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

THE REACTION OF ALKALI METALS WITH POLYCYCLIC HYDROCARBONS: 1,2-BENZANTHRENE, 1,2,5,6-DIBENZANTHRACENE AND METHYLCHOLANTHRENE

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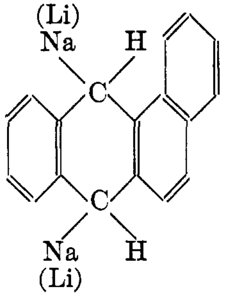
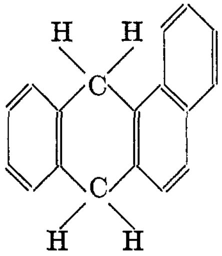
In order to obtain derivatives of polycyclic hydrocarbons we have begun an investigation of the action of alkali metals on the hydrocarbons in organic solvents. Schlenk and Bergmann[1] found that sodium and lithium add to the 9,10 positions of anthracene and give the 9,10-disodium and 9,10-dilithium derivatives of 9,10-dihydroanthracene respectively. We have found that sodium and lithium add to 1,2-benzanthrene in a similar manner. If a solution of 1,2-benzanthrene in ether-benzene is shaken with powdered sodium or with liquid 45 per cent. sodium amalgam a deep blue color develops immediately; this color is gradually replaced by the deep rose-red color of the 7,12-disodium-7,12-dihydro-1,2-benzanthrene (I). The 7,12-dilithium-7,12-dihydro-1,2-benzanthrene, which is formed by interaction of 1,2-benzanthrene and lithium, possesses an intensely blue color. Whether the difference in color of the disodium and the dilithium derivatives is due to *cis-trans* isomerism, as Schlenk and Bergmann suggested for the corresponding alkali derivatives of anthracene, is left undecided at this time. By reaction with methanol the disodium and the dilithium derivatives yield the same colorless 7,12-dihydro-1,2-benzanthrene (II). The structure assigned to the dihydro compound is based on its analysis and on its oxidation to 1,2-benzanthrene-7,12-dione by chromic acid. When heated with sulfur the 7,12-dihydro-1,2-benzanthrene is readily dehydrogenated to 1,2-benzanthrene.



(I)



(II)

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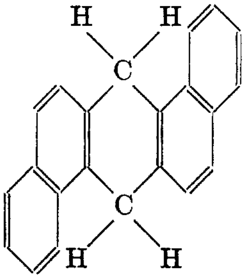
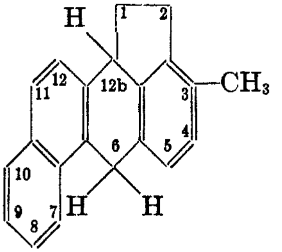
[1] SCHLENK AND BERGMANN, *Ber.*, **47**, 473 (1914); *Ann.*, **463**, 134 (1928).

We were particularly interested in the reactions of the carcinogenic hydrocarbons, α,γ′-dibenzanthracene (1,2,5,6-dibenzanthracene) and 3-methylcholanthrene. A solution of α,γ′-dibenzanthracene immediately becomes deep green in color when shaken with powdered sodium in ether-benzene; when addition of the sodium is complete, the solution is intensely blue in color. The dilithium derivative is also intensely blue. From the disodium and the dilithium derivative the same colorless 7,14-dihydro-α,γ′-dibenzanthracene (III) is obtained on alcoholysis. The dihydro compound is readily oxidized by chromic acid to α,γ′-dibenzanthracene-7,14-dione and is rapidly dehydrogenated by sulfur to α,γ′-dibenzanthracene.



(III)



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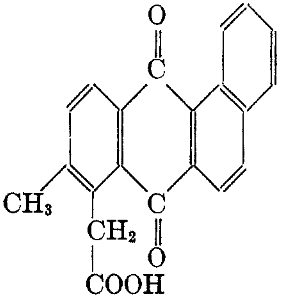

(V)

The yellow hydrocarbon, 3-methylcholanthrene, reacts with powdered sodium and with 45 per cent. sodium amalgam in ether-benzene and gives the intensely purple 6,12b-disodium-6,12b-hydro-3-methylcholanthrene and with two atoms of lithium to give the intensely blue 6,12b-dilithium-6,12b-hydro-3-methylcholanthrene. It is apparent that in all three hydrocarbons the alkali metals add to the *meso* positions of the anthracene portion of the molecule. On alcoholysis of the alkali derivatives the same colorless 6,12b-dihydro-3-methylcholanthrene (IV) is formed. Like 3-methylcholanthrene the dihydro compound is readily oxidized by chromic acid to 5-(6-methyl-1,2-benzanthraquinonyl) acetic acid (V); this reaction is the basis of the structure assigned to the dihydro compound and to the alkali derivatives. 6,12b-dihydro-3-methylcholanthrene is easily dehydrogenated by sulfur at 170° to 3-methylcholanthrene.

