recrystallized from methanol–water to give the amide in long prisms, m. p. 108–110°.

Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.6; H, 7.6. Found: C, 82.4; H, 7.6.

This compound was also prepared from VI as described above for V ($R = C_2H_5$).

9-(2-Piperidino-1-oxoethyl)-9,10-dihydroanthracene Hydrochloride.—The aqueous filtrate from the 0.15 g. of amide above was basified with aqueous ammonia and the liberated base dried in ether. The ethereal solution was acidified with 1.7 cc. of 15% alcoholic hydrogen chloride. Enough acetone and absolute ethanol were added to dissolve the precipitated oil. The amino ketone salt crystallized in a yield of 0.5 g., m. p. 221–223°; flakes from methanol–ether, m. p. 222–224° (d.).

Anal. Calcd. for $C_{21}H_{24}ClNO$: C, 73.8; H, 7.1. Found: C, 74.0; H, 7.1.

Summary

In the reaction of 9-ω-bromoacetyl-9,10-dihydroanthracene with secondary aliphatic amines, the 9-(2-dialkylamino-1-oxoethyl)-9,10-dihydroanthracenes and the corresponding amides of 9-(9,10-dihydroanthryl)-acetic acid were obtained in nearly equal amounts.

Two convenient methods for the preparation of 9,10-dihydro-9-anthroic acid are described.

BETHESDA 14, MD. RECEIVED OCTOBER 23, 1947

[CONTRIBUTION FROM THE DIVISION OF PHYSIOLOGY, NATIONAL INSTITUTE OF HEALTH]

Studies in the Anthracene Series. VI. Derivatives of 1,2,3,4-Tetrahydroanthracene

BY H. GEORGE LATHAM, JR., EVERETTE L. MAY AND ERICH MOSETTIG

As a key substance for further synthetic work, 9-bromo-1,2,3,4-tetrahydroanthracene was needed in quantity. Bachmann and Cronyn[1] have shown that the bromination of tetrahydrophenanthrene gives exclusively and in good yield, the 9-bromo derivative. When tetrahydroanthracene was similarly treated,[2] 9-bromo-1,2,3,4-tetrahydroanthracene (VIII) was formed in a yield of *ca.* 30%. In addition, varying amounts of a dibromo-1,2,3,4-tetrahydroanthracene (IX) could be isolated.

The position of the bromine atom in VIII was established in the following way: VIII was converted, with cuprous cyanide, to the nitrile VI, which was also synthesized from 9-anthroic acid (I) *via* II and III as shown in Fig. 1. Furthermore, we hydrolyzed VI to amide V which, again, was obtained in the catalytic hydrogenation of IV. The dibromo derivative IX appears to be identical with the compound cursorily described by Schroeter[3] as the only bromination product of tetrahydroanthracene. Since it can also be prepared from VIII, one of its bromine atoms must be located in position 9.

The conversion of VI into ketone X constitutes additional evidence for the structure of the latter[4] and supports the formula assigned to the oily acetyltetrahydroanthracene, obtained together with the 6 isomer in the Friedel–Crafts reaction on tetrahydroanthracene.[5]

9-Anthroic acid was conveniently prepared in a yield of 60–70% by heating under reflux, anthracene and oxalyl chloride in nitrobenzene.[6] When 9-bromoanthracene was treated under the same conditions, carboxylation took place to the extent of only 12%. The acid is obviously identical with the 9-bromo-10-anthroic acid of Beyer and Fritsch,[7] since it can be readily oxidized to 9,10-anthraquinone.

Acknowledgment.—We are indebted to Edward A. Garlock, Jr., for much of the preliminary work on the bromination of tetrahydroanthracene and the hydrogenation of 9-anthroic acid.

