The liquid distillate consisted mainly of chlorobenzene. The presence and quantitative amounts of acetone and *t*-butyl alcohol, which formed the major product from the *t*-butyl group in the free radical decomposition of all the peresters, were determined by infrared spectra in chlorobenzene.

A check of the acetone concentration determined in this manner for the reaction product of *t*-butyl α,α-diphenylperpropionate by the iodine titration method of Messinger[22] gave good agreement. This latter method was employed whenever other materials in the reaction product interfered with the carbonyl band of acetone.

(22) F. Wild, "Estimation of Organic Compounds," Cambridge University Press Cambridge, England, 1953, p. 165.

Most of the products from the acid radical of the perester did not distil with the chlorobenzene. This residue was separated into fractions by chromatographing it on acid-washed alumina. The materials thus separated were, for the most part, identified by comparison of their infrared spectra with those of known compounds.

Acknowledgments.—We thank the National Science Foundation for a grant to one of us and a fellowship to the other and the National Institutes of Health for fellowships to the junior author in 1955 and 1956.

CAMBRIDGE 38, MASS.

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

The Synthesis of 5,8-Dimethyl-3,4-benzpyrene, 5,10-Dimethyl-3,4-benzpyrene and 5,8,10-Trimethyl-3,4-benzpyrene[1,2]

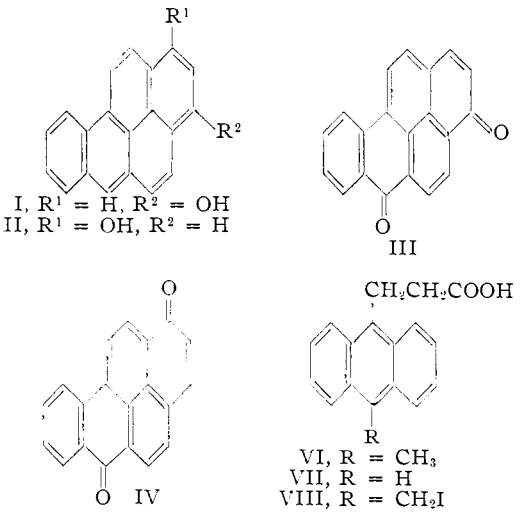
BY JULES L. ADELFANG[3] AND GUIDO H. DAUB

RECEIVED OCTOBER 24, 1957

The substituted malonic ester obtained from the condensation of 10-chloromethyl-9-methylanthracene (V) with diethyl malonate was hydrolyzed and decarboxylated providing β-(10-methyl-9-anthranyl)-propionic acid (VI) in 64% yield from V. The synthesis of VI was also accomplished in 85% yield by stannous chloride reduction of β-(10-iodomethyl-9-anthranyl)-propionic acid prepared by iodomethylation of β-(9-anthranyl)-propionic acid. Reduction of the acid VI with sodium in boiling *n*-amyl alcohol afforded β-(10-methyl-9,10-dihydro-9-anthranyl)-propionic acid which upon cyclization produced 3-keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X). The Stobbe condensation with the ketone X gave β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI) in 85% yield. The half-ester XI was decarbethoxylated providing β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XII). Reduction of the acid XII produced β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid which was cyclized to 8-keto-5-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (XVI). The ketone XVI was treated with methylmagnesium iodide producing a carbinol which was dehydrated and dehydrogenated to 5,8-dimethyl-3,4-benzpyrene (XVII). The hydrocarbon XVII was identical with the compound isolated from Wolff–Kishner reduction of 8-methyl-3,4-benzpyrene-5-aldehyde (XIX) which was obtained by formylation of 8-methyl-3,4-benzpyrene. Cyclization of the half-ester XI provided 10-carbethoxy-8-keto-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX) in 35% yield. The ketone XX was reduced with lithium aluminum hydride and the resulting diol was dehydrated and dehydrogenated producing 5,10-dimethyl-3,4-benzpyrene in 25% yield from XX. Formylation of 8,10-dimethyl-3,4-benzpyrene (XXIII) with N-methylformanilide afforded 8,10-dimethyl-3,4-benzpyrene-5-aldehyde which was directly reduced by the Wolff–Kishner method producing 5,8,10-trimethyl-3,4-benzpyrene in 25% yield from XIX.

