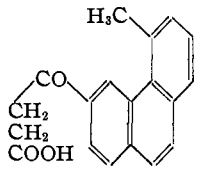
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

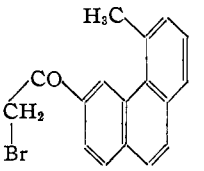
The Synthesis of 1′-Methyl-1,2-benzanthracene and 5-Methylchrysene

BY W. E. BACHMANN AND R. O. EDGERTON[1]

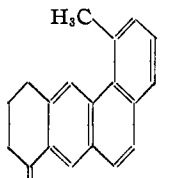
Recently we found that 4-methylphenanthrene reacts with acetyl chloride in the Friedel–Crafts reaction in the 1- and 6-positions.[2] We have now investigated the reaction between the hydrocarbon and succinic anhydride, and have found that the succinoyl group likewise enters the same positions. From the mixture of keto acids formed in the reaction, β-[3-(5-methylphenanthroyl)]-propionic acid (I) (corresponding to substitution in the 6-position of the hydrocarbon) was isolated readily in a pure state. The structure of this keto acid was established by its synthesis from 3-acetyl-5-methylphenanthrene. The latter compound was brominated and the 3-bromoacetyl-5-methylphenanthrene (II) was converted to I through the malonic ester synthesis.



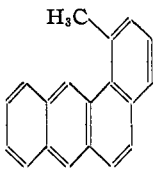
I



II



III

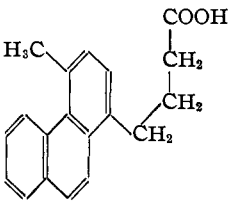


IV

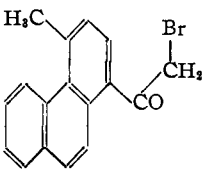
The γ-[3-(5-methylphenanthryl)]-butyric acid obtained by Clemmensen reduction of the keto acid was cyclized through its acid chloride to 1′-methyl-5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene (III); none of the isomeric cyclic ketone was isolated that would be formed by ring closure to the 4-position of the phenanthrene nucleus. The cyclic ketone was reduced to 1′-methyl-5,6,7,8-tetrahydro-1,2-benzanthracene, which on dehydrogenation yielded 1′-methyl-1,2-benzanthracene (IV), identical with that prepared by the method of Cook and Robinson[3] from anthracene. This hydrocarbon has been prepared also by Fieser and Seligman.[4]

The mixture of keto acids remaining after removal of I was reduced by the Clemmensen method. From the product, γ-[1-(4-methylphenanthryl)]-butyric acid (V) was isolated. The structure of this acid was established by two independent syntheses. In one method, 1-acetyl-4-methylphenanthrene was brominated and the 1-bromoacetyl-4-methylphenanthrene (VI) was converted to the keto acid (VII) through the malonic ester synthesis. Clemmensen reduction of this acid yielded V. In the other method, 1-keto-4-methyl-1,2,3,4-tetrahydrophenanthrene was treated with zinc and methyl bromoacetate and the product of the Reformatsky reaction was dehydrated and dehydrogenated to 1-(4-methylphenanthryl)-acetic acid (VIII). By means of two Arndt–Eistert reactions, the acetic acid side-chain was lengthened by two carbon atoms and V was formed.

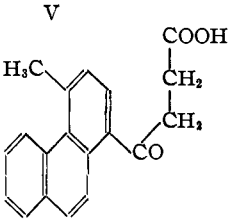
Cyclization of V through its acid chloride yielded 1-keto-1,2,3,4-tetrahydro-11-methylchrysene (IX). This was reduced by the Clemmensen method to 1,2,3,4-tetrahydro-11-methylchrysene, which was dehydrogenated to 5-methylchrysene (X). While this work was in progress, Newman[5]



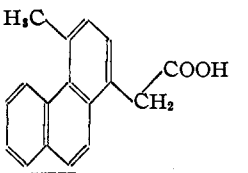
V



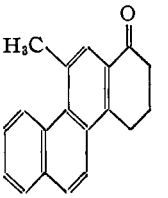
VI



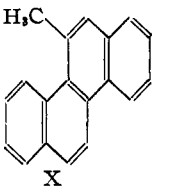
VII



VIII



IX



X

(1) From the Ph.D. dissertation of R. O. Edgerton.
(2) Bachmann and Edgerton, THIS JOURNAL, **62**, 2219 (1940).
(3) Cook and Robinson, *J. Chem. Soc.*, 505 (1938).
(4) Fieser and Seligman, THIS JOURNAL, **60**, 170 (1938).
(5) Newman, *ibid.*, **62**, 870 (1940).

and also Fieser and Joshel[6] reported the preparation of 5-methylchrysene by different methods.

