

THE SYNTHESIS OF METHYLCHRYSENES AND RELATED COMPOUNDS¹

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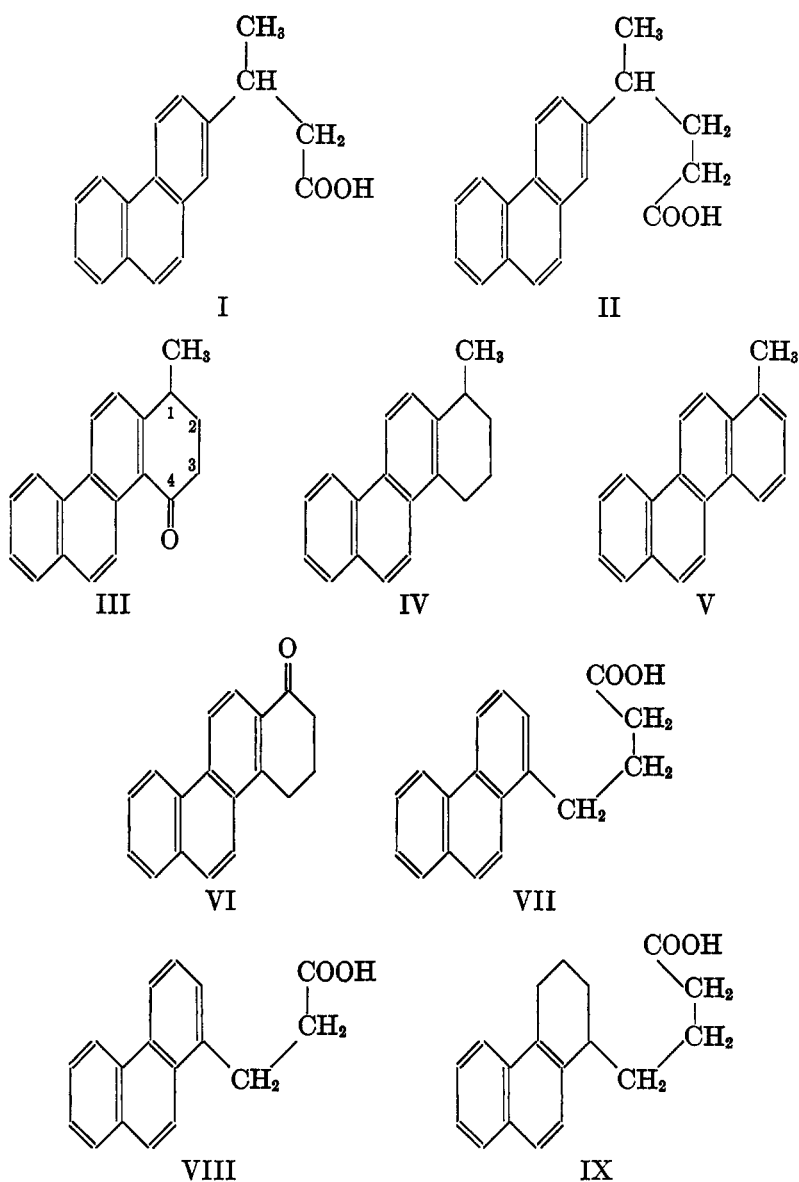
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Only three of the six possible monomethylchrysenes have been synthesized. In a previous paper (1) we have reported the preparation of 2-methylchrysene and 4-methylchrysene. The latter isomer has also been synthesized independently by Fieser and Johnson (2), and 6-methylchrysene has been obtained by Newman (3). In this paper we are reporting the synthesis of 1-methylchrysene and 3-methylchrysene, each by two independent methods, as well as new procedures for obtaining 2-methylchrysene and 4-methylchrysene.

The starting material for the preparation of 1-methylchrysene (V) was 2-acetylphenanthrene, which can be obtained readily by acetylation of phenanthrene. This ketone was reduced to methyl-2-phenanthryl carbinol in excellent yield by means of aluminum isopropoxide (4). The bromide, obtained by interaction of the carbinol and phosphorus tribromide, was condensed with sodio-malonic ester, and the product was converted into β -(2-phenanthryl) butyric acid (I). The side chain of this acid was lengthened by means of the Arndt-Eistert reaction (5) and γ -(2-phenanthryl) valeric acid (II) was obtained in good yield. Cyclization of the acid chloride in carbon disulfide by stannic chloride yielded 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene (III). Clemmensen reduction of this cyclic ketone gave 1-methyl-1,2,3,4-tetrahydrochrysene (IV), which was smoothly dehydrogenated to 1-methylchrysene (V) by palladium on charcoal. This hydrocarbon possesses properties which are quite different from those of 5-methyl-1,2-benzanthracene, which would have resulted if cyclization had occurred in the 3 position of the phenanthrene nucleus. Further proof of the structure of the compound was obtained by its synthesis by the method to be described.

By reaction of 1-methyl-4-ketotetrahydrochrysene (III) with methylmagnesium iodide, followed by dehydration and dehydrogenation of the product, 1,4-dimethylchrysene was prepared.