The dihydro derivatives are being tested for carcinogenic properties. Of especial interest is the dihydro derivative of 3-methylcholanthrene, since 3-methylcholanthrene is the most potent carcinogenic compound discovered so far. The investigation of the alkali derivatives of these and other polycyclic hydrocarbons is being continued. Preliminary experiments on the action of carbon dioxide on the alkali derivatives have yielded acids whose sodium salts are soluble in water; it will be of interest to determine whether these water-soluble derivatives of the carcinogenic hydrocarbons likewise possess cancer-producing properties.

EXPERIMENTAL

1,2-Benzanthrene.—This hydrocarbon was made by pyrolysis of 1-naphthyl *o*-tolyl ketone, which was prepared by means of the Grignard reaction. To the Grignard reagent, which had been prepared from 50 g. of 1-bromonaphthalene in 75 cc. of ether and 75 cc. of benzene, was added 23.4 g. of *o*-tolunitrile. After being refluxed for eight hours the mixture was cooled and hydrolyzed with ice and 100 cc. of concentrated hydrochloric acid. The sparingly soluble ketimine hydrochloride which had crystallized was filtered off from the aqueous and organic solutions and was hydrolyzed by boiling it with water for an hour; when the mixture was cooled the ketone crystallized. Further purification was effected by distillation; b.p. 174°/0.4 mm.; yield, 37.8 g. (76%). After recrystallization from methanol the 1-naphthyl *o*-tolyl ketone melted at 59–61°.

A mixture of 34 g. of the ketone and 10 g. of zinc dust was heated for three hours in a metal bath kept at 410°; the hydrocarbon was distilled from the flask under a pressure of 0.4 mm. and recrystallized several times from benzene-alcohol; weight, 17.2 g. (54%). The yellow color was completely removed from the hydrocarbon by refluxing a solution of the 17.2 g. of hydrocarbon with 1 g. of maleic anhydride in 50 cc. of benzene for three hours.[2] The hot benzene solution was shaken with an aqueous solution of sodium hydroxide, and the benzene solution was filtered, concentrated to a small volume and treated with alcohol; m.p. 155.5–157°. Fieser and Dietz[3] obtained a 10% yield of 1,2-benzanthrene by heating the isomeric ketone, 2-methyl-1-benzoylnaphthalene, at its boiling point for twenty-six hours.

7,12-Dihydro-1,2-benzanthrene (II).—A mixture of 0.5 g. of 1,2-benzanthrene, 1 g. of powdered sodium, 30 cc. of anhydrous ether, 30 cc. of dry benzene (both solvents dried by liquid 40% sodium amalgam) and a few glass beads was shaken in a cylinder (which was nearly completely filled by the mixture). Almost immediately the solution became intensely blue in color; after sixteen hours the solution, which was now intensely rose-red in color, was decolorized by addition of methanol. The solution was quickly filtered through a plug of cotton, shaken with dilute hydrochloric acid, separated, dried and concentrated to a small volume. On addition of alcohol to the hot benzene solution the 7,12-dihydro-1,2-benzanthrene crystallized out; weight, 0.4 g. (80%); m.p. 111–112°. Further recrystallization or purification through the picrate raised the melting point to 112–112.5°. 7,12-Dihydro-1,2-benzanthrene crystallizes from benzene-alcohol and from acetic acid in glistening colorless leaflets; it is little soluble in cold alcohol but is readily soluble in benzene and in acetone.

Anal. Calc'd for $C_{18}H_{14}$: C, 93.89; H, 6.11.
Found: C, 93.88; H, 6.00.

In another experiment a mixture of 1.0 g. of 1,2-benzanthrene, 6 g. of 45% sodium amalgam, 30 cc. of ether and 30 cc. of benzene was shaken for fourteen hours. Alcoholysis of the intensely rose-red solution yielded 0.75 g. (75%) of pure 7,12-dihydro-1,2-benzanthrene.

For the reaction with lithium a mixture of 0.5 g. of 1,2-benzanthrene, 0.8 g. of shining lithium wire (0.5 mm. diameter) in 30 cc. of ether and 30 cc. of benzene was shaken for one week. At the beginning of the experiment the lithium wire was

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[2] Cook, Hieger, Kennaway and Mayneord, *Proc. Roy. Soc.*, **B111**, 469 (1932).