Carcinogenic testing has shown that the 5-,[4] 8-,[5] and 10-monomethyl-3,4-benzpyrenes[5] and 8,10-dimethyl-3,4-benzpyrene[5] are quite active. The synthesis of the remaining 3,4-benzpyrenes having methyl groups in the 5-, 8- and 10-positions, namely the 5,8-dimethyl-, 5,10-dimethyl- and 5,8,10-trimethyl-3,4-benzpyrenes, is presented here.

These compounds are of interest since it has been demonstrated that mice will metabolize 3,4-benzpyrene to non-carcinogenic oxidized products involving the 5-, 8- and 10-positions. Wiegert and Mottram[6] found that the main metabolite obtained from the feces of mice given intravenous injections of 3,4-benzpyrene was 8-hydroxy-3,4-benzpyrene (I). Berenblum and Schoental[7] also found 8-hydroxy-3,4-benzpyrene along with 10-hydroxy-3,4-benzpyrene (II), 3,4-benzpyrene-5,8-quinone (III), and 3,4-benzpyrene-5,10-quinone (IV) in the feces of rats given intraperitoneal injections of 3,4-benzpyrene.



The synthesis of 5,8-dimethyl-3,4-benzpyrene (XVII) and 5,10-dimethyl-3,4-benzpyrene (XXII) was accomplished from β-(10-methyl-9-anthranyl)-propionic acid (VI), an intermediate readily available from anthrone. 9-Methylanthracene, prepared by treatment of anthrone with methylmag-

(1) From the dissertation presented by Jules L. Adelfang to the graduate faculty of the University of New Mexico in partial fulfilment 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, 1956, to August, 1957.

(4) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 2542 (1938).

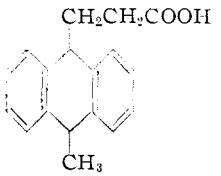
(5) D. W. Stanger, Northwestern University Medical School, unpublished results.

(6) F. Wiegert and J. C. Mottram, *Cancer Research*, **6**, 97 (1946).

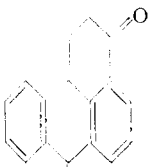
(7) I. Berenblum and R. Schoental, *ibid.*, **6**, 699 (1946).

nesium iodide,[8] was chloromethylated using a solution of paraformaldehyde in acetic acid saturated with hydrogen chloride producing 10-chloromethyl-9-methylanthracene (V)[9] in 76% yield. The substituted malonic ester obtained by condensation of V with diethyl malonate in the presence of sodium ethoxide was hydrolyzed directly with methanolic potassium hydroxide and the resulting dicarboxylic acid was decarboxylated at 205° providing β-(10-methyl-9-anthranyl)-propionic acid (VI) in 64% yield from V. An alternate synthesis of the acid VI was developed starting with β-(9-anthranyl)-propionic acid (VII) prepared from anthrone as previously described by Daub and Doyle.[10] Iodomethylation of the acid VII with 57% hydriodic acid and paraformaldehyde in acetic acid using a procedure suggested by Fieser[11] gave β-(10-iodomethyl-9-anthranyl)-propionic acid (VIII). The unstable iodomethyl acid VIII was reduced with stannous chloride dissolved in a mixture of concentrated hydrochloric acid and dioxane affording the acid VI in 85% yield from VII.

β-(10-Methyl-9-anthranyl)-propionic acid (VI) was reduced with sodium in boiling *n*-amyl alcohol producing a 92% yield of β-(10-methyl-9,10-dihydro-9-anthranyl)-propionic acid (IX) as a mixture of isomers. Cyclization of the acid IX with anhydrous hydrogen fluoride gave 3-keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X) in 77% yield. Cyclization of the acid IX as a mixture of isomers or as the pure predominant isomer, gave the ketone X as a mixture of isomers of approximately the same composition.