With the synthesis of this isomer, all of the monomethylchrysenes have now been prepared. In Table I are presented the melting points of the six monomethylchrysenes as obtained by the various investigators engaged in their synthesis. It is of interest that the melting points of the isomers decrease in regular order from 1- to 5-methylchrysene inclusively.

TABLE I

MONOMETHYLCHRYSENES

Isomer	M. p. (cor.), °C.		
1-	256.5–257[7]	254–255[8]	
2-	229–230[9]		
3-	172.5–173[7]		
4-	151–151.5[9,10]		
5-	118–118.8	117.2–117.8[8]	116.8–117.6[6]
6-	161–161.4[11]		

Experimental

β-[3-(5-Methylphenanthroyl)]-propionic Acid (I). (a) From 4-Methylphenanthrene.—Five grams of succinic anhydride was added in portions to a cold solution (−15°) of 13.3 g. of anhydrous aluminum chloride and 9.6 g. of 4-methylphenanthrene[2] in 55 cc. of nitrobenzene. After being kept in a refrigerator for twenty-two hours, the mixture was hydrolyzed, washed with water and steam distilled. The residue was dissolved in dilute sodium carbonate solution and the solution was heated with Norit, filtered and acidified. A solution of the acids (12.5 g.) in hot acetone was filtered and concentrated until spontaneous crystallization took place. After two recrystallizations from acetone, the β-[3-(5-methylphenanthroyl)]-propionic acid (3.2 g., m. p. 191–193°) was obtained as colorless needles which melted at 195–196.5°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.5; H, 5.4.

(b) From 3-Acetyl-5-methylphenanthrene.—A solution of 0.07 cc. of bromine in 6 cc. of ether was added to a solution of 0.3 g. of 3-acetyl-5-methylphenanthrene[2] in 20 cc. of ether cooled in an ice–salt-bath. Decolorization occurred when the solution was irradiated by two Argon bulbs for thirty-five minutes. After another half-hour, the ether was removed at room temperature. The **3-bromoacetyl-5-methylphenanthrene** (II) crystallized from methanol–acetone in colorless needles (0.3 g.) which melted at 105–107°. The product was added to the sodiomalonic ester prepared from 0.05 g. of powdered sodium, 0.5 cc. of diethyl malonate and 8 cc. of dry benzene. After the mixture had stood at room temperature for twenty-four hours, it was refluxed for two hours. Hydrolysis of the substituted malonic ester by 45% potassium hydroxide solution yielded the dicarboxylic acid (0.31 g.), which was decarboxylated at 160–180°. The keto acid obtained by acidification of an aqueous solution of its potassium salt weighed 0.23 g.; from benzene–acetone it crystallized in prisms which melted at 195–196° alone and when mixed with the keto acid obtained in (a).

γ-[3-(5-Methylphenanthryl)]-butyric Acid.—To 13.5 g. of amalgamated zinc were added in order 13.5 cc. of concentrated hydrochloric acid, 13.5 cc. of acetic acid, 10 cc. of toluene and 4.5 g. of the aforementioned keto acid. The mixture was refluxed for twenty-one hours; during this period 45 cc. of concentrated hydrochloric acid was added. The acid obtained from the toluene layer was distilled under reduced pressure; it crystallized from benzene–petroleum ether in colorless prisms; m. p. 92–94°; yield, 3.79 g. (88%).

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 82.3; H, 6.7.

1'-Methyl-5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene (III).—To a solution of 1 g. of the aforementioned acid in 10 cc. of ether and 2 drops of pyridine was added 0.5 cc. of thionyl chloride. The mixture was allowed to stand at room temperature for one-half hour, and then the ether and excess of thionyl chloride were removed under reduced pressure. One cc. of stannic chloride was added to a cold solution of the acid chloride in 20 cc. of benzene and the solution allowed to stand at room temperature for twenty minutes. The bright-red complex was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide, and the benzene evaporated. The cyclic ketone crystallized from alcohol–acetone in colorless leaflets; yield, 0.84 g. (89%). After three recrystallizations it melted at 153.5–154.5°.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.9; H, 6.1.

