reduced in the manner described and the crude alcohol (obtained by pouring the mixture into dilute hydrochloric acid, filtering and washing the solid with water and with ammonium hydroxide) without purification was heated with 0.2 g. of palladium–charcoal catalyst[11] in a large test-tube in an atmosphere of nitrogen at 310–320° for one and one-half hours. The material which had sublimed up along the sides of the tube was washed down with benzene, the solvent was evaporated and heating was continued for an additional two hours.

The product was separated from the catalyst by means of hot benzene, the solution was passed through a tower of alumina, the solvent was removed under reduced pressure and the 3,4-benzpyrene was recrystallized from benzene–methanol. The first two crops (1.55 g.) were combined and evaporatively distilled at 200–210° at 0.01 mm.; this left behind a trace of high-melting impurity. The product was dissolved in hot acetone, an equal volume of *n*-propyl alcohol was added and the solution was concentrated to incipient crystallization. On cooling, the 3,4-benzpyrene crystallized in large, thin sheets, which began to change to long, pale-yellow needles after a short time; the complete change required an hour or two. The first crop (1.43 g.) melted at 177.5–178.5° cor. (vac.) with slight previous softening and remelted at 178–179°; the second crop (0.05 g.) melted at 175–176° cor.; total yield, 80%. A slightly higher yield of the hydrocarbon was obtained when recrystallized secondary alcohol was used.

A sample was purified further by making and recrystallizing the picrate, and passing the regenerated hydrocarbon through alumina; after recrystallization it melted at 178.6–179.8° cor. (vac.) with slight previous softening and remelted at 179–180° cor. (highest previously recorded value, 178.8–179.3° cor.[12]).

Summary

A procedure has been devised for reducing β-3-pyrenoylpropionic acid to γ-3-pyrenylbutyric acid by the Clemmensen method.

A new procedure for obtaining the carcinogenic hydrocarbon 3,4-benzpyrene from 4'-ketotetrahydrobenzpyrene in good yield is described. The cyclic ketone is reduced to the corresponding alcohol by means of aluminum isopropoxide and the alcohol is dehydrated and dehydrogenated to the hydrocarbon by palladium on charcoal.

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[11] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[12] Fieser and Newman, THIS JOURNAL, **57**, 1602 (1935).

ANN ARBOR, MICHIGAN RECEIVED JANUARY 15, 1941

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

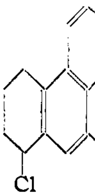
4',5-Dimethylene-3,4-benzpyrene

BY W. E. BACHMANN AND MARVIN CARMACK[1]

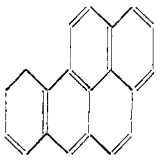
The polycyclic hydrocarbon 4',5-dimethylene-3,4-benzpyrene (VI) is of particular interest in that it combines in one molecule the structural features of the two powerful carcinogens 3,4-benzpyrene and cholanthrene. We were interested in determining whether this compound would surpass its two prototypes in carcinogenic activity.

For its synthesis 4'-chlorotetrahydrobenzpyrene (I) was converted to 4'-tetrahydrobenzpyrenylacetic acid (III) through the malonic ester synthesis, and the acid was cyclized in practically quantitative yield to the ketone IV. A by-product in the malonic ester reaction was 1',2'-dihydro-3,4-benzpyrene (II), which was formed by elimination of the elements of hydrogen chloride from the chloride I. This hydrocarbon was prepared also by heating the chloride with pyridine. As was expected, the dihydro derivative was easily dehydrogenated by palladium to 3,4-benzpyrene.

After a number of unsuccessful trials to reduce the cyclic ketone (IV) by the Clemmensen method and by the Wolff–Kishner reaction, the following method was evolved for obtaining the desired hydrocarbon. The ketone was reduced by means of aluminum isopropoxide and the resulting alcohol was dehydrated to a yellow hydrocarbon to which the structure V is assigned. When this hydrocarbon was heated with palladium on charcoal, it lost hydrogen and was converted to the beautifully crystalline orange colored 4',5-dimethylene-3,4-benzpyrene (VI).