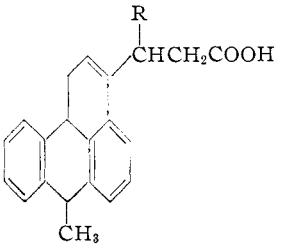


IX

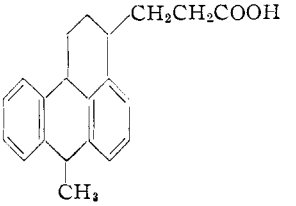


X

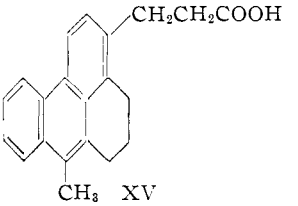
The Stobbe condensation with the ketone X was carried out in the presence of potassium *t*-butoxide affording a mixture of β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI) and isomers in 85% yield. Decarbethoxylation of the crude half-ester XI with a mixture of hydrochloric acid and acetic acid produced β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XII) and a small amount of lactone XIII. The ketone X, either as an oily mixture of isomers or as a single isomer, provided the same acid and lactone in approximately the same yields. Reduction of the acid XII gave β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XIV). An attempt to prepare the acid XIV from the lactone XIII by reduction with phosphorus and iodine gave an abnormal product shown by comparison of ultraviolet absorption spectra[12] to be β-(7-methyl-4,5-dihydro-6H-*meso*-benzanthrenyl-3)-propionic acid (XV).



XI, R = $COOC_2H_5$
XII, R = H

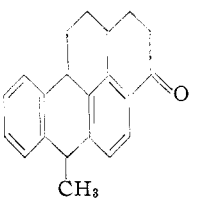


XIV

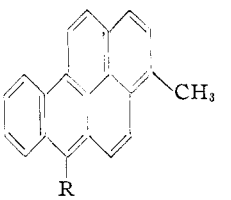


XV

Cyclization of the acid XIV with anhydrous hydrogen fluoride afforded 8-keto-5-methyl-1,2,2a,5,-8,9,10,10a-octahydro-3,4-benzpyrene (XVI) as a mixture of stereoisomers in 88% yield. Reaction of the ketone XVI with methylmagnesium iodide gave 8-hydroxy-5,8-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene which was dehydrated and dehydrogenated over palladium–charcoal at 285–345°, affording the 5,8-dimethyl-3,4-benzpyrene (XVII) in 57% over-all yield. This hydrocarbon also was obtained by Doyle[13] *via* 8-methyl-3,4-benzpyrene (XVIII). Formylation of XVIII with N-methylformanilide gave 8-methyl-3,4-benzpyrene-5-aldehyde (XIX) which was reduced by the Wolff–Kishner method to XVII. Although the hydrocarbon had been prepared previously, the independent synthesis from XVI described above proves it to be 5,8-dimethyl-3,4-benzpyrene.



XVI



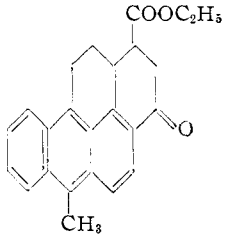
XVII, R = CH_3
XVIII, R = H
XIX, R = CHO

The synthesis of the 5,10-dimethyl derivative was accomplished by using a sequence of reactions developed by Campbell[14] in the preparation of 10-methyl-3,4-benzpyrene. Cyclization of the crude β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI) in the presence of anhydrous hydrogen fluoride produced an oily mixture of isomeric keto esters in 35% yield. It was assumed from the results obtained by Campbell[14] that cyclization had occurred with rearrangement producing 10-carbethoxy-8-keto-5-methyl-1,-2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX) as the predominant product. Reduction of XX with lith-

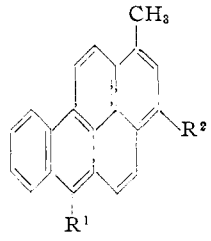
(8) F. Krollpfeiffer and F. Branscheid, *Ber.*, **56**, 1617 (1923).
(9) G. M. Badger and R. S. Pearce, *J. Chem. Soc.*, 2317 (1950).
(10) G. H. Daub and W. C. Doyle, THIS JOURNAL, **74**, 4449 (1952).
(11) R. B. Sandin and L. F. Fieser, *ibid.*, **62**, 3098 (1940).
(12) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, no. 341.
(13) W. C. Doyle, Doctoral Dissertation, University of New Mexico, 1955.
(14) A. D. Campbell, *J. Chem. Soc.*, 1938 (1956).

ium aluminum hydride afforded 8-hydroxy-10-hydroxymethyl-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XXI) which was directly dehydrated and dehydrogenated over a palladium–charcoal catalyst at 285–355° producing 5,10-dimethyl-3,4-benzpyrene (XXII) in 26% over-all yield from XX.

