ammonolyzed as described for the α-anomer XIa, affording crude XVIIb as a slightly yellowish, viscous oil weighing 3.54 g. (125%). It showed no epoxide absorption at 11.6 μ. A 435-mg. portion was dried at 100° and 0.15 mm. until the decrease in weight was less than 1% per hour. The final weight was 316 mg. (91%).

The crude product of an ammonolysis performed at 90° for 17 hr. (showing weak absorption at 11.6 μ) was purified on Amberlite IRC-50 (H)[18] as described for the α-anomer XVIIa. This afforded a 21% yield of neutral material, mainly recovered XIb, and a 73% yield of XVIIb as a pale oil. A 239-mg. portion of the latter was heated at 100° and 0.10 mm. until the weight loss remained constant at about 7 mg./hour. This sample had $[\alpha]^{24}{}_{589}$ −66.1° (2.51% in H_2O); $[\alpha]^{27}{}_{589}$ −74.4° and $[\alpha]^{27}{}_{546}$ −92.3° (0.34% in $CHCl_3$); and $\lambda_{\max}^{\text{film}}$ 2.99 μ (OH, NH), 6.27 μ (NH_2).

Anal. Calcd. for $C_6H_{13}NO_4$: C, 44.2; H, 8.03; N, 8.58. Found: C, 44.1; H, 8.04; N, 8.45.

Methyl 3-Acetamido-3-deoxy-β-D-xylofuranoside (XXb).—Crude methyl 3-amino-3-deoxy-β-D-xylofuranoside (XVIIb) was treated with acetic anhydride in water as described for the α-anomer XXa. The crude derivative crystallized on trituration in ethyl acetate, affording 549 mg. (107% based on XIb) of white crystals, m.p. 97–104°. Three recrystallizations from ethyl acetate–ethanol yielded 243 mg. of white crystals, m.p. 105–106°; $[\alpha]^{25}{}_{589}$ −31.2° and $[\alpha]^{25}{}_{546}$ −37.0° (1.16% in H_2O); $\lambda_{\max}^{\text{KBr}}$ 2.96, 3.05 μ (OH, NH), 6.06 μ (amide C=O); 6.47 μ (amide NH). Paper chromatographic results are given in Table II.

Anal. Calcd. for $C_8H_{15}NO_5$: C, 46.8; H, 7.36; N, 6.83. Found: C, 46.9, 46.9; H, 7.50, 7.28; N, 6.59, 6.44.

The residue from the combined mother liquors from the purification of the analytical sample also moved as a single spot in solvents D (R_f 0.47 ± 0.02), E (R_f 0.79 ± 0.01) and F (R_f 0.90) (*cf.* Table II).

Isomerization of Methyl 3-Amino-3-deoxy-D-xylofuranoside (XVII) to Methyl 3-Amino-3-deoxy-β-D-xylopyranoside (XIV). (A) α-Anomer.—A solution of 1.56 g. of crude XVIIa (86% pure) in 50 ml. of 1% methanolic hydrogen chloride was refluxed for 22 hr. (protected from moisture) and evaporated to dryness *in vacuo*. The residue, dissolved in 25 ml. of water, was neutralized by being stirred with 12 g. of Dowex 2 (CO_3)[24] for 1 hr. at 60–70°. The resin was removed by filtration and the combined filtrate and water washings (3 × 10 ml.) were again treated with 10 g. of Dowex 2 (CO_3). The filtered solution was evaporated to dryness *in vacuo*. Several recrystallizations of the residue from 95% ethanol gave a total of 72 mg. (5.4%) of pure XIV, m.p. 193–195° cor. A mixture with authentic XIV melted at 193–196° cor., and a comparison of their infrared spectra confirmed this identity.

(B) **β-Anomer.**—Isomerization of 1.53 g. of crude XVIIb (76% pure) as described for the α-anomer gave 147 mg. (13%) of pure XIV, m.p. 193–196° cor. A mixture with authentic XIV melted at 194–196° cor., and the two samples had identical infrared spectra.

Paper Chromatography.—The paper chromatograms were run by the descending technique on Whatman No. 1 paper in these several solvent systems: A, 1-butanol/acetic acid/water (5/2/3)[25]; B, ethyl acetate/pyridine/water (2/1/2)[26]; C, 1-butanol/ethanol/water (4/1/5)[27]; D, water-saturated 1-butanol[28]; E, methyl Cellosolve/water (9/1)[29]; and F, 5% disodium hydrogen phosphate[30] (without the usual organic phase). For the aminoxylosides, 250-γ applications were used; for the acetamidoxylosides, 100-γ.