[3] Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

pressed with a glass rod in several places in order to start the reaction. Treatment of the intensely blue colored solution with methanol yielded 0.48 g. (96%) of 7,12-dihydro-1,2-benzanthrene melting at 110–112°.

7,12-Dihydro-1,2-benzanthrene Picrate.—The dihydro compound combines with two molecules of picric acid in benzene solution. The dipicrate, which is very soluble in hot benzene, somewhat soluble in cold benzene but sparingly soluble in ligroïn, crystallizes from benzene-ligroïn in fine yellow needles; m.p. 139–139.5°.

Anal. Calc'd for $C_{18}H_{14}\cdot 2C_6H_3N_3O_7$: N, 12.2. Found: 12.3.

Dehydrogenation of 7,12-Dihydro-1,2-benzanthrene.—A mixture of 0.1 g. of 7,12-dihydro-1,2-benzanthrene and 0.02 g. of sulfur was heated in a metal bath; hydrogen sulfide was evolved as soon as the temperature reached 130°. After being kept at 170° for three hours the product was dissolved in benzene and the solution was shaken with mercury for several hours in order to remove excess of sulfur. The filtered solution was evaporated to dryness and the residue was recrystallized from benzene-alcohol, yielding 0.9 g. (90%) of pure 1,2-benzanthrene of melting point 158–158.5°.

Oxidation of 7,12-Dihydro-1,2-benzanthrene.—A mixture of 0.12 g. of 7,12-dihydro-1,2-benzanthrene and 0.1 g. of chromic acid anhydride in 5 cc. of acetic acid containing two drops of water was heated at the boiling point for a few minutes. The product obtained by addition of water was recrystallized from toluene, and proved to be 1,2-benzanthrene-7,12-dione (0.8 g.); m.p. 166–167°. Mixed with authentic 1,2-benzanthrene-7,12-dione (m.p. 167–168°) the melting point was 166.5–167.5°.

α,γ′-Dibenzanthracene.—1-(2-methylnaphthyl) 2-naphthyl ketone, obtained by Clar[4] through the Friedel and Crafts reaction, was prepared by means of the Grignard reaction. A mixture of 54 g. of 1-bromo-2-methylnaphthalene, 6 g. of magnesium and a crystal of iodine was refluxed in 75 cc. of ether and 125 cc. of benzene for two days, the mixture being protected from air by a mercury trap. To the Grignard reagent was added 33 g. of 2-naphthonitrile and the mixture was kept warm for twenty-four hours. Hydrolysis with ice and 100 cc. of concentrated hydrochloric acid gave the ketimine hydrochloride as an insoluble crystalline precipitate (78 g.), which was filtered off from the aqueous and organic solutions. The ketimine is not hydrolyzed appreciably by boiling water. Complete hydrolysis was effected by heating five sealed tubes, each containing 15.6 g. of ketimine hydrochloride, 4 cc. of concentrated hydrochloric acid and 100 cc. of water, at 180° for six hours. The contents of the tubes were combined, the ketone was extracted by benzene, the benzene solution was heated with charcoal, filtered and evaporated. The ketone was then recrystallized from acetone-alcohol, yielding 40 g. (63%) of product melting at 139.5–141°, which was sufficiently pure for the next step.

By heating a mixture of 30 g. of the ketone and 10 g. of zinc dust for one and three-quarters hours in a metal bath kept at 420°, 14 g. (50%) of purified α,γ′-dibenzanthracene was obtained, a yield higher than that previously reported.[3] The compound was obtained completely colorless by the maleic anhydride treatment.[2]

7,14-Dihydro-α,γ′-dibenzanthracene (III).—A mixture of 0.5 g. of α,γ′-dibenzanthracene and 1 g. of powdered sodium was shaken in 40 cc. of ether and 40 cc. of benzene for three days. The initial deep green color gave way to an intensely blue color. Treatment with methanol followed by purification described for the dihydro derivative of 1,2-benzanthrene gave 7,14-dihydro-α,γ′-dibenzanthracene, which was obtained as colorless, glistening leaflets by recrystallization from benzene-alcohol; weight, 0.42 g. (84%); m.p. 218–219°. Further recrystallization or purification through the picrate raised the melting point to 218.5–219.5°. The compound is

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[4] Clar, *ibid.*, **62**, 350 (1929).

nearly insoluble in cold alcohol, sparingly soluble in hot alcohol and very little soluble in cold benzene.

