

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

The Synthesis of 10-Methyl-3,4-benzopyrene and 8,10-Dimethyl-3,4-benzopyrene¹⁻³BY JULES L. ADELFGANG⁴ AND GUIDO H. DAUB

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The Reformatsky reaction with 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV) followed by chain lengthening *via* the Arndt-Eistert synthesis yielded β -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-butyric acid (IX) which upon cyclization gave 8-keto-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzopyrene (X). The ketone (X) was reduced by the Meerwein-Ponndorf method or methylated with methylmagnesium iodide producing carbinols which were dehydrated and dehydrogenated to 10-methyl-3,4-benzopyrene (XI) and 8,10-dimethyl-3,4-benzopyrene (XII), respectively. The over-all yield of each hydrocarbon from anthrone was approximately 9%. The new 3,4-benzopyrenes gave ultraviolet absorption spectra similar to the parent hydrocarbon, 3,4-benzopyrene. Samples of these new hydrocarbons are being evaluated for carcinogenic activity at the Northwestern University Medical School, Evanston, Ill.

Nine of the possible twelve monomethyl-3,4-benzopyrenes, namely, the 1',^{5a,5b} 2',^{5a,5c} 3',^{5a,5c} 4',^{5d} 2-^{5e} 5-^{5f} 6-^{5f} 8-^{5g} and 9-^{5h} methyl-3,4-benzopyrenes, have been previously reported.

This paper reports the synthesis of a tenth isomer, 10-methyl-3,4-benzopyrene (XI), as well as a new dimethyl derivative, 8,10-dimethyl-3,4-benzopyrene (XII) from readily available anthrone (I). Anthrone (I) was converted to β -(9,10-dihydro-9-anthryl)-propionic acid (III) in 60% over-all yield using the procedures described by Daub and Doyle.⁶ Cyclization of the acid III with anhydrous hydrogen fluoride afforded an 87% yield of 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV) previously reported by Cook, Ludwiczak and Schoental.⁷

The hydroxy ester formed by the Reformatsky reaction of the ketone IV with ethyl α -bromopropionate was dehydrated with anhydrous formic acid and then hydrolyzed with dilute alkali to give α -(1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (V) in 77% over-all yield from the ketone IV. Another acid, probably α -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrylidene-3)-propionic acid (VI) was also isolated but in small quantities (less than 2% yield). Attempts to prove the position of the double bonds in the two isomeric unsaturated acids by oxidation experiments with potassium permanganate or ozonolysis failed to give identifiable products.

The ultraviolet absorption spectra of the two unsaturated acids were measured and comparison of the curves with that of the known β -(1-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (VII)⁸ showed the more abundant isomer to contain

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(2) This work was supported in part by a grant 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 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 30-April 7, 1955.

(4) Graduate Research Assistant, February, 1954, to August, 1954.

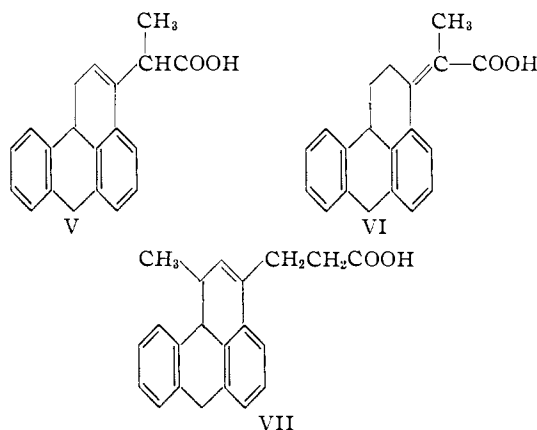
(5) (a) W. E. Bachmann and M. Carmack, *THIS JOURNAL*, **63**, 2494 (1941); (b) G. A. R. Kon and E. M. F. Roe, *J. Chem. Soc.*, 143 (1945); (c) L. F. Fieser and E. B. Hershberg, *THIS JOURNAL*, **60**, 1658 (1938); (d) L. F. Fieser and M. Fieser, *ibid.*, **67**, 782 (1935); (e) L. F. Fieser and H. Heyman, *ibid.*, **63**, 2333 (1941); (f) L. F. Fieser and E. B. Hershberg, *ibid.*, **60**, 2542 (1938); (g) J. M. L. Cameron, J. W. Cook, and R. Schoental, *J. Chem. Soc.*, 257 (1952); (h) L. F. Fieser and F. C. Novello, *THIS JOURNAL*, **62**, 1855 (1940).