Acknowledgments.—We wish to thank Dr. Peter Lim for interpretation of the infrared data; Miss C. M. Brown and staff for the microanalyses; Mr. O. P. Crews, Jr., and staff for large-scale preparation of some intermediates; Dr. L. K. Moss and group for the periodate oxidations, optical rotations, and paper and column chromatography; and Mr. A. Benitez for certain initial preparations.

[24] An anion-exchange resin purchased from Microchemical Specialties Company, Berkeley, California.

[25] D. M. Brown, A. Todd and S. Varadarajan, *J. Chem. Soc.*, 2388 (1956).

[26] M. A. Jermyn and F. A. Isherwood, *Biochem. J.*, **44**, 402 (1949).

[27] P. W. Kent, G. Lawson and A. Senior, *Science*, **113**, 354 (1951).

[28] J. G. Buchanan, C. A. Dekker and A. G. Long, *J. Chem. Soc.*, 3162 (1950).

[29] A. E. Bender, *Biochem. J.*, **48**, xv (1951).

[30] C. E. Carter, THIS JOURNAL, **72**, 1466 (1950).

MENLO PARK, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The Synthesis of 1-Methyl-3,4-benzpyrene and 1,8-Dimethyl-3,4-benzpyrene[1-3]

BY WILLIAM CARTER DOYLE, JR.,[4] AND GUIDO H. DAUB

RECEIVED APRIL 25, 1958

Condensation of anthrone (I) with ethyl methacrylate in the presence of potassium *t*-butoxide followed by acid hydrolysis and reduction gave β-(9-anthranyl)-isobutyric acid (II) in 71% yield. Reduction of II with sodium in *n*-amyl alcohol gave β-(9,10-dihydro-9-anthranyl)-isobutyric acid (III) (87% yield) which was cyclized to 2-methyl-3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV) in 81% yield. The Stobbe condensation of IV with dimethyl succinate using W. S. Johnson's procedure for hindered ketones gave a 95% yield of crude oily half-ester. Saponification of the half-ester with alcoholic potassium hydroxide yielded a mixture of isomeric unsaturated dibasic acids. Decarboxylation of the dibasic acids yielded a mixture from which β-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic acid (VII) was isolated in 40% yield. Reduction of the entire crude mixture of acidic material from the decarboxylation with sodium in *n*-amyl alcohol followed by cyclization with anhydrous hydrogen fluoride gave a mixture of neutral and acidic ketonic material. The neutral fraction (36.5% yield from IV) was shown to contain 8-keto-1-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (VIII) and 8-keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX). This neutral fraction was readily converted into 1-methyl-3,4-benzpyrene (XII) *via* Wolff–Kishner reduction and then by dehydrogenation, and into 1,8-dimethyl-3,4-benzpyrene (XIII) *via* a Grignard reaction with subsequent dehydration and dehydrogenation. The over-all yield for each of these two hydrocarbons from anthrone was 9%.

Previous papers in this series have reported the synthesis of the 10-,[5] 2-[6] and 9-[7] monomethyl-3,4-benzpyrenes, the 8,10-,[5] 2,8-,[6] 8,9-,[7] 5,8-[8] and 5,10-[8] dimethyl-3,4-benzpyrenes and 5,8,10-trimethyl-3,4-benzpyrene.[8] We are now reporting the synthesis of two more new 3,4-benzpyrenes, namely, 1-methyl-3,4-benzpyrene and 1,8-dimethyl-3,4-benzpyrene.

[1] From the dissertation presented by William Carter Doyle, Jr., to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

[3] Presented before the Division of Organic Chemistry at the 128th Meeting of The American Chemical Society, Minneapolis, Minn., September 11–16, 1955.

[4] Graduate Research Assistant, February, 1952, to December, 1955.

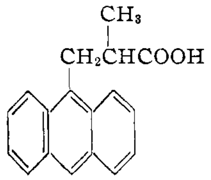
[5] J. L. Adelfang and G. H. Daub, THIS JOURNAL, **77**, 3297 (1955)

[6] J. W. Patton and G. H. Daub, *ibid.*, **79**, 709 (1957).

