tive evaluation and suggest possibilities of modified action.

Further experiments are in progress.

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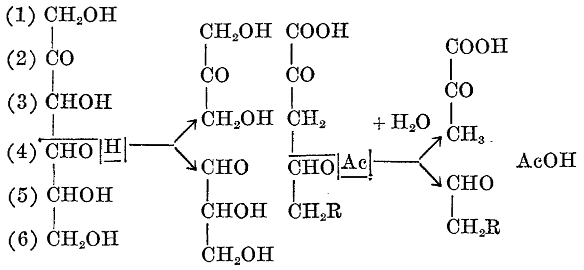
A REVERSED ALDOL CONDENSATION

During the past years many steps in the mechanism of glycolysis in muscle as well as in yeast have been cleared up. One of the remaining questions is: What causes the disruption of the easily fermentable hexose diphosphate ("primaeres Veresterungsproduct" of Meyerhof, etc.), to form two triose phosphates? Another open question is the position of the phosphoric acid rests in this hexose diphosphate. I would like to record an observation made a few years ago which may throw some light on these questions. Further work (which I am unable to undertake) is necessary to test whether this is a true or a false light.

The splitting of the hexose carbon chain to form two trioses is, chemically speaking, the reversal of an aldol condensation (I). I could observe a similar breakdown of a carbon chain in the case of α-keto γ-acetoxy acids. When incubating α-keto γ-acetoxy valeric acid [(II: $R - H$)] at 37° with water, the thick oil slowly dissolved within a few days and pyruvic acid, acetic acid and acetaldehyde could be isolated and identified in form of derivatives. The next higher homologue [(II: $R - CH_3$)] gave the same decomposition, while aldol, acetaldol, β-acetoxybutyric acid and β-acetoxy δ-keto-pentane were quite stable under these conditions. It appears that an acid pH of the solution or an acid group in the molecule is an essential condition for this breakdown, as well as an oxo-group in β-position to an esterified alcoholic one; this latter alcoholic group forms the new aldehyde group after the rupture of the chain. In analogy one is tempted to suppose that the readily fermentable hexose diphosphate ("primaeres Veresterungsproduct") is a ketose, carrying one phosphoric acid group in position 4. This might weaken the C–C-link between carbon atoms 3 and 4 sufficiently to cause a spontaneous formation of two trioses under our experimental conditions and the zymohexase might only be needed to catalyze this reaction to proceed with the necessary speed.

I II



Heinz Fraenkel-Conrat

THE PRODUCTS OF THE CYCLIZING DEHYDRATION OF 1-BETA-PHENYLETHYLCYCLOHEXANOL-1 AND THE SYNTHESIS OF SPIROCYCLOHEXANE-1,1-INDANONE-3

By a cyclizing dehydration of 1-*beta*-phenylethylcyclohexanol-1 with 85 per cent. sulfuric acid, Perlman, Davidson and Bogert[1] observed the simultaneous formation of octahydrophenanthrene and spirocyclohexane-1,1-indane.

Recently, Cook, Hewett and Lawrence,[2] and Cook, Hewett and Robinson,[3] by cold oxidation with chromic acid of a glacial acetic acid solution of the mixture of hydrocarbons resulting from the cyclization of *beta*-phenylethylcyclohexene-1, obtained a mixture of ketones, which they converted into the corresponding oximes, and then separated the latter by fractional crystallization. They thus isolated three oximes, which melted, respectively, at 187.5°, 175–177° and 124°. The first of these, they believed to be the oxime of spirocyclohexane-1,1-indanone, the second that of the *trans*-ketoöctahydrophenanthrene, and the third (m.p. 124°) that of its *cis*-isomer.

We have been occupied lately in the synthesis and study of the pure spirocyclohexane-1,1-indane, to learn more about its behavior when subjected to dehydrogenation reactions, and how its monacetyl derivative compares with those of the *cis*- and *trans*-octahydrophenanthrenes reported by Van de Kamp and Mosettig.[4]

In the course of this investigation, we synthesized the spirocyclohexane-1,1-indanone (VI), and found that its oxime melted at 137–137.8° (corr.). This wide divergence from the melting-point of 187.5° recorded by Cook *et al.* for their oxime, led us to reinvestigate the aforementioned hydrocarbon mixture, by a procedure essentially identical with that of our English colleagues with the result that we isolated the following oximes:

(1) An oxime, m.p. 187–188° (corr.).

(2) An oxime, m.p. 136.5–137° (corr.), which m.p. was not depressed when the compound was mixed with the oxime (m.p. 137–137.8°, corr.) of our synthetic spiroketone (VI). Each oxime was nitrated separately in cold concentrated sulfuric acid with powdered potas-

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[1] Perlman, Davidson and Bogert, *Jour. Org. Chem.*, 1: 288, 300, 1936. See also Perlman and Bogert, *Jour. Am. Chem. Soc.*, 59: 2534, 1937.

[2] Cook, Hewett and Lawrence, *Jour. Chem. Soc.*, 1936, 71.