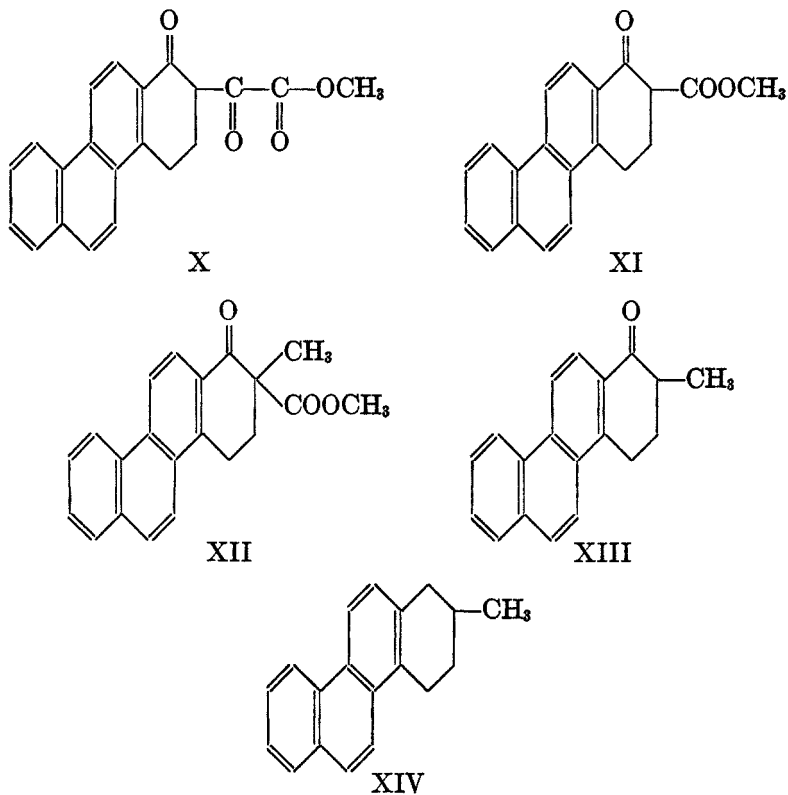
¹ From the Ph.D. dissertation of W. S. Struve.



In the second synthesis, 1-methylchrysenes were obtained by dehydration and dehydrogenation of the carbinol formed by interaction of methylmagnesium iodide and 1-keto-1,2,3,4-tetrahydrochrysenes (VI). The latter compound was first prepared by Hoch (6) by cyclization of γ -(1-phenanthryl)butyric acid (VII) by means of stannic chloride. We em-

ployed the acid chloride rather than the free acid for cyclization. The acid was obtained in two ways: from 1-keto-1,2,3,4-tetrahydrophenanthrene according to Hoch's procedure, and from β -(1-phenanthryl)propionic acid, which can be prepared readily from 1-phenanthraldehyde. In the first method we dehydrogenated the methyl ester of the intermediate γ -[1-(1,2,3,4-tetrahydrophenanthryl)]butyric acid (IX) by palladized charcoal in excellent yields, whereas Hoch used sulfur for this purpose. In the second method the Arndt-Eistert reaction was employed to convert the β -(1-phenanthryl)propionic acid (VIII) to γ -(1-phenanthryl)butyric acid. The products obtained by the two methods were identical. 1-Ethylchrysene was obtained by dehydration and dehydrogenation of the product formed by interaction of the 1-ketotetrahydrochrysene and ethylmagnesium bromide.

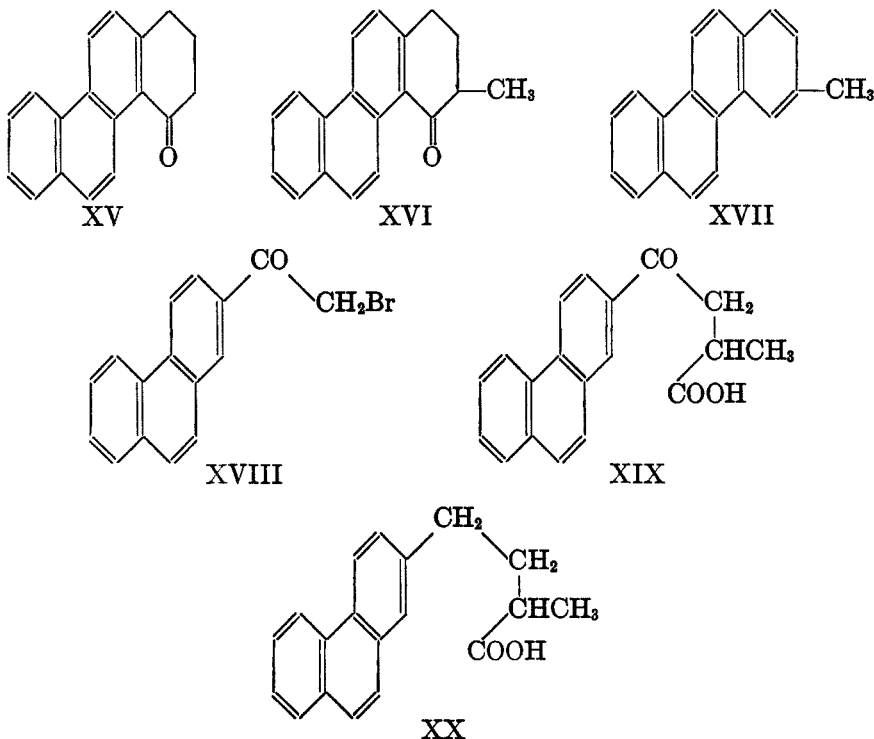
In order to prepare 2-methylchrysene, the 1-ketotetrahydrochrysene was condensed with methyl oxalate by means of sodium methoxide in an



atmosphere of nitrogen to give methyl 1-keto-1,2,3,4-tetrahydrochrysene-2-glyoxalate (X). The yield of glyoxalate was lower when the reac-

