[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. XI. Acetylation and Succinoylation of 3-Methylphenanthrene

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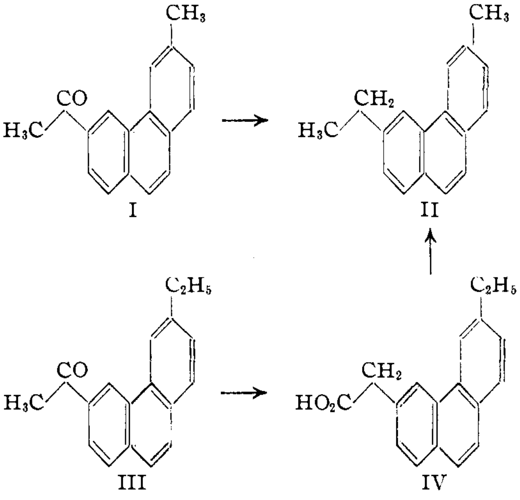
In previous publications,[2] the results of the Friedel–Crafts reaction of 4-methylphenanthrene with acetyl chloride and with succinic anhydride were described. As an extension of such studies on orientation in the phenanthrene nucleus we have investigated the reaction of 3-methylphenanthrene with acetic anhydride, with acetyl chloride and with succinic anhydride. With acetic anhydride, 3-methylphenanthrene gave 3-methyl-6-acetylphenanthrene (I) in 40% yield. With acetyl chloride, 3-methyl-9-acetylphenanthrene (V) was formed in 60% yield. These results bring out the interesting fact that the position taken by the acetyl group depends on the acetylating agent used. Succinic anhydride reacted in the 6 position and gave β-6-(3-methylphenanthroyl)-propionic acid (XI).

In the investigation we were first concerned with the preparation of 3-methylphenanthrene. In two of our methods we made use of Haworth's[3] syntheses with certain modifications which are described in the experimental section. In a third method, α-allylnaphthalene was allowed to react with hydrogen bromide to give 1-(α-naphthyl)-2-bromopropane. Malonic ester condensation followed by hydrolysis and decarboxylation converted the bromide into γ-(1-naphthyl)-β-methylbutyric acid. This acid was cyclized through its acid chloride to 1-keto-3-methyl-1,2,3,4-tetrahydrophenanthrene. The latter was reduced with aluminum isopropoxide to the corresponding carbinol, which was then dehydrated and dehydrogenated with palladium–charcoal catalyst to 3-methylphenanthrene. In a fourth procedure, 3-acetylphenanthrene was converted to 3-phenanthrylacetamide by the Willgerodt reaction. Acid hydrolysis of the amide gave 3-phenanthrylacetic acid. The potassium salt of this acid was heated with soda-lime under reduced pressure to give 3-methylphenanthrene. Of the four methods mentioned, the last one offers the advantage of being short without suffering from the objection of giving low yields, and we consider it the best method of preparing the hydrocarbon.

To prove the structure of 3-methyl-6-acetylphenanthrene (I), it was reduced to 3-methyl-6-ethylphenanthrene (II), and the structure of the latter was established definitely by synthesis. In the synthesis, 3-ethylphenanthrene, obtained by reduction of 3-acetylphenanthrene, was acetylated to give 3-ethyl-6-acetylphenanthrene (III). A Willgerodt reaction followed by hydrolysis yielded 3-ethyl-6-phenanthrylacetic acid (IV). Pyrolysis of a mixture of the potassium salt of this acid and soda-lime gave 3-ethyl-6-methylphenanthrene (or 3-methyl-6-ethylphenanthrene). The structural formulas indicate that these two hydrocarbons can be identical only when the acetyl group in both the 3-methylphenanthrene and 3-ethylphenanthrene derivatives is in the 6 position.



The structure of 3-methyl-9-acetylphenanthrene (V) was determined by reducing it to the hydrocarbon, 3-methyl-9-ethylphenanthrene, whose structure was established by synthesis. In the synthesis, 1-ethylnaphthalene was allowed to react with propionyl chloride in a Friedel–Crafts reaction to give 1-ethyl-4-propionylnaphthalene (VII). Bromination of this ketone yielded 4-(α-bromopropionyl)-1-ethylnaphthalene. Malonic ester condensation followed by hydrolysis and decarboxylation converted the