Experimental[8,9]

9-Anthroic Acid (I).—A mixture of 50 g. of anthracene,[10] 30 cc. of oxalyl chloride, and 150 cc. of dry nitrobenzene in a one-liter flask was heated in a metal-bath. A gentle reflux was maintained by raising the temperature of the bath from 120 to 240° during five to six hours. After steam-distillation of the nitrobenzene, 100 cc. of 10 *N* sodium hydroxide and enough water to make the total volume 700 cc. were added, and the mixture was refluxed for one-half hour. Insoluble material (11 g. of anthracene after purification)[11] was collected. The filtrate was washed with ligroin (b. p. 30–60°), treated with decolorizing carbon (Norit), filtered hot, and the Norit washed with 2 *N* sodium carbonate. Acidification of the combined filtrate and washings gave 41.6 g. (67%) of I, m. p. 208–212°.

9-Bromo-10-anthroic Acid.[7]—This acid was prepared from VIII, as described for I (reaction time twenty-five hours), in a yield of 12%, m. p. 263–266° (dec.). The

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[1] Bachmann and Cronyn, *J. Org. Chem.*, **8**, 456 (1943).

[2] The preliminary experiments of the bromination were carried out by E. A. Garlock, Jr.

[3] Schroeter, *Ber.*, **57**, 2014 (1924).

[4] See Paper III of this series, May and Mosettig, THIS JOURNAL, **70**, 686 (1948).

[5] Garlock and Mosettig, THIS JOURNAL, **67**, 2255 (1945).

[6] We were unable to duplicate the experiments of Liebermann and Zsuffa [*Ber.*, **44**, 208 (1911)] who obtained 9-anthroic acid in yields of 70–80% by heating anthracene and oxalyl chloride in a sealed tube at 160–170°. In our hands the experiment yielded only 15–20% of 9-anthroic acid. Furthermore, Nenitzescu, *et al.* [*Ann.*, **491**, 210 (1931)] prepared 9-benzoylanthracene in nearly quantitative yields by refluxing a solution of anthracene and benzoyl chloride in nitrobenzene. In repeated attempts to reproduce the results of these authors, anthracene was hardly attacked and was recovered nearly quantitatively.

[7] Beyer and Fritsch, *Ber.*, **74**, 494 (1941).

[8] All melting points given are uncorrected.

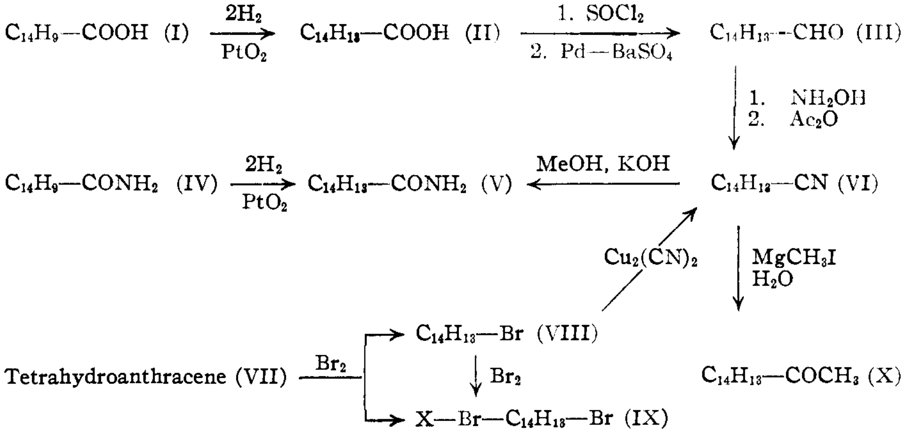
[9] The microanalyses were carried out by the microanalytical Laboratory of this Institute under the direction of C. A. Kinser.

[10] See Garlock and Mosettig[5] for the grade of anthracene used.

[11] During some preliminary work on this reaction, appreciable amounts of a yellow solid, m. p. 260–262°, were encountered.

Anal. Calcd. for $C_{29}H_{18}O$: C, 91.1; H, 4.7. Found: C, 90.8; H, 5.0.