(6) G. H. Daub and W. C. Doyle, *ibid.*, **74**, 4449 (1952).

(7) J. W. Cook, R. S. Ludwiczak and R. Schoental, *J. Chem. Soc.*, 1112 (1950).

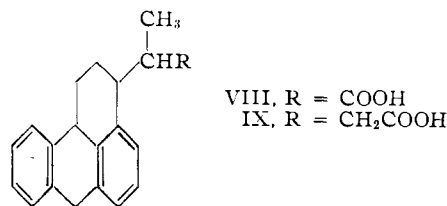
(8) J. W. Patton, Masters Thesis, University of New Mexico, 1954.

the endocyclic double bond (V) with the isomer obtained in low yield probably having the exocyclic double bond (VI).



Attempts were made first to lengthen the chain of the unsaturated acid V using the Arndt-Eistert synthesis. Attempted rearrangement of what was probably the unsaturated diazoketone by prescribed methods⁹⁻¹¹ failed to give tractable acidic material.

Catalytic hydrogenation of the unsaturated acid V over Adams catalyst at atmospheric pressure yielded α -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (VIII) as a highly viscous oil. The acid chloride of VIII prepared from the acid with phosphorus trichloride was allowed to react with an excess of diazomethane and the resulting diazoketone was rearranged in the presence of 95% ethanol and silver oxide.¹⁰ Alkaline hydrolysis of the ethyl ester formed in the rearrangement gave β -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-butyric acid (IX) in an over-all yield of 78% from the unsaturated acid V. This basic hydrolysis was complete in one hour, indicating that the hindering α -methyl group was not present in



(9) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

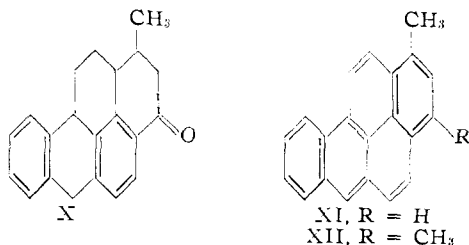
(10) M. S. Newman and A. S. Hussey, *THIS JOURNAL*, **69**, 3023 (1947).

(11) A. L. Wilds and A. L. Mender, *J. Org. Chem.*, **13**, 763 (1948).

the acid IX and the Arndt-Eistert synthesis had been successful. Complete saponification of the unsaturated ester from the Reformatsky reaction in which an α -methyl group was present required 32 hours.

Cyclization of the acid IX with anhydrous hydrogen fluoride afforded 8-keto-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (X) as a mixture of stereoisomers in 82% yield.

Preparation of 10-methyl-3,4-benzpyrene (XI) was accomplished by reduction of the ketone X with aluminum isopropoxide in isopropyl alcohol, to 8-hydroxy-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene which was directly dehydrated and dehydrogenated over palladium-charcoal at 280–315°. The hydrocarbon XI was obtained in 46% over-all yield from the ketone X and formed a dark purple picrate derivative.



Reaction of the ketone X with methylmagnesium iodide gave 8-hydroxy-8,10-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene which was dehydrated and dehydrogenated over a palladium-charcoal catalyst at 300–325°, affording 8,10-dimethyl-3,4-benzpyrene (XII) in 37% over-all yield. The hydrocarbon XII formed a dark brown picrate derivative which could not be obtained analytically pure due to the very low solubility of the parent hydrocarbon.

The ultraviolet absorption curves for 10-methyl-3,4-benzpyrene (XI) and 8,10-dimethyl-3,4-benzpyrene (XII), shown in Fig. 1 with the curve for 3,4-benzpyrene,¹² substantiate the presence of the parent ring system in these new hydrocarbons.