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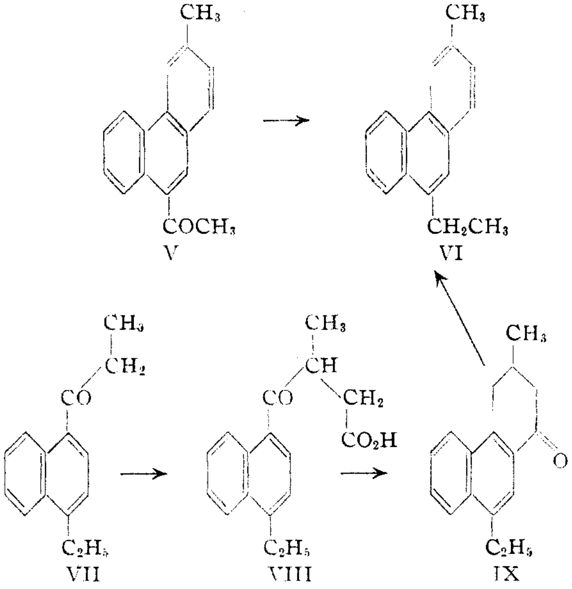
[1] From the Ph.D. dissertation of G. D. Cortes.

[2] Bachmann and Edgerton, THIS JOURNAL, **62**, 2219, 2250 (1940).

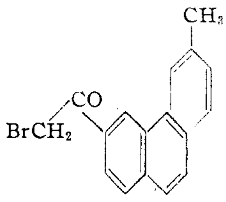
[3] Haworth, *J. Chem. Soc.*, 1125 (1932).

bromo compound into β-(1-ethyl-4-naphthoyl)-butyric acid (VIII). By Clemmensen reduction γ-(1-ethyl-4-naphthyl)-β-methylbutyric acid was obtained. Cyclization of the reduced acid resulted in the cyclic ketone, 1-keto-3-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene (IX). Aluminum isopropoxide reduction, followed by simultaneous dehydration and dehydrogenation gave 3 - methyl - 9 - ethylphenanthrene. This hydrocarbon was identical with that prepared from 3-methyl-9-acetylphenanthrene.



V VI VII VIII IX

The position of the succinoyl group in the 3-methylphenanthrene derivative was established by synthesizing this keto acid (XI) from 3-methyl-6-acetylphenanthrene, in which the orientation of the acetyl group is definitely known. Cold bromination of the acetyl derivative gave 3-methyl-6-bromoacetylphenanthrene (X). Malonic ester condensation with subsequent hydrolysis and decarboxylation yielded β-6-(3-methylphenanthroyl)-propionic acid (XI) which was identical with the keto acid obtained by succinoylating 3-methylphenanthrene.



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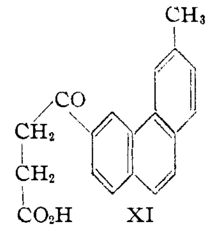
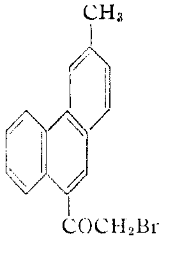


XI

From 3-methyl-9-acetylphenanthrene the known hydrocarbon, 2-methyltriphenylene,[4,5] was synthesized. The acetyl compound was brominated and 3-methyl-9-bromoacetylphenanthrene (XII) was isolated. Reaction with sodiomalonic ester followed by hydrolysis and decarboxylation gave β-9-(3-methylphenanthroyl)-propionic acid (XIII). Clemmensen reduction yielded the butyric acid derivative which was then cyclized to give 10-methyl-1-keto-1,2,3,4-tetrahydrotriphenylene (XIV). Reduction, followed by dehydration and dehydrogenation, converted the ketone into 2-methyltriphenylene (XV). This was identical with 2-methyltriphenylene prepared according to Fieser and Joshel.[4]



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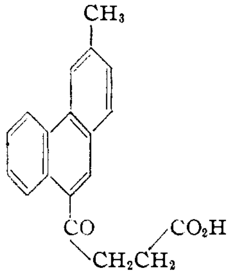
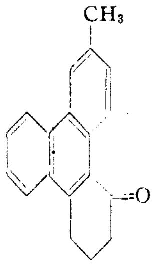


XIII



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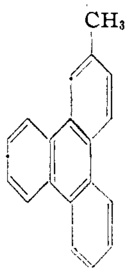
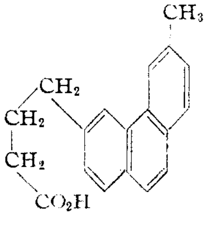
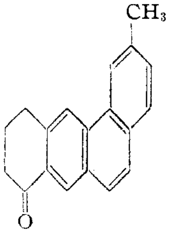