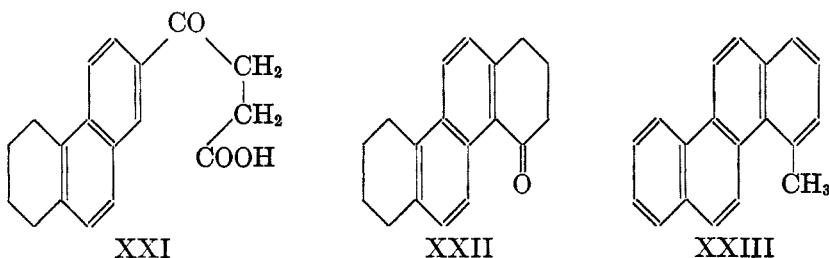
tion was carried out in air, presumably through the susceptibility of the sodio derivative to oxygen. The glyoxalate was smoothly converted to 1-keto-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XI) by loss of carbon monoxide when it was heated to 180–190° with powdered soft glass, the procedure recently developed by Bachmann, Cole, and Wilds (7). By treating the sodio derivative of this compound with methyl iodide, 1-keto-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XII) was obtained. The latter compound, on hydrolysis and subsequent decarboxylation, gave 1-keto-2-methyl-1,2,3,4-tetrahydrochrysene (XIII) in excellent yield. Clemmensen reduction of the ketone gave 2-methyl-1,2,3,4-tetrahydrochrysene (XIV), identical with that which had previously been made by a different method. The dehydrogenation of the compound to 2-methylchrysene was described in the previous paper (1).

In a similar manner, 4-keto-1,2,3,4-tetrahydrochrysene (XV) was condensed with methyl oxalate and the product converted to 3-methylchrysene (XVII) by the reactions just described. The intermediate 3-methyl-4-keto-1,2,3,4-tetrahydrochrysene (XVI) was also prepared from ω -bromo-2-acetylphenanthrene (XVIII). Condensation of this compound with sodio-methylmalonic ester, followed by hydrolysis and decarboxylation of the product of the reaction, gave β -(2-phenanthroyl)- α -methyl-



propionic acid (XIX) in poor yield. Clemmensen reduction of the keto acid gave a good yield of γ -(2-phenanthryl)- α -methylbutyric acid (XX), which was cyclized through its acid chloride by stannic chloride to XVI.

In a previous paper (8) we reported that tetrahydrophenanthrene reacts with succinic anhydride chiefly in the 9 position to give β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid, but there was some evidence of the formation of an isomeric acid. We have now succeeded in isolating the isomeric acid and have shown it to be β -[7-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid (XXI). The structure of the acid followed from the formation of γ -(2-phenanthryl)butyric acid when the reduced acid (γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid) was dehydrogenated (in the form of its methyl ester) by palladized charcoal. Cyclization of the γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid through its acid chloride by stannic chloride gave 4-keto-1,2,3,4,7,8,9,10-octahydrochrysen



(XXII). From this compound 4-methylchrysen (XXIII) was obtained through the action of methylmagnesium iodide, followed by dehydration and dehydrogenation of the product. The formation of this product constitutes further proof of the structure of the keto acid and shows that ring closure took place from the 7 to the 8 position in the 1,2,3,4-tetrahydrophenanthrene molecule.

EXPERIMENTAL

All melting points are uncorrected.

Methyl-2-phenanthryl carbinol. To a solution of aluminum isopropoxide prepared by refluxing 10 g. of aluminum wire, 5 drops of carbon tetrachloride, a pinch of mercuric chloride, and 250 cc. of isopropyl alcohol was added 10 g. of 2-acetylphenanthrene (9) and 250 cc. of isopropyl alcohol. The mixture was refluxed for one hour, and then 250 cc. of isopropyl alcohol was distilled off over a period of two hours. The complex was decomposed with ice-cold 10% sulfuric acid, the carbinol was taken up in benzene, the benzene extract was washed with dilute ammonium hydroxide and then with water, and the benzene was evaporated at room temperature. The residue crystallized from benzene-petroleum ether; weight, 9.60 g. (95%); m.p. 131-131.5°. Mosettig and van de Kamp (10), who prepared the compound by catalytic hydrogenation of the ketone, give 134-135° as the melting point of the carbinol.

α -(2-Phenanthryl)ethyl bromide. To an ice-cold suspension of 10 g. of the above

carbinol in 70 cc. of dry ether was added 2.95 cc. of phosphorus tribromide. The mixture was allowed to stand for an hour in the cold, the ether was evaporated at room temperature, and the residue was triturated with a small amount of methanol, cooled, and filtered; weight, 11.47 g. (89%); m.p. 84–85.5°. For further purification the bromide was dissolved in benzene, the benzene solution was washed with dilute sodium bicarbonate solution, the benzene was evaporated at room temperature, and the residue was crystallized several times from benzene-petroleum ether, from which it was obtained as colorless leaflets; m.p. 86–88°.

Anal. Calc'd for $C_{16}H_{13}Br$: Br, 28.1. Found: Br, 28.5.