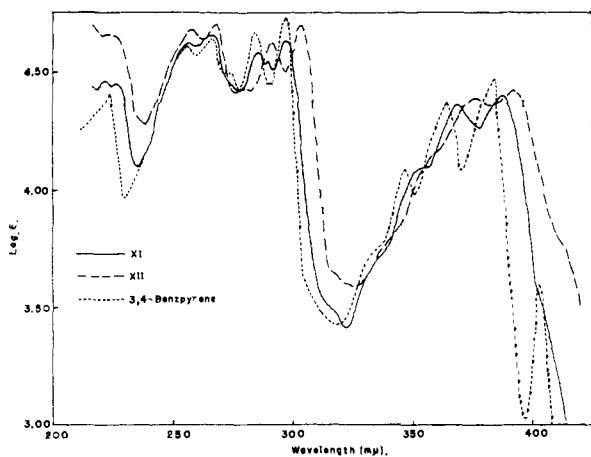


Fig. 1.—The ultraviolet absorption spectra of 3,4-benzpyrene, 10-methyl-3,4-benzpyrene (XI) and 8,10-dimethyl-3,4-benzpyrene (XII).

(12) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, No. 554.

Samples of these hydrocarbons are being tested for carcinogenic activity at Northwestern University Medical School under the direction of Dr. D. Warren Stanger.

Experimental¹³

β -(9,10-Dihydro-9-anthranyl)-propionic Acid (III).—According to a procedure previously described⁶ 58.3 g. (0.3 mole) of anthrone (I) was converted to 66.5 g. (87.5% yield) of β -(9-anthranyl)-propionic acid (II), m.p. 189–193°, reported m.p. 190–193°. Reduction of this acid with sodium and *n*-amyl alcohol gave 51.0 g. (76% yield) of β -(9,10-dihydro-9-anthranyl)-propionic acid (III), m.p. 138–140°, reported m.p. 139–140°.

3-Keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV).—Cyclization of 62.5 g. (0.252 mole) of III with 440 ml. of anhydrous hydrogen fluoride was carried out in a polyethylene beaker. After standing for two hours the excess hydrogen fluoride was removed with a stream of nitrogen and the reaction mixture was poured on crushed ice. The crude ketone was taken up in benzene and washed with water. Several extractions with aqueous sodium bicarbonate solution yielded no uncyclized acid. After drying over anhydrous sodium sulfate the benzene solution was passed through an alumina column. The benzene elutions were concentrated to 100 ml. and upon addition of an equal volume of petroleum ether (b.p. 70–90°) 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV) crystallized as bright yellow needles, m.p. 129.5–130.5°, reported⁷ m.p. 131–132°, 51.6 g. (87% yield). On standing for several months samples of the ketone became discolored and could be purified by recrystallization from 95% alcohol with good recovery.

The Reformatsky Reaction on 3-Keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (IV).—Forty grams (0.17 mole) of the ketone IV was dissolved in an anhydrous mixture of 600 ml. of C.P. benzene and 600 ml. of C.P. ether in a two-liter three necked flask equipped with ground glass joints, fitted with a mercury sealed Hershberg stirrer, a condenser fitted with a drying tube, and a glass stopper. Initially the apparatus had been flame-dried and swept with nitrogen. After the addition of 100 g. of amalgamated zinc,¹⁴ 28 ml. of ethyl α -bromopropionate (Eastman Kodak Co. 1041), and a trace of iodine, the mixture was refluxed for two days. An additional 100 g. of amalgamated zinc and 28 ml. of ethyl α -bromopropionate were added after 17 hours. The dark complex coated the sides of the flask and caked the zinc during the second day. After standing at room temperature for two days the reaction mixture was hydrolyzed with a solution of 20 ml. of concentrated hydrochloric acid in 200 ml. of water. The organic layer was washed with water and sodium bicarbonate solution and dried over anhydrous sodium sulfate. Removal of the benzene-ether mixture under reduced pressure left a light red oil which was dehydrated with 240 ml. of anhydrous formic acid by warming on a steam-bath for 15 minutes. The formic acid was removed under reduced pressure and the remaining oil was refluxed for 32 hours with 56 g. of sodium hydroxide in 1400 ml. of water. The alkaline solution was filtered, extracted with a mixture of ether and benzene, and acidified yielding 46.5 g. (96% yield) of crude acidic material as a pink granular solid, m.p. 143–148°. The benzene-ether extracts gave 0.75 g. of recovered crude ketone (IV). Two crystallizations of the crude acid from ethyl acetate afforded 28.0 g. of α -(1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (V), m.p. 151.5–153°. An additional 9.5 g. of the acid V, m.p. 148–153°, was obtained from the mother liquors to make the total yield 37.5 g. (77%). Repeated crystallization from ethyl acetate gave an analytical sample as almost colorless crystals, m.p. 151.5–153°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_2$: C, 82.74; H, 6.25; neut. equiv., 290. Found: C, 82.34; H, 6.20; neut. equiv., 287.

