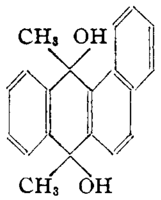
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

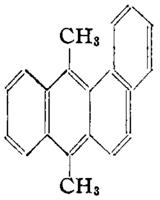
The Synthesis of 9,10-Dimethyl-1,2-benzanthracene, 9,10-Diethyl-1,2-benzanthracene and 5,9,10-Trimethyl-1,2-benzanthracene

BY W. E. BACHMANN AND J. M. CHEMERDA[1]

Recently 9,10-dimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene (I) was synthesized from 1,2-benzanthraquinone and methylmagnesium iodide.[2] This compound offered us the opportunity of obtaining 9,10-dimethyl-1,2-benzanthracene (II), a compound of particular interest because of its close relation to a number of potent carcinogenic hydrocarbons. Treatment of the diol with reducing agents such as hydriodic acid or zinc and acetic acid failed to give the desired hydrocarbon. The hydrocarbon was finally obtained in the following manner. The diol was converted to its dimethyl ether (III) by reaction with methanol in the presence of a small amount of sulfuric acid. Treatment of the dimethyl ether with 45% sodium amalgam replaced the methoxy groups by sodium atoms to yield the intensely colored 9,10-disodio-9,10-dimethyl-9,10-dihydro-1,2-benzanthracene, from which 9,10-dimethyl-9,10-dihydro-1,2-benzanthracene (IV) was obtained by reaction with methanol. The dihydro compound was dehydrogenated by sulfur to the desired 9,10-dimethyl-1,2-benzanthracene. By this method 20–30% yields of the hydrocarbon were obtained from the diol dimethyl ether.



(I)



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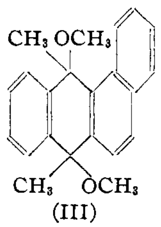

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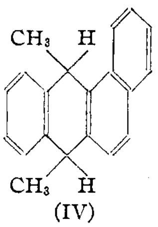
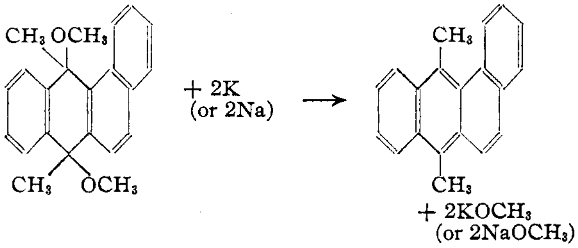
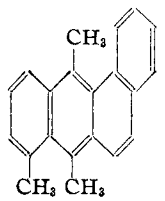


(IV)

A simpler and much better method of converting the dimethyl ether of the diol to 9,10-dimethyl-1,2-benzanthracene was discovered in the use of exactly two atomic equivalents of potassium or sodium. The mechanism of the reaction is still under investigation but the over-all reaction may be written as follows



Through this reaction 9,10-dimethyl-1,2-benzanthracene was obtained directly from the dimethyl ether of the diol in yields as high as 96% (or 72% on the basis of the readily available 1,2-benzanthraquinone). The same procedure gave an equally high yield of 9,10-diethyl-1,2-benzanthracene from the dimethyl ether of 9,10-diethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene. At the end of the reaction between the dimethyl ether and potassium, the reaction mixture was perfectly colorless. In a similar manner we have prepared 5,9,10-trimethyl-1,2-benzanthracene (V) from the diol (VI), which was obtained by interaction of 5-methyl-1,2-benzanthraquinone and methylmagnesium iodide.



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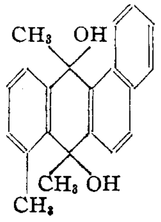

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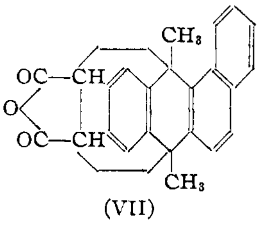
The reaction between 9,10-dimethyl-1,2-benzanthracene and maleic anhydride to form the addition product (VII) was of interest in view of



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

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

some results which we reported recently on the rate of addition of maleic anhydride to polycyclic hydrocarbons.[3] We had found that methyl groups in the 9,10-positions of anthracene greatly increased the reactivity of these positions with respect to addition of maleic anhydride, while a 1,2-benzo group decreased the reactivity of the molecule. In 9,10-dimethyl-1,2-benzanthracene both the activating methyl groups and the inhibiting benzo group are present. It was found that the influence of the methyl groups predominated, for the hydrocarbon reacts very rapidly with maleic anhydride to give the addition compound. Similarly, 5,9,10-trimethyl-1,2-benzanthracene reacts rapidly with the anhydride. Ethyl groups in the 9,10-positions have very little activating effect, for 9,10-diethyl-1,2-benzanthracene reacts slowly with maleic anhydride, although more rapidly than does 1,2-benzanthracene.

