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

The Synthesis of 9,10-Dialkyl-1,2-benzanthracenes

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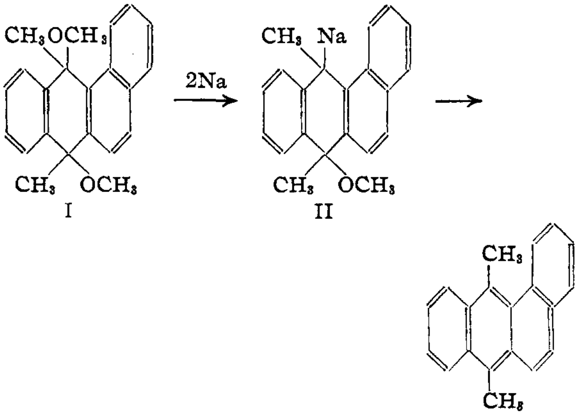
Recently[2] we described the synthesis of 9,10-dimethyl-1,2-benzanthracene and two other hydrocarbons containing alkyl groups in the 9,10-positions of the 1,2-benzanthracene molecule.[3] The mechanism by which 9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene (I) is converted to 9,10-dimethyl-1,2-benzanthracene (III) by reaction with sodium has now been investigated.

In considering a mechanism the following facts must be kept in mind: (1) the reaction occurs between one mole of the dimethyl ether of the diol and two equivalents of sodium; (2) the 9,10-dimethyl-1,2-benzanthracene is present in the reaction mixture as the hydrocarbon and not in the form of a derivative; (3) the reaction mixture remains practically colorless throughout the reaction, an indication that no disodio derivative of the hydrocarbon is present. All of these facts receive a satisfactory explanation if we assume that the diol dimethyl ether reacts with sodium to give the intermediate II, which yields 9,10-dimethyl-1,2-benzanthracene by transannular elimination of sodium methylate.



We consider this reaction more probable than the simultaneous elimination of both methoxy groups by reaction with sodium.

Apparently the hydrocarbon begins to be formed as soon as the reaction is initiated. Since the solution remains practically colorless, our mechanism implies that none of the hydrocarbon which is formed reacts with the sodium as long as any diol dimethyl ether is present. Although this did not seem reasonable in view of the rapidity with which the 9,10-dimethyl-1,2-benzanthracene reacts with sodium in the absence of the diol dimethyl ether, an experiment designed to test this point showed that this is indeed the case. When equimolar amounts of 9,10-dimethyl-1,2-benzanthracene and 9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene were allowed to compete for two equivalents of sodium, no disodio addition product was formed and the diol dimethyl ether was converted completely to the hydrocarbon. One other mechanism, involving the intermediate formation of 9,10-dimethyl-9,10-disodio-9,10-dihydro-1,2-benzanthracene and its subsequent reaction with the diol dimethyl ether, was excluded from consideration when it was found that the two compounds did not react to produce any appreciable quantity of 9,10-dimethyl-1,2-benzanthracene.

We also examined the utilization of other ethers for the sodium reaction. Of the four alcohols, ethyl, *n*-propyl, isopropyl, and *n*-butyl alcohol, only the ethyl alcohol yielded an ether under the conditions employed for the preparation of the dimethyl ether. From the diethyl ether and sodium, 9,10-dimethyl-1,2-benzanthracene was obtained although in lower yield. The diol dimethyl ethers are undoubtedly the best intermediates as they form easily and crystallize readily. In the case of the product from the interaction of 1,2-benzanthraquinone and *n*-propylmagnesium bromide the diol has not been obtained crystalline[4]; the diol dimethyl ether, however, crystallizes readily and yields 9,10-di-*n*-propyl-1,2-benzanthracene by reaction with sodium.

