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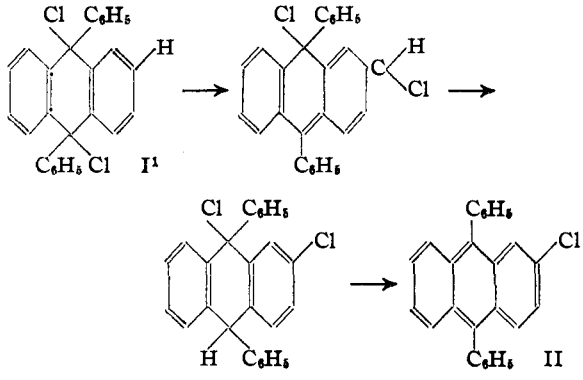
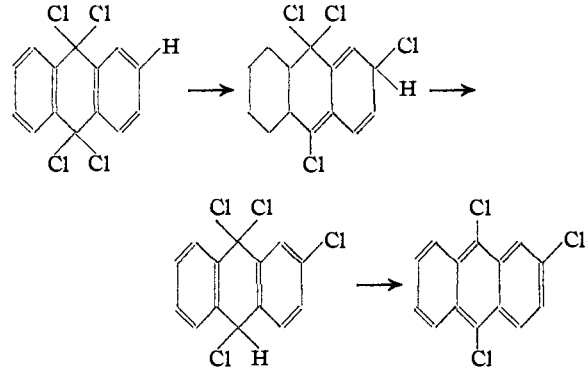
Tautomerization Reactions in the Anthracene Series

BY ERNST BERGMANN AND O. BLUM-BERGMANN

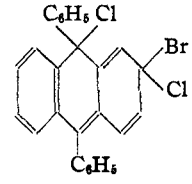
While in the heterocyclic series the heteronuclear *p-quinoidization* of a tricyclic system is a common fact, no similar effect has been detected so far in the anthracene series. In this paper, such a case is recorded. 9,10-Dichloro-9,10-diphenyl-9,10-dihydroanthracene (I) melts with decomposition, whereby a new compound is formed containing one molecule of hydrogen chloride less than the starting material. It exhibits the physical properties of a true anthracene derivative and was identified, by comparison with synthetic samples of 1- and 2-chloro-9,10-diphenylanthracene, as the latter substance (II). We do not see any explanation other than the following. The dichloro compound (I) rearranges via a quinolid system into 2,9-dichloro-9,10-diphenyl-9,10-dihydroanthracene which loses 1 mol. of hydrogen chloride from the middle ring.[1]



In the case of 9,10-di-α-naphthyl-9,10-dichloro-9,10-dihydroanthracene, it has been observed already by Guyot and Staehling[2] that decomposition gives an *x*-chloro-9,10-di-α-naphthylanthracene. We have identified it as the 2-compound by comparison with a synthetic specimen. The dinaphthyl-di-chloro compound is so unstable that treatment of 9,10-dihydroxy-9,10-di-α-naphthyl-9,10-dihydroanthracene with gaseous hydrogen chloride in boiling benzene solution gives the rearranged product directly. The well-known formation of 2,9,10-trichloroanthracene on exhaustive chlorination of anthracene or anthraquinone[3] may also be explained conveniently as proceeding through an intermediate *quinolid* product.



The above effect resembles the observation made by Ingold and Marshall[4] that 2-bromo-9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene, on heating, rearranges to a certain extent to give 2-chloro-9,10-diphenylanthracene. Here again a *quinolid* intermediate stage



explains sufficiently the course of the reaction; one has only to consider that dihalogenides of the mentioned type easily lose one mol. of halogen.

In view of the recorded facts, the possibility of *quinolid* tautomerization has to be borne in mind and may be used to obtain a better insight into the mechanism of the following known but strange reactions.

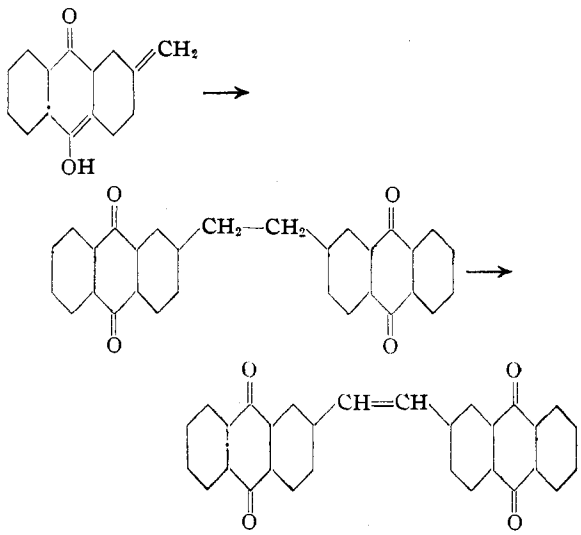
(1) The methyl group of 2-methylanthraquinone is oxidized with surprising ease by means of lead oxide to give anthraflavone. One may assume that the underlying principle of this oxidation is the tautomeric enol form

(1) The dichloro compound has *cis*-structure, as substantiated by unpublished dipole moment measurements in this Laboratory. There seems to be no connection between the steric configuration and the above rearrangement.

