Summary

It is possible to identify many leaf and flower pigments by suitable treatment with methyl alcohol, butyl alcohol, amyl alcohol and ether in acid and alkaline solutions.

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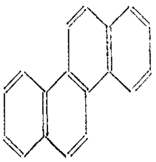
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Synthesis of Chrysene Derivatives

BY MELVIN S. NEWMAN

The desirability of preparing methyl derivatives of all of the five polycyclic aromatic hydrocarbons of the formula $C_{18}H_{12}$ has been pointed out previously.[1] Of these, derivatives of 1,2-benzanthracene have received the greatest attention. With the recent synthesis of 8-methyl-1,2-benzanthracene[2] all of the monomethyl derivatives of 1,2-benzanthracene have been made available for the study of the effect of structure on cancer-producing activity.[3] Of the other members of this class of hydrocarbons chrysene, I, offered a most promising field for research not only because of the similarity of its carbon skeleton to that of the steroids but also because the active carcinogenic agent in coal tar, 3,4-benzpyrene, II,[4] may be considered as a chrysene substituted in positions 4 and 5.



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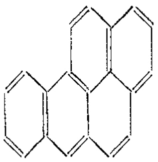

II

Of the known methods for the synthesis of chrysene and its derivatives[5] none seemed adequate for the preparation of various methyl- and dimethylchrysenes desired for biological testing. The work herein reported was undertaken in an effort to find a general method suitable for the preparation of variously substituted derivatives of chrysene.

The successful synthesis proceeds from benzalacetophenone by well-known reactions to α,γ-diphenylbutyric acid.

$$C_6H_5COCH{=}CHC_6H_5 + HCN \longrightarrow$$

$$C_6H_5COCH_2CH(CN)C_6H_5 \xrightarrow[H_2SO_4]{CH_3OH}$$

$$C_6H_5COCH_2CH(COOCH_3)C_6H_5 \xrightarrow{H_2O}$$

$$C_6H_5COCH_2CH(COOH)C_6H_5 \xrightarrow[HCl]{Zn-Hg}$$

$$C_6H_5CH_2CH_2CH(COOH)C_6H_5$$

The acid chloride of α,γ-diphenylbutyric acid was cyclized in benzene solution by aluminum chloride to 1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene III (87% yield) and the remaining steps in the synthesis are indicated below. This part of the synthesis consists essentially of an extension of the phenanthrene synthesis of Cook.[6]

Although one might expect the ketone III to be somewhat hindered, the Reformatsky reaction proceeded vigorously and the yield of the acid IV varied from 60 to 68%. The double bond is placed in the ring instead of the alternate position of conjugation with the carboxyl group because of the failure to isolate III from the products of ozonization. Surprisingly, low pressure catalytic reduction of this acid, its sodium salt, or its methyl ester using palladium or platinum catalysts failed almost completely. Invariably the acid was recovered for the most part unchanged. Reduction in excellent yield was finally effected by the action of 2% sodium amalgam on an aqueous alcoholic solution of the sodium salt, *using acid which had been recovered from unsuccessful attempts at catalytic hydrogenation.* When freshly prepared pure acid was used, *no reduction took place.* While an exhaustive search into the reason for this phenomenon was not made, the effect was noted in several different runs. If an alcoholic solution of the pure acid were shaken with Adams platinum catalyst and hydrogen and then recovered, this acid could be reduced by sodium amalgam. It may be that

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(1) Newman and Joshel, THIS JOURNAL, **60**, 485 (1938).

