The concentration of the acid should not vary too widely from that suggested. If the acid is much more dilute, the action is too slow; if much more concentrated, the reaction products are pale green rather than deep blue.

The point at issue can easily be understood by a class without any statement of the composition of the brown solution or that of the blue reaction products.

G. S. FORBES.

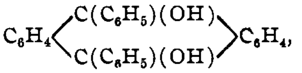
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ACTION OF ETHYL MAGNESIUM BROMIDE ON ANTHRAQUINONE.[1]

BY LATHAM CLARKE AND PAUL WHITTIER CARLETON.

Received August 30, 1911.

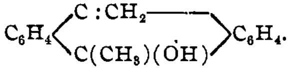
It has been shown by Haller and Guyot[2] that an excess of phenyl magnesium bromide reacts with anthraquinone forming 9,10-diphenyl-9,10-dihydroxydihydroanthracene,



$$C_6H_4\left\langle\begin{matrix}C(C_6H_5)(OH)\\C(C_6H_5)(OH)\end{matrix}\right\rangle C_6H_4,$$

while an excess of the quinone gives phenyloxanthrone (or phenyloxanthranol).

Guyot and Staehling[3] prepared analogous compounds from methyl anthraquinone, using phenyl and naphthyl magnesium bromides. They also treated anthraquinone with methyl magnesium bromide, which produced 9,10-dimethyl-9,10-dihydroxydihydroanthracene, and this compound readily lost one molecule of water, giving 9-methene-10-methylhydroxydihydroanthracene,



$$C_6H_4\left\langle\begin{matrix}C:CH_2 \text{———}\\C(CH_3)(OH)\end{matrix}\right\rangle C_6H_4.$$

The action of ethyl magnesium bromide on anthraquinone was studied in this laboratory in 1907 by Clarke and Victor Cobb, who found that the normal action was to give 9,10-diethyl-9,10-dihydroxydihydroanthracene, but certain other compounds were formed by side reactions. These last we were prevented from studying, on account of the departure of Mr. Cobb from Cambridge.

In the autumn of 1910 this study was taken up by the present writers. We have found that with an excess or ethyl magnesium bromide, the anthraquinone is converted into the di-ol; and when an excess of the quinone is used, the product is ethyloxanthranol. The di-ol is very sus-

---

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Paul Whittier Carleton.

[2] *Compt. rend.*, 138, 327, 1251 (1904); *Bull. soc. chim.*, 31, 795, 979 (1904).

[3] *Bull. soc. chim.*, 33, 375 1104 (1905).

ceptible to the action of dehydrating agents, and the side products obtained in the experiments of Clarke and Cobb and later by us, are dehydration products, formed from the di-ol by the excess of acid used to acidify the reaction mixture after the usual decomposition of the organo-magnesium compound with water.

The di-ol is a white crystallin compound, which melts at 172°. The crystals obtained from ether or alcohol solutions contain ether or alcohol of crystallization, but in either case so loosely held that on standing in the air the crystals quickly effloresce to a white powder. Both hydrogen atoms of the di-ol could be replaced by alkyl groups, and the dimethyl and diethyl ethers were prepared. All attempts to substitute the hydroxyl groups by halogens failed.

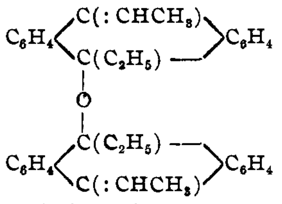
Dilute hydrochloric or sulfuric acid acted on the di-ol, quickly turning it to a yellow color, and giving a mixture of two new substances, which could be separated only by a laborious process of fractional crystallization. These new substances were lemon-yellow in color, one crystallized in rhombic plates and melted at 161°, the other crystallized in prisms and melted at 226°. The longer the standing with dilute acid, the greater was the proportion of the higher melting compound, from which it seemed that the higher melting was formed from the lower melting.