The methyl ester of V was prepared with diazomethane. Crystallization from methanol gave methyl α -(1,11b-di-

(13) All melting points are uncorrected.

(14) Twenty mesh zinc (J. T. Baker C.P.) was amalgamated by the method described by Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 598. The freshly amalgamated zinc was washed with acetone and benzene and stored under benzene before use.

hydro-7H-*meso*-benzanthrenyl-3)-propionate as colorless needles, m.p. 91.5–92.5°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: C, 83.09; H, 6.54.

The mother liquors from the isolation of the acid V afforded a second acid (0.65 g.), probably α -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrylidene-3)-propionic acid (VI), m.p. 173–176°. An analytical sample was obtained, by repeated recrystallization from ethyl acetate, as hard irregular pellets, m.p. 177–178.5°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.74; H, 6.25; neut. equiv., 290. Found: C, 82.50; H, 6.07; neut. equiv., 288.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the acids V and VI in 95% ethanol were measured with a Model DU Beckman spectrophotometer. Maxima and ($\log \epsilon$) values are: α -(1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (V), 265 $m\mu$ (3.90); α -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrylidene-3)-propionic acid (VI), 259 $m\mu$ (3.95), 334 $m\mu$ (3.68), and 349 $m\mu$ (3.80).

α -(1,2,3,11b-Tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic Acid (VIII).—At atmospheric pressure, 10.15 g. (0.035 mole) of α -1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (V), dissolved in 125 ml. of ethanol, was reduced in the presence of 0.1 g. of Adams catalyst. After 25 hours, at room temperature, when 90% of the theoretical amount of hydrogen had been taken up, the solution was filtered and the ethanol removed under reduced pressure. Last traces of ethanol were removed by the addition of benzene followed by further distillation. The highly viscous oil remaining, α -1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid (VIII), was a mixture of isomers which could not be crystallized.

β -(1,2,3,11b-Tetrahydro-7H-*meso*-benzanthrenyl-3)-butyric Acid (IX).—The crude reduced acid VIII from above was dissolved in 85 ml. of anhydrous C.P. benzene and refluxed for two hours with 2.2 ml. (0.025 mole) of phosphorus trichloride (J. T. Baker, C.P.). The solution of the acid chloride was filtered and the benzene and excess phosphorus trichloride were removed under reduced pressure.

Diazomethane was prepared as described by Arndt¹⁵ in an all glass distilling apparatus fitted with two traps cooled to 0°, each containing 45 ml. of anhydrous ether. To the distilling flask containing 80 ml. of 50% potassium hydroxide and 270 ml. of ether, 25 g. of nitrosomethylurea was added. The mixture was swirled and the diazomethane formed was distilled with the ether. The expected yield of diazomethane was 6.5 g. (0.15 mole). Before use, the ether solution of diazomethane was dried over C.P. potassium hydroxide pellets for two hours at 0°.