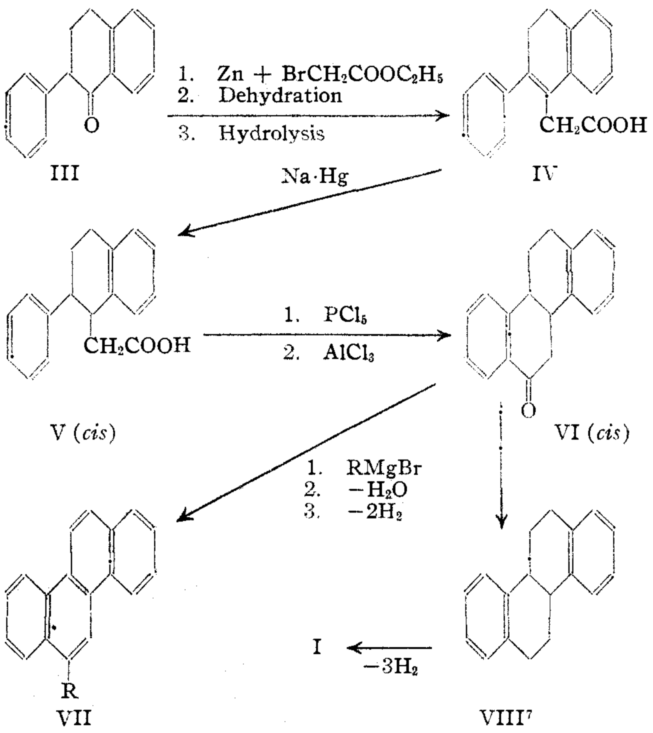
(2) Cook and Robinson, *J. Chem. Soc.*, 505 (1938).

(3) For the most recent report on the activity of methyl-1,2-benzanthracenes see Shear, *Am. J. Cancer*, **33**, 499 (1938); Fieser, *ibid.*, **34**, 37 (1938).

(4) Cook, Hewett and Hieger, *J. Chem. Soc.*, 395 (1933).

(5) Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Rheinhold Publishing Corporation, New York, N. Y., 1936 or 1937, p. 22.

(6) Cook, Hewett and Lawrence, *J. Chem. Soc.*, 71 (1936).



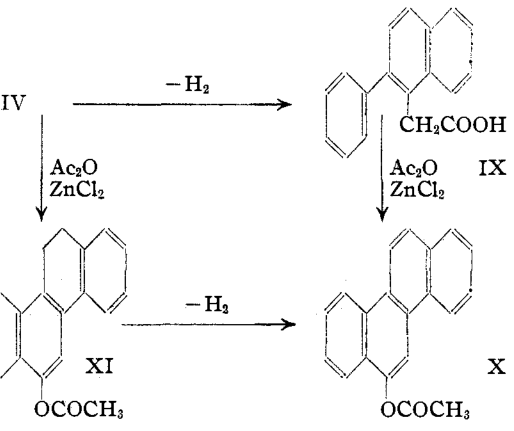
some colloidal platinum is the cause of the results noted for in a patent[8] it is claimed that spongy metals or alloys act as a catalyst for the reaction of sodium amalgam with aqueous solutions. The reduction proceeded in excellent yield to give a mixture of two racemates, one of which easily was isolated pure in 62% yield by fractional crystallization. The remainder of the reduced acids consisted of a difficultly separable mixture.[9]

The ketone VI was prepared in 81% yield by an intramolecular Friedel–Crafts condensation of the chloride of V. Upon Clemmensen reduction the known *cis* 5,6,11,12,13,14-hexahydrochrysene,[7] m. p. 76.8–77.8°, corr., was obtained. This fact forms the basis for assigning the *cis* structure to the acid V and the ketone VI. The formation of chrysene by heating this hydrocarbon with selenium[7] was confirmed. By treating the ketone VI with the appropriate Grignard reagent, followed by dehydration and dehydrogenation, both 6-methylchrysene,[10] m. p. 161.0–161.4°, and 6-ethylchrysene,[11] m. p. 126.4–126.8°, were prepared in 82 and 50% yields, respectively.

Upon oxidation, 6-methylchrysene gave a mixture of products from which a small yield of 6-methyl-11,12-chrysenequinone, m. p. 210–212°, dec., was obtained. This structure is assigned on the basis of the fact that the quinone readily formed a yellow phenazine derivative, m. p. 220–221°, with *o*-phenylenediamine. For comparison the phenazine derivative of chrysenequinone, m. p. 215–216°, was prepared, the mixed melting point being depressed over 20°, whereas a mixed melting point of the two quinones showed no depression.