We have employed our method of synthesis to prepare 5-ethyl-9,10-dimethyl-1,2-benzanthracene (IV) and 5-*n*-propyl-9,10-dimethyl-1,2-benzanthracene (V). For the preparation of the intermediate 5-ethyl-1,2-benzanthracene we employed the reaction between 5-keto-tetrahydro-

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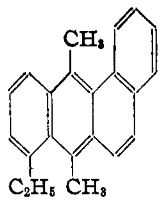
[1] From the Ph.D. dissertation of J. M. Chemerda.

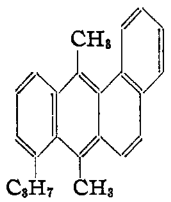
[2] Bachmann and Chemerda, THIS JOURNAL, **60**, 1023 (1938).

[3] For the carcinogenic properties of these compounds see Bachmann, Kennaway and Kennaway, *Yale J. Biol. Med.*, **11**, 97 (1938).

[4] Bachmann and Bradbury, *J. Org. Chem.*, **2**, 175 (1937).

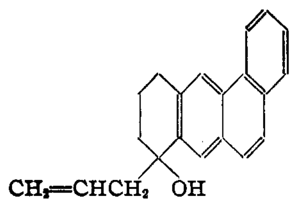


IV

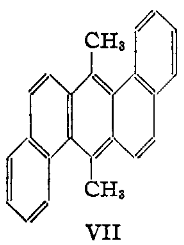


V

1,2-benzanthracene and ethylmagnesium bromide, followed by treatment of the resulting carbinol with palladium on charcoal as was done in the preparation of 5-methyl-1,2-benzanthracene.[5] When the cyclic ketone was treated with *n*-propylmagnesium bromide, considerable reduction took place. The 5-*n*-propyl-1,2-benzanthracene was best prepared by the catalytic dehydration and isomerization of the carbinol VI, which was obtained in good yield by interaction of the cyclic ketone and allylmagnesium bromide.



VI



VII

Our reaction also offers a convenient preparation of 9,10-dimethyl-1,2,5,6-dibenzanthracene (VII). This hydrocarbon has been prepared previously by Cook[6] by cautious reduction of the corresponding diol and by Akin and Bogert[7] by means of the Pschorr synthesis.

Experimental

Reaction of Sodium with a Mixture of 9,10-Dimethyl-1,2-benzanthracene and Diol Dimethyl Ether.—A mixture of 1.0 g. of 9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene and 0.80 g. of 9,10-dimethyl-1,2-benzanthracene (equimolar proportions) in 25 cc. of benzene and 25 cc. of ether was shaken with 0.14 g. of powdered sodium and some sharp glass particles. After one day's shaking, a nearly colorless solution was obtained and all of the sodium had reacted. From the solution 1.59 g. (99%) of the calculated amount of the 9,10-dimethyl-1,2-benzanthracene was isolated; m. p. 122–123°.

Reaction of 9,10-Dimethyl-9,10-disodio-9,10-dihydro-1,2-benzanthracene with Diol Dimethyl Ether.—The disodium derivative was prepared by shaking 1.25 g. of 9,10-dimethyl - 9,10 - dimethoxy - 9,10 - dihydro - 1,2 - benzanthracene with 0.36 g. of powdered sodium in 30 cc. of ether and 30 cc. of benzene. After a week, the solution had a color reminiscent of the permanganate ion. The addition of 1.25 g. of the diol dimethyl ether did not decolorize the solution; the solution seemed to take on a brighter tinge of red. After a week, no further change was observed and the solution was treated with carbon dioxide to remove the disodium derivative. From the benzene–ether solution 0.75 g. (58%) of pure diol dimethyl ether was isolated. The mother liquor gave lower melting material from which no 9,10-dimethyl-1,2-benzanthracene could be isolated.

In another experiment, the disodium derivative was prepared by shaking the hydrocarbon with the theoretical amount of sodium. In the same manner as described above, 80% of the added diol dimethyl ether was recovered.

