[Contribution from the Chemistry Laboratory of the University of Michigan]

THE SYNTHESIS OF 9,10-DIALKYLANTHRACENES

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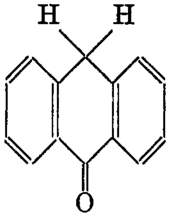
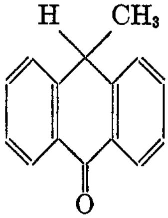
9,10-Dimethylanthracene has been prepared by the reaction of 9-methylanthrone (II) with methylmagnesium iodide[1]. The 9-methylanthrone was obtained by hydrolysis of the methyl ether of 9-methylanthranol which was formed when anthrone (I) was methylated with methyl iodide in strong potassium hydroxide solution[2]. We found it is difficult to obtain 9-methylanthrone by this method, and employed the action of methyl iodide on the sodium compound formed by reaction of anthrone with sodium ethylate. By treating the product with methylmagnesium iodide, low (15–20 per cent.) but reproducible yields of 9,10-dimethylanthracene were obtained. The method was also applicable to the preparation of 9,10-dibenzylanthracene.

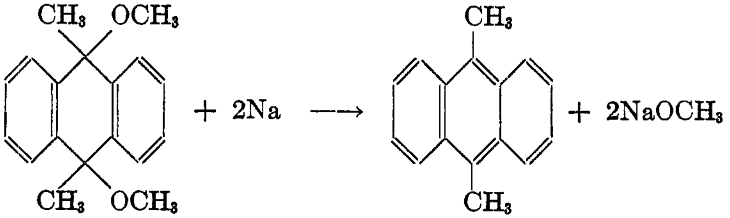


I



II

A much more satisfactory procedure for preparing 9,10-dimethylanthracene and other 9,10-dialkylanthracenes consisted in the extension of the method which was described recently for preparing 9,10-dimethyl-1,2-benzanthracene and related hydrocarbons[3]. In this method 9,10-dimethyl-9,10-dimethoxy-9,10-dihydroanthracene was allowed to react with exactly two equivalents of sodium in a mixture of ether and benzene.



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[1] Barnett and Matthews, *Ber.*, **59**, 767, 1437 (1926).

[2] Meyer and Schlösser, *Ann.*, **420**, 126 (1920).

[3] Bachmann and Chemerda, *J. Am. Chem. Soc.*, **60**, 1023 (1938).

By this reaction a nearly quantitative yield of 9,10-dimethylanthracene was obtained. Similarly 9,10-diethylanthracene was prepared in nearly quantitative yield.

If more than two equivalents of sodium are employed in the reaction, the hydrocarbon which is formed reacts with the sodium to give a deeply-colored 9,10-disodio addition product. With exactly two equivalents of the metal, only the diol dimethyl ether enters into the reaction. In only one instance was there evidence of reaction of the hydrocarbon with sodium before all of the diol dimethyl ether had been converted to the hydrocarbon. In the preparation of 2,9,10-trimethylanthracene some of the disodio addition product was formed and only an 85 per cent. yield of the hydrocarbon was obtained. It is of interest that Schlenk and Bergmann[4] were of the opinion that 9,10-diphenylanthracene was an intermediate in the conversion of 9,10-diphenyl-9,10-dimethoxy-9,10-dihydroanthracene to 9,10-diphenyl-9,10-disodio-9,10-dihydroanthracene by reaction of the diol dimethyl ether with excess of sodium.

EXPERIMENTAL

Preparation of 9,10-dimethylanthracene from anthrone.—To 20 g. of anthrone, partially dissolved in 120 cc. of absolute alcohol, was added 2.4 g. of sodium. Ten cubic centimeters of methyl iodide was added to the dark-brown solution, and the mixture was refluxed overnight. Water and acetic acid were added to the solution, and the oil which precipitated was extracted with benzene. Evaporation of the benzene gave an oil with some unreacted anthrone which was separated by filtration. Attempts to crystallize the oil failed.

