alkyl group transfer. *m*-Diethylbenzene by contrast is of about the same basicity as *m*-xylene, can compete favorably with *m*-xylene for protons and should thus be able to transfer an ethyl group to the *m*-xylene ring.

WHITING, IND.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW MEXICO]

The Synthesis of 7-Methyl-, 10-Methyl-, 6,7-Dimethyl- and 7,10-Dimethyl-3,4-benzpyrenes[1,2]

BY JOSEPH L. COMP[3] AND GUIDO H. DAUB

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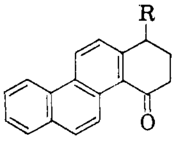
The Reformatsky reaction of 4-keto-1,2,3,4-tetrahydrochrysene (III) with ethyl α-bromopropionate followed by dehydration, hydrolysis and reduction of the Reformatsky product afforded α-(1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (V) which was cyclized to 6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (VI). Reduction, dehydration and dehydrogenation of VI afforded 7-methyl-3,4-benzpyrene (10% over-all yield from phenanthrene). The reaction of methylmagnesium iodide with VI followed by dehydration and dehydrogenation gave 6,7-dimethyl-3,4-benzpyrene (VIII) (6% over-all yield from phenanthrene). 2-Acetylphenanthrene, prepared in two steps from 9,10-dihydrophenanthrene, underwent the Stobbe condensation with diethyl succinate in the presence of sodium hydride to give a mixture of half-esters. The half-ester mixture was decarbethoxylated and reduced to γ-(2-phenanthryl)-valeric acid (X), which was cyclized to 4-keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI). The Reformatsky reaction of XI with ethyl bromoacetate, followed by dehydration, hydrolysis and reduction of the hydroxy-ester thus produced, gave 1-methyl-1,2,3,4-tetrahydro-4-chrysenylacetic acid (XIII). The acid XIII was cyclized with anhydrous hydrogen fluoride to 6-keto-10-methyl-6,7,7a,-8,9,10-hexahydro-3,4-benzpyrene (XIV) and this ketone upon reduction followed by dehydration and dehydrogenation afforded 10-methyl-3,4-benzpyrene (XV) (4% over-all yield from phenanthrene). The Reformatsky reaction of XI with ethyl α-bromopropionate, followed by dehydration, hydrolysis and reduction, gave α-(1-methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (XVII). Cyclization of XVII with anhydrous hydrogen fluoride gave 6-keto-7,10-dimethyl-6,7,7a,-8,9,10-hexahydro-3,4-benzpyrene (XVIII), which upon reduction and dehydrogenation was converted to 7,10-dimethyl-3,4-benzpyrene (XIX) (6% over-all yield from phenanthrene). These hydrocarbons are being evaluated for carcinogenic activity at Northwestern University Medical School, Evanston, Ill.

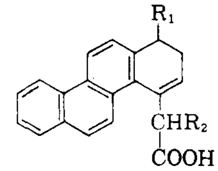
We wish to report new syntheses of the 7-[4] and 10-[5] monomethyl-3,4-benzpyrenes as well as the synthesis of two new dimethyl-3,4-benzpyrenes, namely, the 6,7- and 7,10-dimethyl derivatives.[6]

The Friedel–Crafts acylation of 9,10-dihydrophenanthrene[7] with succinic anhydride in nitrobenzene[8] gave a 98% yield of β-(9,10-dihydro-2-phenanthroyl)-propionic acid (I). Reduction of I by either the Clemmensen method[9] or Wolff–Kishner method[10] afforded γ-(9,10-dihydro-2-phenanthryl)-butyric acid (II) in 84 and 97% yields, respectively. The acid II was converted to 4-keto-1,2,3,4-tetrahydrochrysene (III) in four steps as described by Bachmann and Struve.[9]