β -(2-Phenanthryl)butyric acid (I). To a solution of ethyl sodio-malonate prepared from 0.48 g. of sodium, 4.2 cc. of malonic ester, and 20 cc. of absolute alcohol was added 3.89 g. of purified 2-phenanthrylethyl bromide dissolved in 30 cc. of benzene. The solution was allowed to stand at room temperature overnight and was then refluxed for two hours. If the bromide is added to a hot suspension of sodio-malonic ester in benzene and the whole is refluxed for twelve hours, the yield of product is low. As much alcohol as possible was distilled off, benzene and dilute hydrochloric acid were added, the benzene layer was washed with water, the benzene was evaporated, and the residue was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salt and acidified. The dicarboxylic acid was heated at 180° for a half hour, and the decarboxylated product was crystallized from chloroform-petroleum ether; weight, 3.14 g. (87%); m.p. 128–130°, resolidifying on further heating and remelting at 137–138°. After two recrystallizations from chloroform-petroleum ether and seeding with the high-melting form, the acid melted at 138–139°. It is not necessary to use purified bromide; in a run, using 5 g. of the crude bromide, 3.83 g. (83%) of acid softening at 129°, resolidifying on further heating and melting completely at 137.5–138.5°, was obtained. Bergmann and Hillemann (11), who prepared this acid by the Reformatsky reaction, give 125–127° as the melting point of this compound.

γ -(2-Phenanthryl)valeric acid (II). To a suspension of 1.32 g. of β -(2-phenanthryl)butyric acid in 2 cc. of dry ether and 1 drop of pyridine was added 1 cc. of thionyl chloride, and the mixture was allowed to stand at room temperature for a half hour. The ether and thionyl chloride were then evaporated under reduced pressure, the acid chloride was dissolved in ether, and was added drop by drop to a solution of diazomethane in 25 cc. of ether, the diazomethane being prepared from 3 cc. of ethyl N-methyl-N-nitrosocarbamate. After standing at room temperature for two hours, the ether was evaporated under reduced pressure and the oily diazo ketone was dissolved in 15 cc. of dry methanol. The methanol solution was refluxed for one hour, with addition of silver oxide from 2.5 cc. of 10% silver nitrate solution. Half of the silver oxide was added at the beginning of the heating and the rest in five portions at five minute intervals. The methanol solution was filtered and the residue from evaporation of the methanol was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts, filtered, and acidified; weight, 1.34 g.; m.p. 124–130°. The crude acid was sublimed at 230° and 0.4 mm. and the sublimate was crystallized from benzene-petroleum ether; weight, 1.15 g. (83%); m.p. 132–134°. After several further crystallizations from benzene-petroleum ether the acid was obtained as colorless leaflets; m.p. 136.5–138.5°.

Anal. Calc'd for $C_{17}H_{14}O_2$: C, 82.0; H, 6.5.

Found: C, 81.9; H, 6.5.

1-Methyl-4-keto-1,2,3,4-tetrahydrochrysene (III). To a suspension of 2.85 g. of γ -(2-phenanthryl)valeric acid in 30 cc. of ether and 2 drops of pyridine was added 6

cc. of thionyl chloride. After standing at room temperature for a half hour, the ether and thionyl chloride were removed under reduced pressure. The acid chloride was dissolved in 30 cc. of carbon disulfide (benzene proved less satisfactory) and 4.5 cc. of stannic chloride was added to the chilled solution. After standing at room temperature for one hour, the mixture was hydrolyzed with ice and hydrochloric acid, the carbon disulfide layer was washed with water, and the carbon disulfide was evaporated. The residue was dissolved in benzene, the benzene solution was washed with ammonium hydroxide and then with water, the benzene was evaporated, and the ketone was crystallized from acetone-alcohol; weight, 1.91 g. (72%); m.p. 94-96.5°. After two further crystallizations from alcohol-acetone, colorless prisms of the ketone were obtained; m.p. 98.5-99.5°. Sometimes on crystallization the ketone separates as leaflets which melt at 75-77° and can be changed to the higher-melting form by seeding with it.

Anal. Calc'd for $C_{19}H_{18}O$: C, 87.7; H, 6.2.

Found: C, 88.0; H, 6.1.

1-Methyl-1,2,3,4-tetrahydrochrysene (IV). A mixture of 1 g. of 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene, 10 g. of amalgamated zinc, 20 cc. of acetic acid, 12 cc. of concentrated hydrochloric acid, and 5 cc. of toluene was refluxed for twenty-four hours, an additional 20 cc. of a 1:1 mixture of acetic and concentrated hydrochloric acids being added in portions over that time. The toluene layer was separated, the toluene was evaporated, and the residue was sublimed at 200° and 0.4 mm. The sublimate crystallized from alcohol-acetone as colorless leaflets; yield, 0.81 g. (86%); m.p. 120-121°. After two further crystallizations from alcohol-acetone the compound melted at 120.5-121°.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.7; H, 7.3.

Found: C, 92.3; H, 7.4.

The *picrate* crystallizes from absolute alcohol in yellowish-orange needles; m.p. 124-124.5°.

Anal. Calc'd for $C_{19}H_{18} \cdot C_6H_3N_3O_7$: N, 8.8. Found: N, 8.7.

1,4-Dimethylchrysene. To a Grignard reagent made from 0.5 cc. of methyl iodide and 0.15 g. of magnesium in 5 cc. of dry ether was added 0.5 g. of 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene and 10 cc. of dry benzene. The mixture was allowed to stand at room temperature overnight and was then decomposed with ice and ammonium chloride. To the residue from evaporation of the benzene-ether layer was added 0.05 g. of palladium-charcoal catalyst (12) and the mixture was heated at 300-320° for one hour. The mixture was then taken up in benzene, the filtered benzene solution was evaporated, and the hydrocarbon was crystallized from benzene-petroleum ether; yield, 0.39 g. (79%); m.p. 140-141°. After two recrystallizations from benzene-petroleum ether, the compound was obtained as clusters of small, colorless needles; m.p. 141.5-142.5°.