This analysis indicates that the compound might be 9,9′-dianthryl ketone.



$C_{14}H_9$ = Anthracyl-9, $C_{14}H_{13}$ = Tetrahydroanthracyl-9

Fig. 1.

methyl ester melted at 112–114°. Oxidation of the acid with chromic acid gave 9,10-anthraquinone in a yield of 70%, m. p. 277–278°. The m. p. of the quinone was not depressed by authentic material.

1,2,3,4-Tetrahydro-9-anthroic Acid (II).[12]—A mixture of 10 g. of I (recrystallized from aqueous acetic acid), 0.3 g. of platinum oxide and 200 cc. of absolute ethanol absorbed 2000 cc. of hydrogen during two to three hours. The reaction was interrupted, catalyst was filtered, and the filtrate concentrated to one-fourth its volume. Ice-cooling gave 6.4 g. of II, m. p. 198–201°. This material was pure enough for use in the next reaction.

1,2,3,4-Tetrahydro-9-anthracenecarboxaldehyde (III).—A mixture of 5 g. of II and 10 cc. of thionyl chloride was refluxed for two hours, and excess reagent was distilled *in vacuo*. The resulting acid chloride was dissolved in 20 cc. of dry decalin, 0.6 g. of 5% palladium–barium sulfate was added, and a rapid stream of dry hydrogen bubbled through the mixture, heated to 175–180°. After one and one-half to two hours, hydrogen chloride evolution had almost ceased. The catalyst was filtered, and the solvent was distilled *in vacuo*. The residue was distilled at 0.05 mm. (bath temperature 175°) and the distillate crystallized from ether–ligroin, (b. p. 30–60°) to give 2.0 g. (49%) of III, m. p. 53.5–55°. The analytical sample melted at 54.5–56°; light yellow prisms.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.9; H, 6.8.

The oxime, prepared from hydroxylamine hydrochloride, sodium carbonate, and aqueous ethanol, crystallized from methanol in long prisms of m. p. 158.5–160°.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 80.0; H, 6.7. Found: C, 79.8; H, 6.7.

1,2,3,4-Tetrahydro-9-anthronitrile (VI).—The above oxime (0.5 g.) and 5 cc. of acetic anhydride were refluxed for fifteen minutes. Addition of water and cooling gave a solid which, after recrystallization from ethanol (Norit), weighed 0.3 g. (65%), m. p. 84.5–86°. The analytical sample melted at 85–86.5°, plates.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.9; H, 6.3. Found: C, 87.0; H, 6.4.

9-Bromo-1,2,3,4-tetrahydroanthracene (VIII).—To a mixture of 100 g. of VII,[5] 10 g. of reduced iron powder, and 800 cc. of benzene was added (stirring at 3° to 6°) during three-fourths hour, 90 g. of bromine in 200 cc. of benzene. After stirring at 0 to 5° for four hours, the mixture was filtered. The filtrate was washed three times with 5 *N* sodium carbonate and dried over sodium sulfate. Evaporation of solvent and distillation of the residue at 3 mm. gave (1) 10–15 g. of mainly VII, b. p. 160–170°, (2) 85 g., b. p. 180–190° and (3) about 10 g., b. p. 190–201°. Fraction (2) was dissolved in about 60 cc. of ligroin (b. p. 85–100°) and the solution cooled in ice for fifteen minutes. The supernatant liquid was decanted from a mass of prisms which were washed with a little cold ligroin. The prisms were dissolved in 300 cc. of absolute ethanol to give, after cooling at room temperature for three to four hours, 27 g. of VIII, m. p. 59–61°. It crystallized from ethanol in prisms of m. p. 60.5–61.5°.

Anal. Calcd. for $C_{14}H_{13}Br$: C, 64.4; H, 5.0. Found: C, 64.7; H, 4.8.

