

*Anal.* Calcd. for  $C_{11}H_{19}O_3N_3$ : C, 54.8; H, 7.9. Found: C, 54.9; H, 7.8.

(2) **Ethyl Alcohol as the Hydroxyl-Forming Component.**—The oxidative cleavage of 1.65 g. of 3-hydroxycamphor with lead tetraacetate in the presence of dry ethyl alcohol was carried out in the usual way, yielding after two distillations 1.0 g. (48%) of the ethyl ester of camphoric acid hemialdehyde (secondary); b. p. (0.55 mm.) 88.5–89.5°,  $n_D^{19.5}$  1.4712,  $n_D^{21.5}$  1.4708,  $[\alpha]_D^{20} +21.2^\circ$  (concn. 5.0, dry benzene). A solution of the ester in methyl alcohol reduces an ammoniacal solution of silver promptly at room temperature.

*Anal.* Calcd. for  $C_{12}H_{20}O_4$ : C, 67.9; H, 9.4. Found: C, 68.1; H, 9.3.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethyl alcohol, m. p. 175–176°.

*Anal.* Calcd. for  $C_{18}H_{24}O_6N_4$ : C, 55.1; H, 6.1. Found: C, 54.9; H, 5.9.

**Acknowledgment.**—Grateful acknowledgment is made to Dr. C. C. Lucas for assistance in preparing this manuscript for publication.

## Summary

1. Cyclic  $\alpha$ -ketoalcohols are cleaved by lead tetraacetate in the presence of substances which, by addition, form pseudoglycols (e. g., water, alcohols). The reaction is rapid, exothermic and quantitative.

2. The products are aldehyde-acids or their esters.

3. This cleavage reaction should prove to be a useful tool in the elucidation of structure of cyclic ketoalcohols. The way in which the reaction may be utilized in this connection is indicated by its application to 3-hydroxycamphor and 2-hydroxy-epi-camphor.

4. The hitherto unknown camphoric acid hemialdehyde (secondary) has been prepared and described.

TORONTO, CANADA

RECEIVED FEBRUARY 7, 1942

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

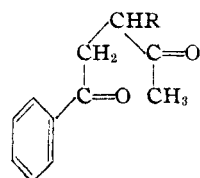
## The Synthesis of 2'-Ketodihydro-1,2-cyclopentenophenanthrene and Derivatives of Phenanthro[1,2-*b*]furan

BY A. L. WILDS

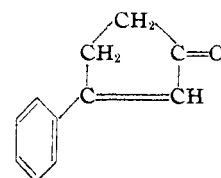
Paal<sup>1</sup> and Borsche<sup>2</sup> showed that 1,4-diketones of the type Ia could be cyclized to the cyclopentenone derivative (II). They also found that the more readily available diketo ester (Ib), prepared from  $\alpha$ -bromoacetophenone and acetoacetic ester, underwent cyclization to the same cyclopentenone (II). In this case hydrolysis of the ester group and decarboxylation occurred in addition to cyclization. This type of ring closure of a diketone has been applied by other investigators to the preparation of numerous cyclopentenone and cyclohexenone derivatives,<sup>3–7</sup> including polycyclic ketones related to the sex hormones.<sup>8</sup>

The reaction has now been extended to the diketo ester (VIII) and the diketone (IX), in

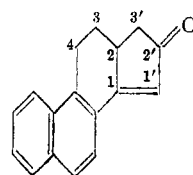
order to prepare the cyclic ketone  $\Delta^{1,1'-2'}$ -keto-3,4-dihydro-1,2-cyclopentenophenanthrene (III).



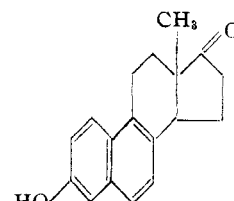
Ia R = H  
Ib R = COOC<sub>2</sub>H<sub>5</sub>



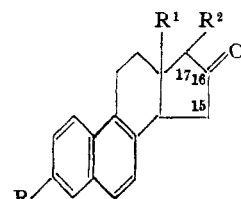
II



III



IV



V R = R<sup>1</sup> = R<sup>2</sup> = H

(1) Paal, *Ber.*, **16**, 2865 (1883); **17**, 2756 (1884).

(2) Borsche and Fels, *ibid.*, **39**, 1809, 1922 (1906); Borsche and Menz, *ibid.*, **41**, 190 (1908).

(3) Weltner, *ibid.*, **17**, 66 (1884).

(4) Blaise, *Compt. rend.*, **158**, 708 (1914).

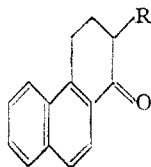
(5) du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937); Koebner and Robinson, *ibid.*, 1994 (1938); Rapson and Robinson, *ibid.*, 1285 (1935).

(6) (a) Weidlich, Daniels, Knauber and Kübler, *Ber.*, **72**, 1590 (1939); (b) Weidlich and Meyer-Delius, *ibid.*, **72**, 1941 (1939).

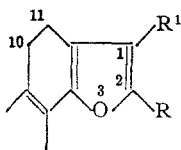
(7) Goldberg and Müller, *Helv. Chim. Acta*, **23**, 831 (1940).

(8) Springall, in "Annual Reports on the Progress of Chemistry," 1939, pp. 294–300.

This method of building up the cyclopentenophenanthrene ring system affords a new approach to compounds related in structure to female sex hormones of the equilenin type (IV).



- VI    R = H  
 VII   R = Br  
 VIII   R = CH(COCH<sub>3</sub>)COOC<sub>2</sub>H<sub>5</sub>  
 IX    R = CH<sub>2</sub>COCH<sub>3</sub>  
 X    R = CH(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 XI    R = CH<sub>2</sub>COOH



- XII   R = OH; R<sup>1</sup> = COCH<sub>3</sub>  
 XIII   R = OH; R<sup>1</sup> = COOC<sub>2</sub>H<sub>5</sub>  
 XIV   R = CH<sub>3</sub>; R<sup>1</sup> = COOC<sub>2</sub>H<sub>5</sub>  
 XV    R = CH<sub>3</sub>; R<sup>1</sup> = COOH  
 XVI   R = CH<sub>3</sub>; R<sup>1</sup> = H

The intermediates VIII and IX have been prepared from the readily available 1-ketotetrahydrophenanthrene (VI) through the bromo derivative (VII). When VIII was treated with various cyclizing agents, it was found that the reaction proceeded in several different directions. However, a detailed investigation showed that the course of the reaction was critically determined by the nature of the reagent, and in each case a single product could be obtained in good yield. Cyclization of VIII to the ketone III was brought about in 84% yield by dilute aqueous alkali. The diketone IX was also cyclized to III by the same reagent, in 90% yield. Weidlich and co-workers<sup>6a</sup> reported an unsuccessful attempt to carry out an analogous cyclization on the tetralone derivative corresponding to VIII.