XV

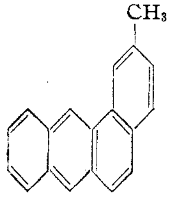
The hydrocarbon, 2′-methyl-1,2-benzanthracene (XVIII), was synthesized readily from β-6-(3-methylphenanthroyl)-propionic acid (XI). The keto acid was reduced to γ-6-(3-methylphenanthryl)-butyric acid (XVI) by the Clemmensen method. Cyclization of the reduced acid yielded the corresponding ketone (XVII) which



XVI



XVII



XVIII

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(4) Fieser and Joshel, This Journal, **61**, 2958 (1939).

(5) Rapson, *J. Chem. Soc.*, 15 (1941).

was reduced to the carbinol and the latter dehydrated and dehydrogenated to 2′-methyl-1,2-benzanthracene. The properties of the compound agreed with those of the hydrocarbon prepared by Cook.[6]

Experimental

Preparation of 3-Methylphenanthrene. (a) From 3-Methyl-4-keto-1,2,3,4-tetrahydrophenanthrene.—This ketone was prepared from 4-keto-1,2,3,4-tetrahydrophenanthrene and from γ-(2-naphthyl)-α-methylbutyric acid. A solution of 6 g. of γ-2-naphthylbutyric acid[3] in 40 cc. of benzene was treated with 7.5 g. of powdered phosphorus pentachloride. After standing for one hour, the mixture was cooled in an ice-bath and 6 cc. of anhydrous stannic chloride was added. At the end of fifteen minutes, the reaction product was poured into a mixture of ice and hydrochloric acid and the benzene layer was then washed successively with dilute acid, water, dilute alkali and water. After removing the benzene, the residue was purified by evaporative distillation at 0.01 mm. and by crystallization from acetone-alcohol, which gave colorless prismatic needles of **4-keto-1,2,3,4-tetrahydrophenanthrene**; weight, 4.6 g. (85%); m. p. 67–68°. Haworth[3] obtained a 70–75% yield of the same ketone (m. p. 69°) by cyclization of the acid with 85% sulfuric acid.

The condensation of 1 g. of the aforementioned ketone with methyl oxalate was carried out in the manner described for a similar compound.[7] The **methyl-4-keto-1,2,3,4-tetrahydrophenanthrene-3-glyoxalate** crystallized from alcohol in lemon-yellow needles; yield 0.8 g. (85%); m. p. 69–71°. After three more recrystallizations, a sample melted at 70–71°.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0. Found: C, 72.2; H, 4.9.

By means of the procedure described,[7] a mixture of 1.5 g. of the glyoxalate and 0.75 g. of powdered soft glass was heated at 180° until the evolution of carbon monoxide ceased (about half an hour). A hot benzene solution of the product was treated with Norite, filtered, and concentrated, and the residue was crystallized from methanol; weight, 1.29 g. (92%); m. p. 87–89°. After two more recrystallizations from methanol. a sample of the **4-keto-3-carbomethoxy-1,2,3,4-tetrahydrophenanthrene** was obtained as colorless needles; m. p. 91–92°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.6. Found: C, 75.5; H, 5.6.

The foregoing compound (1 g.) in 5 cc. of benzene and a solution of sodium methoxide, prepared from 0.4 g. of sodium and 8 cc. of methanol, were warmed for an hour on a steam-bath. To the cooled mixture, 2 cc. of methyl iodide was added and the mixture was kept at 40° for one hour and on a steam-bath for three hours. Then an additional 2 cc. of methyl iodide was added and refluxing was continued for another hour. The cooled reaction mixture was neutralized with acetic acid and evaporated nearly to dryness. After extracting the residue with benzene and water, the benzene layer was washed with dilute alkali and water and was then dried over anhydrous sodium sulfate. After removing the benzene, 0.94 g. (89%) of **3-methyl-4-keto-3-carbomethoxy-1,2,3,4-tetrahydrophenanthrene** was obtained; m. p. 68–71°. After several recrystallizations from methanol, a sample was obtained as colorless needles which melted at 83.5–84°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.0; H, 6.1.