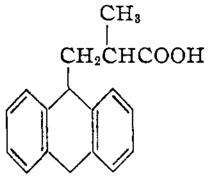
[7] J. L. Adelfang and G. H. Daub, *ibid.*, **79**, 1751 (1957).

[8] J. L. Adelfang and G. H. Daub, *ibid.*, **80**, 1405 (1958).

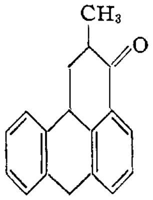
Anthrone (I) condensed readily with ethyl methacrylate in the presence of potassium *t*-butoxide in like manner to the condensation with acrylonitrile described in an earlier paper.[9] Acid hydrolysis of the condensation product followed by reduction with zinc and ammonium hydroxide gave β-(9-anthranyl)-isobutyric acid (II) in 71% over-all yield. Reduction of II with sodium in boiling *n*-amyl alcohol afforded an 87% yield of β-(9,10-dihydro-9-anthranyl)-isobutyric acid (III) which was cyclized with anhydrous hydrogen fluoride to 2 - methyl - 3 - keto - 1,2,3, 11b - tetrahydro - 7H - *meso*-benzanthracene (IV) in 81% yield.



II



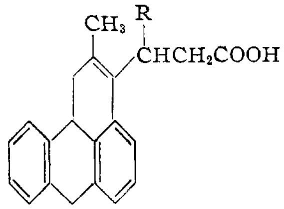
III



IV

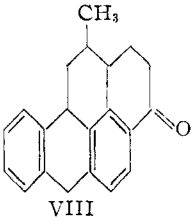
The Stobbe condensation of the ketone IV with dimethyl succinate using the procedure developed for hindered ketones by Johnson[10] gave an oily mixture of half-esters (V) in 95% yield. Saponification of the oily half-ester mixture with aqueous sodium hydroxide produced a mixture of dibasic acids from which two isomers of α-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-succinic acid (VI) were isolated.

Decarbomethoxylation of the crude half-ester V was best effected by saponification with alcoholic potassium hydroxide and then by decarboxylation of the resultant mixture of unsaturated dibasic acids with a mixture of pyridine, hydrochloric acid and oxalic aid.[11] The mixture of decarboxylated acidic material yielded upon trituration with ether 40% of β-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic acid (VII).

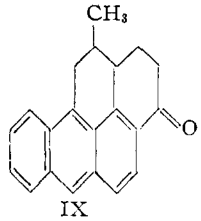


V, R = $COOCH_3$
VI, R = COOH
VII, R = H

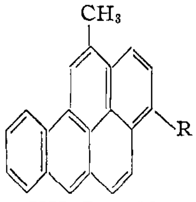
Reduction of the entire crude mixture of acidic material, from the decarboxylation, with sodium in *n*-amyl alcohol followed by cyclization with anhydrous hydrogen fluoride gave a mixture of neutral and acidic ketonic material. The neutral fraction (36.5% yield from IV) was shown to contain 8-keto - 1 - methyl - 1,2,2a,5,8,9,10,10a -octahydro-3,4-benzpyrene (VIII) and 8-keto-1-methyl-1,2,8,9,10,-10a-hexahydro-3,4-benzpyrene (IX). Reduction of the ketone mixture by the Wolff–Kishner method gave 1-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (X) and 1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XI). The structure of the latter compound (XI) was proved by comparison of its ultraviolet absorption spectrum with that of anthracene.



VIII



IX



XII, R = H
XIII, R = CH_3

Dehydrogenation of the hydrocarbon mixture from the reduction of VIII and IX afforded 1-methyl-3,4-benzpyrene (XII) in 57.5% yield. The reaction of VIII and IX with the methylmagnesium iodide and then dehydration and dehydrogenation over a palladium–charcoal catalyst gave 1,8-dimethyl-3,4-benzpyrene (XIII) in 49% yield. The over-all yield of each hydrocarbon from anthrone was approximately 9%.

Both hydrocarbons gave dark purple picrate derivatives and have ultraviolet absorption spectra similar to that for 3,4-benzpyrene. These compounds are being tested for carcinogenic activity at Northwestern University Medical School, Evanston, Ill.