The acid chloride prepared above was dissolved in C.P. anhydrous benzene and added dropwise to the cold diazomethane solution. Evolution of nitrogen began immediately and continued for about one-half hour. After the reaction mixture was allowed to stand at room temperature for 45 minutes the ether was removed under reduced pressure. The remaining highly viscous, yellow diazoketone was dissolved in 150 ml. of 95% ethanol and at 65–70° was treated with 1.5 g. of freshly precipitated silver oxide over a period of two hours. The copious evolution of nitrogen ceased after one and three-quarters hours. The resulting ethanol solution of ethyl β -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-butyrate was treated with norit and passed through an alumina column. The ethanol was removed under reduced pressure and the red oily ester was refluxed for one hour with 175 ml. of 5% sodium hydroxide solution. After one-half hour the insoluble sodium salt precipitated as a gummy mass. The salt was dissolved in hot water and acidification yielded a red oil which was taken up in ether and treated with norit. The ether solution was dried over anhydrous sodium sulfate and removal of the solvent yielded 8.4 g. (78% yield from V) of β -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-butyric acid (IX) as a light red oil.

8-Keto-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzopyrene (X).—Cyclization of 2.6 g. (0.0090 mole) of crude β -(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-butyric acid (IX) was accomplished with 30 ml. of anhydrous hydrogen fluoride. A benzene solution of the crude ketone was passed through an alumina column. Concentration of

the benzene eluants yielded 2.0 g. (82%) of 8-keto-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzopyrene (X) as a light yellow oil. Trituration of this oil with ether gave a solid which was crystallized from methanol giving the ketone X as a mixture of isomers, m.p. 140–155°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 6.99. Found: C, 87.28; H, 7.01.

A sample of the mixture of isomeric ketones was converted to the 2,4-dinitrophenylhydrazones. Crystallization twice from acetone gave a mixture of bright red needles and dark red star-like crystals which had a diffuse melting point range higher than 220° accompanied by decomposition.

Anal. Calcd. for $C_{27}H_{24}O_4N_4$: C, 69.22; H, 5.16. Found: C, 69.22; H, 5.35.

10-Methyl-3,4-benzopyrene (XI).—Reduction of 3.75 g. (0.013 mole) of the oily ketone X was carried out with 6.1 g. (0.038 mole) of aluminum isopropoxide and 150 ml. of anhydrous isopropyl alcohol in a 250-ml. round bottom flask fitted with a Hahn condenser.¹⁶ After 11 hours of slow distillation the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent and the remainder of the isopropyl alcohol was removed under reduced pressure. The reaction mixture then was treated with 20 ml. of concentrated hydrochloric acid in 80 ml. of water and the yellow oil was taken up in benzene and washed with water. The benzene solution was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure leaving 8-hydroxy-10-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzopyrene as a viscous oil.

The crude alcohol was dehydrated and dehydrogenated over 0.38 g. of 10% palladium-charcoal in an apparatus suggested by Fieser.¹⁷ The reaction was carried out in a carbon dioxide atmosphere and the hydrogen evolved was measured in a gas buret protected by an alkali trap. After about one-half hour at 280–315°, 55% of the theoretical amount of hydrogen was given off. After cooling, the hard cake was pulverized in a mortar, dissolved in benzene, and the solution filtered. The benzene solution was twice chromatographed through alumina and concentration of the eluants yielded 1.7 g. of 10-methyl-3,4-benzopyrene (XI), m.p. 170–175°. Recrystallization from benzene-ethanol yielded 1.2 g. of minute yellow needles, m.p. 177–178°. Chromatography and crystallization of the combined mother liquors from benzene-methanol yielded an additional 0.4 g., m.p. 178–178.5°, making the total yield of 10-methyl-3,4-benzopyrene (XI) 1.6 g. (46% yield from X). An analytical sample prepared by crystallization from ethanol was obtained as small yellow needles, m.p. 178–178.5°.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.75; H, 5.23.

A picrate of XI was prepared using a saturated solution of picric acid in absolute ethanol. Crystallization of the picrate from benzene yielded dark purple needles, m.p. 179.5–180.5°.

Anal. Calcd. for $C_{27}H_{17}O_7N_3$: C, 65.45; H, 3.46. Found: C, 65.41; H, 3.09.