A mixture of 0.94 g. of the aforementioned compound, 30 cc. of acetic acid, 15 cc. of hydrochloric acid and 5 cc. of water was refluxed in an atmosphere of nitrogen for eight hours. The cooled solution was diluted with water and chilled. The **3-methyl-4-keto-1,2,3,4-tetrahydrophenanthrene** was filtered off and purified by evaporative distillation at 0.01 mm. Crystallization from alcohol yielded 0.655 g. (88%) of colorless plates, m. p. 64–65°. Haworth[3] obtained this compound (m. p. 64–65°) in low yields by distilling the product obtained by methylating the ethyl ester of the aforementioned glyoxalate.

This ketone was also prepared by cyclization of γ-(2-naphthyl)-α-methylbutyric acid.[8] A solution of 1.6 g. of the acid in 15 cc. of benzene was treated with 2 g. of phosphorus pentachloride. The acid chloride, without being isolated, was then cyclized with 1.6 cc. of anhydrous stannic chloride. After working up the reaction mixture in the usual manner, the product was evaporatively distilled at 0.01 mm.; the **3-methyl-4-keto-1,2,3,4-tetrahydrophenanthrene** separated from an alcoholic solution in colorless plates, m. p. 64–66°. A second crop of 0.22 g., m. p. 61–64°, raised the yield to 89%. A 70% yield of the same ketone was reported,[8] in which sulfuric acid was employed for cyclizing the acid.

A mixture of 0.53 g. of the foregoing compound and 20 cc. of a *M* solution of aluminum isopropoxide in anhydrous isopropyl alcohol was refluxed for thirty minutes. The liquid was distilled slowly until no test for acetone could be obtained in the distillate with 2,4-dinitrophenylhydrazine reagent. The residue was hydrolyzed by pouring it into a cold solution of 3 cc. of sulfuric acid in 60 cc. of water. The precipitate was filtered off and washed with dilute ammonia and with water. The light-colored **3-methyl-4-hydroxy-1,2,3,4-tetrahydrophenanthrene**, weight 0.49 g. (91.8%), m. p. 89–93°, was used directly in the next reaction.

The above carbinol (0.2 g.) and 0.02 g. of palladium-charcoal catalyst were heated in an atmosphere of nitrogen for thirty minutes at 300–310°. The product which was separated from the catalyst by extraction with benzene, was evaporatively distilled at 0.01 mm. at 150–160°. Crystallization from alcohol gave colorless needles of **3-methylphenanthrene**; weight, 0.165 g. (95%); m. p. 61–62° (reported, 60–61°,[3] 65°,[8] 62°[9]).

(b) From 3-Methyl-1-keto-1,2,3,4-tetrahydrophenanthrene.—This compound was prepared readily by a series of reactions starting from α-allylnaphthalene. A mixture of 20 g. of α-allylnaphthalene[10] and 100 g. of a 30% solution of hydrobromic acid in acetic acid was warmed at 40–50° with occasional shaking for three hours and was then mechanically shaken for two days, at room temperature. The mixture was poured into cracked ice, the insoluble

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[6] Cook, *J. Chem. Soc.*, 470 (1932).

[7] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[8] Pschorr, *Ber.*, **39**, 3112 (1906).

[9] Kruber, *ibid.*, **71B**, 2478 (1938).

[10] Fieser and Hershberg, THIS JOURNAL, **60**, 1658 (1938).

bromo compound was separated, and the aqueous portion was extracted with petroleum ether. The combined extracts were washed with 5% sodium carbonate solution and with water and were dried over anhydrous sodium sulfate. After removal of the organic solvent, the 1-(α-naphthyl)-2-bromopropane distilled at 130–135° at 0.01 mm. as a colorless liquid; at 1.5 mm. it distilled at 152–156°; yield, 22.5 g. (75.3%).

Anal. Calcd. for $C_{13}H_{13}Br$: Br, 32.07. Found: Br, 31.90.

To a cooled solution of sodiomalonic ester prepared from 0.5 g. of sodium, 5 g. of ethyl malonate and 5 cc. of ethyl alcohol, was added a solution of 4 g. of the 1-(α-naphthyl)-2-bromopropane in 10 cc. of benzene, and the mixture was warmed at 70–80° for eight hours and refluxed on a steam-bath for four hours. The warm solution was poured cautiously into a hot solution of 6 g. of potassium hydroxide in 8 cc. of water and 10 cc. of alcohol; the benzene and alcohol were evaporated, more water was added and the resulting solution was heated for two hours on a steam-bath. After extraction with benzene to remove any neutral constituents, the cooled solution was acidified. The filtered and dried dicarboxylic acid (1.6 g.) was heated at 160° for about thirty minutes. After treatment of a benzene solution of the product with Norite, the benzene was removed and the **γ-(1-naphthyl)-β-methylbutyric acid** crystallized from alcohol in colorless crystals; yield 1.42 g. (43%); m. p. 89–91°. Repeated recrystallizations raised the melting point of a sample to 92–93°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.7; H, 7.0.