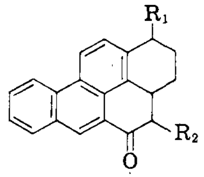
The Reformatsky reaction of the chrysenone III with ethyl α-bromopropionate produced an intermediate hydroxy-ester, which was dehydrated and hydrolyzed to give an 81.5% yield of a mixture of isomeric chrysenyl-propionic acids from which a 33% yield of one isomer, probably α-(1,2-dihydro-4-chrysenyl)-propionic acid (IV), was obtained by crystallization from methanol. Hydrogenation of IV over Adams catalyst gave a 75.5% yield of α-(1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (V), which was cyclized with anhydrous hydrogen fluoride to give a quantitative yield of 6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (VI) as an oily mixture of isomers



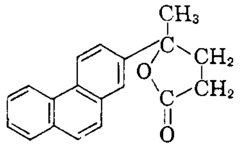
III, R = H
XI, R = CH$_3$



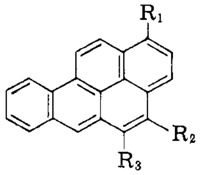
IV, R$_1$ = H, R$_2$ = CH$_3$
XII, R$_1$ = CH$_3$, R$_2$ = H
XVI, R$_1$ = R$_2$ = CH$_3$



VI, R$_1$ = H, R$_2$ = CH$_3$
XIV, R$_1$ = CH$_3$, R$_2$ = H
XVIII, R$_1$ = R$_2$ = CH$_3$



IX



VII, R$_1$ = R$_3$ = H, R$_2$ = CH$_3$
VIII, R$_1$ = H, R$_2$ = R$_3$ = CH$_3$
XV, R$_1$ = CH$_3$, R$_2$ = R$_3$ = H
XIX, R$_1$ = R$_2$ = CH$_3$, R$_3$ = H

One isomer was isolated from this mixture in 52% yield. The Meerwein–Ponndorf–Verley reduction of VI, with subsequent dehydration and dehydro-

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[1] From the dissertation presented by Joseph L. Comp 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] Graduate Research Assistant, February, 1952, to February, 1956.

[4] D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 4360 (1958).

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

[6] For reference to previous papers in this series see W. C. Doyle and G. H. Daub, *ibid.*, **80**, 5252 (1958).

[7] D. D. Phillips, *Org. Syntheses*, **34**, 31 (1954).

[8] A. Burger and E. Mosettig, THIS JOURNAL, **59**, 1302 (1937).

[9] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 456 (1939).

[10] D. D. Phillips, THIS JOURNAL, **75**, 3223 (1953).

genation over 10% palladium–charcoal, afforded a 77.5% yield of 7-methyl-3,4-benzpyrene (VII).

The ketone VI was allowed to react with an excess of methylmagnesium iodide, and the carbinol thus obtained was dehydrated and dehydrogenated directly over 10% palladium–charcoal to give a 48% yield of 6,7-dimethyl-3,4-benzpyrene (VIII).

2-Acetylphenanthrene was prepared by the acetylation of 9,10-dihydrophenanthrene as described by Burger and Mosettig[11] followed by dehydrogenation of the resulting 2-acetyl-9,10-dihydrophenanthrene according to the procedure of Riegel.[12] The Stobbe condensation of 2-acetylphenanthrene with diethyl succinate using sodium hydride[13] afforded a 96% yield of a mixture of half-esters as a light yellow oil. The half-ester mixture was directly decarbethoxylated with 48% hydrobromic acid and acetic acid to give an 80.5% yield of γ-(2-phenanthryl)-valerolactone (IX) along with some unsaturated acid. The lactone IX was reduced with red phosphorus and iodine in glacial acetic acid to γ-(2-phenanthryl)-valeric acid (X) in 88.5% yield. Cyclization of γ-(2-phenanthryl)-valeryl chloride was accomplished with stannic chloride in carbon disulfide solution as described by Bachmann[14] and gave a 67% yield of 4-keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI).