The ligroin filtrate and washings above gave an additional 19 g. of VIII (total yield 32%) after tedious fractional crystallizations from ethanol and from ligroin.

9,x-Dibromo-1,2,3,4-tetrahydroanthracene (IX).—Fraction (3) was recrystallized three times from ligroin (b. p. 85–100°) to give 3.2 g. of IX, m. p. 165–166°[7]. In addition 5 g. of IX was obtained in the course of the isolation of the 19 g. of VIII; needles.

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.4; H, 3.6. Found: C, 49.4; H, 3.6.

Compound IX was also obtained in a yield of 20% by brominating VIII according to the above procedure. It melted at 164–166° and the m. p. was not depressed by the IX isolated as described above.

Conversion of VIII to VI.—A mixture of 5 g. of VIII and 2.5 g. of cuprous cyanide was heated for two to three hours at 245–255°. Distillation at 0.1 mm. (bath temperature 180–200°) followed by recrystallization of the distillate from 95% ethanol gave 3.0 g. (75%) of plates, m. p. 85–87.5°. Mixed with VI prepared from I *via* II and III, it melted at 85.5–87°.

1,2,3,4-Tetrahydro-9-anthramide (V). (a) **By Hydrolysis of VI.**—A mixture of 0.5 g. of VI, 5 g. of potassium hydroxide, 25 cc. of methanol and 1 cc. of water was refluxed for twenty hours and diluted with water to give 0.4 g. of V, m. p. 203–207°. It crystallized from methanol–water in prisms, m. p. 210–211.5°.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 80.0; H, 6.7. Found: C, 80.3; H, 6.7.

(b) **By Hydrogenation of 9-Anthramide.**—A mixture of 0.5 g. of 9-anthramide,[13] 0.05 g. of platinum oxide, and 10 cc. of methanol absorbed two moles of hydrogen in seventeen hours. The filtered solution was concentrated to about 5 cc. and diluted with a little water to give 0.4 g. of prisms, m. p. 209–211°. When mixed with the V prepared as described under (a), the melting point was unchanged.

9-Acetyl-1,2,3,4-tetrahydroanthracene (X).—Two grams of VI in 10 cc. of dry benzene was added dropwise to a

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[12] Meerwein and Migge, *Ber.*, **62**, 1046 (1929).

[13] See Paper V of this series, May and Mosettig, This Journal, **70**, 1077 (1948).

stirred mixture of 12 cc. of 1 *M* methylmagnesium iodide in 25 cc. of dry benzene. The mixture was stirred and refluxed for 3.5 hours and poured into 75 cc. of saturated ammonium chloride. The benzene layer was extracted with two 50-cc. portions of *N* hydrochloric acid. To the combined extracts was added 10 cc. of concentrated hydrochloric acid and the solution refluxed for fifty hours. The resulting dark oil was dried in ether and evaporatively distilled at 150–170° (0.5 mm.). Recrystallization of the distillate from methanol gave 0.15 g. of prisms, m. p. 71–73°. The m. p. was not depressed by mixture with X previously prepared.

Summary

In the bromination of tetrahydroanthracene, 9-bromo-1,2,3,4-tetrahydroanthracene is formed in a yield of *ca.* 30%.

Its structure has been established by linking it with 9-anthroic acid.

A simple and efficient preparative method for 9-anthroic acid is described.