1'-Methyl-5,6,7,8-tetrahydro-1,2-benzanthracene.—A mixture of 10 g. of amalgamated zinc, 12 cc. of concentrated hydrochloric acid, 10 cc. of acetic acid, 5 cc. of toluene and 1 g. of the aforementioned cyclic ketone was refluxed for twenty-four hours; during this period 10 cc. each of hydrochloric acid and acetic acid was added in portions. The hydrocarbon obtained from the toluene layer was distilled under reduced pressure (0.2 mm.) and recrystallized from acetone–alcohol, from which it was obtained as colorless plates; m. p. 81.5–84°; yield, 0.81 g. (85%). A sample after two more recrystallizations melted at 83.5–84.5°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.7; H, 7.3. Found: C, 92.4; H, 7.4.

The **picrate** crystallized from alcohol in orange-yellow needles; m. p. 135–138°. After two recrystallizations, it melted at 140.5–142°.

Anal. Calcd. for $C_{19}H_{18}\cdot C_6H_3N_3O_7$: N, 8.84. Found: N, 8.95.

1'-Methyl-1,2-benzanthracene (IV).—A mixture of 0.5 g. of the tetrahydro derivative and 0.05 g. of palladium charcoal catalyst[12] was heated at 300–320° for one-half

(6) Fieser and Joshel, THIS JOURNAL, **62**, 1211 (1940).

(7) Bachmann and Struve [*J. Org. Chem.*, **5**, 416 (1940)] reported 249.5–250° and 170–170.5° for the uncorrected melting points of the 1- and 3-methylchrysene, respectively. The corrected melting points have now been determined.

(8) Ruzicka and Markus, *Helv. Chim. Acta*, **23**, 385 (1940).

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

(10) Fieser and Johnson, THIS JOURNAL, **61**, 1654 (1939).

(11) Newman, *ibid.*, **60**, 2947 (1938).

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

hour. The 1'-methyl-1,2-benzanthracene crystallized from alcohol–acetone in colorless leaflets; m. p. 133–135°; yield, 0.35 g. (75%). After two more recrystallizations, the hydrocarbon melted at 135.5–136.5°. The picrate prepared from equal weights of the components melted at 128.5–129.5°, and the quinone melted at 183–184°. These values are in agreement with those reported by Cook and Robinson[3] and Fieser and Seligman.[4] The melting point of a mixture of our hydrocarbon and that prepared by the method of Cook and Robinson showed no depression.

γ-[1-(4-Methylphenanthryl)]-butyric Acid (V). (a) From 4-Methylphenanthrene.—The second and third crops of the keto acids obtained by recrystallization of the mixture produced by succinoylation of 4-methylphenanthrene were combined and reduced by the Clemmensen method. A mixture of 150 g. of amalgamated zinc, 250 cc. of concentrated hydrochloric acid, 100 cc. of toluene, 250 cc. of acetic acid and 30 g. of the mixture of keto acids obtained from several succinoylations was refluxed for twenty-four hours; during this period 250 cc. of hydrochloric acid was added in portions. The aqueous layer was extracted once with benzene and the combined organic extracts were evaporated and the crude acid distilled under reduced pressure. A solution of the distillate in benzene yielded 5 g. of product melting at 147–149°. After three recrystallizations, the γ-[1-(4-methylphenanthryl)]-butyric acid formed colorless needles which melted at 152–152.5°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 82.1; H, 6.6.

(b) **From 1-Acetyl-4-methylphenanthrene.**—A solution of 0.23 cc. of bromine in 20 cc. of anhydrous ether was added to a solution of 1 g. of 1-acetyl-4-methylphenanthrene[2] in 40 cc. of anhydrous ether cooled in an ice-salt-bath. After the solution had been decolorized with the aid of ultraviolet light, it was evaporated in the cold. The **1-bromoacetyl-4-methylphenanthrene** (VI) crystallized from methanol–acetone in prisms; m. p. 80–82°; yield, 0.97 g. Four more recrystallizations raised the melting point to 93–94.5° (needles).

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 26.1.