Experimental

9,10-Dimethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene (III).—A mixture of 0.25 cc. of concentrated sulfuric acid in 10 cc. of methanol was added to a solution of 5.0 g. of 9,10-dimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene[2] in 20 cc. of methanol. After a few minutes the dimethyl ether of the diol began to crystallize from the solution. After half an hour, 4.5 g. of the product was filtered off; from the filtrate an additional 0.5 g. was isolated, making a total yield of 91%. The dimethyl ether was freed from traces of sulfuric acid by dissolving it in benzene, shaking the solution with dilute ammonium hydroxide, concentrating the solution to a small volume and adding methanol. The dimethyl ether of the diol crystallizes from benzene–methanol in colorless needles; m. p. 173.5–174.5°. With concentrated sulfuric acid it gives a dark red color.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 6.8. Found: C, 83.4; H, 6.8.

The dimethyl ether of the diol can be obtained conveniently from 1,2-benzanthraquinone without isolating the intermediate diol in crystalline form. Half an hour after adding 10 g. of 1,2-benzanthraquinone to the Grignard reagent prepared from 10 cc. of methyl iodide and 3.6 g. of magnesium in 60 cc. of ether and 60 cc. of benzene, the mixture was hydrolyzed with ice-cold ammonium hydroxide solution. The ether–benzene solution was concentrated to a small volume and 30 cc. of methanol containing 0.5 cc. of sulfuric acid was added. In this manner 9.2 g. (75%) of the dimethyl ether of the diol was obtained.

9,10-Dimethyl-1,2-benzanthracene.—Five cc. of dry benzene was placed in a warm 30-cc. cylinder fitted with a glass stopper; 0.50 g. of potassium was added, the mixture was heated carefully over a steam-bath until the metal melted, the flask was stoppered and the mixture was shaken in order to powder the metal. Two grams of the aforementioned dimethyl ether and about a dozen sharp particles of glass (made from a glass rod) were introduced and the flask was then filled with anhydrous ether. After the stopper had been sealed with Meloche and Fredrick grease[4] and tied down, the mixture was placed on a revolving wheel. After being agitated for sixteen to twenty hours the mixture had a greenish color, which was removed completely by one drop of methanol; no potassium remained. The solution was washed with dilute hydrochloric acid, filtered and evaporated, and the residue was recrystallized from acetone–alcohol. The first crop of nearly colorless hydrocarbon weighed 1.44 g. and melted at 121.5–123°; from the filtrate an additional 0.1 g. of hydrocarbon melting at 119–121° was obtained, making a total yield of 96%. For purification the hydrocarbon and twice its weight of picric acid were dissolved in hot absolute alcohol; the picrate which precipitated on cooling was recrystallized once or twice from absolute ethanol. A benzene solution of the regenerated hydrocarbon was then passed through a tower of aluminum oxide. The 9,10-dimethyl-1,2-benzanthracene crystallizes from acetone–alcohol in leaflets which possess a faint greenish-yellow tinge; m. p. 122–123°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.2.

The hydrocarbon is readily soluble in benzene, moderately soluble in acetone and only slightly soluble in alcohol.

On cooling a solution of 9,10-dimethyl-1,2-benzanthracene and twice its weight of picric acid in hot absolute alcohol the monopicrate crystallized in beautiful black needles. After being recrystallized from absolute alcohol, the **monopicrate** melted sharply at 112.5–113°.

Anal. Calcd. for $C_{20}H_{16}{\cdot}C_6H_3O_7N_3$: N, 8.6. Found: N, 8.6.

When a suspension of the monopicrate and crystals of picric acid in cold absolute alcohol was allowed to stand for twenty-four hours, the black crystals of the monopicrate were replaced by fine reddish-brown needles of the dipicrate. The latter can be obtained directly from the solution if four to five moles of picric acid are used for each mole of hydrocarbon. The **dipicrate** does not melt sharply; it begins to sinter at about 95° but does not melt until 102–106°.