(2) Guyot and Staehling, *Bull. soc. chim.*, [3] **33**, 1117 (1905).

(3) Radulescu, *Bul. Soc. Stiinte*, **17**, 29 (1908); Liebermann and Beudet, *Ber.*, **47**, 1011 (1914).

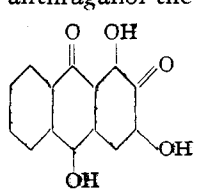
(4) Ingold and Marshall, *J. Chem. Soc.*, 3080 (1926).



which on dehydrogenation[5] will give dihydroanthraflavone. The easy oxidizability of the 2-methyl group may also account for the occurrence in plant cells of 2-methylanthraquinone derivatives in all possible stages of oxidation.

(2) The formation of pyranthrone by intramolecular dehydration of 2,2'-dimethyl-1,1'-dianthraquinonyl involves a reactive methylene group as present in α-picoline, quinaldine and similar substances. Quinolid enolization provides the necessary mobility of an hydrogen atom in the methyl group. It may be mentioned that experiments to prove the reactivity of the methyl group of 2-methylanthraquinone by condensation with aldehydes (*m*-nitrobenzaldehyde) have given no definite results so far, reaction taking place, but giving no crystalline product.

(3) In several cases, similar tautomerization has been suggested already by previous authors, but without substantial foundation. Georgievics,[6] *e. g.*, assigned to anthragallol the formula



in order to explain its difference in behavior from alizarine and Houben[7] explains the reaction between 2-aminoanthraquinone and phosgene and the formation of indanthrene as involving the tautomeric form of 2-aminoanthraquinone.

(5) Compare the conversion of ethyl acetoacetate into ethyl diacetosuccinate.

(6) Georgievics, *Monatsh.*, **32**, 329 (1911).

(7) Houben, "Das Anthracen und die Anthrachinone," Georg Thieme, Leipzig, 1929, pp. 432 and 714.

Experimental

9,10 - Dichloro - 9,10 - diphenyl - 9,10 - dihydroanthracene (I) and its Decomposition.—The dihydroxy compound[8] (7 g., from methyl ethyl ketone, m. p. 257°) was boiled for seven hours with acetyl chloride (200 g.). The solid phase and the residue of the acetyl chloride were identical; from toluene colorless prisms, m. p. 187–189° (dec.); deep blue color reaction with concentrated sulfuric acid. This product was heated for three hours at 200–210°. The brown cake was triturated with ether and recrystallized from glacial acetic acid; prisms of 2-chloro-9,10-diphenylanthracene, (II), m. p. 183–185°, identified by mixed m. p. The decomposition product proved to be absolutely homogeneous.

Synthesis of 2-Chloro-9,10-diphenylanthracene (II).[4,9]—2-Chloro-anthraquinone (11.5 g.) was extracted in a Soxhlet apparatus with the Grignard solution,[10] prepared from bromobenzene (52.3 cc.) and magnesium (12.2 g.), increased with half the volume of benzene in order to enhance the extraction. When the quinone was dissolved, the mass was boiled for eight hours and decomposed with cold dilute sulfuric acid. The ethereal solution, after separation of a small amount of insoluble material, was evaporated and the residue extracted with alkaline hydrosulfite solution several times. The remaining substance apparently was a mixture and therefore (2.7 g.) was boiled with anhydrous formic acid (80 cc.) for three hours. The solution was first dark-red, but the color changed quickly to the violet fluorescence of the desired product, which separated on cooling nearly completely; from glacial acetic acid and then from butanol as needles, m. p. 185°.

Synthesis of 1-Chloro-9,10-diphenylanthracene.[9]—According to the above method, 1-chloroanthraquinone (5.8 g.) was treated with phenylmagnesium bromide (from 6.1 g. of magnesium and 26.2 cc. of bromobenzene). The crude product, after removal of unchanged quinone by means of alkaline hydrosulfite solution (5.2 g.) was boiled for two hours with anhydrous formic acid (160 cc.). The dark solution deposited, while still boiling, a yellow precipitate, which after cooling was collected (4.4 g.) and crystallized from glacial acetic acid as yellowish prismatic plates, m. p. 180–182°. The m. p. was depressed to 152–160° by admixing the 2-chloro isomer or the decomposition product of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene.

2 - Chloro - 9,10 - di - α - naphthylanthracene.—(a) 9,10 - Dihydroxy - 9,10 - di - α - naphthyl - 9,10 - dihydroanthracene[8] (1 g.) was boiled for two hours in benzene (100 cc.) in a stream of dry gaseous hydrochloric acid. The yellowish-brown solution was dried and evaporated, the resinous residue triturated with alcohol and acetone and the solid material recrystallized from methyl ethyl ketone or butanol; prismatic plates, m. p. 270°.

(b) The reaction between 2-chloroanthraquinone and α-naphthylmagnesium bromide was carried out as above. The crude product, after extraction with sodium hydrosulfite, could not be recrystallized due to its low solubility in the common solvents, and was treated (3 g.) with boil-

(8) Kovache, *Ann. chim.*, [9] **10**, 184 (1918).