Both these compounds had the same composition as shown by analysis:

Compound melting at 161°, Found: C, 89.27; H, 7.25.
Compound melting at 226°, Found: I, C, 89.48; H, 7.28.
Compound melting at 226°, Found: II, C, 89.53; H, 6.84.

Determinations of the molecular weights indicated that the molecule of each of these compounds contained two anthracene nuclei; the molecular weight found for the compound melting at 161° was 480; that for the compound melting at 226°, 425. These figures for the analysis and molecular weights point to the formula for each, $C_{36}H_{34}O$. The solubilities of both compounds were quite similar, but in the properties of the solutions there was one striking difference; the lower melting dissolved in alcohol, benzene, and such solvents, giving yellowish solutions, but the solutions of the higher melting were fluorescent.

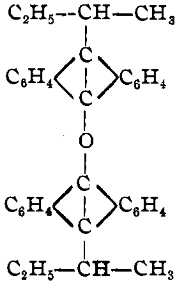
We can now construct a very probable formula for the compound melting at 161°:



$$C_6H_4\left<\begin{array}{l}C(:CHCH_3)\\C(C_2H_5)\end{array}\right>C_6H_4 \\ | \\ O \\ | \\ C_6H_4\left<\begin{array}{l}C(C_2H_5)\\C(:CHCH_3)\end{array}\right>C_6H_4$$

As will be seen, this formula is derived from two molecules of the di-ol, by the elimination of three molecules of water. By the splitting off of one water molecule, the two dihydroanthracene nuclei are joined together, while the splitting off of the other two gives the unsaturated ethylidene groups, which are analogous to the methene groups of Guyot and Staehling. This compound remains a derivative of dihydroanthracene, and *derivatives of dihydroanthracene do not exhibit fluorescence when in solution.*

We may now construct a possible formula for the compound melting at 226°:



This formula is obtained from that for the compound melting at 161°, by a migration of the two ethyl groups from the two different 10-positions in the dihydroanthracene nuclei, to the number 2-position in the ethylidene side chains which thereby become secondary butyl groups, the condition of unsaturation being broken. This migration taking place slowly accounts for the gradual change of the compound melting at 161° into its isomer, and since this new compound is a derivative, not of dehydroanthracene, but of anthracene, the fluorescence of the new compound is explained. A wandering of ethyl groups, similar to the case described above, and likewise brought about through the influence of dilute acids, has been shown by Zincke,[1] while the migrations of other groups in an analogous manner have been described by Bamberger[2] and Auwers.[3]

Experimental Part.

The ethyl magnesium bromide used in this research was prepared in the usual way, in ether solution. Since anthraquinone is but slightly soluble in ether, it was used in suspension and to the ethyl magnesium bromide derived from 90 grams of ethyl bromide, 30 grams of anthraquinone were added, together with about 50 grams of ether. The mixture was heated gently for four hours, then treated with sufficient ice-water to decompose the organomagnesium compounds, and acidified with dilute hydrochloric acid. As much anthraquinone remained visibly

[1] Zincke, *Ber.*, 34, 253 (1901).

[2] Bamberger, *Ibid.*, 38, 3607 (1910).

[3] Auwers, *Ber.*, 36, 1861 (1903); 38, 1697 (1905); 39, 3748 (1906); 43, 3094 (1910); 44, 588 (1911).

unchanged, it was necessary to remove it by filtration, so the ether layer was drawn off and filtered. By setting the clear ether aside and allowing it to evaporate slowly, the di-ol was obtained in the form of rather large white crystals, but as the evaporation proceeded, anthraquinone crystals began to appear, and a reddish colored oil gathered on the sides of the crystallizing dish. It was found, subsequently, that if the acidification of the reaction mixture was so carefully carried out as to avoid an excess of free acid, this reddish oil was practically lacking, while the use of a large excess of hydrochloric acid gave much reddish oil and little or no di-ol. It was also found that by agitating vigorously the mixture of ethyl magnesium bromide and anthraquinone, the yield of the di-ol was much increased, so a mechanical stirring device was used in the later experiments. Without the stirrer, the yield of di-ol was from five to ten per cent. of the theoretical, calculated from the anthraquinone, while with the stirrer the yield was in one case as high as thirty-six per cent. of the theoretical.