The Reformatsky reaction with 4-keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI) and ethyl bromoacetate gave a carbinol, which upon dehydration and hydrolysis afforded 1-methyl-1,2-dihydro-4-chrysenylacetic acid (XII) as a mixture of isomers in 87.5% yield. Since the crude acid could not be purified by crystallization, it was hydrogenated directly over Adams catalyst to 1-methyl-1,2,3,4-tetrahydro-4-chrysenylacetic acid (XIII). Cyclodehydration with anhydrous hydrogen fluoride gave 6-keto-10-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XIV) as an oily mixture of isomers (63.8% over-all yield from crude Reformatsky product). The crude mixture containing 6-keto-10-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene was reduced with aluminum isopropoxide to a carbinol, which was directly dehydrated and dehydrogenated over 10% palladium–charcoal to give a 45% yield of 10-methyl-3,4-benzpyrene (XV).

The Reformatsky reaction of 4-keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI) with ethyl α-bromopropionate gave a hydroxy-ester which was dehydrated and hydrolyzed to give a 79.5% yield of crude acid from which α-(1-methyl-1,2-dihydro-4-chrysenyl)-propionic acid (XVI) was isolated in 46.4% total yield. α-(1-Methyl-1,2-dihydro-4-chrysenyl)-propionic acid (XVI) absorbed 86% of the theoretical amount of hydrogen over Adams catalyst at room temperature and atmospheric pressure, affording a 56.5% yield of one isomer of α-(1-methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (XVII). Cyclization of XVII with anhydrous hydrogen fluoride gave a 97% crude yield of 6-keto-7,10-dimethyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XVIII) which was reduced with aluminum isopropoxide, dehydrated and dehydrogenated to 7,10-dimethyl-3,4-benzpyrene (XIX) in 50.7% yield.

All of these 3,4-benzpyrenes gave ultraviolet absorption spectra similar to that for the parent hydrocarbon. A dark brown picrate was formed with 7,10-dimethyl-3,4-benzpyrene and dark purple picrates were formed with 7-methyl-3,4-benzpyrene and 6,7-dimethyl-3,4-benzpyrene. These compounds are being tested for carcinogenic activity at Northwestern University Medical School, Evanston, Ill.

Experimental[15]

The Reformatsky Reaction of 4-Keto-1,2,3,4-tetrahydrochrysene (III) with Ethyl α-Bromopropionate. The apparatus used was a three-necked 500-ml. round-bottom flask fitted with a rubber sealed Hershberg stirrer, condenser fitted with a calcium chloride tube, and a glass stopper. Baker C.P. 20 mesh zinc was amalgamated according to the method described by Kolthoff and Sandell,[16] washed with acetone and stored under dry benzene. One hundred and twenty-five milliliters of anhydrous benzene and 15 g. of amalgamated zinc were added to the flame-dried apparatus under dry nitrogen; 25 ml. of benzene was distilled from the flask and 5.0 g. (0.0203 mole) of the ketone III, m.p. 124–125°, 100 ml. of anhydrous ether, 5.3 ml. (0.05 mole) of ethyl α-bromopropionate (Eastman 1041) and a crystal of iodine were added. The reaction mixture was refluxed for a total time of 93 hr. At the end of 24 hr. an additional 15 g. of amalgamated zinc and 5.3 ml. of ethyl α-bromopropionate were added. Iodine was added periodically to the reaction mixture, and a yellow oily complex coated the sides of the flask, zinc and the stirrer; 200 ml. of 6 *N* hydrochloric acid was added and the mixture stirred until two clear layers were formed. The organic layer was washed with water, dried over anhydrous magnesium sulfate and filtered. After the benzene and ether had been removed under reduced pressure, the flask containing the oily product was allowed to remain on the steam-bath under reduced pressure for an additional hour to remove the excess ethyl α-bromopropionate. The dark yellow oily residue was dehydrated by heating on a steam-bath for 15 min. with 40 ml. of anhydrous formic acid after which the formic acid was removed under reduced pressure. Hydrolysis of the ester for 12 hr. with 11.2 g. of potassium hydroxide in 100 ml. of water and 100 ml. of alcohol and then dilution of the basic solution with water and extraction with ether gave on acidification 5.31 g. (81.5% yield) of crude acid, m.p. 160–170°. The crude acid crystallized from ethyl acetate as very fine dark brown crystals which were recrystallized from methanol, the brown colored impurities being insoluble in this solvent. A total of 1.67 g. (33% yield) of **α-(1,2-dihydro-4-chrysenyl)-propionic acid** (IV) thus was obtained as colorless needles, m.p. 208–209°. Repeated recrystallization from methanol gave an analytical sample as colorless needles, m.p. 211–212°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.28; H, 6.24.