8,10-Dimethyl-3,4-benzopyrene (XII).—A Grignard reagent was prepared in the usual manner from 1.02 g. (0.042 mole) of magnesium and 6.4 g. (0.045 mole) of methyl iodide in 40 ml. of absolute ether. The oily ketone X, 4.05 g. (0.014 mole), dissolved in 30 ml. of ether and 20 ml. of benzene was added dropwise to the Grignard solution. After standing at room temperature for one hour the reaction mixture was hydrolyzed with 10 ml. of concentrated hydrochloric acid in 40 ml. of water. The organic layer was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent left 8-hydroxy-8,10-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzopyrene as a viscous yellow oil.

The crude alcohol was dehydrated and dehydrogenated by heating with 0.4 g. of 10% palladium-charcoal at 300–325° for one-half hour during which time 60% of the theoretical amount of hydrogen was evolved. After cooling, the hard cake was pulverized in a mortar, dissolved in a large volume of boiling benzene, and the solution filtered to remove the catalyst. The crude hydrocarbon was chromatographed through an alumina column and concentration

(16) A. L. Wilds, "Organic Reactions," Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

(17) L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 462.

(15) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 165.

of the eluants yielded 1.8 g. of 8,10-dimethyl-3,4-benzpyrene (XII) as small yellow plates, m.p. 235–238° dec., m.p. 238–240° *in vacuo*. Recrystallization from benzene followed by sublimation at 200–210° and 0.5–1.0 mm. yielded 1.2 g. of hydrocarbon, m.p. 240.5–241.5° *in vacuo*. An additional 0.25 g., m.p. 240.5–241.5° *in vacuo*, was obtained by similar treatment of the mother liquors. The total yield of purified material was 1.45 g. (37% from X).

Anal. Calcd. for C₂₂H₁₆: C, 94.25; H, 5.75. Found: C, 94.15; H, 5.67.

A picrate was prepared using a saturated solution of picric acid in benzene. Repeated recrystallization of the picrate from benzene yielded dark brown needles, m.p. 202.5–

203.5°. Analysis did not give the expected values due to contamination of the picrate samples with the highly insoluble hydrocarbon.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of 10-methyl- and 8,10-dimethyl-3,4-benzpyrene in 95% ethanol were measured with a Model DU Beckman spectrophotometer (see Fig. 1). Maxima and (log ϵ) values are: 10-methyl-3,4-benzpyrene (XI), 256 m μ (4.62), 266 m μ (4.69), 286 m μ (4.58), 297 m μ (4.64), 369 m μ (4.36), and 387 m μ (4.40); 8,10-dimethyl-3,4-benzpyrene (XII), 257 m μ (4.68), 268 m μ (4.70), 290 m μ (4.62), 304 m μ (4.69), 376 m μ (4.39) and 392 m μ (4.42).

ALBUQUERQUE, NEW MEXICO

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

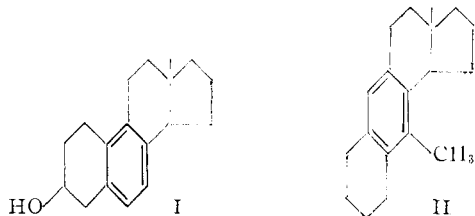
The Spectral Characterization of Benzenoid Systems Derivable from $\Delta^{5,7}$ -Steroids

BY IRVING SCHEER, WILLIAM R. NES AND PHYLLIS B. SMELTZER

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The neosteroids (I) and the anthrasteroids (II) which possess, respectively, a tetrasubstituted benzenoid ring with angular annulation and a pentasubstituted benzenoid ring with linear annulation have been characterized by their absorption in the spectral regions from 220–400 m μ , 1630–1565 cm.⁻¹, and 900–720 cm.⁻¹. Differentiation of the two classes of compounds is possible in either the infrared or ultraviolet region. The spectra of some related aromatic compounds are discussed.