An attempt to prepare 5,8,10-trimethyl-3,4-benzpyrene (XXV) from the keto ester XX failed to give a pure sample of the hydrocarbon. Inverse addition of methylmagnesium iodide to XX gave an oil containing 10-carbethoxy-8-hydroxy-5,8-dimethyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XXVI). Reduction of XXVI with lithium aluminum hydride followed by dehydration and dehydrogenation over palladium–charcoal gave a small amount of hydrocarbon, m.p. 282.5–284.5° vac. Formylation of 8,10-dimethyl-3,4-benzpyrene (XXIII)[15] with N-methylformanilide provided 8,10-dimethyl-3,4-benzpyrene-5-aldehyde (XXIV) which was reduced by the Wolff–Kishner method affording 5,8,10-trimethyl-3,4-benzpyrene (XXV) in 26% over-all yield, m.p. 289–291.5° vac.



XX



XXII, $R^1 = CH_3$, $R^2 = H$
XXIII, $R^1 = H$, $R^2 = CH_3$
XXIV, $R^1 = CHO$, $R^2 = CH_3$
XXV, $R^1 = CH_3$, $R^2 = CH_3$

All of these new 3,4-benzpyrenes give unstable dark purple or brown picrates; the ultraviolet absorption spectra of the hydrocarbons substantiate the presence of the parent ring system.

Samples of the hydrocarbons have been sent to Northwestern University Medical School for carcinogenic testing.

Experimental[16]

10-Chloromethyl-9-methylanthracene (V).—A solution of 13.8 g. (0.46 mole) of paraformaldehyde (Eastman Kodak Co. 421) in 140 ml. of acetic acid was saturated with hydrogen chloride and added to a solution of 34.5 g. (0.180 mole) of 9-methylanthracene,[8] m.p. 79–80°, in 210 ml. of acetic acid. The reaction mixture was stirred intermittently for 2.0 hr. at 45°. After standing at room temperature for an additional 0.5 hr. the reaction mixture was poured into water and the resulting yellow precipitate was collected, washed with water, and crystallized from benzene affording 32.7 g. (76%) of 10-chloromethyl-9-methylanthracene (V) as pale yellow needles. This compound is reported as pale yellow needles, m.p. 192° dec.[9]; however, the compound actually does not appear to melt but chars at 180–190°.

β-(10-Methyl-9-anthranyl)-propionic Acid (VI). (a) From 10-Chloromethyl-9-methylanthracene (V).—To a solution of 11.1 g. (0.48 g.-atom) of sodium in 335 ml. of absolute ethanol, 169 g. (1.06 moles) of diethyl malonate and 113 g. (0.47 mole) of V were added. After the mixture was refluxed for one hour, a solution containing 300 g. of potassium hydroxide, 900 ml. of methyl alcohol and 900 ml. of water was added, and refluxing was continued for an additional 1.5 hr. The reaction mixture was allowed to cool, diluted with water, and then extracted with ether. Acidification yielded the substituted malonic acid as a flocculent yellow precipitate which was collected, washed with water, and dried. This material was decarboxylated by heating for 5 min. at 205°. The resulting mass of dark brown crystals was dissolved in ethyl acetate, treated with Norit and allowed to crystallize, providing 65.5 g. of **β-(10-methyl-9-anthranyl)-propionic acid (VI)** as small yellow needles, m.p. 194–196.5°. Further concentration of the mother liquor yielded an additional 13.5 g. of VI, m.p. 194.5–196.5°, making the total yield 79 g. (64%). An analytical sample, m.p. 195–196°, was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.00; H, 5.79.

(b) From **β-(9-Anthranyl)-propionic Acid (VII).**—To a solution of 50 g. (0.20 mole) of β-(9-anthranyl)-propionic acid (VII)[10] in 750 ml. of acetic acid, was added 50 g. of paraformaldehyde (Eastman Kodak Co. 421) dissolved in a mixture of 215 ml. of 57% hydriodic acid and 125 ml. of acetic acid. After the reaction mixture was allowed to stand at room temperature for one hour with occasional stirring the insoluble **β-(10-iodomethyl-9-anthranyl)-propionic acid (VIII)** was collected by filtration and washed with 110 ml. of cold acetic acid.