An interesting variation leading to the formation of the acetates of 6-chrysenol and 11,12-dihydro-6-chrysenol is indicated below.

The dehydrogenation of the unsaturated acid IV to IX by heating with sulfur proceeded in 79% yield and the cyclization by a new application of the procedure of Fieser and Hershberg[12] yielded the acetate of 6-chrysenol, X, in 80% yield. The yields in the alternate procedure were 87% for the acetylative cyclization and 50% for the dehydrogenation. On hydrolysis, X and XI were converted into 6-chrysenol,[13] m. p. 248–250° with decomposition, and 11,12-dihydro-6-chrysenol, m. p. 156.2–156.6°, respectively. The former yielded chrysenequinone on oxidation and 6-methoxychrysene,[14] m. p. 127.2–127.8°, on methylation.



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[7] Ramage and Robinson, *J. Chem. Soc.*, 607 (1933).

[8] German patent 652,549 (1937).

[9] The author is indebted to Dr. E. B. Hershberg for reducing a small sample in a high pressure hydrogenator using copper chromite. The mixture of reduced acids produced by this reduction was very similar to that mixture produced by sodium amalgam reduction.

[10] Sen-Gupta, *Current Sci.*, **5**, 295 (1936), reported the synthesis of 6-methylchrysene and gave its melting point as 152–153°. Because of the melting point recorded, it seems likely that some other hydrocarbon—possibly 3-methyl-1,2-benzanthracene, m. p. 155°, synthesized by Cook, *J. Chem. Soc.*, 1087 (1930)—was at hand.

[11] Funke and Müller, *J. prakt. Chem.*, **144**, 242 (1936), give the melting point of 6-ethylchrysene as 126°.

[12] Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

[13] Kern, U. S. Patent 1,996,475; *C. A.*, **29**, 3356^1 (1935), gives the melting point of 6-chrysenol as 240–242°.

[14] French Patent 794,534 (1936); *C. A.*, **30**, 5238^6 (1936), gives the melting point of 6-methoxychrysene (called 2-methoxychrysene) as 126°.

Experimental[15]

α-Phenyl-β-benzoylpropionitrile.—Conditions were found which make possible the preparation of this intermediate in much less time than recommended.[16] A solution of 108 g. of potassium cyanide in 200 cc. of water was added under the surface to a solution at 55° of 135 g. of benzalacetophenone in 700 cc. of alcohol. The addition was made over a period of five minutes with continual shaking. After five minutes, the contents were warmed to 60°, the flask was wrapped with several towels and allowed to stand undisturbed for ninety to one hundred minutes, the temperature being maintained at 60° by the heat of reaction. After cooling the crystals were collected by filtration and washed colorless with cold 50% alcohol. The yield was 146 g. (95%) of material melting at 124.4 to 126°.

α,γ-Diphenylbutyric Acid.—The above nitrile was converted into methyl α-phenyl-β-benzoylpropionate[17] and hence to the free acid by alkaline hydrolysis.

In a typical reduction[18] the product obtained from 120 g. of α-phenyl-β-benzoylpropionic acid was distilled at 3 mm. The fraction, 101 g., boiling at 199–203° was dissolved in 250 cc. of warm petroleum ether (b. p. 65–110°) and on cooling 91 g. of white crystals, m. p. 68–71°, was obtained. From the mother liquor only 2 g. more of good product crystallized, making the yield 82%. On one recrystallization the melting point rose to 72–3°[19] with little loss. In an experiment in which the entire crude product at each stage was used directly for the next step, there was obtained 128 g. (62%) of α,γ-diphenylbutyric acid, m. p. 72–73°, from 183 g. of benzalacetophenone. Separate attempts were made to hydrolyze and reduce α-phenyl-β-benzoylpropionitrile, and methyl α-phenyl-β-benzoylpropionate in one step using the Clemmensen procedure but the yield of reduced acid was small, a considerable amount of both starting materials being recovered.