α-(1,2,3,4-Tetrahydro-4-chrysenyl)-propionic Acid (V).—One and seven-tenths grams (0.00558 mole) of α-(1,2-dihydro-4-chrysenyl)-propionic acid (IV), m.p. 210–211°, was hydrogenated at atmospheric pressure over 0.17 g. of Adams catalyst in ethanol solution. In 40 min. the theoretical amount of hydrogen had been absorbed and the catalyst was removed by filtration. The ethanol solution was concentrated and 1.20 g. (70.5% yield) of **α-(1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid** (V) was obtained as colorless needles, m.p. 200–203°. Repeated crystallizations from ethanol gave an analytical sample as colorless needles, m.p. 205–206°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 83.33; H, 6.89.

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(11) A. Burger and E. Mosettig, THIS JOURNAL, **58**, 1857 (1936).

(12) B. Riegel, M. Gold and M. Kubico, *ibid.*, **64**, 221 (1942).

(13) G. H. Daub and W. S. Johnson, *ibid.*, **72**, 501 (1950).

(14) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **5**, 416 (1940).

(15) All melting points are uncorrected.

(16) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 598.

6-Keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzyprene (VI).—Cyclization of 1.53 g. (0.00504 mole) of V, m.p. 200–203°, with 25 ml. of anhydrous hydrogen fluoride was carried out in a polyethylene beaker. After standing overnight the hydrogen fluoride had evaporated and the orange-yellow solid that remained was dissolved in benzene. The benzene solution of the ketone was washed with water, 5% ammonium hydroxide solution and saturated sodium chloride solution. After drying over anhydrous magnesium sulfate the solution was passed through an alumina column and the ketone eluted with benzene. Evaporation of the benzene afforded a quantitative yield of oily ketone, which was crystallized from alcohol to give 0.75 g. (52.0% yield) of **6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (VI)**, m.p. 137–142°. Repeated recrystallization from alcohol gave an analytical sample as yellow needles, m.p. 142–144°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 88.08; H, 6.34. Found: C, 88.21; H, 6.55.

The 2,4-dinitrophenylhydrazone was prepared and crystallized from benzene as dark orange needles, m.p. 278–279°.

Anal. Calcd. for $C_{27}H_{22}O_4N_4$: C, 69.15; H, 4.75. Found: C, 69.24; H, 4.81.

7-Methyl-3,4-benzpyrene (VII).—Reduction of 7.7 g. (0.0269 mole) of the crude oily ketone VI was carried out with 22 g. (0.1076 mole) of aluminum isopropoxide and 125 ml. of dry toluene in a flask fitted with a Hahn condenser.[17] After 50 hr. of slow distillation the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent. Toluene was added periodically during the distillation to maintain the initial volume. The reaction mixture was worked up in the usual manner and the toluene removed under reduced pressure. The yellow gummy solid that remained was transferred to a dehydrogenation apparatus with ether. After removal of the ether 1.54 g. of 10% palladium–charcoal was added and the dehydration and dehydrogenation were carried out in a carbon dioxide atmosphere at 175–360°. The hydrogen evolved was measured in a gas buret using an alkali trap to remove the carbon dioxide. Dehydration occurred between 175 and 200° and most of the hydrogen was liberated between 275 and 300°. After the theoretical amount of hydrogen was collected, the reaction mixture was cooled and the solid residue was dissolved in benzene. The catalyst was removed by filtration and the benzene solution chromatographed. A total of 5.53 g. (77.5% yield) of **7-methyl-3,4-benzpyrene (VII)** was obtained as bright yellow needles, m.p. 188–189°. Repeated recrystallizations from benzene gave an analytical sample, m.p. 190–191°, reported[4] m.p. 188–189°.