The crude acid VIII was dissolved in a boiling solution of 224 g. of stannous chloride, 675 ml. of concentrated hydrochloric acid and 1125 ml. of dioxane. The clear, light yellow solution was cooled and poured into 2250 ml. of water. The precipitated solid was collected and washed successively with 15% hydrochloric acid and water. Crystallization of the crude acid from ethyl acetate afforded 45.1 g. (85%) of β-(10-methyl-9-anthranyl)-propionic acid (VI), m.p. 192–196.5, no depression on admixture with the product from (a) above.

β-(10-Methyl-9,10-dihydro-9-anthranyl)-propionic Acid (IX).—The reduction of 79.0 g. (0.30 mole) of VI, m.p. 194–196.5°, was carried out in 1975 ml. of boiling *n*-amyl alcohol by the addition of 72 g. (3.1 g.-atoms) of sodium metal over a period of 7.0 hr. After removal of the alcohol by steam distillation, the basic solution was acidified yielding a light tan solid. Crystallization of this material from ethyl acetate afforded 40.2 g. of the A-isomer of **β-(10-methyl-9,10-dihydro-9-anthranyl)-propionic acid (IX)** as colorless crystals, m.p. 135.5–138°. Recrystallization of this isomer from ethyl acetate and then from methyl alcohol provided an analytical sample, m.p. 138–139.5°. Further concentration of the mother liquor yielded an additional 33.1 g. of IX as a mixture of isomers, m.p. 118–135°, making the total yield 73.3 g. (92%). Fractional crystallization of the mixture from ethyl acetate yielded an analytical sample of the B-isomer of IX, m.p. 139–140°, depression on admixture with the A-isomer.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found for A-isomer: C, 81.01; H, 6.74. Found for B-isomer: C, 80.83; H, 6.82.

3-Keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X).—Cyclization of 33.3 g. (0.125 mole) of crude β-(10-methyl-9,10-dihydro-9-anthranyl)-propionic acid (IX), m.p. 118–135°, was accomplished with 230 ml. of anhydrous hydrogen fluoride. The crude ketone was taken up in benzene and ether, washed with water and sodium carbonate solution, and dried by azeotropic distillation. The benzene solution was allowed to stand for two weeks and then was passed through an alumina column. Concentration of the eluates produced 23.8 g. (77%) of **3-keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X)** as a light red oil. Trituration of the oil with anhydrous ether yielded an oily solid which was crystallized from methyl alcohol providing 12.2 g. of the **A-isomer of X** as colorless needles, m.p. 104–107.5°. An analytical sample, m.p. 106–107.5°, was prepared by crystallization from methyl alcohol.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.54; H, 6.60.

The *p*-nitrophenylhydrazone of the A-isomer of X crystallized from benzene as small orange needles, m.p. 225.5–227° dec.

Anal. Calcd. for $C_{24}H_{21}O_2N_3$: C, 75.17; H, 5.52. Found: C, 74.96; H, 5.77.

The mother liquor remaining after isolation of the A-isomer was concentrated, the residue dissolved in benzene, and fractionally chromatographed on alumina. The in-

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

(16) All melting points are uncorrected.

itial fractions contained a small quantity of the B-isomer of X which after three crystallizations from methyl alcohol afforded an analytical sample as clusters of colorless needles, m.p. 156–157°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.18; H, 6.33.

The Stobbe Condensation with 3-Keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X).—To a solution of 0.43 g. (0.011 g.-atom) of potassium in 10 ml. of *t*-butyl alcohol, was added a mixture of 2.61 g. (0.015 mole) of diethyl succinate and 2.48 g. (0.010 mole) of the ketone X, m.p. 104.5–106.5°. After refluxing for 0.75 hr. the reaction mixture was cooled and hydrolyzed with 2 ml. of concentrated hydrochloric acid in 8 ml. of water. Ether and benzene were added and the organic layer was washed with water and extracted with dilute ammonium hydroxide solution. Acidification of the alkaline extracts yielded a purple semi-solid which was dissolved in benzene, washed with water, and dried by azeotropic distillation. The benzene solution was treated with Norit and concentrated, providing 3.2 g. (85%) of **β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI)** as a dark red oil.