9,10 - Dimethyl - 9,10 - diethoxy - 9,10 - dihydro - 1,2-benzanthracene.—A suspension of 1.0 g. of 9,10-dimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene[4] in 5 cc. of absolute alcohol was treated with 0.05 cc. of sulfuric acid in 1 cc. of absolute alcohol. In ten minutes a clear solution was obtained and the diol diethyl ether crystallized out. After standing at room temperature for one hour the diol diethyl ether was collected, dissolved in benzene and washed with ammonium hydroxide to remove traces of sulfuric acid. It is highly essential that the ether be as pure as possible for the successful preparation of the hydrocarbon in the sodium reaction. The benzene solution was concentrated, alcohol was added and the diol diethyl ether crystallized in clumps of colorless narrow prisms; yield 0.84 g., m. p. 167.5–171°. After two recrystallizations from benzene–alcohol the **9,10-dimethyl-9,10-diethoxy-9,10-dihydro-1,2-benzanthracene** melted at 172–173.5°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.2; H, 7.6. Found: C, 83.1; H, 7.4.

A mixture of 0.84 g. of the above diol diethyl ether and 0.11 g. of powdered sodium in 15 cc. of benzene and 20 cc. of ether was shaken with a half-dozen sharp glass particles. In the course of a day, a greenish-blue mixture was obtained. The mixture was decolorized with methanol and washed with dilute hydrochloric acid. By recrystallization of the product from acetone–alcohol, 0.38 g. (61%) of 9,10-dimethyl-1,2-benzanthracene was obtained.

9,10-Di-*n*-propyl-1,2-benzanthracene.—The reaction mixture from 5.16 g. of 1,2-benzanthraquinone and *n*-propylmagnesium bromide, obtained according to the procedure of Bachmann and Bradbury,[4] was hydrolyzed and the solvent evaporated at room temperature. Treatment of the oil with a solution of 0.25 cc. of sulfuric acid in 50 cc. of methanol resulted in an immediate crystallization of the diol dimethyl ether. After standing overnight at room temperature, the diol dimethyl ether (3.9 g.) was filtered off and treated in the manner already described. From benzene–methanol, 3.25 g. of **9,10-di-*n*-propyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene** was obtained as colorless needles; m. p. 174–176°. One recrystallization from benzene–ethyl acetate raised the melting point to 176.5–177.5°. The compound gives a brown color with sulfuric acid.

Anal. Calcd. for $C_{26}H_{30}O_2$: C, 83.4; H, 8.1. Found: C, 83.5; H, 8.2.

A mixture of 2.31 g. of the diol dimethyl ether in 25 cc.

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(5) Bachmann and Wilds, THIS JOURNAL, **60**, 624 (1938).

(6) Cook, *J. Chem. Soc.*, 489 (1931).

(7) Akin and Bogert, THIS JOURNAL, **59**, 1564 (1937).

of benzene and 25 cc. of ether shaken with 0.28 g. of powdered sodium for one day gave 1.83 g. (95%) of **9,10-di-*n*-propyl-1,2-benzanthracene;** m. p. 98.5–100°. After purification through the picrate and recrystallization from benzene–alcohol, the hydrocarbon formed thick colorless needles; m. p. 100.5–101°.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.5.

The **picrate** of the hydrocarbon crystallized from absolute alcohol in black needles; m. p. 107.5–108°.

Anal. Calcd. for $C_{24}H_{24}{\cdot}C_6H_3O_7N_3$: N, 8.1. Found: N, 8.0.