The above-mentioned reddish oil was treated with alcohol with which a few drops of benzene had been mixed, and after a series of crystallizations, yielded two light yellow-colored compounds, one melting at 161° and the other at 226°, also some unchanged anthraquinone and a residue of a red tar, from which nothing definit could be isolated. The two yellow-colored compounds were later found to be identical with the substance formed from the di-ol by the action of dilute acids, an account of which is given later in this paper. The red tar was subjected to a distillation *in vacuo* and the distillate, which consisted only of a small fraction of the weight of the substance taken, was found to be diethyl anthracene, and was evidently some decomposition product of the red tar.

9,10-Diethyl-9,10-dihydroxydihydroanthracene.—The di-ol obtained as already described was crystallized from ether or benzene. A sample was dried *in vacuo* for analysis.[1]

Calculated for $C_{18}H_{20}O_2$: C, 80.55; H, 7.50.
Found: I. C, 80.39; H, 7.08.
II. C, 80.71; H, 5.83.

A determination of the molecular weight was made in benzene by the freezing-point method.

0.0758 gram substance in 17.67 grams benzene gave Δ 0.080°.

0.1583 gram substance in 17.67 grams benzene gave Δ 0.130°.

In this last case the substance was not entirely dissolved.

Molecular weight:

Calculated for $C_{18}H_{20}O_2$: 268.
Found: I, 268, II, 344.

---

[1] One of us had previously shown that this substance, when crystallized from ether, retains one molecule of ether of crystallization (*Ber.*, 41, 936). This compound also crystallizes with other solvents, as, for example, alcohol.

Although in the second case the substance was not entirely dissolved, the simpler molecule was indicated and the one trustworthy value was confirmed. Since the solubility in benzene was exceeded, it is possible to calculate the solubility in benzene at its freezing point. We find that the 0.1583 gram should have caused a depression of 0.167°.

Evidently, then, 0.130/0.167 multiplied by 0.1583 is the approximate solubility in 17.67 grams of benzene. This gives one part of the di-ol as soluble in 140 parts of benzene.

Properties.—The di-ol crystallizes in white hexagonal prisms, cut off obliquely, which melt at 172°. The substance crystallizes well from other solvents; from acetone especially, beautifully formed crystals can be obtained. Soluble in alcohol, ether, acetone, chloroform, carbon tetrachloride and carbon disulfide; slightly soluble in cold benzene, but soluble in warm benzene; in naphtha it is not very soluble; glacial acetic acid dissolves it, especially if warmed, but soon acts upon it in a dehydrating manner. It is not soluble in sodium hydroxide. In acetic acid it is an oxidizing agent, acting upon potassium iodide to set iodine free. On standing exposed to the air of the laboratory, the white color changes to a dull yellow, and the melting point falls. It dissolves in concentrated sulfuric acid with an intense red color. If boiled in higher boiling neutral solvents, as xylene, the solution turned yellow, and on evaporation gave a yellow oil which could not be crystallized. Dehydrating agents had the same effect when attempts were made to split out two molecules of water. The benzene solutions in various experiments, zinc chloride, phosphorus pentoxide, calcium chloride, concentrated sulfuric acid, and hydrochloric acid gas were added, but in all cases uncrystallizable yellow oils were obtained. The di-ol was also fused with potassium acid sulfate in order to completely dehydrate it, if possible, but here also the resulting product was an oil.

Just as all attempts to completely dehydrate the diethyldihydroxydihydroanthracene failed, so all attempts to replace the two hydroxyls by halogen failed. Hydrochloric and hydrobromic acid gases were tried in benzene solution both with and without anhydrous sodium phosphate to take up the water. Phosphorus trichloride, oxychloride and pentachloride reacted violently with the substance giving off hydrochloric acid and leaving an oil. The yellow oil resulting from the action of phosphorus pentachloride was dissolved in low-boiling naphtha and this evaporated by a blast of air, when it left some rhombic plates, but any attempt to recrystallize these converted them into an oil.