The picrate was prepared and crystallized from benzene as dark purple needles, m.p. 187–187.5°, reported[4] m.p. 188–189°.

The oily mixture of isomers that remained in the mother liquor after crystallization of the α-(1,2-dihydro-4-chrysenyl)-propionic acid (IV) in 33% yield was reduced with hydrogen over Adams catalyst at room temperature and atmospheric pressure. Cyclization of the crude reduced acid obtained gave 6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,-4-benzpyrene (VI) as an oily mixture of isomers. Reduction of the chromatographed ketone with aluminum isopropoxide and then dehydration and dehydrogenation at 175–360° with 10% palladium–charcoal afforded additional 7-methyl-3,4-benzpyrene.

Ultraviolet Absorption Spectrum of 7-Methyl-3,4-benzpyrene (VII).—The ultraviolet absorption spectrum of 7-methyl-3,4-benzpyrene in alcohol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 212 mμ (4.53), 222 mμ (4.39), 230 mμ (4.28), 256 mμ (4.64), 266 mμ (4.72), 274 mμ (4.50), 286 mμ (4.66), 298 mμ (4.74), 347 mμ (4.10), 365 mμ (4.39), 380 mμ (4.41), 385 mμ (4.47) and 404 mμ (3.48).

6,7-Dimethyl-3,4-benzpyrene (VIII).—A solution of 8.32 g. (0.029 mole) of the oily ketone VI dissolved in 225 ml. of anhydrous benzene and 260 ml. of anhydrous ether was added dropwise to a Grignard solution prepared from 8.8 g. (0.36 g.-atom) of magnesium and 20 ml. (0.4 mole) of methyl iodide in 320 ml. of dry ether. The reaction mixture was refluxed for 6 hr. and then cooled in an ice-bath. To the cooled mixture was added 400 ml. of 10% sulfuric acid and the benzene–ether solution was separated, washed with water and dried over anhydrous magnesium sulfate. The benzene and ether were removed under reduced pressure, and the residual oil was dehydrated and dehydrogenated over 1.76 g. of 10% palladium–charcoal at 175–360° as described previously for the 7-methyl derivative. The hard solid residue was dissolved in benzene and the catalyst removed after which the benzene solution was chromatographed. The benzene solution was concentrated and 3.88 g. (47.5% yield) of **6,7-dimethyl-3,4-benzpyrene (VIII)** was obtained as bright yellow needles, m.p. 181–184°. Purification of this material through the picrate and then recrystallization from benzene gave an analytical sample as bright yellow needles, m.p. 190–191°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.24; H, 5.75. Found: C, 94.54; H, 5.68.

The picrate was prepared and crystallized from benzene as dark purple needles, m.p. 203–204°.

Anal. Calcd. for $C_{28}H_{19}O_7N_3$: C, 66.01; H, 3.67. Found: C, 65.89; H, 3.70.

Ultraviolet Absorption Spectrum of 6,7-Dimethyl-3,4-benzpyrene (VIII).—The ultraviolet absorption spectrum of 6,7-dimethyl-3,4-benzpyrene in alcohol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 212 mμ (4.54), 222 mμ (4.40), 267 mμ (4.72), 276 mμ (4.51), 287 mμ (4.66), 351 mμ (4.08), 367 mμ (4.37), 386 mμ (4.40) and 404 mμ (3.55).

The Stobbe Condensation with 2-Acetylphenanthrene.—A three-necked round-bottom flask equipped with a stirrer, reflux condenser and stopper was flame-dried, swept with dry nitrogen and charged with 30 g. (1.25 moles) of sodium hydride, 52 ml. of anhydrous benzene and 10 ml. of absolute ethanol. When the reaction of ethanol with sodium hydride had subsided 500 ml. of anhydrous benzene, 167.5 ml. (1.0 mole) of diethyl succinate and 110.1 g. (0.5 mole) of 2-acetylphenanthrene,[12] m.p. 142–143°, were added. As the reaction proceeded hydrogen was evolved rapidly, and after stirring for 7 hr. at room temperature 100 ml. of acetic acid was added to decompose the excess sodium hydride. Ether and water were added, and the organic layer was extracted several times with 5% sodium carbonate solution. Acidification of the carbonate extracts gave 168.8 g. (96.5% yield) of a **mixture of half-esters** as a light yellow oil.

