

H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>: C, 60.73; H, 6.02; N, 10.12. Found: C, 60.58; H, 5.98; N, 10.18.

Taken by themselves these formulas would seem to support Kharasch and Legault's contention, but all other available evidence points to the identity of the substances. It is therefore probable that the apparent difference in elementary composition is not real, and that further analyses of ergotocin and its salts may yet lead to the establishment of its complete identity with ergometrine.

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RECEIVED JULY 22, 1935

### THE SYNTHESIS OF BIS-2,2'-(1,3-DIPHENYL-INDENOL-3)

Sir:

In connection with attempts to synthesize rubrene we have prepared bis-2,2'-(1,3-diphenylindolenol-3) by the following series of reactions

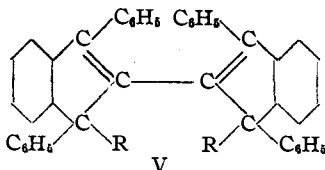
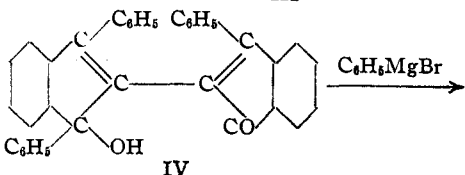
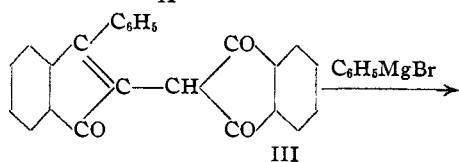
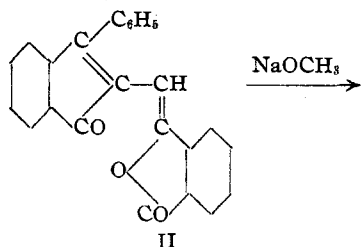
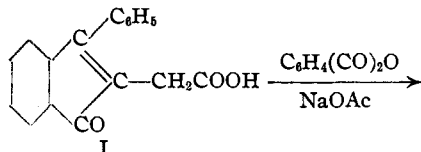
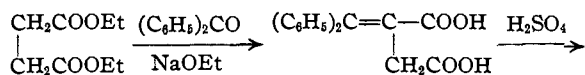


TABLE I

PROPERTIES OF COMPOUNDS INVOLVED

Compound	M. p., °C.	Formula	Analyses, %		Found	
			Calcd. C	H	C	H
I	166-167	C <sub>17</sub> H <sub>12</sub> O <sub>3</sub>	<sup>a</sup>			
II	173.5-174	C <sub>24</sub> H <sub>14</sub> O <sub>3</sub>	82.2	4.0	81.9	4.3
III	190.5-191.5	C <sub>24</sub> H <sub>14</sub> O <sub>3</sub>	82.2	4.0	82.0	3.9
IV	244-245	C <sub>38</sub> H <sub>24</sub> O <sub>2</sub>	88.5	4.9	88.0	4.8
V, R = OH	292	C <sub>42</sub> H <sub>30</sub> O <sub>2</sub>	89.0	5.3	89.0	5.5
V, R = Cl	237-242	C <sub>42</sub> H <sub>25</sub> Cl <sub>2</sub>	83.6	4.6	83.6	4.6

<sup>a</sup> Stobbe and Vieweg, *Ber.*, 35, 1728 (1902).

The product is identical with the one obtained by a different method by Eck and Marvel [THIS JOURNAL 57, 1898 (1935)].

TABLE II

PROPERTIES OF BIS-2,2'-(1,3-DIPHENYLINDENE) DERIVATIVES

Compound	Source	M. p., °C. <sup>c</sup>	Mixed m. p., °C. <sup>d</sup>
V, R = OH	<sup>a</sup>	293	291
	<sup>b</sup>	292	
V, R = Cl	<sup>a</sup>	240-245	237-242
	<sup>b</sup>	237-242	

<sup>a</sup> Eck and Marvel. <sup>b</sup> Koelsch and Richter. <sup>c</sup> Melting involves decomposition, and the temperature at which it occurs depends to some extent on the stage of subdivision of the compound and on the rate of heating. <sup>d</sup> We are indebted to Professor Marvel for the melting points reported here.

Like these authors we have found the derived dichloride to be unreactive toward metals (zinc or mercury). The dichloride, however, appears to give an alkali derivative with 40% sodium amalgam and we hope to make use of this reaction in converting it into the di-radical.