I



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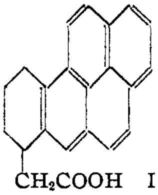
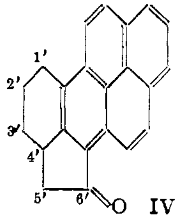


III



IV

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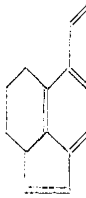
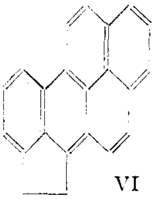
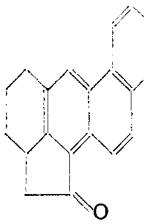
[1] From the Ph.D. dissertation of Marvin Carmack.



V



VI



VII

During the treatment with palladium the double bond in the cyclopentene ring became reduced, a reaction for which there is precedent in the behavior during dehydrogenation of hydroaromatic compounds containing an exocyclic double bond.[2] Further confirmation of the correctness of the structure of the new hydrocarbon was obtained by carrying out the same series of reactions on 1-keto-tetrahydrocholanthrene (VII), whereby cholanthrene was obtained as the final product.

The curve for the absorption spectrum of 4′,5-dimethylene-3,4-benzpyrene in ether is shown in Fig. 1 along with the curve for 3,4-benzpyrene in alcohol as determined by Mayneord and Roe.[3]

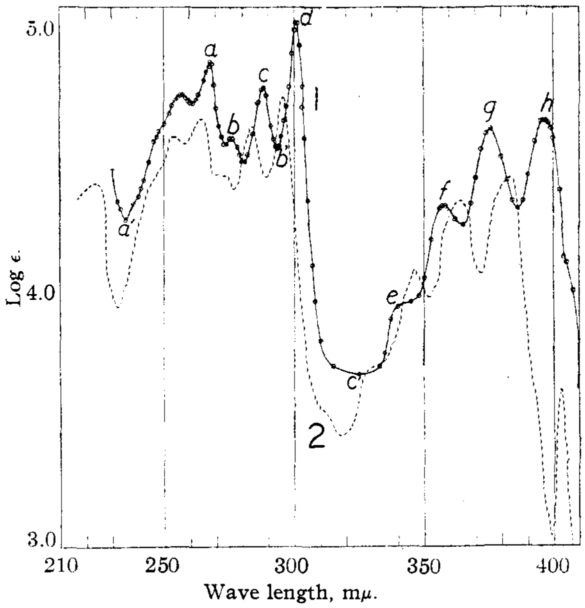


Fig. 1.—Curve 1, 4′,5-dimethylene-3,4-benzpyrene; curve 2, 3,4-benzpyrene.

Following the procedure of Fieser and Hershberg,[4] we have marked significant inflections in the curve by means of letters and have recorded the wave lengths of these points in Table I. The values for 3,4-benzpyrene are subject to a slight error since they were estimated from the published smooth curve of Mayneord and Roe.

Table I

Comparison of Absorption Characteristics

Maxima and minima	4′,5-Dimethylene-3,4-benzpyrene λ, mμ	3,4-Benzpyrene[3] λ, mμ
a′	235	232
a	267.5	264
b	275.5	272[a]
c	288	284
b′	293.5	289
d	300.7	295.5
c′	325	319
e	342[a]	331[a]
f	357.5	346
g	376	364
h	396	384

[a] Point of inflection.

From the curves and the table it is apparent that the absorption spectrum of 4′,5-dimethylene-3,4-benzpyrene is very similar to that of 3,4-benzpyrene and that there is a general shift throughout toward the region of longer wave length. The shift in the near ultraviolet is more pronounced than that in the region of short wave length, being about 110–120 Å. for peaks e, f, g, and h, and only 35–50 Å. for peaks a, b, c and d. Although the values of log ε appeared to be slightly higher than for 3,4-benzpyrene, the difference may not be significant; one reason for this is the fact that the measurements were made in different solvents.