γ-(2-Phenanthryl)-valerolactone (IX).—A mixture of 155 g. (0.445 mole) of the crude oily half-ester, 138 ml. of water, 483 ml. of 48% hydrobromic acid and 621 ml. of glacial acetic acid was refluxed for 15.5 hr. after which the evolution of carbon dioxide had ceased. The water, acetic acid and hydrobromic acid were removed under reduced pressure, and the residue was triturated with 750 ml. of ether to give 98.9 g. (80.5% yield) of the colorless lactone IX, m.p. 124–126°. Repeated recrystallization from ether gave **γ-(2-phenanthryl)-valerolactone (IX)** as colorless plates, m.p. 132–133°.

Anal. Calcd. for $C_{19}H_{16}O_2$: H, 82.58; C, 5.84. Found: C, 82.65; H, 5.71.

γ-(2-Phenanthryl)-valeric Acid (X).—A mixture of 5.0 g. (0.0181 mole) of the lactone IX, m.p. 124–126°, 67 ml. of glacial acetic acid, 4.03 g. (0.13 mole) of red phosphorus, 4.34 g. (0.0172 mole) of iodine and 1.3 ml. of water was refluxed for 6 hr. The dark red solution was decanted through glass wool into 600 ml. of water containing some sodium bisulfite, and 4.81 g. (95.5% yield) of a light cream colored solid, m.p. 131–134°, was obtained. Crystallization from ethyl acetate gave 4.47 g. (88.5% yield) of γ-(2-phenanthryl)-valeric acid (X), m.p. 136–138°, reported[14] m.p. 136.5–138.5°.

The Reformatsky Reaction of 1-Methyl-4-keto-1,2,3,4-tetrahydrochrysene (XI) with Ethyl Bromoacetate.—Activated zinc was prepared by heating Baker C.P. 20 mesh zinc with concentrated sulfuric acid, that contained a few drops of concentrated nitric acid, at 100° for 0.25 hr. The apparatus was flame-dried and swept with nitrogen, and 12.6 g. (0.192 g. atom) of the activated zinc, 5 g. (0.0195 mole) of the ketone XI,[14] m.p. 98–99°, 4.3 ml. (0.0385 mole) of ethyl bromoacetate, 50 ml. of dry benzene, 50 ml. of dry ether and a crystal of iodine were added. The reaction mixture was refluxed with stirring for a total of 26.5 hr., with additions of 12.6 g. of zinc and 4.3 ml. of ethyl bromoacetate at the end of 8 and also at the end of 16 hr. The reaction mixture was worked up and the ester dehydrated with formic

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(17) A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

acid as described above. The unsaturated ester was hydrolyzed for 5 hr. with 5.6 g. (0.1 mole) of potassium hydroxide dissolved in 50 ml. of water and 50 ml. of ethanol. The basic solution was diluted with water, extracted with ether and acidified with concentrated hydrochloric acid to give 5.08 g. (87.5% yield) of **1-methyl-1,2-dihydro-4-chrysenylacetic acid** (**XII**) as a light tan, flocculent precipitate, m.p. 100–110°. All attempts to purify this crude acid by crystallization failed, so the crude material was reduced directly in the next step.

1-Methyl-1,2,3,4-tetrahydro-4-chrysenylacetic Acid (XIII).—The hydrogenation of 14.6 g. (0.048 mole) of the crude acid XII, m.p. 100–110°, over 0.1 g. of Adams catalyst in 400 ml. of ethanol was allowed to proceed for 18 days at room temperature and atmospheric pressure. At the end of this period 70% of the theoretical amount of hydrogen was absorbed, and the catalyst was removed. After removal of most of the ethanol by distillation, 1 l. of ether was added, and the acid was extracted with 5% sodium carbonate solution. Acidification produced 14.5 g. of a tan, amorphous, inseparable mixture of isomers, m.p. 80–90°. The crude acid thus obtained was used directly in the next step.