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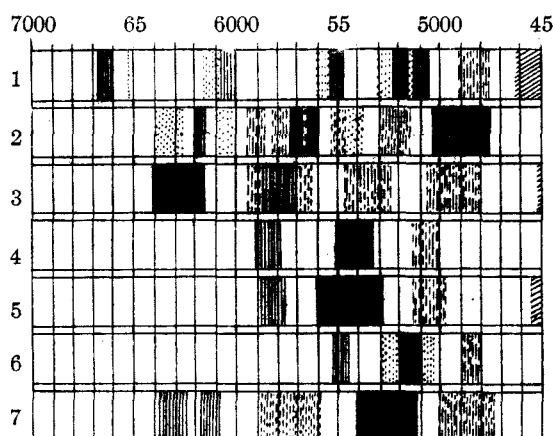
RECEIVED SEPTEMBER 18, 1935

### FORMATION OF PORPHYRINS FROM PYRROLE AND ALDEHYDES

Sir:

Porphyrin formation was observed under the following conditions: pyrrole, c. p., was dissolved in a solution of gaseous acetaldehyde (I) or formaldehyde (II) in methanol (saturated in the cold), and the reaction mixture was either (a) kept at room temperature for several weeks, or (b) heated under reflux for fifteen to twenty-five hours, or (c) heated in a sealed tube to 85-90° for ten to twenty hours in a water-bath.

The reaction mixture was then subjected to vacuum distillation to remove the methanol and the aldehyde; the oily residue was taken up in warm pyridine, transferred into ether and the ether solution was fractionated with hydrochloric acid. The results are indicated in a somewhat abbreviated form in the chart of the absorption spectra.



Absorption spectra.

(1) Porphyrin from reaction I (pyrrole + acetaldehyde) in ether. (2) Porphyrin from reaction II (pyrrole + formaldehyde) in ether. (3) Porphyrin from reaction I in 0.05% hydrochloric acid. (4) Porphyrin from reaction II in 3.0% hydrochloric acid. (5) Copper complex salt of porphyrin from reaction I in ether. (6) Copper complex salt of porphyrin from reaction II in ether. (7) 3% hydrochloric acid fraction from the reaction pyrrole + furfuraldehyde in ether.

The main fraction in case I enters 0.5% hydrochloric acid and has a hydrochloric acid number of 0.075. The main fraction in case II enters 3% hydrochloric acid, its hydrochloric acid number is 3.3. The porphyrin from I crystallized in rhomb-shaped crystals, the one from II in platelets. The corresponding copper complex salts and hemins were prepared.

The yield increased upon addition of pyridine to the original solution, or when suitable agents (*e. g.*,  $\text{CaCO}_3 + \text{MgO}$ ,  $\text{PbCrO}_4$ ) were added; the resulting porphyrins were different from the ones mentioned above when the reaction was performed in presence of  $\text{PbO}_2$ .

Further studies are in progress to secure information on the structure of the porphyrins formed, and to determine the applicability of the reaction to other aldehydes; a comprehensive report of the research will soon be published. From theoretical considerations and in the light of numerous porphyrin syntheses, by H. Fischer

[*Ann.* since 1926; H. Fischer and H. Orth, "Die Chemie des Pyrrols," Leipzig, 1934 and 1935], the main porphyrin formed from acetaldehyde and pyrrole seems to be  $\alpha, \beta, \gamma, \delta$ -tetramethylporphin. The reaction between formaldehyde and pyrrole apparently leads to porphin, the as yet hypothetical tetracyclic parent ring system of the porphyrins, and hence, also the fundamental structure in the physiologically important pigments, hemin and chlorophyll.

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RECEIVED AUGUST 23, 1935

#### CONTRIBUTION TO THE KNOWLEDGE OF THE TESTICULAR HORMONE

Sir:

The communication of E. S. Wallis and E. Fernholz [THIS JOURNAL, 57, 1511 (1935), received July 15] occasions the present note. In an article accepted on June 1 and published in the number of *Helv. Chim. Acta* [18, 986 (1935)] which appeared on July 1, we described the preparation of androstene-3,17-dione (I) and suggested the probability that the testicular hormone (not then isolated) is identical either with this diketone or with androstene-3-one-17-ol (II).

At our request, Dr. E. Tschopp in Basel began the investigation of this hypothesis by submitting (I) to the usual tests on capons and castrated rats. The details of his study, which were communicated to the League of Nations committee in London (July 15-17), will be published elsewhere; they are summarized in the table.

Substance investigated	Capon unit	Seminal vesicle wt. in mg. after 20 days <sup>a</sup>		
		50 $\gamma$ daily	100 $\gamma$ daily	200 $\gamma$ daily
(I) Androstene-3,17-dione	100 $\gamma$	25	51	285
(III) Androstane-3,17-dione	100 $\gamma$	16	27	51
(IV) Androstane-3,17-diol	15 $\gamma$	14	25	40
(V) Androsterone	60 $\gamma$	11	14	17

<sup>a</sup> The control animals had a seminal vesicle weight of about 6 mg.

Compared in terms of capon units, (I) is five times as effective on seminal vesicle growth as (V), on the basis of the 50  $\gamma$  daily dose; on the basis of the 200  $\gamma$  daily dose, however, (I) is 25 times as effective as (V). The corresponding activity ratios for (IV) and (I) are 1:12 and 1:50, respectively.

This constituted the first description of the physiological activity of a substance of known