1-Keto-2-phenyl-1,2,3,4-tetrahydronaphthalene, III.—In the best of several experiments 91 g. of α,γ-diphenylbutyric acid was converted into the acid chloride with 83 g. of phosphorus pentachloride. After removing all volatile phosphorus compounds on the water pump at 100°, the pale yellow oil was dissolved in 380 cc. of thiophene-free benzene and 53 g. of aluminum chloride was added during one-half hour (external cooling). After stirring for three hours at room temperature, the deep red reaction mixture was heated to 40° several times during the next seven hours, cooled, and poured on ice and hydrochloric acid. The benzene was removed by steam and the organic matter collected and dissolved in 300 cc. of alcohol. The first crop of pale buff crystals was distilled, b. p. 182–183 at 2.5–3 mm. The product in the mother liquors was also distilled and the combined distillates yielded a total of 73.0 g. (87%) of white plates, m. p. 76–77°. If the entire reaction product were distilled before a preliminary crystallization the yield was reduced from 5 to 10%. On standing the ketone frequently took on a pink tinge. A sample recrystallized for analysis melted at 76.2–77.0°.

*Anal.** Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.11; H, 6.61.

The semicarbazone melted with decomposition at 250–251.4° after sintering at 245°.

*Anal.** Calcd. for $C_{17}H_{17}ON_3$: N, 15.04. Found: N, 15.18.

3,4-Dihydro-2-phenyl-1-naphthaleneacetic Acid, IV.—In a typical experiment, a mixture of 10 g. each of ketone and granulated zinc, 16 g. of ethyl bromoacetate, 40 cc. of dry thiophene-free benzene, and a pinch of the copper salt of the enol form of ethyl acetoacetate was heated until reaction commenced, after which the heat of reaction was sufficient to reflux the solvent. In larger runs cooling was necessary. After ten minutes, the mixture was heated on the steam-bath for thirty minutes. The cooled reaction mixture was poured into dilute hydrochloric acid and the organic matter collected in the benzene layer. After removing the solvent, the product was dehydrated by heating with a small crystal of iodine at 210–215° for thirty minutes under 100 mm. pressure, following which a pale yellow viscous oil, b. p. 180–200° at 3 mm., was distilled. The distillate was saponified with alcoholic potassium hydroxide. By crystallization and recrystallization from benzene there was obtained 8.1 g. (68%) of the acid IV as dense colorless prisms which contained benzene of crystallization removed by drying at 100°. The melting point was 155–156° and a portion was crystallized from benzene and alcohol to a constant melting point of 156.2–156.8°.

Anal.† Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.17; H, 5.98.

A carbon tetrachloride solution of the acid readily decolorized bromine.

An ozonolysis, for which the author is indebted to Dr. Shinowara, was carried out in acetic acid. The neutral portion of the products of ozonolysis yielded only intractable oils from which no semicarbazone could be obtained. The acid fraction consisted mainly of starting unsaturated acid, m. p. 152–156°.

***cis*-2-Phenyl-1,2,3,4-tetrahydro-1-naphthaleneacetic Acid, V.**—Attempts were made to reduce IV using both platinum and palladium catalysts in acetic acid and in 95% alcohol. There was no further absorption of hydrogen after the catalyst was reduced. The entire crude acid as recovered from the solvent had a melting range of 20° but on one crystallization from benzene, over 65% was recovered with a good melting range, 152–156°, not depressed by the authentic acid. No better results were obtained using the methyl ester in alcohol solution or the sodium salt in aqueous solution. Further unsuccessful attempts at reduction involved the Clemmensen reduction and boiling with phosphorus and hydriodic acid. In a typical reduction with sodium amalgam, 4.90 g. of acid IV was dissolved in 20 cc. of 95% alcohol (distilled over potassium hydroxide), and an equivalent amount of sodium hydroxide in 200 cc. of water was added, followed by 360 g. of 2% sodium amalgam (made by dropping mercury on molten sodium under sulfur-free xylene). After standing for three days at 35–40°, the solution was heated to 100° to dissolve the insoluble sodium salt which had crys-

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(15) All melting points corrected. Analyses marked * by H. S. Clark, † by K. Eder, University of Chicago.