In the course of aromatization studies in this Laboratory, two types of rearrangement products have been obtained.^{1,2} Thus, photodehydrogenation and subsequent pyrolysis of steroidal $\Delta^{5,7}$ -dienes or $\Delta^{5,7,9(11)}$ -trienes³ yields neosteroids (I), while acid-catalyzed rearrangement of $\Delta^{5,7,9(11)}$ -trienes yields anthrasteroids (II).⁴ Although some



spectral data for such systems are recorded in the literature,⁵ we undertook a study of the spectral properties of a number of anthrasteroids, neosteroids and other benzenoid compounds in the infrared and ultraviolet regions in order to determine whether these compounds had definite and differential characteristics. This indeed has been found to be the case.

Results and Discussion

A. Infrared Absorption Spectra. The 900–720 Cm.⁻¹ Region.—It is known^{6,7} that the out-of-plane deformation vibrations of the C–H bands of an aromatic nucleus absorb with moderate to strong intensity in the 900–650 cm.⁻¹ region. Orr and Thompson⁶ reported that the strong band at 810–800 cm.⁻¹ exhibited by polycyclic aromatic com-

pounds such as phenanthrene can be attributed to the 1,2,3,4-tetrasubstituted ring, and they have predicted that simple (*i.e.*, with only one aromatic ring) 1,2,3,4-tetrasubstituted benzene derivatives also would exhibit a strong band close to this value. We have found that the neosteroids (steroids with an aromatic B-ring) in fact do exhibit a single sharp band of moderate to strong intensity at 812–803 cm.⁻¹ (Fig. 1), thus confirming this prediction.⁸ Compounds of this type without the D-ring, such as *sym*-octahydrophenanthrene, also exhibit a strong band in this region, although it is shifted to 795 cm.⁻¹. However, the results, as shown in Table I, reveal that this absorption is *not* exclusively characteristic of the 1,2,3,4-tetrasubstituted benzene derivatives, for the anthrasteroids (II) which have a double bond conjugated with the aromatic ring show a strong band in this region at 813–812 cm.⁻¹ (Fig. 2). Steroids with an aromatic A-ring or with aromatic A/B-rings also exhibit a sharp band of moderate to strong intensity at 819–803 cm.⁻¹.⁹ The band near 810 cm.⁻¹ for the neosteroids, for the anthrasteroids with a double bond in conjugation with the aromatic ring, and for compounds like *sym*-octahydrophenanthrene is by far the strongest one (*ca.* 60% absorption for 15 mg./ml. in a 1-mm. cell) in the 900–720 cm.⁻¹ region (Figs. 1, 2), while the band near 810 cm.⁻¹ for the aromatic A-ring and aromatic A/B ring compounds is not always the strongest in this region (Fig. 3).

The compounds which contain a pentasubstituted aromatic ring, *e.g.*, the anthrasteroids, exhibit a band of weak to moderate intensity at 869–859 cm.⁻¹.¹⁰ The strong absorption near 810 cm.⁻¹ is not exhibited, however, by those compounds, such

(1) E. Mosettig and I. Scheer, *J. Org. Chem.*, **17**, 764 (1952).

(2) (a) W. R. Nes and E. Mosettig, *THIS JOURNAL*, **76**, 3182 (1954); (b) **76**, 3186 (1954).

(3) A. Windaus and C. Roosen-Runge, *Ber.*, **73**, 321 (1940).

(4) An alternate formula for the anthrasteroids is equally possible but it does not alter the substitution on the aromatic ring (ref. 2a.)

(5) See ensuing discussion for references.

(6) S. F. D. Orr and H. W. Thompson, *J. Chem. Soc.*, **218** (1950), and references cited therein.

(7) C. G. Cannon and G. B. B. M. Sutherland, *Spectrochimica Acta*, **4**, 371 (1951), and references cited therein.

(8) Recently P. J. Launer and D. A. McCauley (*Anal. Chem.*, **23**, 1875 (1951)) have shown that 1,2,3,4-tetramethylbenzene likewise exhibits a band in this region as predicted.

(9) The acetates of the aromatic A-ring compounds exhibit a doublet of weak to moderate intensity at 822–813 cm.⁻¹.

(10) C. G. Cannon and G. B. B. M. Sutherland (ref. 6) have attributed this band to a pentasubstituted aromatic ring.