The action of acetyl chloride, benzoyl chloride and acetic anhydride resulted similarly in most cases, that is, neither an acetate nor benzoate could be isolated, but instead there was produced a yellowish oil. The action of acetyl chloride on the dimethyl ether of the di-ol was tried, which procedure was suggested by the fact that the acetate of triphenylcarbinol can be made only in this way, but this was not successful. When the action of acetyl chloride on the di-ol was tried at room temperature, there resulted a cream-colored substance which caused blue fluorescence in methyl alcohol, and crystallized from it in clusters of needles, melting at 135.5–136°. These were dried *in vacuo* to constant weight and analyzed.

Found: C, 85.30, 85.36; H, 7.50, 7.75.

These analyses correspond to a formula $C_{16}H_{17}O$, but what such a formula could represent is not known.

By the action of zinc dust and glacial acetic acid, the di-ol was converted into diethylanthracene.

Dimethyl Ether of Diethyldihydroxydihydroanthracene.—This was made by adding to a hot concentrated solution of the dihydroxy compound in methyl alcohol a few drops of methyl alcohol in which hydrochloric acid gas had been dissolved. At once, the crystals of the dimethyl ether separated and were recrystallized from methyl alcohol, which acquired a slight blue fluorescence on the first crystallization, but on subsequent recrystallizations the fresh solvent remained colorless. The dimethyl ether is much less soluble than the dihydroxy compound, melts at 178°, and dissolves in concentrated sulfuric acid with a red color. It was dried to constant weight *in vacuo* over sulfuric acid and analyzed.

Calculated for $C_{18}H_{18}O_2(CH_3)_2$: C, 81.03; H, 8.14.
Found: C, 80.68; H, 8.25.

The diethyl ether was made by the same method. It is more soluble in ethyl alcohol than the methyl ether is in methyl alcohol.

Calculated for $C_{18}H_{18}O_2(C_2H_5)_2$: C, 81.43; H, 8.70.
Found: C, 80.90; H, 8.26.

Action of Dilute Hydrochloric Acid on the Di-ol.—When the di-ol was heated on the steam bath with water alone for several hours no change took place, but if the water were acidified with hydrochloric acid, the di-ol changed in color to yellowish orange. A solution containing but one per cent. of acid brought this about. With twice-normal hydrochloric acid, the di-ol turned yellow as soon as the suspension became warm on the steam bath, while several minutes were required when acid of a strength of one per cent. was used. On heating for some minutes with twice normal acid, the di-ol was completely transformed into a red oil, which, on cooling, solidified. This was warmed with ethyl alcohol, whereby an extract was obtained, and a yellow mass remained behind. The last was very slightly soluble in most solvents with the exception of benzene, but could not well be crystallized from benzene, however, as it separated as an oil. Alcohol was not at all a convenient solvent, since it dissolved so little substance, and it was ultimately found best as a process of crystallization to first use alcohol with a little benzene, then, on the next recrystallization, to use a mixture of two parts of alcohol and one of benzene. This yellow mass was soon found to be a mixture of two substances, one crystallizing in rhombic plates or octahedra, the other in prisms. The separation of these two was tedious since the solubilities were similar; but by continued fractional crystallization from the benzene and alcohol mixture it was possible to obtain small amounts of each in a pure condition. The rhombic form melted at 161°, the other at 226°. They were both lemon-yellow in color; both decolorized a chloroform solution of bromine as well as bromine water; both were oxidized by potassium dichromate to anthraquinone.