(16) *Org. Syntheses*, **10**, 80 (1930), John Wiley and Sons, New York, N. Y.

(17) Kohler, Peterson and Bickel, This Journal, **56**, 2000 (1934).

(18) Martin, *ibid.*, **58**, 1438 (1936).

(19) Compare Kohler and Kimball, *ibid.*, **55**, 4632 (1933).

tallized. The acids precipitated on acidification were crystallized from 80 cc. of benzene. The first crop melted at 170–172° and the next two crops somewhat lower. On recrystallization from alcohol a total of 3.06 g. (62%) of white needles, m. p. 171–172°, was obtained. A portion recrystallized for analysis melted at 172.0–172.8°.

Anal.† Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.26; H, 6.74.

The acids in the mother liquors were saturated as shown by a failure to decolorize bromine in carbon tetrachloride. These acids undoubtedly formed a mixture of the two racemates.

***cis*-6-Keto-5,6,11,12,13,14-hexahydrochrysene, VI.**—In the best experiment, 4.29 g. of acid V was warmed with 3.5 g. of phosphorus pentachloride for one hour after which phosphorus compounds were removed under reduced pressure on the water-bath at less than 90°. The pale yellow acid chloride was dissolved in 30 cc. of dry sulfur-free benzene and 2.18 g. of powdered aluminum chloride added in portions. The reaction mixture warmed up and took on a green color. After three hours at 30–50°, the mixture was poured into dilute hydrochloric acid and the benzene layer separated and washed successively with hydrochloric acid, sodium hydroxide, water, and saturated sodium chloride solution. After removing the benzene the product crystallized from alcohol. In all 3.23 g. (81%) of ketone which crystallized in dense prisms, m. p. 74.4–76.4°, was obtained. A sample recrystallized for analysis melted at 75.8–76.8° and formed colorless prisms.

Anal.† Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.53, 87.53; H, 6.74, 6.58.

The semicarbazone formed very small crystals from pyridine–alcohol, m. p. 255–258°, dec., after sintering at 251°.

Anal.† Calcd. for $C_{19}H_{19}ON_3$: N, 13.76. Found: N, 13.74.

***cis*-5,6,11,12,13,14-Hexahydrochrysene, VIII.**—By a modified[18] Clemmensen reduction, from 1.0 g. of *cis*-ketone, VI, there was obtained 0.52 g. (55%) of hexahydrochrysene, m. p. 74.4–75.8°. After two recrystallizations from alcohol, thick white plates, m. p. 76.8–77.8°, were obtained. Ramage and Robinson[7] give the melting point for *cis*-hexahydrochrysene as 75°. A mixture of VI and VIII melted at 61–66°.

6-Methylchrysene, VII (R = CH_3).—To a solution of 0.461 g. of VI in 3 cc. of ether and 3 cc. of benzene was added 2 cc. of 2.7 *M* methylmagnesium bromide in ether. A white complex separated immediately but soon dissolved. After thirty minutes of refluxing, the reaction mixture was decomposed with dilute hydrochloric acid and the organic material heated at 220° for ten minutes to effect dehydration. The residue was heated with 0.120 g. of sulfur at 230° for twenty minutes during which time hydrogen sulfide was evolved copiously. Distillation at 3 mm. yielded a yellow distillate which immediately solidified. By crystallization from benzene there was obtained a total of 0.368 g. (82%) of **6-methylchrysene**, m. p. 160.2–161.2°. Recrystallization from benzene–alcohol resulted in colorless stout needles, m. p. 161.0–161.4°. **The picrate,** from benzene–alcohol, formed bright orange needles, m. p. 170.0–170.6°.