Anal. Calc'd for $C_{22}H_{16}$: C, 94.25; H, 5.75.
Found: C, 94.10; H, 5.72.

In another experiment 0.5 g. of α,γ'-dibenzanthracene was shaken with 0.8 g. of lithium wire in ether-benzene for nine days, after first starting the reaction by pressing the metal with a glass rod. On treatment with methanol the intensely blue colored solution yielded 0.4 g. (80%) of pure 7,14-dihydro-α,γ'-dibenzanthracene identical with the product obtained through the sodium reaction. Cook[5] obtained 7,14-dihydro-α,γ'-dibenzanthracene of m.p. 196–198° in 18% yield by catalytic hydrogenation of α,γ'-dibenzanthracene.

7,14-Dihydro-α,γ'-dibenzanthracene Picrate.—Mixing of hot saturated benzene solutions of picric acid (0.7 g.) and of the dihydrocompound (0.4 g.) precipitated the sparingly soluble dipicrate of 7,14-dihydro-α,γ'-dibenzanthracene in nearly quantitative yield. The dipicrate crystallizes from toluene in long, fine, yellow needles. The melting point depends on the rate of heating, for it decomposes near the melting point. When put in a bath at 210° and heated rapidly, the dipicrate melted with decomposition at 221–222°; when put in at 150° the compound melted at 216–217°.

Anal. Calc'd for $C_{22}H_{16}\cdot 2C_6H_3N_3O_7$: N, 11.4. Found: 11.4.

Dehydrogenation of 7,14-Dihydro-α,γ'-dibenzanthracene.—A mixture of 0.2 g. of 7,14-dihydro-α,γ'-dibenzanthracene and 0.04 g. of sulfur was heated for a few minutes at 220–230°. After removal of the excess of sulfur by mercury, followed by recrystallization from benzene-alcohol, 0.15 g. of α,γ'-dibenzanthracene of m.p. 258–260° was obtained.

Oxidation of 7,14-Dihydro-α,γ'-dibenzanthracene.—A mixture of 0.1 g. of the dihydro compound and 0.5 g. of sodium dichromate in 10 cc. of acetic acid was refluxed for one-half hour. After addition of 50 cc. of water containing a little sulfuric acid the crude quinone was filtered off, washed with water and dried; it was then sublimed at 230°/0.2 mm. The sublimate was recrystallized twice by dissolving it in a small amount of hot xylene and adding alcohol to the solution; in this manner 0.09 g. of α,γ'-dibenzanthracene-7,14-dione of m.p. 244–244.5° was obtained. There was no change in melting point when the substance was mixed with a sample of the quinone (m.p. 244–244.5°) prepared from α,γ'-dibenzanthracene.

3-Methylcholanthrene.—This hydrocarbon was prepared according to the method of Fieser and Seligman[6] with one modification. Fieser and Seligman obtained the intermediate ketone, 4-(1-naphthoyl)-7-methylindan, as an uncrystallizable oil by coupling the Grignard reagent of 4-bromo-7-methylindan with 1-naphthoyl chloride. By substituting 1-naphthonitrile for the latter compound we have obtained the ketone in crystalline form. No difficulty was encountered in preparing the Grignard reagent. A solution of 22 g. of 4-bromo-7-methylindan, 2.6 g. of magnesium ribbon, and a few drops of methyl iodide in 75 cc. of ether and 20 cc. of benzene was refluxed for two days, a mercury trap protecting the solution from air. Practically the theoretical amount of magnesium was used up. After addition of 17 g. of 1-naphthonitrile the mixture was refluxed for six hours, after which it was cooled and hydrolyzed with ice-cold ammonium chloride solution. Addition of 100 cc. of concentrated hydrochloric acid to the ether-benzene solution precipitated the ketimine hydrochloride as an oil which soon crystallized. The precipitate was filtered off and heated with

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[5] Cook, *J. Chem. Soc.*, **1933**, 1596.

[6] Fieser and Seligman, *J. Amer. Chem. Soc.*, **57**, 942 (1935).

water at 100° for two hours in order to hydrolyze the ketimine to the ketone. The ketone was taken up in benzene, the solution was dried over sodium sulfate and filtered, and after removal of the benzene the ketone was distilled; b.p. 225–228°/0.8 mm.; weight, 14.6 g. (49%). By recrystallization from acetone-alcohol and then from petroleum ether (60–75°) 11.3 g. of 4-(1-naphthoyl)-7-methylindan was obtained in the form of fine, colorless needles; m.p. 82.7–83.5°. The ketone gives a deep yellow color with concentrated sulfuric acid.