In another experiment the crude half-ester XI was triturated with anhydrous ether providing a light purple solid which was crystallized from methyl alcohol and ethyl acetate providing an analytical sample of the half-ester XI as a mixture of isomers, m.p. 153–156° vac.

Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.58; H, 6.43. Found: C, 76.75; H, 6.58.

β-(7-Methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic Acid (XII).—The crude oily half-ester obtained above (3.2 g.) was decarbethoxylated by refluxing for 7.5 hr. with a mixture of 20 ml. of acetic acid, 10 ml. of concentrated hydrochloric acid and 15 ml. of water. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with water and extracted with sodium carbonate solution. Acidification of the carbonate extracts yielded 1.25 g. of a dark brown solid, m.p. 130–137°, which was dissolved in ethyl acetate, treated with Norit, and allowed to crystallize providing 0.92 g. (30% from X) of **β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XII)** as clusters of almost colorless needles, m.p. 140–145°. This acid gave an immediate reaction with bromine in carbon tetrachloride. An analytical sample, m.p. 147–148°, was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 83.24; H, 6.82.

Concentration of the ether layer remaining after extraction with sodium carbonate solution afforded 1.0 g. of a dark purple semi-solid which was dissolved in ethyl acetate, decolorized with Norit, and allowed to crystallize to give 0.30 g. (10% from X) of **lactone XIII** as colorless prisms, m.p. 166.5–167.5°. An analytical sample, m.p. 168.5–170°, was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 82.98; H, 6.86.

β-(7-Methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic Acid (XIV).—At atmospheric pressure, 2.40 g. (0.0079 mole) of β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XII), dissolved in 40 ml. of ethanol, was reduced in the presence of 0.1 g. of Adams catalyst. After 2.25 hr. at room temperature, when 95% of the theoretical amount of hydrogen had been taken up, the solution was filtered. Removal of the ethanol yielded **β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XIV)** as a viscous oil which solidified upon trituration with a mixture of methyl alcohol and cyclohexane. Crystallization of this material from methyl alcohol afforded an analytical sample of XIV as a mixture of isomers, m.p. 161–169°.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.31; H, 7.24. Found: C, 82.32; H, 7.22.

An attempt to prepare β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XIV) by reduction of the lactone XIII with phosphorus and iodine in glacial acetic acid failed to give the desired product. The dark granular solid which was obtained was crystallized four times from an ethyl acetate–benzene mixture providing an analytical sample of **β-(7-methyl-4,5-dihydro-6H-*meso*-benzanthrenyl-3)-propionic acid (XV)** as light yellow needles, m.p. 222.5–224.5° vac.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 82.62; H, 6.56.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectrum of β-(7-methyl-4,5-dihydro-6H-*meso*-benzanthrenyl-3)-propionic acid (XV) in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ε) values are: 262 mμ (4.77), 284 mμ (4.14), 294 mμ (4.01), 306 mμ (4.02), 329 mμ (3.21) and 342 mμ (3.24).

8-Keto-5-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (XVI).—Cyclization of 2.4 g. (0.0078 mole) of β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XIV) was accomplished with 25 ml. of anhydrous hydrogen fluoride. The crude ketone was taken up in benzene, washed with water, and extracted with sodium carbonate solution. Passage of the dried benzene solution through an alumina column and concentration of the benzene eluates yielded 2.0 g. (88%) of **8-keto-5-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (XVI)** as a yellow semi-solid. Crystallization from methyl alcohol and ethyl acetate provided an analytical sample of XVI as a mixture of isomers, m.p. 161–164°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 6.99. Found: C, 87.96; H, 7.17.

5,8-Dimethyl-3,4-benzpyrene (XVII).—A Grignard reagent was prepared in the usual manner from 0.96 g. (0.040 g.-atom) of magnesium and 6.1 g. (0.043 mole) of methyl iodide in 40 ml. of absolute ether. The oily ketone XVI, 1.75 g. (0.0061 mole), dissolved in 20 ml. of anhydrous benzene was added dropwise to the Grignard solution. After standing at room temperature for 0.5 hr. the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried by azeotropic distillation. Removal of the solvent left **8-hydroxy-5,8-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene** as a viscous oil.