A more convenient way of preparing this mixture was not to heat at all, but to allow the di-ol to stand in dilute acid at room temperature using either hydrochloric or sulfuric acids, although hydrochloric was to be preferred. In the course of a few hours the color was changed perceptibly, but the mixture was allowed to stand four days, when the yellow mixture was filtered and washed free from acid. The wash waters had a slight blue fluorescence. The mass was then extracted with hot alcohol from which unchanged substance crystallized on cooling, while the substance which remained was largely that yellow compound which had the rhombic form, melting at 161°, but which required several crystallizations to purify it entirely. If the acid mixture were allowed to stand two weeks, a much larger proportion of the compound melting at 226° was found to be present. A mixture was nearly always obtained, but the longer the reaction mixture remained standing, the more of the higher melting form was produced.

The yellow compound melting at 161° was dried *in vacuo* and analyzed.

Calculated for $C_{36}H_{34}O$: C, 89.57; H, 7.10.
Found: C, 89.27; H, 7.25.

A molecular weight determination by the freezing-point method was made, although only a small sample of pure material was available.

Molecular weight:

Calculated for $C_{36}H_{34}O$: 484.
Found: 480.

Properties.—Yellow rhombic plates, melting at 161°. This compound is soluble to a slight extent in methyl alcohol, ethyl alcohol, acetone, ether, and glacial acetic acid. The solubility in the hot solvents is only slightly greater. Soluble in benzene and toluene.

The yellow substance melting at 226° was dried and analyzed.

Calculated for $C_{36}H_{34}O$: C, 89.57; H, 7.10.
Found: C, 89.53, 89.48; H, 7.27; 6.84.

The only sample at hand sufficiently pure for a molecular weight determination was small and was somewhat impure, due to a slight admixture of the lower melting substance. The freezing-point method was used.

Molecular weight:

Calculated for $C_{36}H_{34}O$: 484.
Found: 425.

Properties.—Yellow prisms, melting at 226°. Soluble in benzene and toluene; slightly soluble in methyl alcohol, ethyl alcohol, ether, acetone, and glacial acetic acid. The solutions show fluorescence.

Part of the expenses of this research were defrayed by a grant from the C. M. Warren Fund for Research, for which we wish to express our gratitude.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

HYDANTOINS: THE SYNTHESIS OF 2-THIOHYDANTOIN.

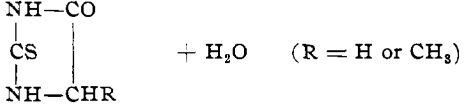
[SEVENTH PAPER.]

BY TREAT B. JOHNSON AND BEN H. NICOLET.

Received November 13, 1911.

Two methods of synthesizing 2-thiohydantoin have recently been described in the literature. Komatsu[1] has prepared this compound by the action of potassium thiocyanate on glycocoll. He states that this amino acid reacts with the thiocyanate, in the presence of acetic anhydride, giving the hitherto unknown thiohydantoic acid, $NH_2CSNHCH_2COOH$, which can be converted into the hydantoin by the action of strong hydrochloric acid. He also examined the behavior of potassium thiocyanate towards alanine and obtained 2-thio-4-methylhydantoin. The general reactions involved in these condensations are represented by him as follows:

$$NH_2.CHR\,.\,COOH + HSCN = NH_2CSNH.CHR\,.\,COOH \longrightarrow$$



$$\begin{array}{l} NH{-}CO \\ |\qquad | \\ CS \qquad | \qquad + H_2O \quad (R = H \text{ or } CH_3) \\ |\qquad | \\ NH{-}CHR \end{array}$$

The second method of synthesis has recently been described in a publication from this laboratory.[2] We showed, for example, that ethyl acetyl- and benzoyldithiocarbamates, I, react smoothly with glycocoll or its ethyl ester, giving the corresponding acyl derivatives of thiohydantoic acid, II, with evolution of ethyl mercaptan. When these acyl derivatives, II, were digested with hydrochloric acid they were converted smoothly into 2-thiohydantoin, III. We also prepared 2-thio-4-methylhydantoin from alanine. The various transformations are represented as follows:

---

[1] *Memoirs Coll. Sci. and Eng.*, Kyoto Univ. (Japan), 3, 1 (1911).

[2] Wheeler, Nicolet and Johnson, *Am. Chem. J.*, 46, 456 (1911).