A dried solution of the crude methylanthrone in toluene was added to an ice-cold solution of methylmagnesium iodide prepared from 18.5 cc. of methyl iodide and 75 cc. of ether. After standing at room temperature overnight, the solution was hydrolyzed, and the solvent was evaporated. A solution of the residue in benzene, when seeded with 9,10-dimethylanthracene, deposited 4.3 g. of the hydrocarbon; m.p. 171–179°. After treatment of a benzene solution of the product with sodium hydrosulfite-sodium hydroxide solution 3.4 g. of 9,10-dimethylanthracene was obtained as yellow needles; m.p. 180.5–181°.

Preparation of 9,10-dibenzylanthracene from anthrone.—To 10 g. of anthrone in 50 cc. of absolute alcohol was added 1.2 g. of sodium. When 6.2 cc. of benzyl chloride was added, a vigorous reaction took place, accompanied by the precipitation of sodium chloride. The solution was refluxed for five hours, and then 200 cc. of water was added. Extraction of the precipitated oil with benzene gave 14.5 g. of a dark-colored oil.

Seven grams of the above oil was added to an ice-cold solution of benzylmagnesium chloride prepared from 12 cc. of benzyl chloride and 50 cc. of ether. A brown addition product was formed, but disappeared in two hours at room temperature to give a light-green fluorescent solution. After the mixture had been worked up in the usual fashion and steam-distilled to remove dibenzyl, the crude product recrystallized from acetic acid gave 2.6 g. (17%) of 9,10-dibenzylanthracene; m.p. 243–245°.

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[4] SCHLENK AND BERGMANN, *Ann.*, **463**, 134 (1928).

Barnett and Cook[5] prepared 9,10-dibenzylanthracene from 9,9,10-tribenzyl-9,10-dihydroanthranol; they reported 245° for the melting point.

9,10-Dimethyl-9,10-dihydroxy-9,10-dihydroanthracene.—The general procedure for the reactions of anthraquinone with Grignard reagents is described in the case of the methyl diol. Attempts to carry out the reaction by adding solid anthraquinone to the Grignard reagent provided only small amounts of the diol with much unchanged quinone. Apparently the insoluble addition product which is formed in the reaction coats the undissolved quinone. By working with solutions of anthraquinone this difficulty can be avoided, but large volumes of solvent are required to dissolve the anthraquinone. We found it more convenient to extract the quinone into the Grignard reagent using a Soxhlet extractor or some suitable modification.

The Grignard reagent was prepared from 10 cc. of methyl iodide in 100 cc. of ether. A Soxhlet thimble was slit vertically, and a piece of cellophane was pasted in to allow observation of the progress of the extraction. In the thimble was placed 10.4 g. of anthraquinone, the extractor was attached to the flask, and the mixture was refluxed over a water bath. The almost colorless dilute solution of anthraquinone reacted immediately with the Grignard reagent with precipitation of a yellow complex. After two and one-half days, 0.5 g. of the quinone remained in the thimble. The ether suspension was hydrolyzed, the ether was evaporated, and the insoluble diol was removed by filtration. When dry it was dissolved in hot methanol, and an additional 0.5 g. of anthraquinone was separated by filtration. The hot methanol solution was treated with sodium hydroxide-sodium hydrosulfite solution and much water. The diol (8.5 g.) was filtered off and washed with much water. Recrystallization from methanol gave colorless needles of the diol containing solvent of crystallization which was easily driven off when heated; m.p. 185–195°. Guyot and Staehling[6] reported 181°.

A more rapid extraction resulted when a thimble containing the quinone was suspended from copper wires into the reaction flask directly below the reflux condenser. Using ether as a solvent, thirty hours was required to extract 19.6 of anthraquinone from a charge of 20.8 g. When ether-benzene (2:3) was used as a solvent and the mixture refluxed upon a steam bath, only six hours was required to extract 20.1 g. from 20.8 g. The last portion of quinone was always extracted more slowly. The yield of diol did not vary markedly with the method of extraction.