This bathochromic shift of the spectrum of 4′,5-dimethylene-3,4-benzpyrene is of interest in connection with the tests for carcinogenic activity which are being carried out on the hydrocarbon. Jones[5] has observed that "some correlation can be traced between the carcinogenic activity and the bathochromic shift of band D" (of which d is the maximum) of various derivatives of 1,2-benzanthracene. Thus, the d peak of the carcinogen cholanthrene (2950 Å.) is shifted 80 Å. to the long wave region with reference to the corresponding band of 1,2-benzanthracene (2870 Å.), and in 3,4-benzpyrene there is a shift of 85 Å., although this hydrocarbon was included in the comparison with

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(2) Compare Bachmann and Wilds, This Journal, **60**, 624 (1938); Bachmann and Chemerda, *ibid.*, **61**, 2358 (1939).

(3) Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).

(4) Fieser and Hershberg, This Journal, **60**, 940 (1938).

(5) Jones, *ibid.*, **62**, 148 (1940).

some reservation since its spectrum differs from that of 1,2-benzanthracene in the long wave part. In 4',5-dimethylene-3,4-benzpyrene the peak d is located at 3007 Å., corresponding to a shift of 137 Å., which is greater than the shift in the spectrum of cholanthrene and of 3,4-benzpyrene. The hydrocarbon 1',2'-dihydro-3,4-benzpyrene is also being tested for carcinogenic activity.

Experimental

4'-Chloro-1',2',3',4'-tetrahydro-3,4-benzpyrene (I).—Dry hydrogen chloride was passed through a suspension of 7 g. of 4'-hydroxy-1',2',3',4'-tetrahydro-3,4-benzpyrene[6] in 35 cc. of dry benzene at room temperature for thirty-five minutes. The needle-like crystals of the alcohol change rapidly to fine rhombic crystals of the chloride. After the addition of 10 cc. of petroleum ether, the mixture was cooled and the crystals were filtered off; yield, 7.04 g. (94%); m. p. 145°, dec., when placed in a bath at 140°. The product so obtained was used immediately in the next step without further purification since the chloride decomposes readily. A sample after two recrystallizations from benzene formed pale-yellow rhombic crystals; m. p. 150° (cor.), dec.

Anal. Calcd. for $C_{20}H_{15}Cl$: C, 82.6; H, 5.2. Found: C, 82.6; H, 5.5.

4'-(1',2',3',4'-Tetrahydro-3,4-benzpyrenyl)-acetic Acid (III).—To the sodio-malonic ester prepared from 2 g. of powdered sodium and 17.5 cc. of malonic ester in 50 cc. of benzene was added 7.7 g. of the aforementioned chloride and 25 cc. of benzene. The mixture was warmed gradually with continuous swirling and then refluxed on a steam-bath for fourteen hours. The benzene was evaporated in a current of air and the ester was hydrolyzed by heating it with 40 cc. of 40% aqueous potassium hydroxide on a steam-bath for two hours. Water was added to dissolve the crystalline salt which had separated, the solution was filtered from a small amount (0.2–0.3 g.) of crystalline 1',2'-dihydro-3,4-benzpyrene (II), and the filtrate was poured into dilute hydrochloric acid. The practically colorless substituted malonic acid weighed 8.8 g. (93%).

Five grams of the product was decarboxylated at 190–200° and the tetrahydrobenzpyrenylacetic acid was recrystallized from a mixture of benzene and acetic acid, from which it separated as light tan crystals suitable for the next step; yield, 3.86 g. (88%); m. p. 187.5–188.5°. After evaporative distillation at 0.01 mm. and recrystallization from acetic acid a sample of the acid formed colorless needles which exhibited two melting points. When heated slowly it melted at 188–193°; when placed in a bath at 189°, it melted completely, the melt solidified and remelted at 194–195°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.0; H, 5.8. Found: C, 83.9; H, 5.7.

1',2'-Dihydro-3,4-benzpyrene (II).—A mixture of 0.46 g. of 4'-chlorotetrahydrobenzpyrene (I) and 5 cc. of pyridine was refluxed for fifteen minutes and then poured into dilute hydrochloric acid and benzene. From the benzene layer 0.17 g. of crystalline dihydrobenzpyrene was isolated. After evaporative distillation at 0.5 mm. and three recrystallizations from ether–alcohol, it formed light-yellow platelets; m. p. 149.5–150°. The warm acid solution deposited nearly colorless crystals (0.26 g.) of what were probably the pyridinium salt of the chloride. When heated at 250° the salt decomposed and from the product practically pure dihydrobenzpyrene was obtained by evaporative distillation under reduced pressure.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.4; H, 5.6. Found: C, 94.2; H, 5.6.

