

*Anal.* Calcd. for  $C_{14}H_{11}O_2Cl$ : Cl, 25.24. Found: Cl, 25.08, 25.16.

**4-(4-Chlorophenyl)-2,6-dichlorophenol (XI).**—The impure 4-(4-chlorophenyl)-2,6-dichlorophenol was prepared according to the method of Colbert, Meigs and Mackin.<sup>10</sup> This was crystallized several times from carbon tetrachloride, thus yielding the pure compound with a constant melting point of 144°. (A 9% yield was obtained.) When a melting point was taken on a mixture of this compound with the chlorophenylphenol obtained from III it was lowered to 120°.

**4-(4-Chlorophenyl)-2,6-dichlorophenyl Acetate (XII).**—This product was obtained by acetylating 2,6,4'-trichlorophenylphenol in the same manner used to prepare VI and X. After two recrystallizations from ethanol, the product was obtained as white needles which melted at 79.5°, in a yield of 75%.

*Anal.* Calcd. for  $C_{14}H_9O_2Cl_3$ : Cl, 33.72. Found: Cl, 33.50, 33.57.

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tance of Mr. T. R. Thompson in the analyses of the compounds.

### Summary

1. Chlorination of 4-phenylphenyl acetate in the presence of iodine catalyst gave rise to 4-(4-chlorophenyl)-phenyl acetate. Hydrolysis of this ester gave a quantitative yield of 4-(4-chlorophenyl)-phenol. Proof of the structure of 4-(4-chlorophenyl)-phenol was given by an independent synthesis of this compound from benzidine.

2. Purification of 4-(4-chlorophenyl)-2,6-dichlorophenol to a constant melting point (144°) was accomplished by several recrystallizations of the impure substance (m. p. 135.5–137°) previously reported. The acetates of 4-(4-chlorophenyl)-phenol, 2-chloro-4-phenylphenol, 2,6-dichloro-4-phenylphenol and 2,6-dichloro-4-(4-chlorophenyl)-phenol were prepared in good yield.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## A Method for the Synthesis of Certain 2-Substituted Phenanthrenes

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A good general method for the preparation of a number of 2-acyl and amino phenanthrenes was required for the synthesis of polynuclear hydrocarbon derivatives. A few such derivatives have been prepared from phenanthrene, but in low yields because the orientation for substitution is chiefly to the 3-position. Not only are the yields low but the separation is quite often difficult.

By the use of the Friedel-Crafts reaction on phenanthrene a 15% yield of the 2-acetylphenanthrene has been obtained. The major product of this reaction<sup>2</sup> was a 65% yield of the 3-acetylphenanthrene. It is possible to separate readily the 2-acetyl derivative because it has the higher melting point and is less soluble. Using the same method, the 2-propionylphenanthrene could be isolated only in an 8% yield,<sup>3</sup> while with succinic anhydride no 2-succinoylated phenanthrene could be isolated.<sup>4</sup> When there is no particular need for the 3-acylphenanthrenes such reactions constitute

an unnecessary waste of laboriously purified phenanthrene.

It has been shown that the 2-position is exclusively involved in the substitution reactions<sup>5</sup> of 9,10-dihydrophenanthrene. The reactions with 9,10-dihydrophenanthrene are not accompanied by the usual resinous products encountered with phenanthrene. We have found that 2-acyl-9,10-dihydrophenanthrenes could be easily dehydrogenated by means of sulfur. Although this method requires three steps in contrast to one step by the older method, they are all readily performed in over-all yields as listed in Table I. The amino

2-Substituted phenanthrene	Over-all yield, %
Acetyl	53
Propionyl	45
Isobutyryl	48
Methoxysuccinyl	70
Amino	25

derivative was made in four steps from phenanthrene, through the 2-amino-9,10-dihydrophene-

(1) Anna Fuller Fund Research Associate.  
 (2) E. Mose tig and J. van de Kamp, *THIS JOURNAL*, **52**, 3704 (1930); **54**, 3328 (1932).  
 (3) W. E. Bachmann and W. S. Struve, *ibid.*, **58**, 1659 (1936).  
 (4) R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1012 (1933).