The structure of the ketone III was proved by Clemmensen reduction to the hydrocarbon and dehydrogenation of the latter to the known 1,2-cyclopentenophenanthrene. The melting points of this hydrocarbon, its picrate and trinitrobenzene derivative agreed with the values reported in the literature. The location of the double bond has not yet been determined in III; however, the position shown is believed to be the most probable one. Hydrogenation experiments on the unsaturated ketone bear this out, since with a palladium-charcoal catalyst one mole of hydrogen was absorbed to give the ketone V, as shown by

its conversion in good yield to a semicarbazone and an oxime. If the double bond was located between the rings, the formation of a ketone on reduction would be less likely. As would be anticipated, V was a mixture of ketones from which two diastereoisomers were obtained.

One of the main uses of this method of preparing the ketones III and V lies in its extension to the preparation of related compounds carrying substituents in the three positions indicated in V. These positions are the ones in which substitution occurs in many of the steroids, including the sex hormones. With the compound V (where R = OH, R<sup>1</sup> = CH<sub>3</sub>, and R<sup>2</sup> = H) an isomer of the sex hormone equilenin (IV) would result, in which the ketone group is shifted from the 17 to the 16 position. In the extension of these reactions to introduce an angular methyl group (V, R<sup>1</sup> = CH<sub>3</sub>), the bromoketone analogous to VII would contain a tertiary bromine atom. It would not be expected that the method could be used unmodified in this case. Work is in progress in this direction employing the sodium enolate of 2-methyl-1-keto-tetrahydrophenanthrene.

When the diketo ester VIII was treated with sodium ethoxide, an insoluble compound, C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>, was obtained in 84% yield. The same compound could be prepared in 81% over-all yield from VII, without isolation of the intermediate VIII. This compound, m. p. 223° with the evolution of gas, formed an insoluble sodium salt and gave a green color with ferric chloride solution. Upon heating with a mixture of hydrochloric and acetic acids for twelve hours it was changed into an isomeric compound; m. p. 331°. Both isomers were converted in good yield to IX by long heating with acid. To the isomer melting at 223° is assigned the structure of 1-acetyl-2-hydroxy-10,11-dihydrophenanthro[1,2-b]furan<sup>9</sup> (XII), arising through lactonization of the carbethoxyl group of VIII and the enolic form of the 1-keto group, with loss of alcohol. To the other isomer melting at 331° is assigned the structure of 2-methyl-10,11-dihydrophenanthro[1,2-b]furan-1-carboxylic acid (XV), arising through loss of water between the two ketone groups in VIII after enolization.

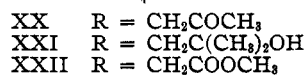
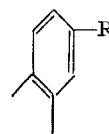
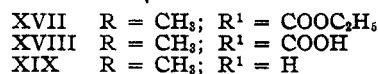
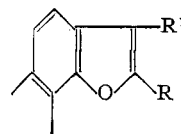
This assignment of structure follows principally from esterification experiments on the two compounds. Treatment of the 331° isomer XV with alcoholic hydrogen chloride gave the

(9) For this system of numbering see Patterson and Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940. No. 2488; also the Subject Index of C. A.

ethyl ester XIV, which also resulted from VIII in 83% yield when the latter compound was cyclized by short heating with acid. Diazomethane converted XV to the methyl ester corresponding to XIV in 85% yield, and an identical product was obtained with methanol and hydrogen chloride. This identity shows that no rearrangement occurs in the esterification with hydrogen chloride in this case. When XII was treated with alcoholic hydrogen chloride, it gave an ethyl ester identical with that from XV, namely, XIV. However, since alkaline hydrolysis of the ester gave XV, a rearrangement occurred during this esterification. In harmony with this, it was found that diazomethane, while reacting with XII, did not give the methyl ester corresponding to XIV. No crystalline reaction product could be isolated in this case. These esterification results, coupled with hydrolytic opening of the furan ring of both isomers to form the diketone IX, show that the structures are as assigned. It may be pointed out that XII is remarkably stable toward alkali, and can be recovered mainly unchanged after long heating with methanolic potassium hydroxide. This stability points to the hydroxyfuran structure, rather than to a lactone form having a carbonyl group at position 2. Paal,<sup>1</sup> and Borsche, Fels and Menz<sup>2</sup> have reported the preparation of analogous furan derivatives from Ib. Treatment of this diketo ester with acid gave a furan carboxylic acid similar to XV, while treatment with sodium ethoxide resulted in an enolic lactone analogous to XII. Some of the corresponding furan derivatives have been obtained in the cyclohexanone series by Ebel, Huber and Brunner,<sup>10</sup> and Weidlich, *et al.*,<sup>6a</sup> have obtained from 2-bromo-1-tetralone the corresponding analog of XV. Recently Smith and Carlin<sup>11</sup> observed that the manner of cyclization of 3-acetoxy-6-hydroxy-2,4,5-trimethylbenzylacetoacetic ester was dependent upon the reagent. Treatment with alkali resulted in an acetyl dihydrocoumarin, and with acid, in a  $\gamma$ -chromene carboxylic acid, analogous to XII and XV, respectively.

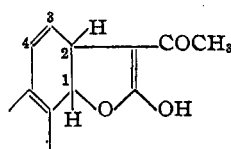
When the ester XIV was treated with palladium-charcoal at 200°, the dehydrogenated ester XVII resulted in excellent yield. Although both of the acids XVIII and XV are stable toward heat, decarboxylation occurred when they were heated in quinoline with copper chromite catalyst,

giving 2-methylphenanthro[1,2-*b*]furan (XIX) and its dihydro derivative XVI, respectively.

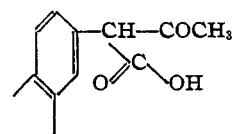


A curious reaction was observed to take place with the hydroxyfuran XII upon heating. Carbon dioxide was lost and the product formed in 79% yield was a ketone, C<sub>17</sub>H<sub>14</sub>O, therefore, an isomer of the cyclic ketone III. However, in this case the presence of a fully aromatic phenanthrene nucleus could be demonstrated by Clemmensen reduction of the ketone to 2-propylphenanthrene identical with the hydrocarbon of Bachmann and Struve,<sup>12</sup> obtained by reduction of 2-propionylphenanthrene. This indicated that the ketone was 2-phenanthreneacetone (XX), and the structure was confirmed by converting XX into the tertiary carbinol (XXI) with methylmagnesium iodide. The compound was identical with the carbinol prepared by the action of excess methylmagnesium iodide on methyl 2-phenanthreneacetate (XXII). Reduction of XX with aluminum isopropoxide occurred readily to give the corresponding secondary alcohol.