The preceding compound was cyclized through its acid chloride (without isolation) in the usual manner using 1.5 g. of phosphorus pentachloride and 1 cc. of stannic chloride. After evaporative distillation at 0.01 mm., the **3-methyl-1-keto-1,2,3,4-tetrahydrophenanthrene** crystallized from alcohol in fine colorless needles; weight 0.84 g. (91%); m. p. 103–104°. Several recrystallizations raised the melting point of a sample to 105–106°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.8; H, 6.7.

The foregoing cyclic ketone (1 g.) was reduced to the carbinol with 20 cc. of a *M* solution of aluminum isopropoxide. The **3-methyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene** crystallized from alcohol in colorless needles; yield, 0.85 g. (85%); m. p. 90–92°. A sample after repeated recrystallizations melted at 92–93°. The carbinol gave a violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 84.5; H, 7.6.

A mixture of 0.7 g. of the carbinol and 0.07 g. of palladium–charcoal catalyst was heated in a nitrogen atmosphere at 300–310° for thirty minutes. Evaporative distillation of the product and crystallization from alcohol, yielded colorless needles of **3-methylphenanthrene**, m. p. 61–62°; weight 0.52 g. (81%). A second crop (0.6 g.), m. p. 59–60°, raised the yield to 89%.

(c) **From 3-Acetylphenanthrene.**—Following the excellent procedure of Fieser and Kilmer,[11] a mixture of 4 g. of 3-acetylphenanthrene, 16 cc. of dioxane and 20 cc. of ammonium polysulfide reagent was heated in a sealed tube at 165–167° for fourteen hours. The **3-phenanthrylacetamide**, which separated in rosets of light yellow needles, was washed with ammonium sulfide and dioxane; best yield, 3.4 g. (81%); m. p. 172–176°. When four runs of 2 g. each of 3-acetylphenanthrene were carried out at the same time, the yields varied from 40 to 80%. The combined yields averaged 65–70%.

The amide (1 g.) was hydrolyzed by refluxing it with 10 cc. of acetic acid and 3 cc. of hydrochloric acid for three hours. After adding another 3 cc. of hydrochloric acid, the mixture was chilled for a few hours. The precipitated **3-phenanthrylacetic acid** was purified by treating an aqueous solution of its sodium salt with Norite. The dried, regenerated acid melted at 177–178° (reported,[12] 175–177°); yield, 0.7 g. (76%).

The dried potassium salt of 7.3 g. of 3-phenanthrylacetic acid was thoroughly mixed with 30 g. of powdered soda-lime, in a two-bulb flask with a wide side-arm and the mixture was heated under reduced pressure (20 mm.) until distillation of 3-methylphenanthrene took place. Crystallization of the distillate from alcohol gave colorless needles of **3-methylphenanthrene**, weight, 4.53 g.; m. p. 61–62°. A second crop of 0.21 g., m. p. 59–61°, brought the yield up to 84%.

Acetylation of 3-Methylphenanthrene. With Acetic Anhydride.—To an ice-cold, stirred solution of 1.5 g. of anhydrous aluminum chloride in 10 cc. of nitrobenzene, 1.5 cc. of acetic anhydride was added. After standing overnight in a refrigerator, the mixture was poured into ice and hydrochloric acid and the organic layer was washed a few times with water. The product obtained after removal of the nitrobenzene by steam distillation was evaporatively distilled at 0.01 mm. A light yellow viscous liquid, weighing 0.93 g., distilled at 165–175°. As the liquid could not be made to crystallize, presumably because it was a mixture of isomers, a separation was made by preparing the semicarbazones in alcoholic solution. A crystalline semicarbazone, m. p. 213–215°, was isolated and this was hydrolyzed by refluxing it with 10 cc. of a mixture of 1:1 hydrochloric acid and alcohol for three hours to regenerate the acetyl derivative. After evaporative distillation at 0.01 mm., the **3-methyl-6-acetylphenanthrene** (I) crystallized from alcohol in fine colorless needles; weight, 0.485 g. (40%); m. p. 86–89°. Repeated recrystallizations raised the melting point of a sample to 95–96°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.1; H, 6.1. Found: C, 87.0; H, 6.1.