The crude alcohol was dehydrated directly and dehydrogenated by heating with 0.25 g. of 10% palladium–charcoal at 285–345° for 1.5 hr. during which time about 65% of the theoretical amount of hydrogen was evolved. After cooling, the hard cake was dissolved in boiling benzene and the solution filtered to remove the catalyst. The solution of the crude hydrocarbon was chromatographed through an alumina column and concentration of the benzene eluates yielded 0.92 g. of **5,8-dimethyl-3,4-benzpyrene (XVII)** as small yellow needles, m.p. 239–239.5° vac. The material obtained by concentration of the mother liquor was crystallized from ethyl acetate providing an additional 0.05 g. of hydrocarbon, m.p. 239–239.5° vac., making the total yield 0.97 g. (57% from XVI).

This hydrocarbon was shown by mixed melting point determination to be identical with a dimethyl-3,4-benzpyrene, m.p. 239.5–240.5, prepared by Doyle[18] from 8-methyl-3,4-benzpyrene (XVIII) *via* formylation with N-methylformanilide and then Wolff–Kishner reduction of the aldehyde XIX.

Anal.[13] Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.71; H, 5.68.

The formylation of 8-methyl-3,4-benzpyrene (XVIII) was repeated using Doyle's procedure, and after reduction the crude product was extracted with boiling benzene. The benzene extracts were filtered, dried, and passed through an alumina column. Concentration of the benzene eluates yielded 3.20 g. of 5,8-dimethyl-3,4-benzpyrene (XVII), m.p. 245–245.5° vac., mixed m.p. with material prepared by Doyle gave no depression. The mother liquors provided an additional 0.64 g. of hydrocarbon, m.p. 242.5–243.5° vac., making the total yield 3.84 g. (61% from XVIII).

10-Carbethoxy-8-keto-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX).—Cyclization of 53 g. (0.14 mole) of crude β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI) obtained from 40.5 g. of the ketone X was accomplished with 400 ml. of anhydrous hydrogen fluoride. After allowing the reaction mixture to stand for 13 hr., water was added and the organic material was taken up in a mixture of ether and benzene. The organic layer was washed with water and extraction with sodium carbonate solution provided a large quantity of intractable acidic material. The benzene–ether solution

was dried by azeotropic distillation and passed through an alumina column. Concentration of the benzene eluates afforded 17.7 g. (35%) of **10-carbethoxy-8-keto-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX)** as a light red oil which did not solidify.

5,10-Dimethyl-3,4-benzpyrene (XXII).—A solution of 17.7 g. (0.0493 mole) of 10-carbethoxy-8-keto-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX), from above, in 100 ml. of anhydrous ether was added over a period of one hour at room temperature to 10 g. (0.26 mole) of lithium aluminum hydride suspended in 500 ml. of anhydrous ether. After refluxing for 2.75 hr. the reaction mixture was cooled and hydrolyzed with 35% sulfuric acid. Benzene was added and the organic layer was filtered, washed with water, and dried by azeotropic distillation. Concentration of the benzene solution afforded **8-hydroxy-10-hydroxymethyl-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XXI)** as a viscous oil.

The crude diol XXI was directly dehydrated and dehydrogenated by heating with 3.0 g. of 10% palladium–charcoal at 285–355° for 1.25 hr. After cooling, the hard cake was dissolved in boiling benzene and the solution was chromatographed through alumina, and the material obtained by concentration of the benzene eluates was crystallized three times from ethyl acetate producing 2.85 g. of **5,10-dimethyl-3,4-benzpyrene (XXII)** as minute yellow plates, m.p. 227.5–230° vac. The material remaining in the mother liquors was purified *via* the picrate providing an additional 0.80 g. of XXII, m.p. 228–230° vac., making the total yield 3.65 g. (26% from XX). An analytical sample, m.p. 229.5–231° vac., was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 93.73; H, 5.66.

The hydrocarbon XXII gave an unstable, purple picrate, m.p. 195–197°.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectrum of 5,10-dimethyl-3,4-benzpyrene (XXII) in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 258 mμ (4.57), 268 mμ (4.63), 290 mμ (4.55), 302 mμ (4.65), 378 mμ (4.38) and 398 mμ (4.47).