6-Keto-10-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XIV).—The cyclization of 14.5 g. of the crude reduced acid XIII, m.p. 80–90°, with approximately 150 ml. of anhydrous hydrogen fluoride was carried out in a polyethylene beaker. The reaction mixture was allowed to stand overnight, during which time the hydrogen fluoride had evaporated, and the dark brown complex was dissolved in ether and extracted with 5% sodium carbonate solution. Acidification of the carbonate extracts gave 4.31 g. of brown acidic material, m.p. 100–140°, which failed to give more ketonic material when treated again with anhydrous hydrogen fluoride. The ether solution was evaporated, the residue dissolved in benzene and the benzene solution chromatographed over alumina. Evaporation of the benzene gave 8.8 g. (63.8% yield) of **6-keto-10-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XIV)** as a light yellow oil which resisted all efforts to crystallize.

10-Methyl-3,4-benzpyrene (XV).—In a round-bottom flask fitted with a Hahn condenser were placed 1.34 g. (0.00468 mole) of the oily ketone XIV, 3.82 g. (0.0187 mole) of aluminum isopropoxide, and 25 ml. of dry toluene. After 73 hr. of slow distillation, the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent. The reaction mixture was worked up as previously described and the oily product transferred to a dehydrogenation apparatus. Dehydration and dehydrogenation were carried out over 0.27 g. of 10% palladium-charcoal by heating to 360° until no more hydrogen was evolved. The compound dehydrated between 175 and 200°, and the main portion of hydrogen was liberated between 275 and 300°. The hard cake of 10-methyl-3,4-benzpyrene (XV) was dissolved in benzene and the catalyst removed. The benzene solution was chromatographed, and the product was purified *via* the picrate. Crystallization from benzene gave 0.56 g. (45% yield) of 10-methyl-3,4-benzpyrene (XV) as fine yellow needles, m.p. 177–178°, reported[5] m.p. 178.0–178.5°.

The Reformatsky Reaction of 4-Keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI) with Ethyl α-Bromopropionate.—A mixture of 20 g. (0.076 mole) of the ketone XI, m.p. 98–99°, 500 ml. of anhydrous benzene, 500 ml. of anhydrous ether, 50 g. (0.76 g. atom) of amalgamated zinc,[16] 50 ml. (0.385 mole) of ethyl α-bromopropionate and a crystal of iodine was allowed to reflux gently with stirring for a total of 47 hr. Further additions of 25 g. (0.38 g. atom) of amalgamated zinc and 25 ml. (0.192 mole) of ethyl α-bromopropionate were made at the end of 9, 18, 27 and 40 hr. The cooled reaction mixture was worked up and the ester dehydrated with formic acid as described above.

The dehydrated ester was hydrolyzed for 11 hr. with 56.1 g. (1.0 mole) of potassium hydroxide in 500 ml. of water and 500 ml. of ethanol. The clear, light yellow, alkaline solution was diluted with 1 l. of water, extracted with ether and acidified with hydrochloric acid to give 19.3 g. (79.5% yield) of a cream colored solid, m.p. 90–100°. Trituration with 25 ml. of ether gave 11.26 g. (46.4% yield) of **α-(1-methyl-1,2-dihydro-4-chrysenyl)-propionic acid (XVI)** as fine colorless needles, m.p. 199–201. Several recrystallizations from methanol gave an analytical sample of colorless needles, m.p. 207–208°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.47; H, 6.45.

The isomeric acids remaining in the ether solution from the trituration were carried on to 7,10-dimethyl-3,4-benzpyrene without further purification.