Anal. Calcd. for $C_{20}H_{16}{\cdot}2C_6H_3O_7N_3$: N, 12.3. Found: N, 12.3.

The reaction of the diol dimethyl ether with sodium was carried out in the same manner as for potassium, except that the powdered sodium was prepared outside of the reaction vessel and then transferred to the latter. In one run a mixture of 5 g. of the diol dimethyl ether, 0.75 g. of powdered sodium, a dozen particles of glass, 20 cc. of benzene and 40 cc. of ether was shaken for twenty hours. From the mixture 3.6 g. (90%) of 9,10-dimethyl-1,2-benzanthracene melting at 121.5–123° was isolated.

In the early experiments in which sodium amalgam was employed, 1.0 g. of the diol dimethyl ether and 10 g. of 45% sodium amalgam in 30 cc. of ether and 30 cc. of benzene were shaken in the absence of air for four days. The deep green color which was formed initially gradually gave way to an intense red color. The amalgam was frozen by plac-

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[3] Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

[4] Meloche and Fredrick, *ibid.*, **54**, 3264 (1932).

ing the flask in ice water and the solution was decolorized by the addition of methanol. The oily residue (IV) obtained by evaporation of the ether–benzene solution was heated with 0.2 g. of sulfur at 200° for one-half hour. The 9,10-dimethyl-1,2-benzanthracene which was formed by the dehydrogenation process was sublimed from the mixture and purified by the methods already described. The yield of hydrocarbon (m. p. 122–123°) varied, usually amounting to 20–30% of the calculated amount.

9,10 - Dimethyl-1,2-benzanthracene-9,10-*endo*-α,β-succinic Anhydride (VII).—A solution of 0.5 g. of 9,10-dimethyl-1,2-benzanthracene and 0.25 g. of maleic anhydride in 5 cc. of benzene was refluxed for one hour. The orange-yellow color originally present gradually disappeared and the solution was nearly colorless after twenty minutes (in another experiment it was found that the reaction was 94% complete in this time). On cooling, 0.6 g. of the addition compound crystallized in colorless needles. The compound is readily soluble in ethyl acetate but little soluble in benzene and it may be recrystallized from a mixture of the two solvents; m. p. 238–240° with decomposition.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.3; H, 5.1. Found: C, 81.1; H, 5.1.

9,10 - Diethyl-9,10-dimethoxy-9,10-dihydro-1,2-benzanthracene.—A 94% yield of the dimethyl ether was obtained when a solution of 5 g. of 9,10-diethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene[2] in 15 cc. of warm methanol was cooled and treated with a solution of 0.25 cc. of concentrated sulfuric acid in 10 cc. of methanol. The product was purified in the manner described for the methyl analog. The compound can also be obtained conveniently from 1,2-benzanthraquinone without isolation of the intermediate diol by following the procedure outlined for the methyl compound. Any 1,2-benzanthraquinone present in the solution of the crude diol can be extracted by a concentrated solution of sodium hydrosulfite and sodium hydroxide. From benzene–methanol the diol dimethyl ether crystallizes in colorless needles; m. p. 172–173°. With concentrated sulfuric acid it gives an intense red color.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.2; H, 7.6. Found: C, 82.6; H, 7.6.

9,10-Diethyl-1,2-benzanthracene.—A mixture of 2.0 g. of the aforementioned diol dimethyl ether and 0.46 g. of powdered potassium was allowed to react under the conditions described for the methyl analog. After twenty hours, no potassium remained and the solution was perfectly colorless, containing a white suspension of potassium methylate. From the mixture was isolated 1.58 g. (96%) of 9,10-diethyl-1,2-benzanthracene melting at 97–99°. After being purified through the picrate and by passage of its benzene solution through aluminum oxide, the hydrocarbon melted at 98.5–99.5°. 9,10-Diethyl-1,2-benzanthracene crystallizes from acetone–alcohol in thin, perfectly colorless plates. The hydrocarbon was obtained in yields of 90% or more by reaction of the diol dimethyl ether with powdered sodium.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 92.5; H, 6.8.

Since the picrate dissociates readily into the two components in hot alcohol, it was made with excess of picric acid present. The crystals of picric acid which precipitated along with the picrate from the cooled solution were dissolved by adding cold absolute alcohol to the mixture. The picrate crystallizes in heavy black plates, which appear deep orange in color by transmitted light; m. p. 97–98.5°.