Experimental[12]

β-(9-Anthranyl)-isobutyric Acid (II).—A solution of 17.4 g. (0.45 g.-atom) of potassium in 750 ml. of *t*-butyl alcohol was treated under nitrogen with 58.3 g. (0.30 mole) of anthrone, m.p. 153–156°, with stirring. The flask was warmed to approximately 50° and a solution of 49.8 g. (0.45 mole) of ethyl methacrylate (Eastman Kodak Co. practical) in 90 ml. of *t*-butyl alcohol was added dropwise during a 1-hour period. After refluxing for 5 hr., 565 ml. of water and 50 ml. of concentrated hydrochloric acid were added and the solvent removed by distillation, 1000 ml. of distillate being collected. The oil and water remaining in the flask was refluxed for 9 hr. with an additional 600 ml. of water and 480 ml. of concentrated hydrochloric acid. The aqueous layer was decanted, 550 ml. of water, 1080 ml. of concentrated ammonium hydroxide and 150 g. of zinc dust (activated with copper sulfate) were added and the flask heated at 90–95° for 6.5 hr., during which the aqueous solution changed in color from reddish-orange to pale greenish-yellow. This solution was filtered and acidified with hydrochloric acid, giving a pale yellow precipitate which, when collected, washed with water and dried weighed 56.2 g. (71% yield) and melted at 176–180° with preliminary shrinkage. Crystallization from glacial acetic acid–water yielded 46.6 g. of **β-(9-anthranyl)-isobutyric acid (II)**, m.p. 178.5–180.5°, as small yellow needles. An analytical sample, m.p. 180–181.5°, was obtained by crystallization from benzene.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10; neut. equiv., 264. Found: C, 82.14; H, 5.95; neut. equiv., 258.

The methyl ester of II crystallized from methanol as greenish-yellow needles, m.p. 54–56°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.87; H, 6.30.

β-(9,10-Dihydro-9-anthranyl)-isobutyric Acid (III).—Sodium (33.2 g., 1.44 g.-atoms) was added in small pieces over a 5-hr. period to a refluxing solution of 42.4 g. (0.16 mole) of β-(9-anthranyl)-isobutyric acid (II), m.p. 178–180°, in 1000 ml. of *n*-amyl alcohol. The alcohol was removed by steam distillation and the resulting alkaline solution cooled, whereupon the sodium salt of the acid crystallized as colorless plates. These were collected by filtration, dissolved in warm water and acidified with hydrochloric acid, giving **β-(9,10-dihydro-9-anthranyl)-isobutyric acid (III)** as a flocculent white precipitate weighing 39.5 g. (93% yield) and melting at 140–

---

[9] G. H. Daub and W. C. Doyle, This Journal, **74**, 4449 (1952).

[10] W. S. Johnson, J. W. Petersen and V. L. Stromberg, *ibid.*, **71**, 1384 (1949).

[11] W. S. Johnson and V. L. Stromberg, *ibid.*, **72**, 505 (1950).

[12] All melting points are uncorrected.

143°. The analytical sample crystallized from ethyl acetate as colorless micro-crystals, m.p. 142–144°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; neut. equiv., 266. Found: C, 80.83; H, 6.60; neut. equiv., 267.

The methyl ester of III crystallized from methanol as colorless needles, m.p. 101.5–102.5°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.16; H, 6.97.

3-Keto-2-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV).—Anhydrous hydrogen fluoride (350 ml.) was poured over 53.1 g. (0.20 mole) of β-(9,10-dihydro-9-anthranyl)-isobutyric acid, m.p. 132–143°, in a polyethylene beaker. After 4 hr. most of the hydrogen fluoride had evaporated and the viscous residue was poured on cracked ice. A greenish-yellow oil separated and was taken up in benzene. The benzene solution was extracted several times with 10% sodium bicarbonate, washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and passed through a column of alumina. A band of dark colored impurities was held near the top of the column while the almost colorless ketone passed through. The benzene solution was then taken to dryness on a steam-bath, leaving a solid orange residue weighing 46.9 g. Crystallization of this solid from ethanol gave 40.0 g. (80.6% yield) of **3-keto-2-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV)** as greenish-white needles, m.p. 29–131°. Several recrystallizations from ethanol gave colorless needles, m.p. 130–131°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.05; H, 6.49. Found: C, 86.94; H, 6.36.

The 2,4-dinitrophenylhydrazone of IV crystallized from benzene as small reddish-orange needles, m.p. 236.5–237.0° dec.