Anal. Calc'd for $C_{20}H_{18}$: C, 93.8; H, 6.3.

Found: C, 93.6; H, 6.2.

The *picrate* crystallizes from absolute alcohol containing an excess of picric acid as deep red needles; m.p. 140.5-141°.

Anal. Calc'd for $C_{20}H_{18} \cdot C_6H_3N_3O_7$: N, 8.7. Found: N, 8.6.

γ -(1-Phenanthryl)butyric acid (VII). (a) To a suspension of 2.92 g. of β -(1-phenanthryl)propionic acid (VIII) (13) in 5 cc. of dry ether and 1 drop of pyridine was added 3.3 cc. of thionyl chloride. The mixture was allowed to stand at room temperature for a half hour and then the ether and thionyl chloride were evaporated under reduced pressure. The acid chloride was dissolved in a mixture of benzene and ether and added drop by drop to a solution of diazomethane in 60 cc. of dry ether, the

diazomethane being made from 7 cc. of ethyl N-methyl-N-nitrosocarbamate. After standing for two hours at room temperature, the ether and benzene were evaporated under reduced pressure and the crystalline diazo ketone was dissolved in 50 cc. of dry methanol. The methanol solution was refluxed for two hours (one hour was insufficient), with addition of silver oxide from 6 cc. of 10% silver nitrate solution over this time, a quarter at the beginning, another quarter in five portions at five minute intervals after this, another quarter at the end of the first hour, and the last quarter in five portions at five minute intervals after this. The methanol solution was filtered to remove the silver oxide, and the residue obtained from evaporation of the methanol was heated for an hour with an excess of 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts and then acidified. The precipitated acid was sublimed at 230° and 0.4 mm. and the sublimate was crystallized twice from dilute acetic acid; yield, 1.88 g. (61%); m.p. 153-154°. After several further crystallizations from dilute acetic acid, the acid separated as colorless leaflets; m.p. 154.5-155.5°.

(b) Five and seven-tenths grams of γ -[1-(1,2,3,4-tetrahydrophenanthryl)]butyric acid (IX) prepared from 1-keto-1,2,3,4-tetrahydrophenanthrene according to the procedure of Hoch (6) was esterified with an ethereal solution of diazomethane, the ether was evaporated, and the ester was heated for three hours at 250-260° with 0.55 g. of palladium-charcoal catalyst. The mixture was taken up in benzene, and the filtered benzene solution was evaporated. The ester was heated for one hour with 45% potassium hydroxide solution and the solution was diluted and acidified; weight, 5.42 g. (95%); m.p. 149-154°. After two crystallizations from dilute acetic acid, the compound melted at 154-155.5°. Hoch reports 152° as the melting point of this compound.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.9; H, 6.1.

Found: C, 81.5; H, 6.0.

1-Keto-1,2,3,4-tetrahydrochrysene (VI). To a suspension of 5.63 g. of the above acid in 60 cc. of dry ether and 2 drops of pyridine was added 12 cc. of thionyl chloride. After standing at room temperature for a half hour, the ether and thionyl chloride were removed under reduced pressure, the acid chloride was dissolved in 80 cc. of dry benzene, and 9 cc. of stannic chloride was added to the chilled solution. After standing for twenty minutes at room temperature, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene layer was washed with ammonium hydroxide and then with water, the benzene was evaporated, and the ketone was crystallized from benzene; weight, 4.85 g. (92%); m.p. 226.5-228°. After two recrystallizations from benzene the compound was obtained as colorless prisms; m.p. 228-229°. Hoch gives 222° as the melting point of this compound:

Anal. Calc'd for $C_{18}H_{14}O$: C, 88.0; H, 5.7.

Found: C, 87.7; H, 5.7.

1-Methylchrysene (V). (a) A mixture of 0.69 g. of 1-methyl-1,2,3,4-tetrahydrochrysene and 0.07 g. of palladium-charcoal catalyst was heated at 300-320° for one hour and the mixture was taken up in benzene and filtered. The hydrocarbon obtained by evaporation of the benzene solution was crystallized from toluene; yield, 0.63 g. (94%); m.p. 248-250°. After two further crystallizations from toluene, colorless, glistening leaflets were obtained; m.p. 249.5-250°. The mixture melting point with chrysene (m.p. 246-247°) was 243-245°.

(b) To a Grignard solution made from 0.5 cc. of methyl iodide, 0.15 g. of magnesium, and 10 cc. of ether were added 0.5 g. of 1-keto-1,2,3,4-tetrahydrochrysene and 15 cc. of dry benzene. The mixture was allowed to stand at room temperature overnight and was then hydrolyzed with ice and ammonium chloride. The benzene-

ether layer was separated, the benzene and ether were evaporated, and the residue was heated for one hour with 0.05 g. of palladium-charcoal catalyst. The reaction-product was taken up in benzene, and the hydrocarbon obtained by evaporation of the filtered benzene solution was crystallized from benzene, giving colorless, glistening leaflets; weight, 0.42 g. (86%); m.p. 249.5–250°. The melting point was unchanged after two further crystallizations from benzene. The mixture melting point with the material prepared in part (a) was 249.5–250°. The mixture melting point with chrysene was 242.5–244°. The hydrocarbon, like chrysene, does not form a very stable picrate and we were unable to prepare a satisfactory picrate.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 94.3; H, 5.8.