One-half gram of the bromo ketone, condensed with diethyl malonate and the product worked up in the manner described for the isomeric 3-bromoacetyl-4-methylphenanthrene, yielded 0.33 g. (74%) of **β-[1-(4-methylphenanthroyl)]-propionic acid** (VII) melting at 133–136°. After two recrystallizations from benzene, the acid melted at 137–138°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.2; H, 5.2.

The Clemmensen reduction of 0.09 g. of the keto acid was carried out in the manner described for the isomer (I). The reduced acid (0.05 g.) after distillation and two recrystallizations from benzene melted at 151–152.5° alone and when mixed with the acid in (a).

(c) **From 1-Keto-4-methyl-1,2,3,4-tetrahydrophenanthrene.**—This ketone[2] (1.72 g.) was added to a mixture of 2 g. of granulated zinc, 0.05 g. of iodine and 0.6 cc. of methyl bromoacetate in 20 cc. of dry benzene and 20 cc. of dry ether. After the iodine color had disappeared and a yellowish-white precipitate had formed, further additions of zinc and iodine were made every half hour for two hours. At the end of this time 0.6 cc. of methyl bromoacetate was added and the mixture refluxed for four hours more. The mixture was hydrolyzed with cold dilute hydrochloric acid, the aqueous layer extracted with benzene and the combined organic extracts washed with water and dilute ammonium hydroxide. The product obtained from the solution was heated with 0.2 g. of palladium–charcoal catalyst at 240–260° for two hours. The product, after being separated from the catalyst, was hydrolyzed by 45% potassium hydroxide solution. The acid was sublimed and crystallized from alcohol–acetone, forming colorless needles; m. p. 179–183°; yield, 0.98 g. After three recrystallizations the **1-(4-methylphenanthryl)-acetic acid** melted at 188–189°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.3; H, 5.6.

To a suspension of 0.6 g. of the aforementioned acid in 2 cc. of dry ether and 1 drop of pyridine was added 0.6 cc. of thionyl chloride. After one-half hour at room temperature, the ether and excess of thionyl chloride were removed under reduced pressure. A solution of the crystalline acid chloride in benzene was added dropwise to a solution of diazomethane in 35 cc. of dry ether prepared from 1.5 cc. of nitrosomethylurethan. After standing at room temperature for two hours, during which time the diazoketone separated as clusters of colorless needles, the solvents were evaporated under reduced pressure. A boiling solution of the diazo ketone in 15 cc. of anhydrous methanol was treated with 0.1 g. of freshly-prepared silver oxide over a period of three hours. The product was hydrolyzed with aqueous potassium hydroxide solution, and the acid which was formed was sublimed and crystallized from benzene. The **β-[1(4-methylphenanthryl)]-propionic acid** formed clusters of colorless needles; m. p. 155–156°; yield, 0.27 g. (42%). A mixture of this acid and that obtained in (b) melted at 125–130° (depression).

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.0. Found: C, 81.3; H, 6.2.

The Arndt–Eistert reaction carried out in the same manner on 0.3 g. of the β-[1(4-methylphenanthryl)]-propionic acid yielded 0.13 g. (41%) of γ-[1-(4-methylphenanthryl)]-butyric acid melting at 150–151° alone and when mixed with the same acid obtained in (a).

1-Keto-1,2,3,4-tetrahydro-11-methylchrysene (IX).—Cyclization of 1 g. of the aforementioned acid was carried out in the manner described for the isomeric acid. The cyclic ketone crystallized from alcohol–acetone in clusters of colorless needles; yield, 0.85 g. (91%); m. p. 138–140°. After two further recrystallizations from alcohol–acetone, the ketone melted at 139.5–140.5°.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.4; H, 6.2.

1,2,3,4-Tetrahydro-11-methylchrysene.—A mixture of 10 g. of amalgamated zinc, 20 cc. of acetic acid, 12 cc. of concentrated hydrochloric acid, 5 cc. of toluene and 0.93 g. of the aforementioned cyclic ketone was refluxed for twenty-four hours; during this period 10 cc. each of the two acids was added. The hydrocarbon obtained from the toluene layer was distilled under reduced pressure and then

recrystallized. From alcohol–acetone it crystallized in colorless needles; yield, 0.76 g. (86%); m. p. 71–72°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.2.

The **picrate** crystallized from alcohol in clusters of orange needles; m. p. 141–142°.

Anal. Calcd. for $C_{19}H_{18}\cdot C_6H_3N_3O_7$: N, 8.84. Found: N, 8.85.