(9) Barnett, Cook and Wiltshire, *J. Chem. Soc.*, 1724 (1927).

(10) Compare for this method Schlenk, Houben-Weyl's "Methoden der organischen Chemie," Vol. IV, 1924, p. 927.

ing anhydrous formic acid (90 cc.) for three hours. The precipitate was collected and recrystallized from methyl ethyl ketone. The m. p. of the prisms could be raised to 280°, but the mixed m. p. with the above sample proved the identity.

Summary

On heating 9,10-diphenyl-9,10-dichloro-9,10-dihydroanthracene is converted into 2-chloro-9,10-diphenylanthracene (and 1 mole of hydrochloric acid). This reaction is suggested to involve a *p*-quinolid tautomerization.

This mechanism is used for explaining certain known reactions of the anthracene series. It may be responsible, too, for the occurrence in nature of 2-methylanthraquinone in various oxidative stages with regard to the methyl group.

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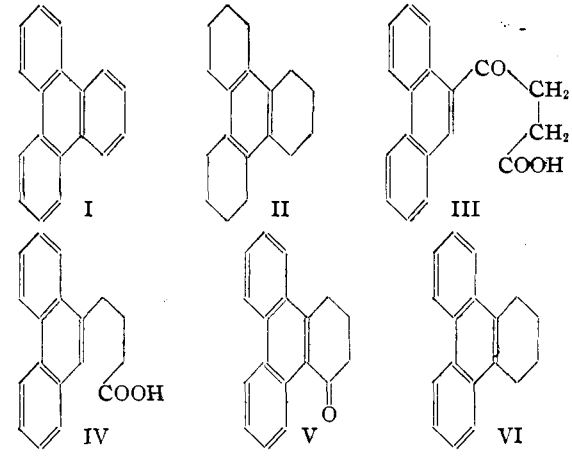
Synthesis of Triphenylene

BY ERNST BERGMANN AND O. BLUM-BERGMANN

For spectroscopic purposes, we required a specimen of pure triphenylene (I). An easy way of synthesis has been devised by Mannich[1] and by Diels and Karstens[2] by dehydrogenation with selenium of dodecahydrotriphenylene (II), which is formed in relatively small yields (3 to 4 g. from 100 g. of cyclohexanone) on treating cyclohexanone with methyl alcoholic sulfuric acid. We thought it advisable to find a synthetic method proving at the same time the constitution of triphenylene, which so far has been based on mere analogy. The method to be described here gives not only the desired proof, but may be extended to include the synthesis of alkyl and aryl derivatives of triphenylene.

By the interaction of 9-phenanthrylmagnesium bromide and succinic anhydride according to the method of Weizmann and co-workers[3] β-(9-phenanthroyl)-propionic acid (III) is formed. It is converted, through its semicarbazone, into γ-(9-phenanthryl)-butyric acid (IV) which subsequently has been cyclized by means of phosphoric oxide to form 4-keto-1,2,3,4-tetrahydrotriphenylene (V). Clemmensen reduction afforded 1,2,3,4-tetrahydrotriphenylene (VI), which could be dehydrogenated easily to (I).

In preparing triphenylene by dehydrogenation of (II), occasionally an intermediate product $C_{18}H_{16}$ has been obtained, which was identified by mixed m. p. as tetrahydrotriphenylene (VI), for which our synthesis gives the exact formula. Obviously, the three hydrogenated rings in (II) lose their supernumerary hydrogen atoms stepwise.[3a]



Experimental

β-(9-Phenanthroyl)-propionic Acid (III).—When a solution of 9-phenanthrylmagnesium bromide (prepared from 5 g. of magnesium and 48.5 g. of 9-bromophenanthrene according to Bachmann[4]) was added to a boiling suspension of succinic anhydride (15 g.) in ether, a violent reaction took place. After one hour's boiling, the product was decomposed with ice and dilute sulfuric acid and the resulting acid extracted with alkali from its solution. The dark brown liquid, on acidifying, deposited an oil, which solidified quickly. The crystals were collected, kept with benzene at 0° for twenty-four hours, filtered, washed with ice-cold benzene and recrystallized from propyl alcohol; m. p. 176°; yield, 9 to 11.5 g. This acid dissolves in concentrated sulfuric acid with dark orange-red color. (Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.0. Found: C, 77.5; H, 5.1.)

The methyl ester, prepared by means of diazomethane in ethereal solution, boiled at 217–220° (1.5 mm.) and crystal-

(1) Mannich, *Ber.*, **40**, 153 (1907); compare Pirrone, *Chem. Zentr.*, **107**, II, 2351 (1936).

(2) Diels and Karstens, *ibid.*, **60**, 2323 (1927).

(3) Weizmann and co-workers, *J. Chem. Soc.*, 1370 (1935).

(3a) Compare Cook and Hewett, *J. Chem. Soc.*, (370 1934), for the case of didecahydrobenzanthracene.

(4) Bachmann, THIS JOURNAL, **56**, 1363 (1934).