX MOLECULES AT CATALYTIC SURFACES

Sir:

It has now become possible to examine the activation of specific bonds in complex molecules at catalytic surfaces, a fundamental problem in surface catalysis, that of specificity. We shall illustrate a method capable of quite general applicability by a specific example, that of the molecule ethane. In this we are concerned with two types of bond, the C–C and the C–H bond. We have followed the activation of these bonds on an active nickel surface by the study of the two reactions (a) the exchange reaction $C_2H_6 + mD_2 \longrightarrow C_2H_xD_y$ where $x + y = 6$ and m may be varied arbitrarily; (b) $C_2H_6 + H_2 = 2CH_4$. The former involves only the C–H, the latter the C–C bond, the other reactant in each case being hydrogen (or deuterium) adsorbed on the surface in the activated form. We find that, on this catalyst, the exchange reaction proceeds quantitatively at 138° under conditions in which reaction (b) is quite negligible. The production of methane sets in, under our conditions about 150° and is sensibly complete around 200°. We thus define the temperature, catalyst and reactant concentration conditions necessary to activated adsorption of ethane molecules producing either the C–H or the C–C bond split or both. By extension of these studies to other catalyst surfaces, to molecules which contain a wide variety of other bonds, *e. g.*, O–H, N–H, C–O, C–N, etc., and to varied operating conditions we plan to determine in detail the factors which produce specific activity of catalysts in general.

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RECEIVED NOVEMBER 8, 1935

SYNTHESIS OF DEUTERO-ACETALDEHYDE

Sir:

By absorbing deutero-acetylene in an acid solution of mercury salts in deuterium oxide we have succeeded in synthesizing deutero-acetaldehyde. About 25 cc. have been prepared so far. The aldehyde freed from deuterium oxide by repeated distillations at low temperatures is a colorless mobile liquid. Preliminary determinations indicate a vapor pressure of 327 mm. at 0°. It shows the usual aldehyde reactions: reducing ammoniacal silver solutions, forming a white crystalline compound with ammonia and a phenylhydrazone with phenylhydrazine.

The D_2O used in generating the acetylene and in the absorbing solution was 99.6% pure. The burning of about 2 cc. of the aldehyde over copper oxide in a current of oxygen gave D_2O of 99.2% purity, both values determined by the interferometer method.

The determination of the physical constants of this compound as well as its chemical properties is proceeding in this Laboratory.

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