With Acetyl Chloride.—To an ice-cold stirred solution of 3.5 g. of anhydrous aluminum chloride in 20 cc. of nitrobenzene, 1.4 cc. of freshly distilled acetyl chloride and 3 g. of 3-methylphenanthrene were added. After being stirred for ten hours at ice-bath temperature, the mixture was worked up as above. Evaporative distillation at 0.01 mm. and crystallization from alcohol gave 2.19 g. of colorless needles of **3-methyl-9-acetylphenanthrene** (V); m. p. 88–90°. Several recrystallizations of a sample raised the melting point to 90–91°. A mixture of this compound and that obtained with acetic anhydride melted at 60–71°.

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[11] Fieser and Kilmer, This Journal, **62**, 1354 (1940).

[12] Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.1; H, 6.1. Found: C, 87.1; H, 6.1.

Structure Proof of I. 3-Methyl-6-ethylphenanthrene (II). (a) **From 3-Methyl-6-acetylphenanthrene.**—A mixture of 6 g. of amalgamated zinc, 8 cc. of hydrochloric acid, 4 cc. of acetic acid, 5 cc. of toluene and 0.15 g. of the ketone was refluxed for thirty-six hours, during which time three portions of 5 cc. of hydrochloric acid and 1 cc. of acetic acid each were added. After separating the toluene layer, the aqueous portion was extracted with benzene and the combined benzene and toluene extracts were washed with water. The solvents were then removed and evaporative distillation of the residue at 0.01 mm. followed by crystallization from methanol gave 0.08 g. (60%) of **3-methyl-6-ethylphenanthrene** in colorless leaflets; m. p. 44–46°. Three more recrystallizations raised the melting point of a sample to 47–48°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.9; H, 7.3.

The **picrate** crystallized from alcohol in fine orange needles, m. p. 156–156.5°.

(b) **From 3-Ethylphenanthrene.**—The Friedel–Crafts reaction between 5 g. of 3-ethylphenanthrene and 3 g. of acetic anhydride in a solution of 5 g. of anhydrous aluminum chloride in 20 cc. of nitrobenzene was carried out as already described for 3-methylphenanthrene. The crude product was evaporatively distilled at 0.01 mm. and the light yellow oil which was obtained yielded a crystalline semicarbazone; m. p. 203–206°. The semicarbazone was hydrolyzed and the product was evaporatively distilled and crystallized from dilute methanol to give 1.95 g. of **3-ethyl-6-acetylphenanthrene** (III) in colorless glistening plates; m. p. 82–83°. After three more recrystallizations, a sample melted at 86–87°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 87.0; H, 6.4.

In the manner described, a Willgerodt reaction was carried out using 0.965 g. of 3-ethyl-6-acetylphenanthrene, 4 cc. of dioxane and 5 cc. of ammonium polysulfide reagent. The crude **3-ethyl-6-phenanthrylacetamide** melted at 172–174°; weight, 0.825 g. (82%). After two recrystallizations of a sample from dilute alcohol, long, light yellow needles were obtained; m. p. 182–183°.

Anal. Calcd. for $C_{18}H_{17}ON$: N, 5.32. Found: N, 5.40.

Hydrolysis of the crude amide (0.245 g.) gave 0.18 g. (77%) of colorless **3-ethyl-6-phenanthrylacetic acid** (IV); m. p. 107–109°. Several recrystallizations raised the melting point of a sample to 110–111°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.4; H, 6.2.

The potassium salt of the above acid (0.2 g.) was heated with 0.8 g. of soda-lime under reduced pressure so that distillation of the product took place. The distillate, which solidified on cooling, was crystallized from methanol and colorless leaflets of **3-ethyl-6-methylphenanthrene** were obtained; yield, 0.11 g.; m. p. 46–47°. A second crop of 0.02 g., m. p. 44–46°, raised the yield to 77%. Repeated recrystallizations yielded a product which melted at 47–48° alone and when mixed with the 3-methyl-6-ethylphenanthrene described above. Likewise the **picrate** melted at 156–156.5° alone and when mixed with the picrate obtained previously.