Anal. Calcd. for $C_{22}H_{20} \cdot C_6H_3O_7N_3$: N, 8.2. Found: N, 8.2.

9,10-Diethyl-1,2-benzanthracene-9,10-*endo*-α,β-succinic Anhydride.—A mixture of 0.5 g. of 9,10-diethyl-1,2-benzanthracene and 0.5 g. of maleic anhydride in 5 cc. of benzene was refluxed for twenty hours; on being cooled the solution deposited the addition compound in the form of stout, colorless needles; m. p. 215–217° with previous sintering; yield 0.5 g. No hydrocarbon was found unchanged.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.6; H, 5.8. Found: C, 81.1; H, 5.4.

When 0.1 g. of 9,10-diethyl-1,2-benzanthracene and 0.05 g. of maleic anhydride in 2 cc. of benzene was heated for twenty minutes only 20% of the addition product was formed. This was determined by converting the addition product to the water-soluble salt of the dicarboxylic acid by treatment with strong aqueous potassium hydroxide. When xylene was used and the mixture was heated for two hours an 84% yield of the adduct was formed. The addition product can be obtained rapidly by using a large excess of maleic anhydride. Thus, 0.5 g. of the hydrocarbon and 5 g. of maleic anhydride in 10 cc. of benzene was refluxed for two hours; the excess of anhydride was extracted from the cooled solution by means of water and the addition product obtained from the benzene was recrystallized from acetic anhydride.

5,9,10 -Trimethyl-9,10-dihydroxy-9,10-dihydro-1,2-benzanthracene (VI).—5-Methyl-1,2-benzanthraquinone was prepared by adding gradually 5.6 g. of powdered sodium dichromate dihydrate to a hot solution of 4.2 g. of 5-methyl-1,2-benzanthracene[5] in 50 cc. of acetic acid. After the addition was complete, the solution was refluxed for ten minutes and then treated with dilute sulfuric acid to precipitate the 5-methyl-1,2-benzanthraquinone. After being filtered and dried, the latter was recrystallized from toluene, with addition of ethanol to the hot solution; yield, 4.06 g. (86%), which included 0.5 g. obtained from the mother liquor by evaporation and sublimation of the residue at 220° (0.3 mm.). The compound possessed the melting point reported by Cook, who prepared the compound by the same method.

To the cooled Grignard reagent prepared from 3.3 cc. of methyl iodide and 1.2 g. of magnesium in 20 cc. of ether was added 15 cc. of benzene, followed by 3.56 g. of 5-methyl-1,2-benzanthraquinone. After the mixture had been allowed to stand at room temperature for two hours, the clear tan-colored solution was hydrolyzed with ice-cold ammonium chloride solution. Most of the diol precipitated as fine colorless crystals at this point; from the ether–benzene solution more of the diol was obtained, making a total yield of 3.6 g. (91%). From dilute acetone the diol crystallized in small thin sheets; m. p. 204–206°. From the behavior of the compound it is not unlikely that both *cis* and *trans* forms were present. With concentrated sulfuric acid the diol gives a purplish-red color.

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(5) Cook, *J. Chem. Soc.*, 1593 (1933); Bachmann and Wilds THIS JOURNAL, **60**, 624 (1938).

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.8; H, 6.6. Found: C, 82.8; H, 6.3.

To a suspension of 3 g. of the diol in 30 cc. of benzene was added a solution of 0.15 cc. of concentrated sulfuric acid in 60 cc. of methanol. As soon as all of the diol had gone into solution, the **dimethyl ether** of the diol began to crystallize as colorless needles. After purification in the manner described for the other diol ethers, the compound melted at 228–229°; yield 3 g. When a benzene suspension and solution of the total crude diol obtained from 3.56 g. of 5-methyl-1,2-benzanthraquinone was treated with methanol containing 0.2 cc. of sulfuric acid, 3.72 g. (85% on the basis of the quinone) of the diol dimethyl ether was obtained. The diol dimethyl ether gives a deep red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.1; H, 7.3. Found: C, 83.1; H, 7.3.