5,8,10-Trimethyl-3,4-benzpyrene (XXV).—A mixture containing 2.50 g. (0.0089 mole) of 8,10-dimethyl-3,4-benzpyrene (XXIII),[15] 2.55 g. (0.019 mole) of N-methylformanilide, 2.55 g. (0.017 mole) of phosphorus oxychloride and 10 ml. of *o*-dichlorobenzene was warmed on a steam-bath for 2.0 hr. The resulting red solution was cooled, treated with a solution of 17 g. of sodium acetate in 75 ml. of water, and steam distilled. The residual brown solid, **8,10-dimethyl-3,4-benzpyrene-5-aldehyde (XXIV)**, was filtered, washed with water, and dried. The crude aldehyde was added to 1.5 g. (0.054 mole) of 95% hydrazine, 2.0 g. of C.P. potassium hydroxide and 25 ml. of diethylene glycol. The resulting mixture was heated at 100–115° for 30 min. and then at 210–235° for an additional 90 min. The reaction mixture was allowed to cool and then was acidified with dilute hydrochloric acid. The resulting brown precipitate was filtered, washed with water, and extracted with boiling benzene. The benzene solution was filtered, dried, and passed through an alumina column. Concentration of the benzene eluates yielded 0.67 g. (26%) of **5,8,10-trimethyl-3,4-benzpyrene (XXV)** as light yellow plates, m.p. 289–291.5° vac. An analytical sample, m.p. 290–292° vac., was prepared by crystallization from benzene.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.92; H, 6.10.

Ultraviolet Absorption Spectrum.—The ultraviolet absorption spectrum of 5,8,10-trimethyl-3,4-benzpyrene (XXV) in 95% ethanol was measured with a model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 258 mμ (4.61), 270 mμ (4.63), 296 mμ (4.58), 308 mμ (4.73), 384 mμ (4.42) and 404 mμ (4.45).

ALBUQUERQUE, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. XII. The *o*-Tolyl/Phenyl Migration Ratios in the Pinacol Rearrangement and in the Deamination Reaction[1]

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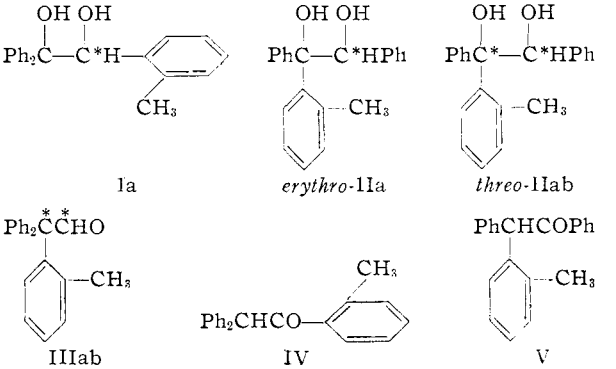
The rearrangements, in cold, concentrated sulfuric acid, of diphenyl-*o*-tolylacetaldehyde (III) and the associated glycols I and II have been studied by means of techniques similar to those previously[2] employed. The *o*-tolyl/phenyl migration ratio has been estimated to be about 3. The *o*-tolyl/phenyl migration ratio in the deamination of 2,2-diphenyl-2-*o*-tolylethyl-1-C^{14}-amine (VI) has been determined as 0.75. These results are explained, in the rearrangement of III, on the basis of open carbonium ion intermediates whose life-times are long enough so that the various conformational isomers are in equilibrium; thus *o*-tolyl group migration predominates over phenyl because of a greater electrical effect and because more steric strain is relieved as a result of tolyl migration. In the deamination of VI, however, it is postulated that the open cationic intermediates are short-lived, do not reach equilibrium with respect to their rotational isomers, and thus phenyl migration predominates over *o*-tolyl migration because conformations VI-1 and VI-2 are sterically more compatible than conformation VI-3.

Introduction and Results

By an application of the same radiochemical techniques previously applied[2] to the acid-catalyzed rearrangements of triphenylethylene glycol,[2a] and closely related trisubstituted glycols and aldehydes,[2b] we have now studied the rearrangements in cold, concentrated sulfuric acid of compounds I, II and III to the ketones IV and V. This series of compounds[3] was selected in order that we might compare the *o*-tolyl/phenyl migration ratio in the aldehyde–ketone rearrangement of III with that



(1) This paper is based upon work performed at Oak Ridge National Laboratory which is operated for the Atomic Energy Commission by Union Carbide Nuclear Co.

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