Proof of Structure of V. 3-Methyl-9-ethylphenanthrene (VI). (a) **From 3-Methyl-9-acetylphenanthrene.**—The Clemmensen reduction of 0.6 g. of this ketone was carried out as described for its isomer (I). Evaporative distillation at 0.01 mm. and crystallization from alcohol gave colorless needles of **3-methyl-9-ethylphenanthrene** (VI); yield, 0.3 g. (56%); m. p. 47–48°. Repeated recrystallizations did not raise the melting point.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.72; H, 7.33.

The **picrate** of the hydrocarbon crystallized from alcohol in reddish-orange needles; m. p. 121–122°.

(b) **From α-Ethylnaphthalene.**—As described for a similar compound,[13] 5.17 g. of α-ethylnaphthalene was allowed to react with 3.5 g. of propionyl chloride in the presence of 5 g. of anhydrous aluminum chloride in carbon disulfide solution. Evaporative distillation of the crude product (0.01 mm.) at 140–150° yielded 5.2 g. (73%) of colorless liquid, **1-ethyl-4-propionylnaphthalene** (VII).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 85.3; H, 7.4.

To an ice-cold solution of 3 g. of the above ketone in 100 cc. of ether, a cold solution of 2.25 g. of bromine in 40 cc. of ether was added. With irradiation of light from two argon bulbs, the mixture turned colorless in one hour. After another half hour, the ether was removed, and the residue was washed with sodium bicarbonate solution and with water and dried over anhydrous magnesium sulfate. The light yellow liquid, **4-(α-bromopropionyl)-1-ethylnaphthalene** (4.15 g.), without further purification was condensed with sodio-malonic ester in the manner already described. The decarboxylated product, **β-(1-ethyl-4-naphthoyl)-butyric acid** (VIII) was dissolved in benzene and treated with Norite and was crystallized from a mixture of benzene and petroleum ether; weight, 1.87 g. (48%); m. p. 123–125°. Two more recrystallizations raised the melting point of a sample to 127–128°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.5; H, 6.7. Found: C, 75.8; H, 6.6.

Clemmensen reduction of 1.8 g. of the keto acid gave 1.29 g. of **γ-(1-ethyl-4-naphthyl)-β-methylbutyric acid**, which was cyclized in the manner described previously. The product, **1-keto-3-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene** (IX) crystallized from alcohol in colorless glistening needles; yield, 0.615 g. (52%); m. p. 95–97°. A sample after two more recrystallizations melted at 97.5–98°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.9; H, 7.5.

One-half gram of the ketone was reduced to the carbinol with aluminum isopropoxide solution and the solid carbinol was converted to the hydrocarbon by heating it with palladium–charcoal catalyst at 310° in a nitrogen atmosphere for thirty minutes. The **3-methyl-9-ethylphenanthrene** (VI) after evaporative distillation and crystallization from dilute alcohol was obtained as colorless fine needles melting at 47–48° alone and when mixed with the same hydrocarbon prepared in (a). Likewise the melting

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(13) Frösche and Harlass, *Monatsh.*, **59**, 282 (1932).

point (121–122°) of the **picrate** was not depressed by the picrate of the hydrocarbon prepared previously.

β-6-(3-Methylphenanthroyl)-propionic Acid (XI). (a) **By Succinoylation of 3-Methylphenanthrene.**—Following the procedure already described, a Friedel–Crafts reaction was carried out with 3 g. of 3-methylphenanthrene, 3 g. of succinic anhydride, 4.5 g. of anhydrous aluminum chloride and 15 cc. of nitrobenzene. After fifteen hours in a refrigerator, the reaction mixture was worked up in the usual way, and the product was decolorized in hot benzene by means of Norite. From the benzene solution fine needles of β-6-(3-methylphenanthroyl)-propionic acid separated; yield, 1.655 g.; m. p. 182–183°. Two recrystallizations raised the melting point of a sample to 184.5–185°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.8; H, 5.4.

(b) **From 3-Methyl-6-Acetylphenanthrene.**—In a manner described for a similar compound, 1 g. of this ketone was brominated in ether solution with the aid of light from two argon bulbs. The crude **3-methyl-6-bromoacetylphenanthrene (X)** separated as yellow needles weighing 1.12 g. (82.5%); m. p. 154–156°. Very pale yellow needles melting at 157–158° were obtained after two recrystallizations from a methanol–acetone mixture.

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 25.3.