5,9,10-Trimethyl-1,2-benzanthracene (V).—A mixture of 2 g. of the aforementioned dimethyl ether and 0.28 g. of powdered sodium was allowed to react in 30 cc. of anhydrous ether in the usual manner; most of the diol dimethyl ether remained undissolved. After twenty-four hours the mixture was purple in color and contained a considerable amount of precipitate; the latter was still present after thirty-six hours and proved to be 5,9,10-trimethyl-1,2-benzanthracene (0.85 g., m. p. 127–128°). From the solution an additional 0.71 g. (m. p. 124–126°) of hydrocarbon was isolated, making a yield of 96%. After purification in the manner described for the other hydrocarbons, the 5,9,10-trimethyl-1,2-benzanthracene crystallized from acetone–alcohol in plates or leaflets which possessed a yellowish tinge; m. p. 127–128°. When potassium was employed, the yield of crude, crystalline hydrocarbon was usually not greater than 80%.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.3; H, 6.7. Found: C, 93.3; H, 6.2.

The picrate, prepared with excess of picric acid, crystallizes from absolute alcohol in beautiful black needles; m. p. 112–113°.

Anal. Calcd. for $C_{21}H_{18}\cdot C_6H_3O_7N_3$: N, 8.4. Found: N, 8.5.

5,9,10-Trimethyl-1,2-benzanthracene-9,10-*endo*-α,β-succinic Anhydride.—A solution of 0.5 g. of the hydrocarbon and 0.5 g. of maleic anhydride in 5 cc. of benzene was refluxed for one-half hour. The solution which was initially yellow became colorless and deposited crystals of the addition product. After cooling, 0.5 g. of the addition product was filtered off; it crystallizes from benzene in colorless needles; m. p. 250° with previous decomposition. The product obtained by evaporation of the benzene filtrate was completely soluble in hot aqueous potassium hydroxide, an indication that the addition of maleic anhydride to the hydrocarbon had been complete.

Anal. Calcd. for $C_{25}H_{20}O_3$: C, 81.5; H, 5.4. Found: C, 82.2; H, 5.1.

Summary

Three new polycyclic hydrocarbons, 9,10-dimethyl-1,2-benzanthracene, 9,10-diethyl-1,2-benzanthracene and 5,9,10-trimethyl-1,2-benzanthracene, have been synthesized for their possible cancer-producing properties.

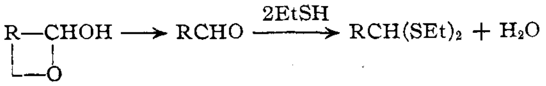
Ann Arbor, Michigan Received March 5, 1938

[Contribution from the Chemical Laboratory of The Ohio State University]

Studies of Cellulose Hydrolysis by Means of Ethyl Mercaptan. II[1]

By M. L. Wolfrom, Louis W. Georges[2] and John C. Sowden[2]

In a previous publication[3] from this Laboratory we have reported a study of the course of hydrolysis of the cellulose molecule. This study was performed by allowing a solution of high viscosity cotton linters in fuming hydrochloric acid to hydrolyze at 16° and following the course of hydrolysis by mercaptalation at various time intervals. Ethyl mercaptan is a reagent that will react with the free reducing groups of carbohydrates in high concentrations of mineral acid to form mercaptals or thioacetals.



$$\underset{\lfloor\!-\!\mathrm{O}}{\mathrm{R{-}CHOH}} \longrightarrow \mathrm{RCHO} \xrightarrow{\mathrm{2EtSH}} \mathrm{RCH(SEt)_2} + \mathrm{H_2O}$$

Sulfur analyses on the resulting mercaptalated hydrolyzed celluloses then gave an estimate of their average molecular size. In the work herein reported, the course of the hydrolysis of the same sample of cotton linters previously studied, was followed in more detail during the first three hours of the hydrolysis by fuming hydrochloric acid at 16°.

The literature concerned with hydrocelluloses and cellodextrins is very large[4] and a great deal of it is concerned with surface alterations of cellulose fibers in relation to textiles. No attempt will be made to review this literature, since so far as we are aware no previous work has been done employing ethyl mercaptan as a reagent for following the course of hydrolysis of the cellulose molecule.

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[1] Presented before the Division of Cellulose Chemistry at the 94th meeting of The American Chemical Society, Rochester, New York, September 9, 1937.

[2] Du Pont Cellulose Research Fellow.

[3] M. L. Wolfrom and Louis W. Georges, This Journal, **59**, 282 (1937).

[4] *Cf.* A. Girard, *Compt. rend.*, **81**, 1105 (1875); E. Heuser and F. Stöckigt, *Cellulosechem.*, **3**, 61 (1922); C. Birtwell, D. A. Clibbens and A. Geake, *J. Text. Inst.*, **17**, T145 (1926).