Anal.† Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.15; H, 5.95. Calcd. for $C_{25}H_{17}O_7N_3$: N, 8.91. Found: N, 8.96.

6-Methylchrysene-11,12-quinone.—6-Methylchrysene (0.32 g.) was oxidized by boiling with 1 g. of sodium dichromate and 10 cc. of acetic acid for five hours. The red oxidation product was recrystallized until its behavior on melting remained constant. The product obtained in very small amount formed beautiful bright red needles which, when the temperature of the melting point bath was raised slowly, darkened slightly above 200° and melted with much decomposition at 210–212°. The temperature of decomposition was higher, the faster the rate of heating and on rapid heating it melted at 218–220°. The decomposition point was not affected by mixing the sample with authentic chrysenequinone, m. p. 242–242.6°. The color of the solution of 6-methylchrysenequinone in cold concentrated sulfuric acid was blue-violet and not quite as pronounced as the deep blue color of chrysenequinone under the same conditions.

Anal.† Calcd. for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.75; H, 4.74.

Chrysophenazine and 5-Methylchrysophenazine.[20]—Condensation products of chrysenequinone and 6-methylchrysenequinone with *o*-phenylenediamine in alcohol–acetic acid were obtained easily. After recrystallization from pyridine–alcohol **chrysophenazine** formed long silky yellow needles, m. p. 215–216°.

*Anal.** Calcd. for $C_{24}H_{14}N_2$: N, 8.48. Found: N, 8.40.

5-Methylchrysophenazine formed small yellow needles, m. p. 220–221°, and a mixed melting point with the above was depressed 20°.

Anal.† Calcd. for $C_{25}H_{16}N_2$: N, 8.14. Found: N, 8.45.

6-Ethylchrysene, VII, (R = C_2H_5).—In a manner entirely analogous to that used in the preparation of 6-methylchrysene there was obtained from 0.765 g. of VI, 0.378 g. of 6-ethylchrysene, m. p. 124–125°. On recrystallization from benzene–alcohol colorless needles, m. p. 126.4–126.8°, were obtained. A solution in warm concentrated sulfuric acid had a blue-violet color as mentioned by Funke.[11] The picrate, bright orange needles, m. p. 136.2–136.8°, was prepared in and recrystallized from benzene–alcohol.

*Anal.** Calcd. for $C_{26}H_{19}O_7N_3$: N, 8.66. Found: N, 8.64, 8.65.

2-Phenyl-1-naphthaleneacetic Acid, XI.—A mixture of 2.64 g. of IV and 0.32 g. of sulfur was heated at 220–225° for ninety minutes. Hydrogen sulfide was evolved copiously for the first twenty minutes but if the reaction were stopped at this point the yield was greatly decreased. The slightly colored reaction product was crystallized from benzene yielding a total of 2.07 g. (79%) of the desired acid IX as colorless prisms, m. p. 192–193°.

*Anal.** Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 81.99; H, 5.52.

6-Chrysenyl Acetate, X.—A solution of 1.60 g. of IX and a small amount of anhydrous zinc chloride in 8 cc. of

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(20) *Chemical Abstracts* numbering.

acetic anhydride and 8 cc. of acetic acid[12] was refluxed for one hour, cooled, and diluted with water. On further cooling there crystallized in colorless needles 1.39 g. (80%) of **6-chrysenyl acetate,** m. p. 157–158°. A sample recrystallized for analysis melted at 158.6–159.2°.

Anal.† Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.58; H, 5.02.

6-Chrysenol.—The acetate was converted into 6-chrysenol by heating with alcoholic potassium hydroxide for five minutes. The cooled yellow solution was diluted with dilute hydrochloric acid, whereupon the color almost disappeared. Soon 6-chrysenol separated in almost colorless needles in quantitative yield. Upon recrystallization from acetone–benzene, 6-chrysenol[13] formed colorless needles, m. p. 248–250°, with decomposition. Darkening and sintering took place as low as 240°. Upon oxidation with sodium dichromate in acetic acid, 6-chrysenol was converted in theoretical yield to chrysenequinone.