The **picrate** crystallized from benzene in brownish-red prisms; m. p. 170–180°, dec.

Anal. Calcd. for $C_{20}H_{14}\cdot C_6H_3N_3O_7$: N, 8.7. Found: N, 8.8.

A mixture of 0.2 g. of dihydrobenzpyrene and 20 mg. of palladium-charcoal catalyst was heated in a nitrogen atmosphere at 320° for one hour. From the mixture was obtained 0.2 g. of 3,4-benzpyrene melting at 172.5–174.5°. By recrystallization from benzene-methanol the hydrocarbon was obtained as pale yellow needles; m. p. 176–176.5°.

6'-Keto-4',5-dimethylene-1',2',3',4'-tetrahydro-3,4-benzpyrene (IV).—A mixture of 2 g. of the tetrahydrobenzpyrenylacetic acid (III) and 1.44 g. of finely powdered phosphorus pentachloride in 40 cc. of benzene was allowed to stand at room temperature for forty minutes with frequent swirling. Then 1 cc. of anhydrous stannic chloride was added dropwise with swirling; a deep-red complex precipitated immediately. After forty-five minutes at room temperature, the complex was hydrolyzed and worked up in the usual manner. The benzene solution after being washed was combined with a similar solution from 1 g. of the acid; from the combined solutions 2.77 g. (98%) of the cyclic ketone was isolated in the form of golden-yellow prisms; m. p. 192–193° (vac.). The melting point was not raised when a sample was sublimed at 0.01 mm. and then recrystallized from benzene. In an open tube the compound darkened and melted at a slightly lower temperature. The ketone gives an orange-red color (green fluorescence) with concentrated sulfuric acid. Alcholic solutions of the ketone show an intense blue fluorescence.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.9; H, 5.4.

4',5-Dimethylene-3,4-benzpyrene (VI).—The ketone (2 g.) was added to a solution of aluminum isopropoxide prepared from 1.35 g. of aluminum wire and 50 cc. of anhydrous isopropyl alcohol. The mixture was alternately refluxed and distilled slowly through an upright column for approximately four hours; an additional 30 cc. of isopropyl alcohol was added during this time. When no further test for acetone could be detected in the distillate by means of 2,4-dinitrophenylhydrazine reagent, the mixture was cooled and hydrolyzed with ice and dilute hydrochloric acid. The light-yellow crystalline solid which was obtained weighed 1.97 g.

The product was dehydrated in three portions in the following manner. Each portion was heated rapidly to 180° under a pressure of 1 mm., whereupon water was evolved for approximately ten minutes. The pressure was then reduced to 0.01 mm. and the temperature raised to 320°, whereupon a yellow crystalline solid collected on the cool

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(6) Bachmann, Carmack and Safir, THIS JOURNAL, **63**, 1682 (1941).

part of the sublimation tube; yield, 1.23 g. (65%); m. p. 203–208°. In one run 0.6 g. (78%) of sublimed product was obtained from 0.81 g. of the cyclic ketone. A sample of the **hydrocarbon** (V) crystallized from benzene in yellow rhombic plates; m. p. 209–213°. It dissolves slowly in concentrated sulfuric acid to give an emerald green solution.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.7. Found: C, 93.7; H, 5.7.

The **picrate** crystallized from benzene in dark-red needles; m. p. 177.5–178°.

Anal. Calcd. for $C_{22}H_{16} \cdot C_6H_3N_3O_7$: N, 8.3. Found: N, 8.3.