9,10-Dimethyl-9,10-dimethoxy-9,10-dihydroanthracene.—Five grams of the diol was dissolved in a solution of 25 cc. of benzene and 25 cc. of methanol containing 5 drops of sulfuric acid. A clear solution was obtained immediately. After standing at room temperature for half an hour, much water was added, and the benzene solution was treated with dilute ammonium hydroxide to remove traces of sulfuric acid which are harmful. Concentration of the benzene solution followed by addition of methanol gave 5.36 g. (96%) of the diol dimethyl ether. Guyot and Staehling[6], who used hydrogen chloride in place of sulfuric acid, reported a melting point of 197°.

9,10-Dimethylanthracene from the diol dimethyl ether.—A mixture of 5.36 g. of the diol dimethyl ether and 0.82 g. of powdered sodium was shaken in 30 cc. of ether and 30 cc. of benzene with about a half-dozen sharp glass particles for four days. The resulting mush was filtered; the residue was washed with water, and dried, giving 2.54 g. of 9,10-dimethylanthracene; m.p. 180–181°. Treatment of the ether-benzene filtrate with hydrochloric acid, and recrystallization of the residue after evaporation

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[5] Barnett and Cook, *J. Chem. Soc.*, **1928**, 566.

[6] Guyot and Staehling, *Bull. soc. chim.*, [3], **33**, 1144 (1905).

from alcohol-acetone gave an additional 1.25 g. (m.p. 179–181°) of hydrocarbon making a total yield of 92%.

9,10-Diethyl-9,10-dihydroxy-9,10-dihydroanthracene.—9,10-Diethyl-9,10-dihydroxy-9,10-dihydroanthracene was prepared from 10.4 g. of anthraquinone, using the modified extractor, and ether as a solvent. Considerable gas was evolved during the reaction, and ether must be added from time to time to replace that lost by evaporation. When purified in the manner described, 4.7 g. of a light-brown product was obtained; m.p. 147–153° with darkening. In another experiment starting with 20.8 g. of quinone, the ether was removed in a current of air at room temperature, and the crude diol dissolved in benzene was extracted with hot sodium hydroxide-sodium hydrosulfite solution. The dried benzene solution, when concentrated carefully, deposited 6.45 g. of colorless 9,10-diethyl-9,10-dihydroxy-9,10-dihydroanthracene; m.p. 169–171° with previous sintering (Clarke and Carleton[7], m.p. 175°).

9,10-Diethyl-9,10-dimethoxy-9,10-dihydroanthracene.—A solution of 3.65 g. of the diol in 17 cc. of methanol was treated with 0.17 cc. of sulfuric acid in 7 cc. of methanol. The precipitated diol dimethyl ether was collected, dissolved in benzene and purified as described above; yield 3.29 g., m.p. 176–178° with previous softening. After one recrystallization from benzene-methanol and one recrystallization from ethyl acetate, it melted constantly at 179–180.5°; yield 1.6 g. Clarke and Carleton[7] reported a melting point of 178°.

9,10-Diethylanthracene.—To 0.255 g. of powdered sodium in 25 cc. of ether and 25 cc. of benzene was added 1.64 g. of the diol dimethyl ether (m.p. 179–180.5°). After two days' shaking, the reaction mixture (slightly green in color) was worked up in the manner described, and a total yield of 1.23 g. (95%) of 9,10-diethylanthracene was isolated; m.p. 144–147°. Sublimation of a portion of the product followed by recrystallizations from alcohol-acetone and acetic acid gave colorless diamond-like prisms; m.p. 146–147°. Hugel and Lerer[8] who prepared 9,10-diethylanthracene by dehydrogenation of the dihydro derivative obtained by the treatment of 9,10-disodio-9,10-dihydroanthracene, with ethyl bromide reported a melting point of 145.5°.