5-Methylchrysene (X).—A mixture of 0.5 g. of the tetrahydro derivative and 0.05 g. of palladium–charcoal catalyst was heated at 300–320° for forty-five minutes. The mixture was digested with hot benzene and filtered, and the benzene evaporated. From alcohol–acetone the 5-methylchrysene crystallized in colorless needles; yield, 0.42 g. (85%); m. p. 116–117°. After a second recrystallization it melted at 118–118.8° (cor.). The hydrocarbon shows strong blue-violet fluorescence in ultraviolet light. The picrate crystallized from alcohol in red needles; m. p. 141–142° (reported: 142.6–143° cor.[5]; 141.6–142.4° cor.[6]). The *s*-trinitrobenzene derivative crystallized from benzene–alcohol in orange needles; m. p. 171–173° (reported: 172.6–173.6° cor.[5]).

Summary

4-Methylphenanthrene reacts with succinic anhydride in the Friedel–Crafts reaction in the 1- and 6-positions.

From the products of this reaction 1′-methyl-1,2-benzanthracene and 5-methylchrysene were synthesized.

ANN ARBOR, MICHIGAN RECEIVED JULY 18, 1940

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

Melibiotol and Maltitol

BY M. L. WOLFROM AND THOMAS S. GARDNER

The classical method of preparing sugar alcohols by the sodium amalgam reduction of the reducing sugars was tedious, gave low yields and was unsatisfactory in general. The electrolytic reduction of *d*-glucose,[1] now carried out on an industrial scale in this country, has made sorbitol and *d*-mannitol commercially available. From a laboratory standpoint, the high pressure catalytic reduction methods pioneered by Ipatieff, now make the reduction of sugars to the corresponding alcohols a comparatively simple procedure when the proper equipment is available. By such methods, Levene and Kuna[2] obtained the disaccharide alcohol cellobiotol in crystalline form and Levene and Tipson[3] crystallized 6-(β-glucosido)-dulcitol by the reduction of the synthetic 6-(β-glucosido)-*d*-galactose of Freudenberg and co-workers.[4] Senderens[5] previously had reduced lactose by high pressure catalytic methods and although he obtained some hydrolytic splitting to dulcitol, he was able to isolate a hydrated form of lactitol.

From this Laboratory, we have reported the crystallization of the anhydrous form of lactitol[6] (lactositol) and we wish now to record crystalline melibiotol and its crystalline nonabenzoate. The structure of our reduced product was verified by its lack of Fehling reduction and by hydrolysis to its components, sorbitol and *d*-galactose, each of which was identified through a crystalline characteristic derivative. The derivative used to characterize *d*-galactose was its diethyl mercaptal, a readily obtainable and easily crystallizable substance. A sirupy melibiotol had been reported by Scheibler and Mittelmeier[7] by the sodium amalgam reduction of an early melibiose preparation.

Karrer and Büchi[8] reduced maltose by high pressure, catalytic methods but were unable to crystallize the product. We have repeated the work of Karrer and Büchi, and while we were likewise unable to crystallize the maltitol, we obtained a definitely crystalline nonaacetate of this substance. Karrer and Büchi also prepared maltitol nonaacetate and characterized it as a "nicht deutlich krystallines Pulver." A comparison of the properties recorded by these workers for their preparation with those of our distinctly crystalline product, would make it appear probable that the maltitol nonaacetate of Karrer and Büchi was microcrystalline. Karrer and Büchi identified the reduced portion of the maltitol by hydrolysis and identification as tribenzylidenesorbitol. We have further characterized the glucose liberated

(1) H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939).

(2) P. A. Levene and M. Kuna, *Science*, **85**, 550 (1937); *J. Biol. Chem.*, **127**, 49 (1939).

(3) P. A. Levene and R. S. Tipson, *ibid.*, **125**, 355 (1938).

(4) K. Freudenberg, A. Noë and E. Knopf, *Ber.*, **60**, 238 (1927).

(5) J. B. Senderens, *Compt. rend.*, **170**, 47 (1920).

(6) M. L. Wolfrom, W. J. Burke, K. R. Brown and R. S. Rose, Jr., THIS JOURNAL, **60**, 571 (1938).

(7) C. Scheibler and H. Mittelmeier, *Ber.*, **22**, 3118 (1889).

(8) P. Karrer and J. Büchi, *Helv. Chim. Acta*, **20**, 86 (1937).