*Anal.** Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.61, 88.75; H, 5.13, 5.26.

6-Methoxychrysene.—An aqueous methyl alcoholic solution of 0.515 g. of 6-chrysenol containing 1 cc. of 50% potassium hydroxide was treated with two 0.5-cc. portions of dimethyl sulfate. After a time pale yellow crystals separated. The reaction mixture was warmed, diluted with water, and cooled in an ice-bath. By crystallization of the reaction product from benzene–alcohol there was obtained 0.464 g. (85%) of white needles, m. p. 125–127°. A sample recrystallized from benzene–alcohol melted at 127.2–127.8°.[14]

*Anal.** Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.46. Found: C, 88.16; H, 5.48.

11,12-Dihydro-6-chrysenyl Acetate, XI.—Under conditions similar to those used in the preparation of 6-chrysenyl acetate, X, 3.00 g. of IV was cyclized to yield 2.80 g. (87%) of XI, m. p. 94–96°. A sample recrystallized from alcohol melted at 95.6–96.2°.

Anal.† Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.31; H, 5.96.

Under conditions identical to those used in the dehydrogenation of IV to IX, **11,12-dihydrochrysenyl acetate** was converted in 50% yield into **6-chrysenyl acetate.**

11,12-Dihydro-6-chrysenol.—By saponification with alcoholic potassium hydroxide for one hour, 0.342 g. (80%) of 11,12-dihydro-6-chrysenol, m. p. 155.6–156.4°, was obtained from 0.50 g. of XI. A sample recrystallized for analysis from alcohol formed colorless elongated prisms, m. p. 156.2–156.6°.

*Anal.** Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.67, 88.15; H, 5.72, 5.85.

An attempt at methylation resulted in the formation of an uninviting brown viscous oil.

Fluorescence in Ultraviolet Light.—The following compounds exhibited vivid blue fluorescence when viewed in ultraviolet light: 2-phenyl-3,4-dihydro-1-naphthaleneacetic acid, *cis*-6-keto-5,6,11,12,13,14-hexahydrochrysene, *cis*-5,6,11,12,13,14-hexahydrochrysene, 6-methylchrysene, 6-chrysenol, and 6-methoxychrysene.

Summary

A new synthesis for hydrocarbons containing the chrysene nucleus is described. The starting material is benzalacetophenone which is converted by well-known reactions into α,γ-diphenylbutyric acid. This acid is cyclized to 1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene. By the Reformatsky reaction, followed by dehydration and saponification, this ketone is converted into 3,4-dihydro-2-phenyl-1-naphthaleneacetic acid which on reduction with sodium amalgam yields *cis*-2-phenyl-1,2,3,4-tetrahydro-1-naphthaleneacetic acid. Upon cyclization this acid yields *cis*-6-keto-5,6,11,12,13,14-hexahydrochrysene from which, by reaction with methyl- and ethylmagnesium bromides, followed by dehydration and dehydrogenation, there is obtained, respectively, 6-methyl- and 6-ethylchrysene. 6-Methylchrysene on oxidation yields 6-methylchrysene-11,12-quinone.

By dehydrogenation with sulfur, 3,4-dihydro-2-phenyl-1-naphthaleneacetic acid is converted into 2-phenyl-1-naphthaleneacetic acid from which is formed 6-chrysenyl acetate by acetylative cyclization. The latter is hydrolyzed to 6-chrysenol, in turn methylated to 6-methoxychrysene. On acetylative cyclization 3,4-dihydro-2-phenyl-1-naphthaleneacetic acid yields 11,12-dihydro-6-chrysenyl acetate which is hydrolyzed to 11,12-dihydro-6-chrysenol and is dehydrogenated to 6-chrysenyl acetate.

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