[3] Cook, Hewett and Robinson, *ibid.*, 1939, 168.

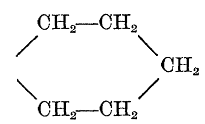
[4] Van de Kamp and Mosettig, *Jour. Am. Chem. Soc.*, 58: 1062, 1936.

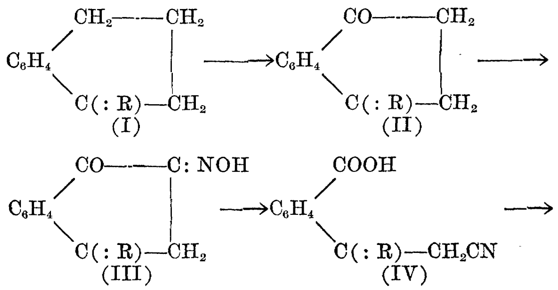
sium nitrate, and the nitro oximes were then hydrolyzed with dilute sulfuric acid. The nitro ketones so obtained were identical and both melted at 192° (corr.). Further, direct nitration of our synthetic spiroketone (VI) gave the same nitro ketone (m.p. 192°, corr.).

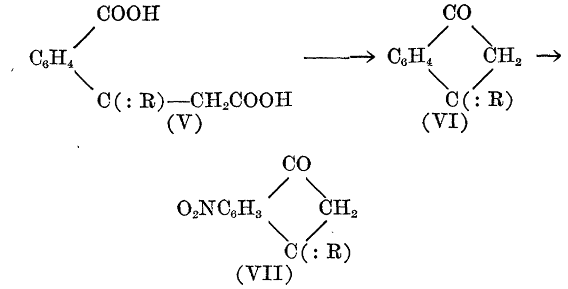
(3) An oxime, m.p. 123–124° (corr.), which yielded a nitro ketone, m.p. 149–150° (corr.). This is evidently the same as the oxime, m.p. 124°, whose nitro ketone melted at 150–150.5°, and which Cook *et al.* suggested was probably the oxime of the *cis*-ketoöctahydrophenanthrene.

The only difference between our operations and those of Cook *et al.* was that our mixture of hydrocarbons was obtained by the action of 85 per cent. sulfuric acid upon the phenylethylcyclohexanol, while theirs was the result either of the action of phosphorus pentoxide upon the cyclohexanol, or of aluminum trichloride upon the corresponding cyclohexene.

The spirocyclohexane-1,1-indanone (VI) was synthesized by the following steps, in which "R" represents the group







The pure spirocyclohexane-1,1-indanone (VI) was obtained as a white crystalline solid, m.p. 58–59° (corr.); oxime, m.p. 137–137.8° (corr.).

All products described in the foregoing gave on analysis figures substantiating the formulas assumed.

SUMMARY

(1) Spirocyclohexane-1,1-indanone (VI) has been found among the oxidation products of the hydrocarbon mixture which results when 1-*beta*-phenylethylcyclohexanol-1 is dehydrated, or when 1-*beta*-phenylethylcyclohexene is cyclized by aluminum trichloride, and its constitution has been proved by synthesis.

(2) Its oxime melts at 137–137.8° (corr.). The oxime of m.p. 187.5°, reported by Cook *et al.* therefore must be derived from some other ketone, perhaps the trans-ketoöctahydrophenanthrene, since we were unable to isolate any oxime of m.p. 177°, the figure which they reported for this compound.

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SCIENTIFIC APPARATUS AND LABORATORY METHODS

AN X-RAY DENSITOMETER FOR MEASURING RELATIVE DENSITIES OF MUSCLE, BONE AND OTHER TISSUES

IN the studies of child growth and development undertaken by the Developmental Health Inquiry of the Associated Foundations it became evident that an objective method for measuring muscle, bone and other tissue densities would be a valuable aid. An x-ray densitometer has been designed and constructed for that purpose and is now in use.

Two other x-ray densitometers have recently been reported, one by P. B. Mack,[1] which is being used at Pennsylvania State College to determine the degree of mineralization of bone in a nutritional study and one by R. G. Bloch,[2] at Chicago University, designed for a study of tuberculous calcifications. Although the apparatus described here is similar in principle to these, its differences are the result of an attempt to obtain an optimum degree of accuracy combined with rapidity of operation and simplicity in interpretation of readings in a unified portable instrument.

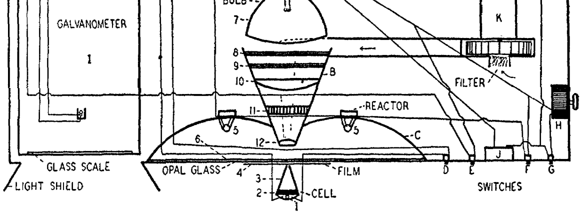

FIG. 1. Top view and circuit diagram.

As shown in Fig. 1, the various components of the

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[1] P. B. Mack *et al.*, SCIENCE, 89: 467, 1939.

[2] R. G. Bloch *et al.*, *Am. Jour. of Roentgenol. and Rad. Therapy*, 41: 642–647, 1939.