While the course of this novel formation of the ketone XX is still uncertain, a plausible explanation is that the transformation involves rearrangement of the 1,2-double bond in the furan XII to the 3,4-position (XXIII; numbering system of phenanthrene), followed by opening of the furan ring with the formation of a new double bond and the fully aromatic nucleus, XXIV. Finally, loss of carbon dioxide from this  $\beta$ -keto acid would re-



XXIII



XXIV

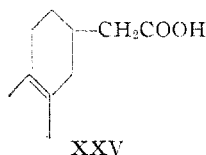
(10) Ebel, Huber and Brunner, *Helv. Chim. Acta*, **12**, 16 (1929).

(11) Smith and Carlin, *THIS JOURNAL*, **64**, 435, 524 (1942).

(12) Bachmann and Struve, *J. Org. Chem.*, **4**, 456 (1939).

sult in the formation of the ketone. The transformation takes place under relatively mild conditions, for it was observed that heating an acetic acid solution of XII gave a 74% yield of XX. This is somewhat analogous to the conversion of  $\alpha$ -methylmorphimethine to methylmorphol upon heating with acetic anhydride.<sup>13</sup> In this case the nitrogen-containing side chain is eliminated and aromatization of the ring occurs through opening of a furan ring.

Cyclization to a hydroxyfuran derivative XIII, similar to the formation of XII from the acetoacetic ester derivative VIII, was found to occur also with the corresponding malonic ester derivative X. This latter compound was obtained from VII upon treatment with sodio-malonic ester. Hydrolysis and decarboxylation of X gave the keto acid XI, which underwent Clemmensen reduction smoothly to 1,2,3,4-tetrahydrophenanthrene-2-acetic acid (XXV). The methyl ester of the latter could be dehydrogenated to XXII with palladium-charcoal in 85% yield.



A preliminary attempt was made to carry out the transformation of XIII to an aromatic derivative similar to XX. If an analogous change took place here, the expected product would be the ethyl ester corresponding to XXII. However, XIII gave a mixture of products from which no pure compound was isolated. Further work is in progress to learn more about the extension and limitations of this transformation. This work and the extension in other directions indicated above will be reported in a future communication.

The author wishes to express appreciation to the Wisconsin Alumni Research Foundation for a grant to purchase some of the chemicals used in this investigation.

### Experimental<sup>14</sup>

**1-Keto-1,2,3,4-tetrahydrophenanthrene (VI).**—The first step in the synthesis of this ketone, the preparation of  $\beta$ -1-naphthylethyl alcohol,<sup>15</sup> has been improved. The

(13) Fischer and Vongerichten, *Ber.*, **19**, 792 (1886); Vongerichten, *ibid.*, **31**, 3198 (1898); see also Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1937, 2nd ed., p. 26.

(14) M. p.'s. above 250° were taken in a copper block similar to that described by Berl and Kullmann, *Ber.*, **60**, 811 (1927).

(15) Ruzicka, Ehmman, Goldberg and Hösli, *Helv. Chim. Acta*, **16**, 836 (1933); Robinson and Walker, *J. Chem. Soc.*, 1531 (1935).

Grignard reagent was prepared from 330 g. of 1-bromo-naphthalene and 39 g. of ground magnesium in 500 cc. of ether and 500 cc. of dry, thiophene-free benzene. Part of the ether was then removed under slight vacuum and additional benzene was added to bring the total volume to one liter. The mixture was cooled below 0° with ice and salt, and a solution of 83 g. of ethylene oxide in 175 cc. of anhydrous ether was added during one-half hour with swirling. After two hours at 0° and one hour at room temperature, the mixture was heated on the water-bath for one hour, then this procedure was repeated with an additional 17 g. of ethylene oxide in 40 cc. of ether. Following hydrolysis and isolation of the product in the usual manner, 231 g. (84%) of  $\beta$ -1-naphthylethyl alcohol was collected at 140–150° at 0.2 mm. as a light yellow, viscous oil suitable for the next step. Without the second treatment with ethylene oxide the yields were 10 to 20% lower.<sup>16</sup>

Using the method of Hoch,<sup>17</sup>  $\beta$ -1-naphthylethyl bromide was obtained in 85% yield, b. p. 135–140° at 0.4 mm. This was converted to  $\gamma$ -1-naphthylbutyric acid as described by Bachmann and Wilds.<sup>18</sup> A few changes were made in the cyclization procedure of the latter authors in using larger quantities. The acid chloride was prepared from 69.5 g. of the acid with 74 g. of powdered phosphorus pentachloride in 300 cc. of dry, thiophene-free benzene. After one hour at room temperature and five minutes on the steam-bath, the clear solution was cooled to 5° and cyclized by adding rapidly 80 cc. of anhydrous stannic chloride dissolved in 80 cc. of benzene. The mixture was hydrolyzed after fifteen minutes at 5° and the product was isolated as previously described,<sup>18</sup> except vacuum distillation was unnecessary. A total of 60.7 g. (95%) of colorless VI was obtained after recrystallization from methanol; m. p. 94–96°.

### 2-Bromo-1-keto-1,2,3,4-tetrahydrophenanthrene (VII).

—The following modification of the procedure of Mosettig and Burger<sup>19</sup> was found to give more consistent results. To a suspension of 20 g. of VI in 200 cc. of anhydrous ether at room temperature was added one drop of bromine and the solution, which was decolorized rapidly, was then cooled to 10°. The remainder of 5.2 cc. (16.2 g.) of bromine was added slowly over a ten-minute period, allowing each drop of bromine to decolorize before more was added. Then the mixture was swirled at room temperature until the yellow, insoluble addition complex which had formed was completely dissolved. After pouring into ice water, the ether layer was washed with water, dilute sodium bicarbonate solution and evaporated. Recrystallization of the residue from a mixture of acetone and methanol gave 24.0–25.4 g.; m. p. 83–86°. A second crop melting at 77–80° brought the total yield to 27.4–27.8 g. (97–99%). This material was suitable for use without further purification. Recrystallization from methanol-acetone gave colorless prisms with the m. p. 87–88° (lit.<sup>19</sup> 84–85°). The compound gave an intense red color with concentrated sulfuric acid.