1-Ethylchrysene. To a Grignard solution made from 0.55 cc. of ethyl bromide and 0.15 g. of magnesium in 10 cc. of ether were added 0.5 g. of 1-ketotetrahydrochrysene and 15 cc. of dry benzene. The mixture was allowed to stand at room temperature for twelve hours, and ice and ammonium chloride were added to decompose the complex. The benzene-ether layer was evaporated and the residue was heated for one hour at 300–320° with 0.05 g. of palladium-charcoal catalyst. The mixture was taken up in benzene, the filtered solution was evaporated, and the hydrocarbon was crystallized from benzene-methanol; yield, 0.38 g. (73%); m.p. 183–184°. After two recrystallizations from benzene-methanol, colorless leaflets were obtained; m.p. 183.5–184°.

Anal. Calc'd for $C_{20}H_{16}$: C, 93.8; H, 6.3.

Found: C, 93.5; H, 6.1.

Methyl 1-keto-1,2,3,4-tetrahydrochrysene-2-glyoxalate (X). Sixty-nine hundredths gram of sodium was dissolved in 15 cc. of methanol and the excess methanol was then evaporated under reduced pressure. A mixture of 3 g. of 1-keto-1,2,3,4-tetrahydrochrysene and 3.6 g. of methyl oxalate was then added, the flask was filled with nitrogen, and 75 cc. of dry benzene was added. After the mixture had stood for five hours with occasional agitation, water and a few drops of 45% potassium hydroxide solution were added, the benzene layer was extracted twice with 2% potassium hydroxide solution, and the alkaline washings were acidified; weight, 3.92 g. (97%); m.p. 167–168°. After two crystallizations from benzene-methanol, deep yellow prisms were obtained; m.p. 176–177° with decomposition. Upon crystallization, two forms usually separate: light yellow, flocculent leaflets and thick, deep yellow prisms. On standing, the leaflets, which melt about 169–170°, change over almost completely to the prisms, and the remaining leaflets can be removed by decantation before filtering. The compound gives an immediate, reddish-brown color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8.

Found: C, 76.0; H, 4.8.

1-Keto-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XI). A mixture of 2.90 g. of the above compound and 1.5 g. of powdered glass was heated at 180–190° for a half hour. The mixture was taken up in benzene and the filtered benzene solution was evaporated. The residue crystallized from benzene-methanol as colorless needles; weight, 2.10 g. (79%); m.p. 156–157.5°. After two recrystallizations from benzene-methanol the compound melted at 156.5–157.5°. This carbomethoxy ketone gives a green color on standing with alcoholic ferric chloride.

Anal. Calc'd for $C_{20}H_{16}O_3$: C, 79.0; H, 5.3.

Found: C, 79.2; H, 5.3.

1-Keto-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XII). To a solution of 0.3 g. of sodium in 10 cc. of methanol was added 1 g. of 1-keto-2-carbomethoxy-

1,2,3,4-tetrahydrochrysene in 30 cc. of benzene. The mixture was refluxed for two hours and then cooled. One and one-half cubic centimeters of methyl iodide was added and the mixture was allowed to stand at room temperature for an hour. Another 1.5 cc. of methyl iodide was then added and the mixture was refluxed for an hour, cooled, and acidified with acetic acid. The benzene and methanol were evaporated, benzene and water were added, the benzene layer was evaporated, and the residue was crystallized from benzene-methanol, giving colorless needles; weight, 0.93 g. (89%); m.p. 154-155°, unchanged after two further crystallizations. The melting point when the compound was mixed with the original 1-keto-2-carbomethoxytetrahydrochrysene was 125-135°. The compound gives no color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{18}O_2$: C, 79.2; H, 5.7.

Found: C, 79.4; H, 5.7.

1-Keto-2-methyl-1,2,3,4-tetrahydrochrysene (XIII). A mixture of 0.75 g. of 1-keto-2-methyl-2-carbomethoxytetrahydrochrysene, 23 cc. of acetic acid, and 12 cc. of concentrated hydrochloric acid was refluxed for three hours, and then water was added to complete the precipitation of the ketone; weight, 0.59 g. (93%); m.p. 183-184.5°. After two crystallizations from benzene-methanol, colorless leaflets were obtained; m.p. 184-184.5°.

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.7; H, 6.2.

Found: C, 87.5; H, 6.2.

2-Methyl-1,2,3,4-tetrahydrochrysene (XIV). A mixture of 0.2 g. of 1-keto-2-methyl-1,2,3,4-tetrahydrochrysene, 5 g. of amalgamated zinc, 10 cc. of acetic acid, 6 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours. An additional 10 cc. of a 1:1 mixture of acetic and hydrochloric acids was added in portions over this period. The organic layer was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone, giving colorless, glistening leaflets; weight, 0.145 g. (77%); m.p. 145-146°, unchanged after two more recrystallizations. The mixture melting point with 2-methyl-1,2,3,4-tetrahydrochrysene (m.p. 141.5-142°) prepared from 2-methyl-4-keto-1,2,3,4-tetrahydrochrysene (1) was 143.5-145°.