The unrecrystallized hydrocarbon (1.23 g.; m. p. 203–208°) and 0.2 g. of palladium–charcoal catalyst[7] were heated in a nitrogen atmosphere at 310–330°. After twenty minutes the material which had sublimed up on the sides of the tube was washed down with a little benzene, the benzene was evaporated and the heating continued for ten minutes. The product was then sublimed directly from the catalyst at 0.01 mm.; the bright orange sublimate weighed 0.97 g. and melted at 240–246.5° (vac.). A solution of 1.2 g. of such sublimed product in benzene was passed through a short tower of alumina and the solution was concentrated under reduced pressure; addition of a little petroleum ether caused the **4′,5-dimethylene-3,4-benzpyrene** to separate as bright orange platelets; yield, 0.78 g.; m. p. 251–252° (255–256° cor.) in an evacuated tube; the melting point in air is somewhat lower because of oxidation. From the filtrate an additional 0.29 g. of practically pure hydrocarbon was isolated. The hydrocarbon is very slightly soluble in cold alcohol and ether, slightly soluble in cold benzene and only moderately soluble in boiling benzene. It gives a violet color with concentrated sulfuric acid; in a few minutes the color changes to a beautiful magenta (yellow-orange fluorescence).

Anal. Calcd. for $C_{22}H_{14}$: C, 94.9; H, 5.1. Found: C, 94.8, 95.23; H, 4.9, 5.0.

The **picrate** crystallized from benzene in almost black needles; m. p. 177–177.5°.

Anal. Calcd. for $C_{22}H_{14} \cdot C_6H_3N_3O_7$: N, 8.3. Found: N, 8.4.

Conversion of 1-Ketotetrahydrocholanthrene (VII) to Cholanthrene.—One-half gram of the ketone[8] was reduced by aluminum isopropoxide in the manner described. The crude **1-hydroxytetrahydrocholanthrene** was recrystallized from benzene, from which it separated in fine colorless rhombic platelets and needles. The first crop weighed 0.32 g. and melted at 146.5–147.5°; this was suitable for the next step. A sample after another recrystallization melted at 150–150.5°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.6; H, 6.8.

Dehydration of 100 mg. of the secondary alcohol by heating it gradually to 240° at 5 mm. and after cessation of frothing evaporatively distilling at 0.05 mm. gave 80 mg. of product melting at 136–137°. When this was dehydrogenated with palladium on charcoal in the manner described, there was obtained 51 mg. of practically pure cholanthrene.

Summary

The polycyclic hydrocarbon 4′,5-dimethylene-3,4-benzpyrene which possesses the basic structures of both cholanthrene and 3,4-benzpyrene has been synthesized from 4′-ketotetrahydro-3,4-benzpyrene and its absorption spectrum has been measured.

The preparation of 1′,2′-dihydro-3,4-benzpyrene is described. The two new polycyclic hydrocarbons are being tested for carcinogenic activity.

ANN ARBOR, MICHIGAN RECEIVED MARCH 4, 1941

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[7] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[8] Bachmann, *J. Org. Chem.*, **3**, 434 (1938).

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

Mesylated Cellulose and Derivatives[1]

BY M. L. WOLFROM, JOHN C. SOWDEN[2] AND E. A. METCALF[2]

A long-known process for the surface alteration of cellulose fibers to make them resistant or "immune" to direct dyes consists in the treatment of alkali cellulose with *p*-toluenesulfonyl chloride (tosyl chloride).[3] The scientific aspects of this process formed the subject of investigations carried out in the laboratories of G. Kita in Japan.[4] The tosylation of cellulose with *p*-toluenesulfonyl chloride in pyridine solution was studied carefully by Hess and Ljubitsch[5] and more recently by Bernoulli and Stauffer.[6]

The tosyl esters of cellulose are of interest because their chemical reactivity resembles that of a

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[1] Presented before the Division of Cellulose Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Missouri, April 9, 1941.

[2] Du Pont Cellulose Research Fellow.

[3] German Patents: Agfa, 200,334 (1907); Casella, 346,883 1919); Textilwerke Horn, 396,926 (1922); Chem. Werke vorm. Sandoz, 545,323 (1929), 521,121 (1929).

[4] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. chem. Research* (Tokyo), **6**, 214 (1927); *C. A.*, **22**, 684 (1928); *Bull. Inst. Phys. Chem. Research* (Tokyo), **8**, 272 (1929); *C. A.*, **23**, 3572 (1929).

[5] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933).

[6] A. L. Bernoulli and H. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940).