**Ethyl 1-Keto-1,2,3,4-tetrahydrophenanthrene-2-acetoacetate (VIII).**—To the clear solution of sodio-acetoacetic ester prepared from 2.8 g. of sodium powder, 20.5 cc. of

(16) Compare Bachmann and Thomas, *THIS JOURNAL*, **64**, 95 (1942).

(17) Hoch, *Bull. soc. chim.*, [5] **5**, 268 (1938).

(18) Bachmann and Wilds, *THIS JOURNAL*, **62**, 2085 (1940).

(19) Mosettig and Burger, *ibid.*, **57**, 2191 (1935).

ethyl acetoacetate, 8 cc. of absolute alcohol and 100 cc. of dry, thiophene-free benzene, was added 20 g. of the bromo-ketone VII and an additional 50 cc. of benzene. The mixture was refluxed for four hours, cooled, acidified with acetic acid and then diluted with water. After the benzene layer was washed with 2% sodium hydroxide, and water and evaporated, the residue was crystallized from alcohol to give 16.1 g. of the substituted acetoacetic ester melting at 107–115°. Additional material (m. p. 103–110°) in the filtrate brought the total yield to 18.1 g. (77%).

Even after repeated recrystallization from alcohol the compound had a wide melting range. Approximately half of the colorless prisms melted at 108–112° and the remainder at 130–135°. However, analytical results were satisfactory. The recrystallized material gave only a light tan color with alcoholic ferric chloride; with concentrated sulfuric acid the ester gave a yellow color which rapidly changed to orange and finally to an intense red.

*Anal.* Calcd. for  $C_{20}H_{20}O_4$ : C, 74.0; H, 6.2. Found: C, 74.2; H, 6.2.

On one run the filtrates from recrystallization contained 0.5 g. of a colorless by-product, m. p. 138–141°, which crystallized from alcohol as colorless prisms. This material gave no color with ferric chloride solution, but gave an initial yellow color changing to red brown with sulfuric acid. *Anal.* Found: C, 77.5; H, 6.0.

**$\Delta^{1,1'}\text{-2'-Keto-3,4-dihydro-1,2-cyclopentenophenanthrene (III)}$ .**—Dilute aqueous potassium hydroxide was found to be the only cyclizing agent of a number which were tried that gave III from VIII. A mixture of 4.8 g. of VIII and 500 cc. of 5% aqueous potassium hydroxide was heated in an oil-bath with mechanical stirring under an atmosphere of nitrogen (without the inert atmosphere the product was red). After one-half hour at 80° the bath temperature was raised to 115° and the solution was refluxed for six hours, then the mixture was cooled and the solid obtained by filtration was washed thoroughly by suspending in hot water. After drying the solid at 100° there was obtained 3.0 g. (86%) of light tan ketone; m. p. 178–181°. This was best purified by evaporative distillation at 200–220° at 0.2 mm. and recrystallization from benzene or acetone. If all of the alkali was not removed in the washing, considerable loss of material occurred here, due to condensation to a red, high boiling solid. With well washed material, however, there was very little loss. In this manner 2.9 g. (84%) of pure III was obtained as cream colored plates; m. p. 185–185.5°. The ketone gave an orange-yellow solution with sulfuric acid.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.4; H, 6.2.

The alkaline filtrate from the preparation of the ketone upon acidification gave 0.50 g. (13%) of crude acid; m. p. 160–180°. No keto acid corresponding to III was found; instead, after recrystallization from acetic acid, there was obtained XI, resulting from cleavage of the substituted acetoacetic ester. The acid had the m. p. 183–185° alone and when mixed with the same acid obtained through the malonic ester synthesis (see below). Variation in the concentration of the potassium hydroxide used in the cyclization from 1% to 10% had very little effect on the relative proportions of ketone and cleavage product obtained. When the time of heating in the cyclization was reduced to

one hour the ketone was impure and was accompanied by considerable amounts of the diketone IX.

The oxime of III was obtained in 90% yield in alcohol-pyridine solution. After recrystallization from alcohol the pale yellow needles of the oxime melted at 247–250° (with gas).

*Anal.* Calcd. for  $C_{17}H_{15}ON$ : C, 81.9; H, 6.1. Found: C, 81.8; H, 6.2.

**Other Cyclization Experiments on VIII.**—The use of a 1% solution of methanol-free sodium methoxide in dry benzene gave the furan derivative XII (see below) in 84% yield; m. p. 220–223°. With a 0.1 *N* solution of potassium hydroxide in methanol, none of the cyclic ketone was formed, and instead cleavage of VIII to the acid XI resulted (53% yield). Likewise, the use of a 0.5% solution of sodium methoxide in anhydrous methanol gave cleavage to the ester of XI. Finally, heating a benzene solution of VIII with piperidine acetate for five hours gave no reaction.

**Cyclization of 1-Ketotetrahydrophenanthrene-2-acetone (IX).**—When 0.5 g. of the diketone (see below) was refluxed for six hours with 5% potassium hydroxide solution exactly as described above for VIII, there was obtained 0.46 g. of solid ketone; m. p. 178–182°. After evaporative distillation at 200° (0.2 mm.) and recrystallization from benzene, there was obtained 0.42 g. (90%) of III; m. p. 181–184°, undepressed by mixture with the same ketone prepared above.

**Conversion of III to 1,2-Cyclopentenophenanthrene.**—Three hundred milligrams of the ketone was heated with a mixture of 5 g. of amalgamated zinc, 10 cc. of acetic acid, 10 cc. of hydrochloric acid, and 2 cc. of toluene for twenty-four hours, during which time an additional 4 cc. of hydrochloric acid was added. The oil which was isolated with benzene was evaporatively distilled at 200° (0.2 mm.) to remove high boiling resin, and was then dehydrogenated by heating under nitrogen with 100 mg. of palladium-charcoal<sup>20</sup> at 300–320° for one hour. A total of 100 mg. of 1,2-cyclopentenophenanthrene could be isolated, and after recrystallization from acetic acid it melted at 131.5–133° (lit.<sup>21</sup> 134–135°). The picrate separated as orange needles from absolute alcohol; m. p. 132–134° (lit. 133–134.5°). The trinitrobenzene complex, also prepared in absolute alcohol, melted at 165–166.5° (lit. 165.5–166.5°).