Anal. Calcd. for $C_{24}H_{18}O_4N_4$: C, 67.28; H, 4.71. Found: C, 67.63; H, 4.90.

The Stobbe Condensation of 3-Keto-2-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene with Dimethyl Succinate.—To 1.98 g. (0.008 mole) of the ketone IV under nitrogen was added 10 ml. of a solution of dimethyl succinate (7.60 g., 0.052 mole), b.p. 92–94° (20 mm.), and potassium *t*-butoxide (prepared from 2.32 g. of potassium and 50 ml. of anhydrous *t*-butyl alcohol). The remainder was added dropwise over a 3-hr. period while the solution was refluxing on a steam-bath. Refluxing was continued for an additional 45 min., at the end of which 6.5 ml. of concentrated hydrochloric acid and 40 ml. of water were added and the *t*-butyl alcohol removed at reduced pressure on the steam-bath. Ether was added to the resultant mixture of oily half-ester and light yellow solid self-condensation product of dimethyl succinate (m.p. 155°) and the ether solution filtered to remove the latter. The filtered ether solution was extracted with three portions of dilute ammonium hydroxide and the combined ammonia extracts washed with ether and acidified yielding 2.75 g. (95% yield) of **β-carbomethoxy-β-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic acid (V)**, or isomers, as a light yellow oil which failed to crystallize.

Saponification of the Half-ester Mixture; Isomers of α-(2-Methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-succinic Acid (VI).—The crude oily half-ester mixture from 1.98 g. (0.008 mole) of IV, m.p. 129–131°, was refluxed with 8% aqueous sodium hydroxide. After 30 min. a heavy precipitate of sodium salt separated and was collected, dissolved in warm water and acidified with concentrated hydrochloric acid, precipitating 0.25 g. of a yellowish solid acid, m.p. 134–137° dec. Three recrystallizations from benzene–methanol gave small fluffy colorless crystals of the A-isomer of **α-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-succinic acid (VI)**, m.p. 186–188° dec.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.85; H, 5.69.

The alkaline filtrate from which the insoluble sodium salt had been removed was refluxed for an additional 36 hr. After cooling and extracting with ether, the solution was acidified with concentrated hydrochloric acid, the gummy precipitate of acidic material was dissolved in methanol, benzene was added and the solution boiled to expel the methanol and water. On cooling, the concentrated benzene solution deposited 0.33 g. of a yellowish solid, m.p. 200–203° dec. Three recrystallizations from benzene–methanol gave small colorless crystals of the B-isomer of **α-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-succinic acid (VI)**, m.p. 218–219° dec.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.56; H, 6.14.

Ultraviolet Absorption Spectra of the Isomers of α-(2-Methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-succinic Acid (VI).—The ultraviolet absorption spectra of the isomeric dibasic acids VI, m.p. 186–188° and 218–219°, in 95% ethanol were measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: A-isomer, 219 mμ (4.19) and 266 mμ (4.15); B-isomer, 220 mμ (4.22) and 262 mμ (4.12).

β-(2-Methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic Acid (VII).—The oily half-ester from 19.8 g. of 3-keto-2-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV), m.p. 129–131°, was refluxed for 13.5 hr. with a solution of 45 g. of potassium hydroxide in 900 ml. of 95% ethanol. At the end of this time, the ethanol was removed at reduced pressure on the steam-bath and the residual potassium salt dissolved in water and acidified with concentrated hydrochloric acid, giving a tan granular solid mixture of the isomeric dicarboxylic acids VI. This mixture of acids was refluxed for 53 hr. with a mixture of 432 ml. of pyridine, 756 ml. of concentrated hydrochloric acid and 252 g. of oxalic acid. During this there was a steady evolution of carbon dioxide, and the oily acidic mixture gradually changed to a yellowish solid. The mixture was cooled and the solid material was collected by filtration and washed with ether. The ether-insoluble material which remained was 9.65 g. of **β-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic acid (VII)**, m.p. 167–171° (40% yield from IV). Crystallization from methanol gave colorless needles, m.p. 167–173°, repeated recrystallizations failing to shorten the range.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 83.06; H, 6.62.

The aqueous filtrate was diluted with water and extracted with ether and this, combined with the ether washings from the isolation of VII, was extracted with dilute ammonium hydroxide. The ammonia extracts were acidified with concentrated hydrochloric acid and a gummy acidic material weighing 11.0 g. was obtained.