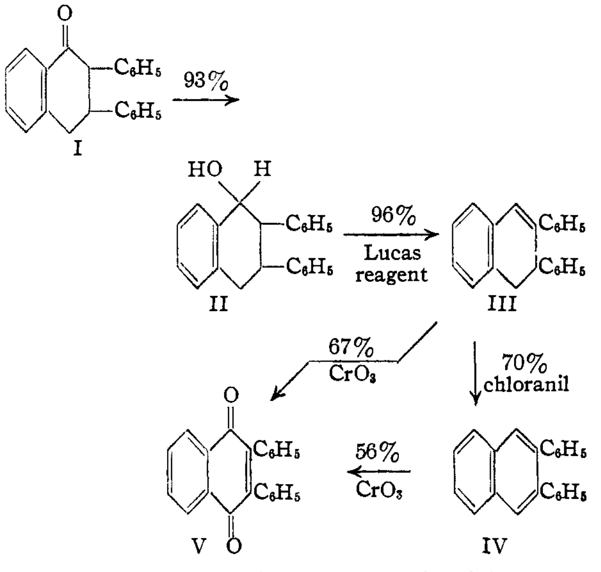
BETHESDA 14, MD. RECEIVED OCTOBER 23, 1947

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

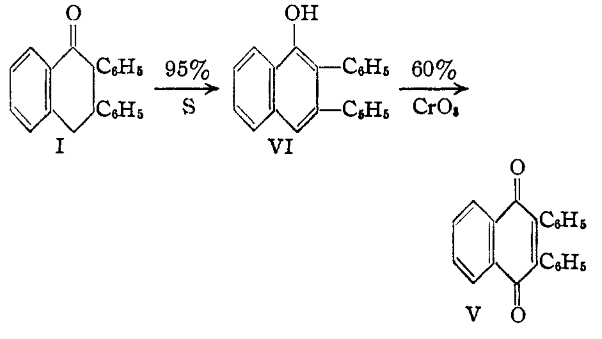
The Preparation of 2,3-Diphenyl-1,4-naphthoquinone and its Reaction with Phenylmagnesium Bromide and Phenyllithium

BY H. MARJORIE CRAWFORD

2,3-Diphenyl-1,4-naphthoquinone has been prepared by Crawford and Nelson[1] by the series of reactions



and by Bergmann and Szmuszkovic[2] as follows:



In preparing this quinone in larger quantities for the study reported here, variations in these procedures were carried out in attempts to improve the yield. Direct oxidation of 2,3-diphenyl-1,2-dihydronaphthalene (III) with chromium trioxide in glacial acetic acid gave 67% of the quinone (V). This makes the over-all yield of the quinone from the tetralone about 60% as compared to 35% when the dehydrogenation step is included. This is a more satisfactory method of preparing the quinone than that described by Bergmann[2] for, although three steps are involved instead of two, the yield is about the same and the products are much more easily purified.

Dehydrogenation of the tetralone (I) by sulfur gave the naphthol (VI) in 85–90% yields but there were red products formed which made the purification of the naphthol by recrystallization very difficult. In variations of the dehydrogenation reaction, selenium and chloranil gave poorer yields than sulfur. In the oxidation of the naphthol (VI) with chromium trioxide, the quinone (V) was obtained in 30–60% yields, accompanied by a high molecular weight white compound melting at 265–267°, and considerable quantities of yellowish oils.

As it has already been shown,[3,4,5] the reactions of phenylmagnesium bromide with methyl substituted naphthoquinones give complex mixtures of products. The solid compounds isolated from these mixtures resulted from both 1,2-additions to the carbonyl group and 1,4-additions to the conjugated systems, as well as reduction of the quinones to the hydroquinones and the accompanying formation of biphenyl. When phenyllithium reacted with these methyl substituted naphthoquinones the only products isolated were those resulting from the 1,2-addition of two molecules of the reagent to the carbonyl groups.

The behavior of 2,3-diphenyl-1,4-naphthoquinone has now been studied, hoping that the phenyl groups would be large enough to prevent the 1,4-

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(1) Crawford and Nelson, THIS JOURNAL, **68**, 134 (1946).

(2) Bergmann and Szmuszkovic, *ibid.*, **68**, 1662 (1946).

(3) Crawford, *ibid.*, **57**, 2000 (1935).

(4) Crawford, *ibid.*, **61**, 3310 (1939).

(5) Crawford, *ibid.*, **63**, 1070 (1941).