(5) A. Burger and E. Mosettig, *THIS JOURNAL*, **58**, 1857 (1936), **59**, 1302 (1937).

nanthrene, previously reported by Krueger and Mosettig.<sup>6</sup>

### Experimental<sup>7</sup>

**2-Acetylphenanthrene.**<sup>2</sup>—The 9,10-dihydrophenanthrene used in this work was prepared by the method described by Fieser and Johnson.<sup>8</sup> The crude 2-acetyl-9,10-dihydrophenanthrene<sup>6</sup> obtained from the reaction of 65 g. of 9,10-dihydrophenanthrene and 31 g. of acetyl chloride was transferred to a 250-ml. Claisen-head sabre flask. After heating the flask to 250°, 12 g. of sulfur was added in 1–2 g. quantities over a period of ten minutes. Heating was continued at 260–280° for about one hour or until no more hydrogen sulfide was evolved. The reaction mixture was allowed to cool somewhat and then distilled at 1–2 mm. By dissolving the crude solid distillate in boiling benzene and adding an equal volume of petroleum ether (b. p. 60–90°), 47 g. of crystalline material (in two crops), m. p. 138–142°, was obtained. This was sufficiently pure for further work and represented an over-all yield of 59% for the two steps or a 53% yield based on phenanthrene. Pure material, m. p. 142–143°, could be obtained by two crystallizations. A high boiling viscous oil remained in the mother liquors.

**2-Propionylphenanthrene.**—The distillate, from the dehydrogenation of 2-propionyl-9,10-dihydrophenanthrene,<sup>5</sup> gave crystalline material, m. p. 99–102°, from ethanol. An over-all yield of 45%, based on phenanthrene, was obtained. Recrystallization from ethanol raised the m. p. to 103–104°. Bachmann and Struve<sup>3</sup> reported its m. p. as 104–105°.

**2-Isobutyryl-9,10-dihydrophenanthrene.**—The crude reaction product from 30 g. of 9,10-dihydrophenanthrene and 19.4 g. of isobutyryl chloride was distilled at 2 mm. giving 36.8 g. (88%) of distillate, a sample of which gave crystals, from ethanol, melting at 71.6–72.6°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O: C, 86.36; H, 7.24. Found: C, 86.90; H, 7.34.

**2-Isobutyrylphenanthrene.**—Dehydrogenation of a 10.1-g. sample of the previously described distillate gave a product which crystallized from benzene-ethanol giving 6.06 g. (61%), m. p. 116.8–117.6°. This represents an over-all yield of 48% for the three steps.

(6) J. W. Krueger and E. Mosettig, *J. Org. Chem.*, **3**, 340 (1938–1939).

(7) All melting points are corrected. Microanalyses by Dr. T. S. Ma, University of Chicago.

(8) L. F. Fieser and W. S. Johnson, *THIS JOURNAL*, **61**, 168 (1939).

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O: C, 87.06; H, 6.50. Found: C, 86.83; H, 6.75.

**Methyl β-[2-Phenanthroyl]-propionate.**—To a suspension of 8 g. of β-[9,10-dihydro-2-phenanthroyl]-propionic acid<sup>8</sup> in 100 ml. of methanol was added slowly, while swirling, 10 ml. of acetyl chloride. The reaction mixture became hot and the solid acid dissolved. After standing for three hours at room temperature, water and ether were added. The ether extract was washed with a dilute solution of sodium carbonate and treated with Norite and anhydrous sodium sulfate. It was then filtered and the solvent removed under reduced pressure. The residual oil crystallized from methanol giving 7.6 g. (90%) of material sufficiently pure for further reactions. Recrystallization from methanol gave prisms melting at 73.5–74°. Fieser and Johnson<sup>9</sup> reported the m. p. 77–78°. The above esterification is most convenient and is similar to the method described by Freudenberg and Jakob.<sup>10</sup>

Dehydrogenation of a 2.756-g. sample of the methyl β-[9,10-dihydro-2-phenanthroyl]-propionate gave 2.382 g. of crude material which crystallized from acetone-methanol giving 2.185 g. (80%) of product melting 105–107°. Two crystallizations including a treatment with Norite gave glistening white plates, m. p. 112.2–112.6°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: C, 78.06; H, 5.53. Found: C, 78.43; H, 5.96.

A small sample was hydrolyzed giving the free acid melting at 203–206° (reported<sup>4</sup> 205–206°).

**2-Aminophenanthrene.**—2-Amino-9,10-dihydrophenanthrene<sup>6</sup> was smoothly dehydrogenated by means of sulfur. The reaction product was isolated in the form of its hydrochloride in a 68% yield. Liberation of the free amine by the addition of alkali gave a product melting at 85–86°. This amine has been prepared by Bachmann and Boatner<sup>11</sup> through the Beckmann rearrangement of the oxime of 2-acetylphenanthrene.

### Summary

1. A convenient and improved method for the preparation of 2-acyl and amino phenanthrenes has been described. This method involves the dehydrogenation of the easily prepared 9,10-dihydrophenanthrene derivatives.

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(9) L. F. Fieser and W. S. Johnson, *ibid.*, **61**, 1647 (1939).

(10) K. Freudenberg and W. Jakob, *Ber.*, **74**, 1001 (1941).

(11) W. E. Bachmann and C. H. Boatner, *THIS JOURNAL*, **58**, 8:7 2194 (1936).