5-Ethyl-1,2-benzanthracene.—To a solution of the Grignard reagent prepared from 22 g. of ethyl bromide and 50 cc. of ether was added 50 cc. of benzene. To the ice-cold solution was added 13.8 g. of 5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene. After standing at room temperature for half an hour, the mixture was hydrolyzed with ice-cold ammonium chloride solution. The reaction product obtained by evaporation of the solvent was heated with 1.0 g. of palladium on charcoal[8] at 310–320° for half an hour in an atmosphere of nitrogen. The cooled solid was extracted with acetone–benzene. After concentrating and adding alcohol, 9.95 g. of slightly yellow hydrocarbon was obtained; m. p. 115–117°. An additional 1.3 g. of hydrocarbon was obtained by treating the product in the mother liquor once more with the catalyst making a total yield of 79% based on the cyclic ketone. After distillation at 0.4 mm. the hydrocarbon crystallized from acetone–alcohol in colorless plates; yield, 9.3 g. (65%); m. p. 118–119°. Cook and his co-workers[9] reported a melting point of 120° for the compound prepared from 5-keto-dodecahydro-1,2-benzanthracene.

In another run with 5.0 g. of the cyclic ketone, the product was heated with 10 g. of powdered potassium bisulfate at 150–160° for one hour. The benzene extract of the hydrocarbon was clarified and concentrated, by addition of alcohol giving 3.46 g. of **5-ethyl-7,8-dihydro-1,2-benzanthracene.** A sample of the hydrocarbon after sublimation under reduced pressure crystallized from alcohol in colorless prisms; m. p. 110–112°.

Anal. Calcd. for $C_{20}H_{18}$: C, 93.0; H, 7.0. Found: C, 92.9; H, 7.1.

Dehydrogenation of the dihydro derivative by palladium on charcoal[8] at 330–340° for one hour gave the hydrocarbon in 70% yield.

5-Ethyl-9,10-dimethyl-1,2-benzanthracene.—Five grams of 5-ethyl-1,2-benzanthracene was dissolved in 50 cc. of hot acetic acid. After cooling to 70°, 5.81 g. of pure sodium dichromate dihydrate was added in portions and the mixture was heated on the steam-bath for an hour. The quinone was precipitated by the addition of 15% sulfuric acid. Recrystallization from acetone–alcohol gave 4.1 g. of 5-ethyl-1,2-benzanthraquinone; m. p. 96–98°. A second recrystallization gave 3.75 g.; m. p. 97–98° (Cook,[9] 97–98°).

5-Ethyl-1,2-benzanthraquinone (3.75 g.) was added to an ice-cold solution of the Grignard reagent prepared from 4 cc. of methyl iodide and 12 cc. of ether and 12 cc. of benzene. After hydrolysis with ice-cold ammonium chloride solution, 3.54 g. of the diol was isolated. Recrystallized twice from ethyl acetate the **5-ethyl-9,10-dimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene** formed microscopic needles; m. p. 201.5–204.5°. It gives a purple color with sulfuric acid. Since the diol retains solvent of crystallization tenaciously, it was analyzed as the dimethyl ether. The latter was prepared by treating a suspension of the diol (3.0 g.) in 15 cc. of methanol with a solution of 0.15 cc. of sulfuric acid in 5 cc. of methanol. After one hour at room temperature the diol dimethyl ether was filtered off and purified in the usual manner. Recrystallization from benzene–methanol gave colorless needles of **5-ethyl-9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene;** yield, 2.36 g.; m. p. 194–195°. Two more recrystallizations raised the melting point to 197–200°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.2; H, 7.6. Found: C, 83.4; H, 7.9.

A mixture of 2.36 g. of the above diol dimethyl ether (m. p. 194–196°) and 0.31 g. of powdered sodium in 25 cc. of ether and 25 cc. of benzene was shaken with a half-dozen sharp glass particles for one day. Worked up in the usual manner, 1.56 g. (80%) of the hydrocarbon was obtained. The hydrocarbon does not form a stable picrate. After purification by passage of a benzene solution through a tower of anhydrous alumina, **5-ethyl-9,10-dimethyl-1,2-benzanthracene** crystallized from acetone in light yellow plates; m. p. 107–108°.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 92.6; H, 6.8.