Ultraviolet Absorption Spectrum of β-(2-Methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic Acid (VII).—The ultraviolet absorption spectrum of the acid VII in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 220 mμ (4.28) and 270 mμ (4.02).

8-Keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX).—A solution of 1.36 g. (0.0041 mole) of the acid VII, m.p. 167–171°, in 25 ml. of anhydrous hydrogen fluoride was allowed to stand at room temperature for 7 hr. and the viscous residue remaining was poured on cracked ice. The precipitated solid was dissolved in benzene and the benzene solution extracted with dilute ammonium hydroxide, washed with saturated sodium chloride solution and passed through a column of alumina. When concentrated and cooled, the yellow benzene solution deposited 0.28 g. (24% yield) of bright yellow needles, m.p. 200–220°. Several recrystallizations from benzene gave yellow plates, m.p. 235–239.5°, shown to be **8-keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX)** by comparison of its ultraviolet absorption spectrum with that of 2-acetylanthracene.[13]

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.48; H, 6.49.

Ultraviolet Absorption Spectrum of 8-Keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX).—The ultraviolet absorption spectrum of the ketone IX in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 244 mμ (4.29), 267 mμ (4.74), 332 mμ (3.51), 348 mμ (3.72), 366 mμ (3.75) and 390 mμ (3.60).

β-(2-Methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene-3)-propionic Acid (XIV).—The reduction of β-(2-methyl-1,11b-dihydro-7H-*meso*-benzanthracene-3)-propionic acid (VII) was carried out at atmospheric pressure.

---

[13] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, no. 393.

The acid VII (1.0 g., 0.0031 mole) in 100 ml. of absolute ethanol was stirred at room temperature with 0.12 g. of Adams catalyst for 69 hr. at which time the theoretical volume of hydrogen had been consumed. The solution was filtered to remove the catalyst and concentrated, whereupon 0.49 g. (49% yield) of β-(**2-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene-3)-propionic acid (XIV)** crystallized as colorless needles, m.p. 200–202°. Two more recrystallizations from ethanol gave an analytical sample, m.p. 202–203°.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.63; H, 6.82.

The methyl ester of XIV crystallized from methanol as small colorless needles, m.p. 110–111°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.14; H, 8.04.

Reduction of the Total Acidic Materials from Decarboxylation.—To a refluxing solution of 18.3 g. of combined solid (m.p. 167–171°) and gummy acidic material from the decarboxylation of the dicarboxylic acid mixture (VI) in 620 ml. of *n*-amyl alcohol was added 25 g. of sodium (1.09 g.-atoms) in small pieces over a 4-hr. period. The alcohol was removed by steam distillation and the alkaline solution acidified with concentrated hydrochloric acid giving a tan, granular solid weighing 20.9 g., m.p. 65–115°.

8-Keto-1-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (VIII) and 8-Keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX).—The above crude mixture of reduced acidic material (20.9 g.) was cyclized with 150 ml. of anhydrous hydrogen fluoride by the procedure described previously. After being chromatographed, the neutral benzene solution was evaporated to dryness, leaving 8.35 g. of an orange oil (36.5% yield from IV). On cooling an ether solution of this oil, a small amount of a yellow solid, m.p. 221–231°, crystallized. This was recrystallized several times from benzene, obtained as yellow plates, m.p. 235–239.5°, and shown to be 8-keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX).

The remainder of the neutral material gave a dark red **2,4-dinitrophenylhydrazone** (m.p. 254° dec., from benzene) corresponding to that of **8-keto-1-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (VIII)**.

Anal. Calcd. for $C_{27}H_{24}O_4N_4$: C, 69.22; H, 5.16. Found: C, 68.67; H, 5.18.