**2'-Keto-1,2,3,4-tetrahydro-1,2-cyclopentanophenanthrene A and B (V).**—A suspension of 500 mg. of III and 100 mg. of palladium-charcoal catalyst<sup>20</sup> in 25 cc. of pure dioxane was shaken with hydrogen at room temperature and atmospheric pressure. There was a smooth, though slow uptake of hydrogen, and after twelve hours one mole had been absorbed. There was little tendency for a second mole of hydrogen to enter the molecule. In another run using twice as much catalyst, reaction was complete in four and one-half hours. The catalyst was filtered off and the product was crystallized from methanol. A total of 460 mg. (91%) of the stereoisomeric ketones A and B was obtained as a mixture of plates and needles, m. p. 101–112° to a cloudy liquid, clear at 125°. The crystals gave a pale yellow color with sulfuric acid.

*Anal.* Calcd. for  $C_{17}H_{16}O$ : C, 86.4; H, 6.8. Found: C, 86.5; H, 6.9.

(20) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(21) Cook and Hewett, *J. Chem. Soc.*, 1109 (1933).

That the mixture was ketonic in nature was shown by conversion in 91% yield to a semicarbazone mixture, m. p. 240–243°, and in 94% yield to a mixture of oximes, m. p. 155–160°. Another recrystallization of the oxime mixture gave material melting at 163–168° with previous sintering at 155°.

*Anal.* Calcd. for  $C_{17}H_{17}ON$ : C, 81.3; H, 6.8. Found: C, 81.6; H, 6.7.

Simple recrystallization of the ketone mixture showed little promise of effecting a separation. However, it was found that the two ketones crystallized at different rates, and when a methanol solution of 400 mg. of the ketones was seeded while hot with the mixture, the first material to separate was mainly needles. This was separated by decanting the mother liquor, giving 50 mg.; m. p. 119–130°. The next crop to crystallize was mainly plates, 25 mg.; m. p. 110–112°. One recrystallization of the plates gave the isomer A; m. p. 115–116°. Another recrystallization of the needles, with seeding, gave isomer B; m. p. 146–147.5°.

**1-Acetyl-2-hydroxy-10,11-dihydrophenanthro[1.2-*b*]furan (XII).**—This compound was prepared directly from the bromoketone VII without isolation of intermediates. The solution of VIII in benzene which resulted from reaction of 5 g. of VII with sodioacetoacetic ester as described above, was treated at room temperature with a solution of sodium ethoxide from 1 g. of sodium and 20 cc. of absolute alcohol. The clear solution which resulted rapidly deposited the sodium salt of the reaction product, and within a few minutes the mixture had set to a solid gel. After standing for several hours at room temperature, 25 cc. of methanol was added to the mixture and the solid was broken up with a spatula. Following acidification with dilute hydrochloric acid care was taken to crush any lumps of the salt, then the yellow solid was filtered off and washed with water and benzene to give 4.1 g. (81%) of XII melting at 220–223° with the evolution of gas.

In a similar manner, the pure ester VIII gave an 84% yield of XII; m. p. 220–223° (with gas). The compound is quite insoluble in most organic solvents. The sodium and potassium salts also are relatively insoluble in water, but will dissolve in hot methanol containing a little water. XII could be recrystallized from dioxane or a mixture of benzene and acetic acid only with considerable loss due to decomposition (with the formation of XX, see below). The recrystallized product was obtained as fine, yellow, prismatic needles; m. p. 220–223° (gas). A pyridine solution of the compound gave an intense green color with alcoholic ferric chloride solution. Concentrated sulfuric acid gave a brown solution with XII.

*Anal.* Calcd. for  $C_{18}H_{14}O_3$ : C, 77.7; H, 5.1. Found: C, 77.9; H, 4.9.

In one of the preliminary runs the mixture was warmed for a short time after acidification of the insoluble sodium salt. None of the compound XII could be isolated and instead there resulted a 30% yield of the isomeric furan acid XV (see below). Recrystallization of this acid from dioxane-methanol gave small, cream-colored prisms, m. p. 328–331°<sup>14</sup>; mixed with XV prepared from the ethyl ester (see below) it melted at 327–330°. The two samples likewise gave identical colors with sulfuric acid and with ferric chloride.

*Anal.* Calcd. for  $C_{18}H_{14}O_3$ : C, 77.7; H, 5.1. Found: C, 77.6; H, 5.2.

Esterification of this furan carboxylic acid with alcoholic hydrogen chloride gave an 80% yield of the ethyl ester XIV, identical with that prepared below from VIII; m. p. and mixed m. p. 87–88°. The same ethyl ester XIV could also be obtained in 50% yield by the action of alcoholic hydrogen chloride on XII; m. p. and mixed m. p. 88–89°. An attempt was made to prepare a methyl derivative from XII without rearrangement, through the action of excess ethereal diazomethane on a dioxane solution of the compound. Although reaction occurred at room temperature, no crystalline product could be isolated from the dark oil that resulted, even after evaporative distillation.

Efforts to prepare a crystalline benzoyl derivative by the action of benzoyl chloride in pyridine solution at room temperature or at 100° were unsuccessful. An attempt to hydrolyze XII with alkali revealed that this hydroxyfuran was remarkably stable. Even after refluxing for forty-eight hours with 5% potassium hydroxide in 80% methanol, most of the material was recovered unchanged.

**Ethyl 2-Methyl-10,11-dihydrophenanthro[1.2-*b*]furan-1-carboxylate (XIV).**—A mixture of 4 g. of VIII, 50 cc. of acetic acid, 40 cc. of concentrated hydrochloric acid and 20 cc. of water was refluxed for two hours, then cooled, diluted and extracted with benzene. After washing the extract with water and dilute sodium hydroxide, the benzene was removed and the residue was crystallized from alcohol, giving a total of 3.14 g. (83%) of XIV; m. p. 88–90°. Recrystallization of the product from alcohol gave colorless plates; m. p. 88.5–90°. On one occasion recrystallization from acetone-methanol gave a polymorphic form as prismatic needles; m. p. 78–80°. When the melt was seeded with a crystal of the higher melting form it solidified completely and remelted at 89–90°. Sulfuric acid gave an intense red color with the compound.

*Anal.* Calcd. for  $C_{20}H_{16}O_3$ : C, 78.4; H, 5.9. Found: C, 78.4; H, 5.9.

Acidification of the alkaline wash solution from the preparation of the above ester precipitated 0.32 g. (9%) of the corresponding acid XV; m. p. 310–320°. This acid was best prepared by heating 1 g. of the ethyl ester for twenty hours with 50 cc. of methanol and 5 cc. of 45% potassium hydroxide solution. The methanol was then removed in a stream of air and the insoluble salt was dissolved in warm water. Acidification gave 0.91 g. (100%) of the acid after drying at 100°; m. p. 317–320°. By recrystallization from dioxane **2-methyl-10,11-dihydrophenanthro[1.2-*b*]furan-1-carboxylic acid (XV)** was obtained in the form of cream colored prisms, m. p. 328–331°.<sup>14</sup> XV dissolved in sulfuric acid with the production of an intense red color. A pyridine solution of the acid gave an intense orange-red color with alcoholic ferric chloride solution.