5-*n*-Propyl-1,2-benzanthracene.—(a) A mixture of 10 g. of 5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene, 2 g. of magnesium, 20 cc. of ether and 40 cc. of benzene was placed in a dry flask equipped with a reflux condenser. When 10 cc. of allyl bromide was added, a vigorous reaction was initiated in a few minutes. The contents were swirled occasionally until all the cyclic ketone dissolved (ten to twenty minutes) the mixture being cooled in a pan of cold water when necessary. The product began to crystallize from the hot mixture. After twelve hours in a refrigerator, the product was filtered off, washed with benzene and hydrolyzed with ice-cold ammonium chloride solution. The carbinol which crystallized out was filtered off, dissolved in benzene to free it from magnesium salts and returned to the benzene solution of the carbinol. Spontaneous evaporation of the solution gave practically colorless carbinol; yield 9.87 g. (84%). From dilute methanol, **5-allyl-5-hydroxy-5,6,7,8-tetrahydro-1,2-benzanthracene** crystallizes in colorless needles; m. p. 82–82.5°. With sulfuric acid it gives a brown color.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.5; H, 7.0. Found: C, 87.3; H, 7.0.

Five grams of the allylcarbinol was heated with 0.5 g. of palladium on charcoal[8] for half an hour at 300° in an atmosphere of nitrogen. At this temperature there was a sudden evolution of hydrogen which was reabsorbed for the most part by the end of the experiment. The cooled malodorous melt was extracted with acetone, filtered and allowed to evaporate spontaneously. A gum settled out on the bottom and crystalline material along the

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(8) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(9) Cook, Robinson and Gulden, *J. Chem. Soc.*, 393 (1937).

sides. These portions, distilled separately at 0.4 mm. and recrystallized from acetone–alcohol, gave pure colorless needles of 5-*n*-propyl-1,2-benzanthracene; yield 3.55 g.; m. p. 90–92°. Cook and Haslewood[10] prepared the compound (m. p. 92°) from 5-keto-dodecahydro-1,2-benzanthracene.

(b) Five grams of 5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene was added to an ice-cold solution of the Grignard reagent prepared from 4 cc. of *n*-propylmagnesium bromide and 20 cc. of ether followed by the addition of 20 cc. of benzene. The mixture was kept in a refrigerator for twenty-four hours and the crystalline product was filtered off and washed with benzene. The crystalline material was hydrolyzed with ice-cold ammonium chloride solution containing a little benzene. By spontaneous evaporation of the benzene solution and trituration of the residue with benzene–ligroin, 2.2 g. of **5-*n*-propyl-5-hydroxy-5,6,7,8-tetrahydro-1,2-benzanthracene** was obtained. The carbinol crystallized from benzene–ligroin in colorless threads; m. p. 107–108.5°. With sulfuric acid it gives a brownish-yellow color. It was not obtained analytically pure. By dehydrating the carbinol by heating with formic acid and dehydrogenating the product with palladium on charcoal, a 69% yield of 5-*n*-propyl-1,2-benzanthracene (m. p. 86–88°) was obtained.

5-*n*-Propyl-9,10-dimethyl-1,2-benzanthracene.—In the same manner as described for the ethyl homolog, 4.42 g. of 5-*n*-propyl-1,2-benzanthraquinone (obtained in 66% yield by the oxidation of 5-*n*-propyl-1,2-benzanthracene) was treated with methylmagnesium iodide. The clear yellow gum obtained was scratched until crystallization set in and the diol triturated with benzene–ligroin; yield 3.9 g.; m. p. 160–161°. **5-*n*-Propyl-9,10-dimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene** crystallized from ligroin–ethyl acetate in microscopic needles; m. p. 161.5–163°. With sulfuric acid it gives a purple color. It retains solvent of crystallization tenaciously and was analyzed as the dimethyl ether. In the manner previously described, 3. 0 g. of the diol dimethyl ether was obtained from 3.4 g. of the diol. **5-*n*-Propyl-9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene** crystallizes from benzene–methanol in colorless rectangular prisms; m. p. 157–159°.