Wolff–Kishner Reduction of 8-Keto-1-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (VIII) and 8-Keto-1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (IX).—A solution of 8.35 g. of the oily neutral ketonic material (VIII and IX) in 44 ml. of 1,4-butanediol was heated at 115–135° for 45 min. with 4.4 ml. of 99% hydrazine and 6.1 g. of potassium hydroxide. The temperature was then raised to 185° and heating was continued for an additional three hours while the temperature was increased gradually to 205°. The solution was cooled and dilute hydrochloric acid and benzene were added. The benzene layer was washed with water, dried over anhydrous magnesium sulfate and passed through a column of alumina. The chromatographed benzene solution was evaporated to dryness leaving a greenish-yellow oil. Trituration of this oil with petroleum ether (b.p. 60–90°) produced a small amount of a light yellow solid melting at 161–168°. Crystallization of this solid from methanol gave light yellow plates, m.p. 171–172°, shown to be **1-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XI)** by comparison of its ultraviolet absorption spectrum with that of anthracene.[14]

Anal. Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.83; H, 7.44.

Ultraviolet Absorption Spectrum of 1-Methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XI).—The ultraviolet absorption spectrum of the hydrocarbon XI in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ε) values are: 227 mμ (4.13), 262 mμ (5.20), 320 mμ (3.15), 352 mμ (3.72), 371 mμ (3.88) and 390 mμ (3.84).

1-Methyl-3,4-benzpyrene (XII).—The oily mixture of hydrocarbons from the above reduction (about 8 g.) was heated in an atmosphere of carbon dioxide with 1.6 g. of 10% palladium–charcoal. Heating was begun at 260° and the temperature was raised steadily to 370° during which time 2500 ml. of hydrogen was evolved. The mixture was cooled, dissolved in benzene and the catalyst removed by filtration. The benzene solution was passed through a column of alumina and concentrated, whereupon bright yellow, fluffy needles of **1-methyl-3,4-benzpyrene (XII)** crystallized. The yield was 4.46 g. (20% over-all yield from IV) of hydrocarbon melting at 155–156.5°.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.44; H, 5.33.

The picrate of XII crystallized from benzene as small dark purple needles, m.p. 187.5–188.5°.

Anal. Calcd. for $C_{27}H_{17}O_7N_3$: C, 65.45; H, 3.46. Found: C, 65.55; H, 3.50.

1,8-Dimethyl-3,4-benzpyrene (XIII).—A solution of 4.18 g. of the oily neutral ketone mixture (VIII and IX) in 110 ml. of anhydrous benzene and 130 ml. of anhydrous ether was added dropwise over a 1.25-hr. period to the Grignard reagent prepared from 4.4 g. (0.18 g.-atom) of magnesium, 28.2 (0.20 mole) of methyl iodide and 160 ml. of anhydrous ether. The solution was then refluxed for 2 hr., cooled in an ice-bath and 200 ml. of 10% sulfuric acid added carefully. The organic layer was washed with water, dried over anhydrous magnesium sulfate and evaporated to dryness. The residual oil was heated at 260–360° for one hour in an atmosphere of carbon dioxide with 0.8 g. of 10% palladium–charcoal, 1000 ml. of hydrogen being evolved. The product was dissolved in benzene, the catalyst removed by filtration and the benzene solution passed through a column of alumina. Concentration of the benzene solution caused 2.00 g. (48.8% yield) of **1,8-dimethyl-3,4-benzpyrene (XIII)**, m.p. 130–133°, to crystallize. An analytical sample was obtained from benzene as bright yellow micro-crystals, m.p. 136.5–137°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.53; H, 6.00.

The picrate of XIII crystallized from benzene as small, dark purple needles, m.p. 190.5–191.5°.

Ultraviolet Absorption Spectra of 1-Methyl-3,4-benzpyrene (XII) and 1,8-Dimethyl-3,4-benzpyrene (XIII).—The ultraviolet absorption spectra of the hydrocarbons XII and XIII in 95% ethanol were measured with a model DU Beckman spectrophotometer. Maxima and (log ε) values are: 1-methyl-3,4-benzpyrene (XII), 222 mμ (4.42), 228 mμ (4.44), 256 mμ (4.64), 266 mμ (4.72), 286 mμ (4.69), 298 mμ (4.77), 351 mμ (4.11), 368 mμ (4.42) and 390 mμ (4.50); 1,8-dimethyl-3,4-benzpyrene (XIII), 222 mμ (4.41), 228 mμ (4.44), 256 mμ (4.64), 267 mμ (4.66), 290 mμ (4.66), 294 mμ (4.65), 302 mμ (4.79), 356 mμ (4.10), 374 mμ (4.38) and 393 mμ (4.39).

ALBUQUERQUE, N. M.

---

(14) R. A. Friedel and M. Orchin, ref. 13, no. 388.