α-(1-Methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic Acid (XVII).—The reduction of 11.62 g. (0.0368 mole) of the acid XVI, m.p. 207–208°, was carried out over Adams catalyst in 330 ml. of ethanol. After 24 hr. at room temperature and atmospheric pressure 86% of the theoretical amount of hydrogen was absorbed. After removal of the catalyst, the solution was concentrated and 7.82 g. (66.5% yield) of a colorless solid, m.p. 200–215°, was obtained. Repeated recrystallization from alcohol gave 6.64 g. (56.5% yield) of **α-(1-methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (XVII)** as colorless crystals, m.p. 216–217.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 83.18; H, 7.09.

The material left in the mother liquors was carried on to 7,10-dimethyl-3,4-benzpyrene without further purification.

6-Keto-7,10-dimethyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XVIII).—In a polyethylene beaker were placed 7.12 g. (0.0224 mole) of α-(1-methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (XVII), m.p. 216–217°, and approximately 75 ml. of anhydrous hydrogen fluoride. After standing overnight, the dark residue was dissolved in ether, washed with water, 5% sodium carbonate solution and 5% sodium hydroxide sloution. The ether was replaced with benzene, and the benzene solution was chromatographed through alumina. Removal of the benzene gave 6.5 g. (97.0% yield) of a light yellow oily ketone which formed a gummy solid upon standing. Crystallization from methanol gave 2.93 g. (43.7% yield) of **6-keto-7,10-dimethyl-6,7,7a,-8,9,10-hexahydro-3,4-benzpyrene (XVIII)** as light yellow needles, m.p. 153–154°. Repeated recrystallization from methanol afforded an analytical sample as light yellow needles, m.p. 156.0–156.5°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.70; H, 6.76.

The 2,4-dinitrophenylhydrazone was prepared and crystallized from benzene as bright orange needles, m.p. 255.5–256.0°.

Anal. Calcd. for $C_{28}H_{24}O_4N_4$: C, 69.99; H, 5.03. Found: C, 70.10; H, 5.20.

The mother liquor from the crystallization of XVIII was carried on to 7,10-dimethyl-3,4-benzpyrene without further purification.

7,10-Dimethyl-3,4-benzpyrene (XIX).—In a round-bottom flask fitted with a Hahn condenser were placed 2.5 g. (0.0084 mole) of 6-keto-7,10-dimethyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (XVIII), m.p. 153–154°, 7.15 g. (0.0336 mole) of aluminum isopropoxide and 46 ml. of dry toluene. After 12.5 hr. of slow distillation a negative test for acetone was obtained on the distillate. The reaction mixture was worked up in the usual manner, and the light yellow oil which was obtained was dehydrated and dehydrogenated over 0.5 g. of 10% palladium-charcoal at 170–360°. The solid residue was dissolved in benzene and chromatographed through alumina. The benzene solution was concentrated and 1.76 g. (75.4% yield) of **7,10-dimethyl-3,4-benzpyrene (XIX)** was obtained as yellow prisms, m.p. 215–222°. Recrystallization from benzene gave 1.50 g. (64.1% yield) of light yellow prisms, m.p. 222–223°. Repeated recrystallization from benzene gave an analytical sample as bright yellow prisms, m.p. 223.0–223.5°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.24; H, 5.75. Found: C, 94.27; H, 5.73.

The picrate was prepared and crystallized from benzene as dark brown needles, m.p. 189–190°.

Anal. Calcd. for $C_{28}H_{19}O_7N_3$: C, 66.01; H, 3.67. Found: C, 67.84; H, 4.10.

Ultraviolet Absorption Spectrum of 7,10-Dimethyl-3,4-benzpyrene (XIX).—The ultraviolet absorption spectrum of 7,10-dimethyl-3,4-benzpyrene in alcohol was measured with a model DU Beckman spectrophotometer. Maxima and (log ε) values are: 211 mμ (4.50), 222 mμ (4.36), 232 mμ (4.24), 259 mμ (4.63), 268 mμ (4.75), 287 mμ (4.58), 300 mμ (4.64), 351 mμ (4.10), 369 mμ (4.42), 390 mμ (4.51) and 407 mμ (3.49).

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