*Anal.* Calcd. for  $C_{18}H_{14}O_3$ : C, 77.7; H, 5.1. Found: C, 77.4; H, 5.2.

The **methyl ester** was prepared in 85% yield, m. p. 120–121°, by the action of ethereal diazomethane on a dioxane solution of the acid, or in the same yield by refluxing the acid with methyl alcoholic hydrogen chloride. After evaporative distillation of the ester at 200–220° (0.5 mm.) and recrystallization from acetone-methanol, the colorless

prisms melted at 121.5–122.5°. With concentrated sulfuric acid an intense red color was formed.

*Anal.* Calcd. for  $C_{18}H_{16}O_3$ : C, 78.1; H, 5.5. Found: C, 77.8; H, 5.6.

**1-Keto-1,2,3,4-tetrahydrophenanthrene-2-acetone (IX).**—Two grams of VIII was refluxed with a mixture of 100 cc. of acetic acid and 20 cc. of concentrated hydrochloric acid for forty-eight hours, during which time the insoluble solid gradually dissolved. The clear yellow solution was diluted with water, the insoluble oil was extracted with benzene and the extract was washed with water and dilute sodium hydroxide. After removal of the benzene the residue was crystallized from methanol (Norit) giving 1.37 g. of solid melting at 96–98°. A second crop of 0.07 g. brought the total yield to 80%. Evaporative distillation of the diketone at 180–200° (0.2 mm.) and recrystallization from methanol gave colorless prisms melting at 97–98°. The compound gave a yellow solution with sulfuric acid.

*Anal.* Calcd. for  $C_{17}H_{16}O_2$ : C, 80.9; H, 6.4. Found: C, 80.7; H, 6.5.

When the time of heating in the above hydrolysis was shortened to twenty-four hours, appreciable amounts of the acid XV were obtained. As would be expected in view of this, the diketone was also obtained upon hydrolytic cleavage of XV; yield 75%; m. p. 93–95°. Another recrystallization of the diketone raised the m. p. to 97–98° alone, and when mixed with the diketone prepared from XII. IX could be prepared directly from VIII by refluxing with acid as above for forty-eight hours (57% yield).

**Ethyl 2-Methylphenanthro[1.2-*b*]furan-1-carboxylate (XVII).**—Dehydrogenation of 0.5 g. of the ethyl ester XIV was accomplished by heating with 0.1 g. of palladium-charcoal<sup>20</sup> under nitrogen at 200–210° for twenty-five minutes. The product was dissolved in hot benzene, the catalyst filtered off and the residue after concentration was crystallized from acetone-alcohol, giving a total yield of 0.46 g. (92%) of XVII; m. p. 116–123°. The use of a higher temperature for dehydrogenation is disadvantageous due to formation of considerable amounts of the corresponding acid, presumably accompanied by ethylene, as this temperature effect was not observed with the methyl ester.

Evaporative distillation at 200–220° (0.5 mm.) and recrystallization from acetone-alcohol gave colorless prisms of XVII melting at 116.5–124° when immersed in the bath at 110°. When placed in a bath preheated to 120° the crystals melted completely, resolidified quickly and remelted sharply at 123.5–124°, indicating the existence of two crystallographic forms for the compound.

*Anal.* Calcd. for  $C_{20}H_{16}O_3$ : C, 78.9; H, 5.3. Found: C, 78.9; H, 5.5.

The methyl ester was prepared in an analogous manner in 86% yield from the corresponding methyl dihydrophenanthro[1.2-*b*]furan-1-carboxylate. After evaporative distillation and recrystallization from acetone-methanol the colorless needles melted at 142.5–144°.

*Anal.* Calcd. for  $C_{19}H_{14}O_3$ : C, 78.6; H, 4.9. Found: C, 78.7; H, 5.0.

The free acid was obtained by heating 160 mg. of the dehydrogenated ethyl ester with a mixture of 25 cc. of methanol and 3 cc. of 45% potassium hydroxide solution

for twenty hours. Acidification gave 140 mg. (95%) of 2-methylphenanthro[1.2-*b*]furan-1-carboxylic acid (XVIII); m. p. 318–322°. After recrystallization from acetic acid XVIII was obtained as colorless needles; m. p. 323–325°. The acid and its esters, in contrast with the dihydro compounds, gave only a pale yellow color with sulfuric acid.

*Anal.* Calcd. for  $C_{18}H_{12}O_3$ : C, 78.3; H, 4.4. Found: C, 78.0; H, 4.5.

**2-Methyl-10,11-dihydrophenanthro[1.2-*b*]furan (XVI).**—The acid XV was decarboxylated by boiling 0.5 g. in a mixture of 10 cc. of quinoline and 0.2 g. of copper chromite catalyst,<sup>22</sup> for one and one-half hours. After cooling and adding benzene the mixture was filtered, the benzene solution was washed with dilute hydrochloric acid, sodium hydroxide and water, and the residue after concentration was purified by evaporative distillation at 170° (0.2 mm.). Recrystallization of the distillate from methanol-acetone gave long colorless needles; m. p. 72–74°; yield 0.29 g. (69%). An intense orange-red color was formed with XVI and sulfuric acid.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.3; H, 5.8.

**2-Methylphenanthro[1.2-*b*]furan (XIX).**—Decarboxylation of 0.25 g. of the dehydrogenated acid XVIII was carried out with copper chromite and quinoline as described for the dihydro derivative. After evaporative distillation at 180° (0.3 mm.) and recrystallization from methanol-acetone, there was obtained a total yield of 0.14 g. (67%) of colorless needles; m. p. 112–112.5°. With concentrated sulfuric acid only a pale tan color was formed.

*Anal.* Calcd. for  $C_{17}H_{12}O$ : C, 87.9; H, 5.2. Found: C, 87.8; H, 5.1.