Anal. Calcd. for $C_{25}H_{28}O_2$: C, 83.3; H, 7.8. Found: C, 83.3; H, 7.9.

A mixture of 2.23 g. of the diol dimethyl ether reacted with 0.29 g. of powdered sodium in 25 cc. of ether and 25 cc. of benzene in the manner previously described to give 1.64 g. (89%) of **5-*n*-propyl-9,10-dimethyl-1,2-benzanthracene.** Purified by passage of a benzene solution of the hydrocarbon through anhydrous alumina and crystallized from acetone–alcohol, the hydrocarbon formed yellowish nacreous plates; m. p. 84–85°.

Anal. Calcd. for $C_{23}H_{22}$: C, 92.6; H, 7.4. Found: C, 92.4; H, 7.7.

9,10-Dimethyl-1,2,5,6-dibenzanthracene.—One and one-half grams of the crude methyl diol, obtained according to Cook's[6] procedure, was treated with a solution of 0.2 cc. of sulfuric acid in 10 cc. of methanol and 20 cc. of benzene. The diol dissolved and the diol dimethyl ether crystallized in fine needles. After purification in the usual manner the **9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2,5,6-dibenzanthracene** (1.2 g.) crystallized from benzene in fine narrow colorless prisms; m. p. 310–320° with decomposition.

Anal. Calcd. for $C_{26}H_{24}O_2$: C, 84.8; H, 6.6. Found: C, 84.7; H, 6.7.

A mixture of 0.092 g. of powdered sodium and 0.74 g. of the diol dimethyl ether in 20 cc. of ether and 20 cc. of benzene was shaken for two days. A yield of 0.52 g. (85%) of hydrocarbon was obtained; m. p. 202–205°. From the mother liquor an additional 0.06 g. was obtained which gave 0.07 g. of fairly pure picrate; m. p. 174–176°.

The first crop was picrated in benzene and the benzene solution of the regenerated hydrocarbon passed through anhydrous alumina. From benzene the 9,10-dimethyl-1,2,5,6-dibenzanthracene crystallized in glistening yellow plates; m. p. 205.5–206.5°, the same melting point reported by Cook.[6]

9,10-Dimethyl-1,2,5,6-dibenzanthracene and picric acid dissolved in hot alcohol containing a little benzene deposited bright red needles of a **dipicrate;** m. p. 175°.

Anal. Calcd. for $C_{24}H_{18} \cdot 2C_6H_3O_7N_3$: N, 11.0. Found: N, 11.0.

Care must be exercised to avoid undue exposure of solutions of the hydrocarbon to light, for the hydrocarbon readily forms a peroxide. In one experiment, after purification, colorless needles of the peroxide were obtained instead of the usual yellow plates; m. p. 206–207° with decomposition. When placed in a bath at 200°, a melting point of 218–219° with bubbling and complete decomposition was observed. This same compound was prepared by exposure to sunlight of a solution of 0.10 g. of the hydrocarbon in 5 cc. of benzene. After forty-five minutes, 0.07 g. of clumps of colorless needles of **9,10-dimethyl-1,2,5,6-dibenzanthracene peroxide** was filtered off; m. p. 212–213° with decomposition when placed in the bath at 200°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.4; H, 5.5.

Summary

The mechanism by which 9,10-dimethyl-1,2-benzanthracene is formed by interaction of sodium and 9,10-dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene has been investigated.

5-Ethyl- and 5-*n*-propyl-9,10-dimethyl-1,2-benzanthracene, 9,10-di-*n*-propyl-1,2-benzanthracene and 9,10-dimethyl-1,2,5,6-dibenzanthracene have been prepared.

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[10] Cook and Haslewood, *J. Chem. Soc.*, 428 (1934).