Anal. Calc'd for $C_{21}H_{18}O$: C, 88.07; H, 6.34.
Found: C, 88.15; H, 6.38.

Pyrolysis of 11 g. of the pure crystalline ketone followed by purification according to the directions of Fieser and Seligman yielded 4.5 g. (43%) of 3-methylcholanthrene melting at 180.3–180.6° (corr.). Fieser and Seligman reported a value of 178.5–179° (corr.). From propanol the methylcholanthrene was sometimes obtained in the form of large, transparent, yellow plates instead of the usual broad, yellow needles.

Dihydro-3-methylcholanthrene (IV).—A mixture of 0.5 g. of 3-methylcholanthrene and 1 g. of powdered sodium was shaken in 40 cc. of ether and 40 cc. of benzene with several glass beads for forty hours. The solution immediately became intensely purple in color. The solution was decolorized with methanol, filtered from the sodium, shaken with dilute hydrochloric acid, dried, filtered and evaporated; recrystallization of the residue from propanol gave 0.45 g. of cream-colored needles melting at 122–130°. These were found to contain about 0.03 g. of 3-methylcholanthrene. The latter was removed by dissolving the product along with 0.7 g. of picric acid in a small amount of hot benzene; on cooling the solution the picrate of 3-methylcholanthrene precipitated. The solution after being filtered was shaken with dilute sodium hydroxide solution in order to remove the picric acid, and washed thoroughly with water; the product obtained by evaporation of the colorless benzene solution was then recrystallized from propanol, yielding 0.4 g. (80%) of the dihydro compound. Dihydro-3-methylcholanthrene crystallizes from propanol and from benzene-alcohol in long, fine, colorless needles; m.p. 136–137°. The compound is readily soluble in benzene and in acetone but is little soluble in the lower aliphatic alcohols.

Anal. Calc'd for $C_{21}H_{18}$: C, 93.29; H, 6.71.
Found: C, 93.25; H, 6.70.

For addition of lithium a mixture of 0.5 g. of 3-methylcholanthrene and 0.8 g. of lithium wire was shaken in ether-benzene for one week, after first starting the reaction by pressing the lithium with a glass rod. In a few minutes the solution was intensely blue in color. Treatment of the blue solution with methanol yielded the dihydro compound, which after two recrystallizations from propanol was obtained as colorless needles melting at 136–137°; weight, 0.4 g. (80%).

Dehydrogenation of Dihydro-3-methylcholanthrene.—A mixture of 50 mg. of the dihydro compound and 10 mg. of sulfur was heated at 170° for one hour. After shaking a benzene solution of the product with mercury for several hours, the solution was filtered and evaporated to dryness; the residue of 3-methylcholanthrene was obtained pure by recrystallization from propanol; weight, 30 mg. (60%).

Oxidation of Dihydro-3-methylcholanthrene.—A mixture of 0.1 g. of the dihydro compound and 0.5 g. of sodium dichromate in 10 cc. of acetic acid was refluxed for one-half hour; 50 cc. of water containing a little sulfuric acid was added and the 5-(6-methyl-1,2-benzanthraquinonyl) acetic acid (V) which precipitated was filtered off. The product dissolved completely in dilute potassium carbonate solution; addition of hydrochloric acid to this solution reprecipitated the quinone-acid in gelatinous form. This was filtered off and dried (0.1 g.) and recrystallized from xylene, from which it was obtained in the form of microscopic yellow needles. The properties of the compound were identical with those of a sample of 5-(6-methyl-1,2-benzanthraquinonyl) acetic acid prepared by oxidation of 3-methylcholanthrene in exactly the same manner.[7] Further confirmation of the identity of the two acids was obtained by making the methyl ester of each sample in xylene solution by means of diazomethane. In both cases a methyl ester crystallizing from acetone-methanol in broad, thin, lemon-yellow needles was obtained; m.p. 213–214° alone and when mixed with each other.

SUMMARY

Sodium and lithium add to the 7,12 positions of 1,2-benzanthrene and to the 7,14 positions of α,γ'-dibenzanthracene and to the *meso* positions of 3-methyl-cholanthrene, yielding intensely colored organoalkali compounds. On treatment with methanol the corresponding 7,12-dihydro-1,2-benzanthrene, 7,14-dihydro-α,γ'-dibenzanthracene and dihydro-3-methylcholanthrene are formed.

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[7] Cook and Haslewood, *J. Chem. Soc.*, **1934**, 432.