A solution of 0.5 g. of the crude bromo compound was allowed to react with a sodio-malonic ester solution in the usual way. After hydrolysis and decarboxylation, the β-6-(3-methylphenanthroyl)-propionic acid crystallized from benzene in fine colorless needles; yield 0.25 g. (59%). The acid melted at 181–182° alone and when mixed with the succinoylation product of 3-methylphenanthrene.

2-Methyltriphenylene (XV).—This hydrocarbon was prepared by synthesis from 3-methyl-9-acetylphenanthrene. The bromination of 0.6 g. of this ketone was carried out according to the method already described. From an acetone–methanol solution, colorless needles of **3-methyl-9-bromoacetylphenanthrene (XII)** were obtained; weight, 0.67 g. (83%); m. p. 96–97°. A sample, after repeated recrystallizations, melted at 101–102°.

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 25.4.

The condensation of 0.5 g. of the foregoing bromo compound with sodio-malonic ester followed by hydrolysis and decarboxylation gave **β-9-(3-methylphenanthroyl)-propionic acid (XIII)** which crystallized from a benzene–acetone solution in colorless needles; yield, 0.30 g. (71%); m. p. 172–173°. After two more recrystallizations, a sample melted at 174–175°.

Anal. Calcd. for: $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.9; H, 5.6.

Clemmensen reduction of 0.225 g. of the keto acid gave 0.14 g. of **γ-9-(3-methylphenanthryl)-butyric acid** (m. p. 164–170°) which, without purification, was added to a mixture of 5 cc. of ether, 0.4 cc. of thionyl chloride and a drop of pyridine. After one hour at room temperature, the thionyl chloride and ether were removed completely under reduced pressure and the acid chloride was dissolved in 5 cc. of dry benzene. To the ice-cold benzene solution, 0.2 cc. of anhydrous stannic chloride was added. After one-half hour, the orange-red complex was worked up in the usual way, and the **10-methyl-1-keto-1,2,3,4-tetrahydrotriphenylene (XIV)** was obtained as a colorless solid; yield, 0.12 g. (91%); m. p. 80–83°.

The crude ketone was reduced with aluminum isopropoxide solution and the crude carbinol (0.09 g.) was heated with palladium–charcoal catalyst at 220° in an atmosphere of nitrogen for thirty minutes. The temperature was then slowly raised to 300–310° and kept there for 20 minutes. From a benzene-alcohol solution, colorless fluffy needles of **2-methyltriphenylene (XV)** separated; yield, 0.085 g. (65%); m. p. 101–102°. There was no depression in the melting point of a mixture of this hydrocarbon and an authentic sample of 2-methyltriphenylene prepared according to Fieser and Joshel.[4]

The **picrate** melted at 191–192° alone and when mixed with the picrate of the 2-methyltriphenylene.

2′-Methyl-1,2-benzanthracene (XVIII).—Clemmensen reduction of 0.2 g. of β-6-(3-methylphenanthroyl)-propionic acid gave 0.110 g. of crude **γ-6-(3-methylphenanthryl)-butyric acid (XVI)**, m. p. 108–111°, which was cyclized (using 0.2 g. of phosphorus pentachloride and 0.4 cc. of anhydrous stannic chloride) to **1-keto-1,2,3,4-tetrahydro-2′-methyl-5,6-benzanthracene (XVII)**. The pale-yellow solid (54%) melting at 165–168° was reduced with aluminum isopropoxide solution and the crude carbinol, 0.045 g. (89%), m. p. 131–133°, was heated with palladium-charcoal catalyst at 300–310° for thirty minutes. Crystallization from alcohol gave **2′-methyl-1,2-benzanthracene** in colorless elongated leaflets; weight, 0.03 g. (75%); m. p. 148–149° (reported,[6] 149–150°).

The **picrate** of the hydrocarbon crystallized from alcohol in red needles; m. p. 179–180° (reported,[6] 180°).

Summary

Two new methods of synthesizing 3-methylphenanthrene are described.

In the Friedel–Crafts reaction, 3-methylphenanthrene reacts with acetic anhydride and with succinic anhydride in the 6 position and with acetyl chloride in the 9 position. 3-Ethylphenanthrene is acetylated with acetic anhydride in the 6 position.

Two new methylethylphenanthrenes, 3-methyl-6-ethylphenanthrene and 3-methyl-9-ethylphenanthrene, have been prepared.

The known hydrocarbons 2-methyltriphenylene and 2′-methyl-1,2-benzanthracene were synthesized by new methods.

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