**Ethyl 2-Hydroxy-10,11-dihydrophenanthro[1.2-*b*]furan-1-carboxylate (XIII).**—To a solution of sodio-malonic ester from 0.25 g. of sodium powder and 2.5 cc. of ethyl malonate in 20 cc. of dry benzene and 1 cc. of absolute alcohol was added 2 g. of the bromoketone VII and the mixture was refluxed for four hours. The solution of the substituted malonic ester X was then cooled to room temperature and treated with the sodium ethoxide from 0.5 g. of sodium and 10 cc. of absolute alcohol. After allowing the mixture to stand for twelve hours at room temperature, during which time most of the material precipitated from solution, water was added to dissolve the salt. Following acidification the benzene layer was washed and evaporated. The remaining oil crystallized readily from alcohol as a light-yellow solid; 1.34 g. (60%); m. p. 123–126°. Upon recrystallization from acetone-alcohol cream colored prisms of XIII were obtained melting at 126–127.5°. With sulfuric acid an intense green color resulted, and with a pyridine solution of the compound a green color was formed on addition of alcoholic ferric chloride solution.

*Anal.* Calcd. for  $C_{19}H_{16}O_4$ : C, 74.0; H, 5.2. Found: C, 73.9; H, 5.4.

From the filtrate there was obtained 0.16 g. of an unknown compound; m. p. 211–215° (gas). With potassium hydroxide this compound formed an insoluble salt which was soluble in hot dilute alcohol; acidification of the solution gave back the original material. Recrystallization of

the compound from dioxane-alcohol raised the m. p. of the small colorless plates to 220–222° (gas). It gave an intense green color with sulfuric acid and in pyridine solution it gave a light green color with alcoholic ferric chloride solution.

*Anal.* Calcd. for  $C_{22}H_{20}O_5$ : C, 72.5; H, 5.5; neut. equiv., 364. Found: C, 72.2; H, 5.6; neut. equiv., 363.

**1-Keto-1,2,3,4-tetrahydrophenanthrene-2-acetic Acid (XI).**—The sodio derivative from 6 cc. of ethyl malonate and 0.7 g. of sodium powder in 25 cc. of dry benzene and 3 cc. of absolute alcohol was heated with 5 g. of VII for three hours, then the benzene was evaporated with an air jet and the residue was hydrolyzed with a mixture of 15 cc. of 45% potassium hydroxide and 15 cc. of methanol. Following short warming, water was added and after an additional one-half hour of warming the mixture was acidified. The malonic acid derivative was usually completely decarboxylated by refluxing the water suspension for twelve hours, although on one run it was necessary to heat the solid obtained by filtration for five minutes at 180° to finish the reaction. The product was recrystallized from acetic acid or ethyl acetate, using Norit, to give 3.35–3.9 g. (73–84%) of the acetic acid XI; m. p. 184–186°. Another recrystallization from ethyl acetate gave colorless prisms; m. p. 187.5–188.5°. With sulfuric acid XI formed an orange-yellow color.

*Anal.* Calcd. for  $C_{18}H_{14}O_3$ : C, 75.6; H, 5.5. Found: C, 75.5; H, 5.5.

The methyl ester was prepared by refluxing 4.4 g. of the acid for five hours with 50 cc. of methanol saturated with dry hydrogen chloride. After cooling, the mixture was diluted and the ester was extracted with benzene, washed with water and sodium bicarbonate solution and crystallized from methanol; total yield, 4.39 g. (95%); m. p. 105–106°. Evaporative distillation at 220° (0.5 mm.) and recrystallization from methanol gave material melting at 106–106.5°.

*Anal.* Calcd. for  $C_{17}H_{14}O_3$ : C, 76.1; H, 6.0. Found: C, 76.2; H, 5.8.

**1,2,3,4-Tetrahydrophenanthrene-2-acetic Acid (XXV).**—Clemmensen–Martin reduction of 4 g. of XI was carried out according to the procedure of Bachmann and Struve for  $\beta$ -(2-phenanthroyl)-butyric acid.<sup>12</sup> After twenty-four hours of heating, the hot solution was decanted from the zinc and the latter was washed well with hot benzene. The benzene-toluene layer was evaporated from the hot mixture with a stream of air and the crystalline residue was filtered from the water layer which remained. Recrystallization from ethyl acetate gave a total yield of 3.18–3.36 g. (84–89%) of the acid; m. p. 166–168°. For analysis a sample was evaporatively distilled at 200° (0.4 mm.) and recrystallized from acetone-methanol to give a colorless microcrystalline powder; m. p. 167–168°. The acid gave only a pale violet color with sulfuric acid.

*Anal.* Calcd. for  $C_{18}H_{16}O_2$ : C, 80.0; H, 6.7. Found: C, 80.1; H, 6.9.

The methyl ester was obtained in 91% yield with diazomethane in ether. The ester crystallized from methanol as colorless prisms; m. p. 67–68°.

*Anal.* Calcd. for  $C_{17}H_{16}O_2$ : C, 80.3; H, 7.1. Found: C, 80.5; H, 7.1.

**Methyl 2-Phenanthreneacetate (XXII).**—Dehydrogenation of 0.92 g. of the tetrahydro ester was carried out by heating with 0.1 g. of palladium-charcoal<sup>20</sup> at 240–250° for a total of two and one-half hours, at which time the evolution of hydrogen had ceased. The total yield of material recrystallized from methanol was 0.77 g. (85%). Evaporative distillation of XXII at 180° (0.2 mm.) and another recrystallization from methanol gave colorless clusters of needles melting at 78.5–79°. Mosettig and van de Kamp<sup>23</sup> reported 78–78.5° for this ester.

Upon saponification of the ester with 45% potassium hydroxide, 2-phenanthreneacetic acid was obtained in 98% yield; m. p. 192–195°. Evaporative distillation at 200° (0.2 mm.) and recrystallization from methanol gave the acid as colorless clusters of thin plates; m. p. 194.5–195.5°. Mosettig and van de Kamp<sup>23</sup> reported obtaining the acid as needles melting at 183.5–184.5°, but did not report the solvent used. It is possible that two different crystallographic forms are involved here.

**2-Phenanthreneacetone (XX).**—One and one-half grams of the furan XII (m. p. 223°) was melted in a 10-cc. two-bulb distilling flask<sup>24</sup> and then distilled at 0.5 mm. pressure. The distillate crystallized readily from methanol to give 0.56 g. of XX; m. p. 90.5–91.5°. After evaporative distillation of the filtrate an additional 0.44 g. (m. p. 89–91°) was obtained to give a total yield of 79%.

The same ketone was obtained by refluxing a solution of 1 g. of XII for twenty hours in 50 cc. of acetic acid. The diluted mixture was extracted with benzene and the extract was washed with water and dilute sodium hydroxide. After evaporation of the benzene, the residue was crystallized from methanol to give a total of 0.62 g. (74%); m. p. 88–90°. A mixture of this product and the ketone obtained by distillation showed no melting point depression.