β -(2-Phenanthryl)- α -methylpropionic acid (XIX). A mixture of 0.5 g. of powdered sodium, 5.1 cc. of malonic ester, and 30 cc. of benzene was refluxed until the sodium had reacted. The suspension was cooled, 5 g. of ω -bromo-2-acetylphenanthrene (14) (XVIII) was added, and the mixture was allowed to stand at room temperature for twelve hours and then heated for three hours. Dilute hydrochloric acid was added to the cooled solution, the organic layer was evaporated, and the residue was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts and then acidified. The dicarboxylic acid was heated for an hour at 180-200° and the product was crystallized from acetic acid-toluene; yield, 1.8 g. (37%); m.p. 222-224°. After two further crystallizations from acetic acid-toluene, colorless needles with the melting point 228-229° were obtained.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 78.1; H, 5.5.

Found: C, 77.9; H, 5.5.

γ -(2-Phenanthryl)- α -methylbutyric acid (XX). A mixture of 1 g. of β -(2-phenanthryl)- α -methylpropionic acid, 5 g. of amalgamated zinc, 7.5 cc. of acetic acid, 7.5 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours. An additional 7.5 cc. of concentrated hydrochloric acid was added in portions over this period. The organic layer was evaporated and the reduced acid was crystallized from benzene-petroleum ether; weight, 0.89 g. (94%); m.p. 122-124°.

After two recrystallizations from benzene-petroleum ether, colorless leaflets were obtained; m.p. 124-124.5°.

Anal. Calc'd for $C_{18}H_{18}O_2$: C, 82.0; H, 6.5.

Found: C, 82.1; H, 6.4.

Methyl 4-keto-1,2,3,4-tetrahydrochrysen-3-glyoxalate. Twenty-three hundredths gram of sodium was dissolved in 5 cc. of methanol and the excess methanol was removed under reduced pressure. A mixture of 1 g. of 4-keto-1,2,3,4-tetrahydrochrysen (XV) (1) and 1.2 g. of methyl oxalate was added, the apparatus was filled with nitrogen, and 25 cc. of dry benzene was added. After the mixture had stood at room temperature for three hours with occasional shaking, water and a few drops of 45% potassium hydroxide solution were added, the benzene layer was washed with 2% potassium hydroxide solution, and the alkaline washings were acidified; weight, 1.27 g. (95%); m.p. 112-115°. After three recrystallizations from acetone-methanol, lemon-yellow needles of melting point 116-117.5° were obtained. The compound gives an immediate, deep brown color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{18}O_4$: C, 75.9; H, 4.8.

Found: C, 75.5; H, 4.7.

3-Carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysen. A mixture of 0.59 g. of the above glyoxalate and 0.3 g. of powdered soft glass was heated for one hour at 180° and the decarbonylated product was taken up in benzene, the benzene solution was filtered, the benzene was evaporated, and the residue was crystallized from benzene-alcohol; weight, 0.44 g. (82%); m.p. 153-155°. After two further crystallizations from benzene-alcohol, colorless needles were obtained; m.p. 154-155°. This compound gives an emerald-green color on standing with alcoholic ferric chloride.

Anal. Calc'd for $C_{20}H_{16}O_3$: C, 79.0; H, 5.3.

Found: C, 78.8; H, 5.3.

3-Methyl-3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysen. To a solution of 0.45 g. of sodium in 15 cc. of methanol was added 1.5 g. of 3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysen in 30 cc. of benzene and the mixture was refluxed for two hours. To the cooled mixture was added 2.3 cc. of methyl iodide, and the reaction-mixture was allowed to stand at room temperature for an hour. Another 2.3 cc. of methyl iodide was then added and the whole was refluxed for an hour. The mixture was acidified with acetic acid and the benzene and methanol were evaporated. Water and benzene were added, the benzene layer was evaporated, and the residue was crystallized from acetone-methanol, giving colorless needles; weight, 1.32 g. (84%); m.p. 114-116°. After several recrystallizations from acetone-methanol, the melting point was 115.5-117°. The methylcarbomethoxy ketone gives no color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7.

Found: C, 79.2; H, 5.7.

3-Methyl-4-keto-1,2,3,4-tetrahydrochrysen (XVI). (a) To a suspension of 0.75 g. of γ -(2-phenanthryl)- α -methylbutyric acid in 7.5 cc. of dry ether and 1 drop of pyridine was added 1.5 cc. of thionyl chloride and the mixture was allowed to stand at room temperature for a half hour. The ether and thionyl chloride were evaporated under reduced pressure, the acid chloride was dissolved in 7.5 cc. of carbon disulfide, and 1.2 cc. of stannic chloride was added to the solution cooled in ice-water. After standing at room temperature for ten minutes, the mixture was hydrolyzed with ice and hydrochloric acid and the carbon disulfide layer was evaporated. The residue was dissolved in benzene, the benzene solution was washed with ammonium hydroxide, the benzene was evaporated, and the ketone was crystallized from alcohol-acetone; m.p. 108-111°; weight, 0.45 g. (64%). After several recrystalliza-

tions from alcohol-acetone, the ketone was obtained as colorless prisms; m.p. 114–115°.

(b) A mixture of 2.1 g. of 3-methyl-3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysene, 60 cc. of acetic acid, and 30 cc. of concentrated hydrochloric acid was refluxed for four hours. Water was added to the cooled mixture, which was then extracted with benzene. The benzene was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone; weight, 1.58 g. (92%); m.p. 114–115.5°. The mixture melting point with the material prepared in part (a) was 114–115.5°.