9,10-Diethylanthracene dissolved in a hot absolute alcoholic solution of picric acid deposited black needles of a picrate when cooled; m.p. 128–129°. It is somewhat unstable, and cannot be recrystallized without decomposition.

2,9,10-Trimethyl-9,10-dihydroxy-9,10-dihydroanthracene.—This diol could be prepared either by the addition of solid *beta*-methylanthraquinone to an ice-cold solution of the Grignard reagent in ether-benzene and allowing the mixture to stand at room temperature overnight, or by extraction with ether, using the modified extractor (11g. required three hours). Although a yellow addition product was formed, the quinone dissolved before the addition product crystallized. After hydrolysis with ice-cold ammonium chloride solution, it is best to dissolve the diol in benzene, extract any unchanged quinone as described above for the ethyl diol, and allow the benzene solution to evaporate spontaneously.

Much crystalline material was obtained together with a red oil; the oily portion concentrates in the upper portion of the evaporating dish and these portions are separated mechanically, triturated separately with ligroin containing a small amount of acetone and filtered; yield (from 11 g. of quinone by either method) 8–9 g.; m.p.

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[7] CLARKE AND CARLETON, *J. Am. Chem. Soc.*, **33**, 1966 (1911).

[8] HUGEL AND LERER, *Bull. soc. chim.*, **53**, 1497 (1933).

112–130°. This diol retains solvent of crystallization quite tenaciously and was analyzed as the dimethyl ether.

2,9,10-Trimethyl-9,10-dimethoxy-9,10-dihydroanthracene.—Five grams of the diol was dissolved in 20 cc. of methanol and treated with 5 cc. of methanol containing 0.25 cc. of sulfuric acid. The diol dimethyl ether crystallized, and after purification in a manner already described, 4.35 g. of 2,9,10-trimethyl-9,10-dimethoxy-9,10-dihydroanthracene was obtained; m.p. 181–182.5°. Recrystallization from methanol containing a little benzene gave colorless tablets of the diol dimethyl ether; m.p. 181.5–182.5°.

Anal. Calc'd for $C_{19}H_{22}O_2$: C, 80.8; H, 7.9.
Found: C, 80.5; H, 7.8.

2,9,10-Trimethylanthracene.—One and one-half grams of pure diol dimethyl ether and 0.245 g. of powdered sodium in 25 cc. of ether and 25 cc. of benzene were shaken for two days. After a day a light pea-green solution which contained much sodium was obtained. After two days the solution was dark-green. Decolorized with methanol and worked up in the usual fashion, the reaction mixture gave 1.0 g. (85%) of 2,9,10-trimethylanthracene as yellow needles from alcohol-acetone. Evidently this hydrocarbon can exist in two polymorphic modifications. A portion of the hydrocarbon, when sublimed and allowed to crystallize slowly from alcohol, had a melting point of 100–101°. When crystallized rapidly it melted at 95–96°. Often a mixture is obtained which melts at an intermediate temperature. When remelted several times, the higher-melting form changes over gradually to the lower-melting form. A sample for analysis purified through the picrate melted at 96–101°. After two weeks it melted at 99–101°.

Anal. Calc'd for $C_{17}H_{16}$: C, 92.7; H, 7.3.
Found: C, 92.2; H, 7.5.

A solution of the hydrocarbon and picric acid in hot absolute alcohol containing a little benzene deposited jet black needles of a monopicrate when cooled. After recrystallization from benzene the *picrate* melted at 162–162.5°.

Anal. Calc'd for $C_{17}H_{16} \cdot C_6H_3N_3O_7$: N, 9.4. Found: N, 9.3.

SUMMARY

A method has been devised for preparing 9,10-dimethylanthracene, 9,10-diethylanthracene and 2,9,10-trimethylanthracene in excellent yields.