After another evaporative distillation at 0.5 mm. pressure and recrystallization from methanol, the analytical sample was obtained as colorless needles; m. p. 91–91.5°. The ketone gave only a pale yellow color with sulfuric acid.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.0; H, 6.0.

The oxime, prepared in 99% yield in absolute alcohol-pyridine, crystallized from alcohol as colorless plates; m. p. 197–198°.

*Anal.* Calcd. for  $C_{17}H_{15}ON$ : C, 81.9; H, 6.1. Found: C, 81.5; H, 5.9.

**Reduction of XX to 2-Propylphenanthrene.**—Clemmensen reduction of 0.5 g. of XX was carried out according to the general procedure of Martin.<sup>25</sup> The product was extracted with benzene and evaporatively distilled at 150–170° (0.2 mm.). On cooling there was obtained 0.40 g. (85%) of colorless crystalline 2-propylphenanthrene; m. p. 32.5–34°. Bachmann and Struve<sup>12</sup> record 35–36°.

The picrate, prepared in absolute alcohol solution, was obtained as canary yellow needles. The m. p. 91–92° of the picrate was undepressed by an authentic sample (Bachmann and Struve report 92–93°).

The trinitrobenzene complex, prepared in absolute alcohol solution, formed lemon yellow needles; m. p. 102.5–

(23) Mosettig and van de Kamp, *THIS JOURNAL*, **55**, 2998 (1933).

(24) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, 2nd ed., p. 250.

(25) Martin, *THIS JOURNAL*, **58**, 1438 (1936).

103.5° alone and when mixed with a sample prepared from authentic 2-propylphenanthrene.

*Anal.* Calcd. for  $C_{17}H_{16}C_6H_5O_6N_2$ : C, 63.7; H, 4.4. Found: C, 63.7; H, 4.4.

**2-Phenanthrene-*t*-butyl Alcohol (XXI).** (A) **From XX.**—A solution of 100 mg. of the ketone in 5 cc. of benzene was treated with excess methylmagnesium iodide and allowed to stand for twelve hours at room temperature. After hydrolysis and extraction of the product with benzene, the carbinol was crystallized from benzene-petroleum ether giving a total of 100 mg. (93%) of material melting at 118.5–119.5°. Another recrystallization of the compound raised this m. p. to 119–119.5°.

(B) **From XXII.**—When 100 mg. of the ester XXII was refluxed in benzene solution for four hours with excess methylmagnesium iodide and the carbinol isolated as before, there was obtained a total of 95 mg. (95%); m. p. 119–120°. Recrystallization from benzene-petroleum ether gave material melting at 119.5–120°; when mixed with the carbinol prepared in (A) this product melted at 119–120°. Both samples gave dark brown crystals with sulfuric acid with but little color in the liquid.

*Anal.* Calcd. for  $C_{18}H_{18}O$ : C, 86.4; H, 7.2. Found: C, 86.6; H, 7.0.

**1-(2'-Phenanthryl)-propanol-2.**—Reduction of 0.5 g. of the ketone XX with 10 cc. of a *M* solution of aluminum isopropoxide in isopropyl alcohol according to the method of Lund<sup>26</sup> gave 0.44 g. (88%) of the secondary alcohol; m. p. 105–107°. Another recrystallization of the compound from

benzene-petroleum ether raised the m. p. to 107–107.5°.

*Anal.* Calcd. for  $C_{17}H_{18}O$ : C, 86.4; H, 6.8. Found: C, 86.8; H, 6.7.

**Attempt to Convert XIII to Ethyl 2-Phenanthreneacetate.**—Evaporative distillation of this furan derivative at 200° at 0.3 mm. and recrystallization of the acidic material after hydrolysis gave 10% of a mixture; m. p. 200–210°. Similarly, boiling a solution of XIII in acetic acid for fifteen hours, followed by alkaline hydrolysis of the product, gave a mixture of acids melting at 120–170°; after recrystallization from methanol the mixture had the m. p. 145–172°.

### Summary

1. The synthesis of  $\Delta^{1,1'}\text{-2'-keto-3,4-dihydro-1,2-cyclopentenophenanthrene}$  is reported.

2. Catalytic reduction of the unsaturated ketone to 2'-keto-1,2,3,4-tetrahydro-1,2-cyclopentanophenanthrene is described, and the extension of the method to the synthesis of compounds of interest in connection with the sex hormones is discussed.

3. Cyclization of ethyl 1-ketotetrahydrophenanthrene-2-acetoacetate to phenanthro[1.2-*b*]-furan derivatives is described.

4. 1-Acetyl-2-hydroxy-10,11-dihydrophenanthro[1.2-*b*]furan was converted by heat into 2-phenanthreneacetone.

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RECEIVED MARCH 11, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE LIGNIN AND CELLULOSE RESEARCH LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

## Vanillin from Lignin Materials

BY IRWIN A. PEARL\*

Recently numerous investigators<sup>1-6</sup> have reported high yields of vanillin from lignin containing materials by oxidation with nitrobenzene and aqueous alkali under pressure. These successful experiments with nitrobenzene prompted the use of other low potential oxidizing agents in attempts to obtain high yields of vanillin from lignin materials.

The oxidizing mixture of copper hydroxide in alkaline solution reported by Pearl and Dehn<sup>7</sup> was

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(1) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940).

(2) Schulz, U. S. Patent 2,187,366 (1940).

(3) Lautsch, Plankenhorn and Klink, *Angew. Chem.*, **53**, 450 (1940).

(4) Lautsch and Piazolo, *Ber.*, **73**, 317 (1940).

(5) Creighton, McCarthy and Hibbert, *THIS JOURNAL*, **63**, 312 (1941).

(6) Creighton, McCarthy and Hibbert, *ibid.*, **63**, 3049 (1941).

(7) Pearl and Dehn, *ibid.*, **60**, 57 (1938).

tried on sulfite waste liquor solids, butanol lignin, and Meadol. High vanillin yields (10–20%) were obtained. Lautsch, Plankenhorn and Klink<sup>3</sup> reported very low yields (3–5%) of vanillin by oxidation of "Cuproxam" or hydrochloric acid lignin with alkali in the presence of lead, silver or copper oxide.

In addition to the oxidations with alkaline copper hydroxide experiments were made using Fehling solution and using copper hydroxide-calcium hydroxide mixtures on the three previously mentioned lignin materials. Yields of 9–16% vanillin were obtained on the basis of the lignin present (Table I).

Vanillin was determined by extracting the acidified reaction mixture with ether. The ether was then extracted successively with 5% sodium bicarbonate and sodium hydroxide solutions. The