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.7; H, 6.2.

Found: C, 87.2; H, 6.1.

3-Methyl-1,2,3,4-tetrahydrochrysene. A mixture of 1 g. of 3-methyl-4-keto-1,2,3,4-tetrahydrochrysene, 10 g. of amalgamated zinc, 20 cc. of acetic acid, 12 cc. of concentrated hydrochloric acid, and 5 cc. of toluene was refluxed for twenty-four hours, an additional 20 cc. of a 1:1 mixture of acetic and hydrochloric acids being added in portions over this period. The organic layer was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from benzene-petroleum ether, giving colorless needles; weight, 0.82 g. (86%); m.p. 129–130.5°. After several recrystallizations from benzene-petroleum ether, the hydrocarbon melted at 130–131°.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.7; H, 7.3.

Found: C, 92.4; H, 7.3.

3-Methylchrysene (XVII). A mixture of 0.74 g. of 3-methyl-1,2,3,4-tetrahydrochrysene and 0.07 g. of palladium-charcoal catalyst was heated for one hour at 300–320°. The mixture was taken up in benzene, the filtered benzene solution was evaporated, and the residue was crystallized from benzene-petroleum ether, giving colorless, glistening leaflets; weight, 0.67 g. (92%); m.p. 170–170.5°, unchanged after several further crystallizations.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 93.8; H, 5.8.

The *picrate* crystallizes from absolute alcohol as orange needles; m.p. 164–164.5°.

Anal. Calc'd for $C_{19}H_{14} \cdot C_6H_3N_3O_7$: N, 8.9. Found: N, 8.9.

β -[7-(1,2,3,4-Tetrahydrophenanthroyl)]propionic acid (XXI). The combined mother liquors from the crystallizations of about 35 g. of crude β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid (8) deposited about 2 g. of crystals after standing for about two months at room temperature; m.p. 150–154°. After several recrystallizations from toluene-acetic acid, colorless, rhombic prisms of melting point 158–159° were obtained. Concentration of the filtered mother liquors did not give any more acid of this melting point and, although crops were obtained which melted over wide ranges, from 125–165°, no other pure products were isolated.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.

Found: C, 76.8; H, 6.3.

γ -[7-(1,2,3,4-Tetrahydrophenanthryl)]butyric acid. A mixture of 1 g. of the above keto acid, 2.5 g. of amalgamated zinc, 4 cc. of acetic acid, 4 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours. An additional 4 cc. of concentrated hydrochloric acid was added in portions over this time. The organic layer was evaporated, and the residue was crystallized from benzene; weight, 0.80 g. (84%); m.p. 92–95.5°. After several crystallizations, colorless prisms of melting point 95.5–97° were obtained.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5.

Found: C, 81.1; H, 7.3.

The structure of the acid was proved by catalytic dehydrogenation to γ -(2-phenanthryl)butyric acid. Two-tenths gram of γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid was esterified with an ethereal solution of diazomethane, the ether was evaporated, and the ester was heated at 250–270° for two hours with 0.03 g. of palladium-charcoal catalyst. The mixture was taken up in benzene and filtered, the benzene was evaporated, and the residue was heated for an hour with 3 cc. of 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salt and then acidified; weight, 0.162 g. (82%); m.p. 130–131°. After two crystallizations from benzene the acid melted at 133.5–134.5°. The mixture melting point with authentic γ -(2-phenanthryl)butyric acid (1) (m.p. 134–135°) was 134–135°.

4-Keto-1,2,3,4,7,8,9,10-octahydrochrysenes (XXII). To a suspension of 0.24 g. of γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid in 5 cc. of ether and 1 drop of pyridine was added 1 cc. of thionyl chloride. After standing for a half hour at room temperature, the ether and thionyl chloride were removed under reduced pressure, the acid chloride was dissolved in 3 cc. of dry benzene, and to the chilled solution was added 0.4 cc. of stannic chloride. After standing for ten minutes in the cold, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene layer was washed with ammonium hydroxide, the benzene was evaporated, and the residue was crystallized from methanol, giving colorless leaflets; m.p. 91–94°; weight, 0.15 g. (68%). After several recrystallizations from methanol, the ketone was obtained as leaflets which melted at 93.5–95°. Sometimes on crystallization needles are obtained which melt at 89.5–91° and which remelt at 93.5–95°.

Anal. Calc'd for $C_{18}H_{18}O$: C, 86.4; H, 7.2.

Found: C, 86.1; H, 7.55.

4-Methylchrysenes (XXIII). To a Grignard reagent prepared from 0.12 g. of magnesium and 0.40 cc. of methyl iodide in 10 cc. of dry ether was added 0.475 g. of 4-ketoöctahydrochrysenes in 5 cc. of benzene. After standing at room temperature for twelve hours, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene-ether layer was evaporated, and the residue was heated at 300–320° for one hour with 0.1 g. of palladium-charcoal catalyst. The mixture was taken up in benzene and filtered, the benzene was evaporated, and the residue was crystallized from benzene-petroleum ether; weight, 0.28 g. (61%); m.p. 147–149°. After sublimation and several recrystallizations from benzene-petroleum ether, the hydrocarbon melted at 149–149.5°. The mixture melting point with authentic 4-methylchrysenes (1) showed no depression.

SUMMARY

The 1- and 3- methylchrysenes have been prepared, both by two independent syntheses.

New methods of preparation of 2- and 4- methylchrysenes are given.

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