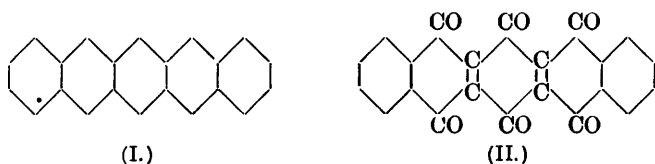


CCXXX.—*The Synthetic Production of Derivatives of Dinaphthanthracene.*

By WILLIAM HOBSON MILLS and MILDRED MILLS.

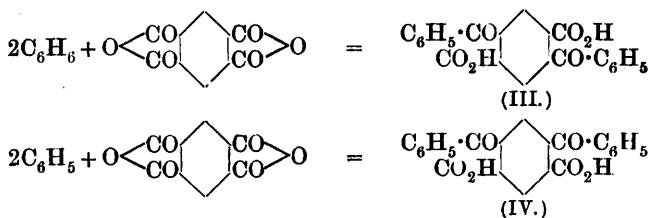
THE knowledge hitherto possessed of $\beta\beta\beta'\beta'$ -dinaphthanthracene (I) or of its derivatives is exceedingly scanty:



Russig (*J. pr. Chem.*, 1900, [ii], 62, 30) obtained a dinaphthanthratriquinone (II) by the action of concentrated sulphuric acid on 1:4-dihydroxy-2-naphthoic acid, and this is apparently the only compound hitherto described which can be regarded definitely as a representative of this group.*

In view of the interest which $\beta\beta\beta'\beta'$ -dinaphthanthracene possesses as a higher member of the series of hydrocarbons, naphthalene, anthracene, naphthacene—composed of benzene nuclei condensed in straight alinement—we have endeavoured to obtain some more extended knowledge of this hydrocarbon and its derivatives in the hope that it might be possible thereby to gain further insight into the constitution of condensed nuclei of this type.

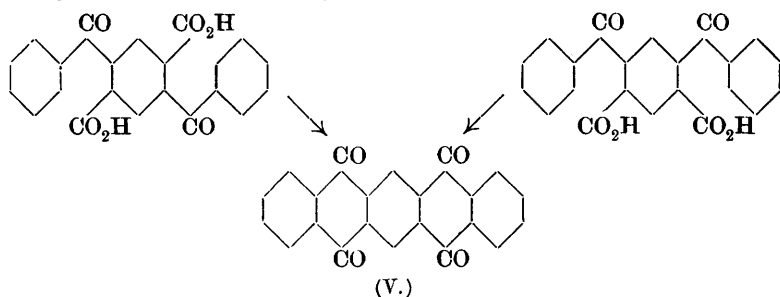
With this end in view we have attempted to bring about by means of aluminium chloride a reaction between benzene and pyromellitic anhydride analogous to the well known condensation of benzene with phthalic anhydride, which results in the formation of benzoylbenzoic acid. In this manner we have obtained two isomeric dibenzoylbenzenedicarboxylic acids, as shown by the following equations:



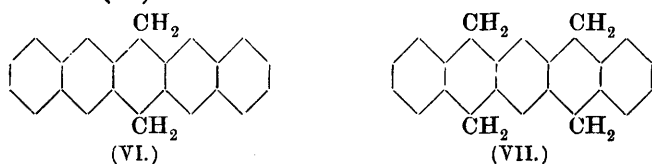
The constitution of these two acids was established by fusion with potassium hydroxide. The acid of higher melting point and

* The question of Russig's dinaphthanthracene (*loc. cit.*, p. 49) is discussed later (p. 2198).

lower solubility undergoes scission under these conditions into benzoic acid and terephthalic acid, and is accordingly 2:5-*dibenzoyl-terephthalic acid* (III). The isomeric acid, being similarly resolved into benzoic acid and *isophthalic acid*, must have the alternative constitution (IV). Both these acids on being warmed with concentrated sulphuric acid undergo intramolecular condensation with the loss of two molecules of water. The product is in each case the same yellow, crystalline compound of exceedingly high melting point (408° corr.), and from its mode of formation it must necessarily be dinaphthanthradiquinone (V):



From this diquinone it has been possible to prepare a series of derivatives of dinaphthanthracene. In the first place, we attempted to obtain dinaphthanthracene itself by reduction with zinc dust and ammonia, and under these conditions the diquinone is, in fact, converted into a hydrocarbon of very sparing solubility. This is, however, not dinaphthanthracene, but a dihydrodinaphthanthracene* (VI):



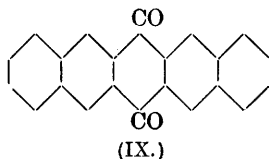
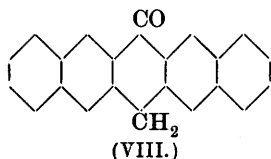
As this method of production presented considerable experimental difficulties, and the yield of dihydrodinaphthanthracene was small, we investigated the behaviour of the diquinone towards fuming hydriodic acid and phosphorus, hoping thus to obtain a tetrahydrodinaphthanthracene (VII), from which it might be possible to obtain dinaphthanthracene by oxidation. The product of the reaction was, however, unexpectedly, not a single compound, but a mixture of two isomeric tetrahydrodinaphthanthracenes. The oxidation of the isomeride present in larger quantity (α -tetrahydrodinaphthanthracene) has been carefully studied. The hydro-

* The constitution of these compounds is discussed later.

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carbon was found to be smoothly oxidised by ferric chloride in acetic acid solution, and by means of the regulated action of this reagent a series of oxidation products has been obtained.

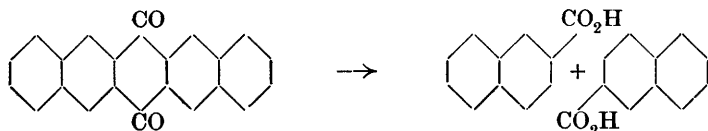
The first of these is dihydrodinaphthanthracene (VI), identical with that produced, as stated above, when the diquinone is reduced with zinc dust and ammonia. As the second oxidation product, dinaphthanthracene might have been expected; we have, however, not been able to isolate it, the next substance obtained being dinaphthanthrone (VIII), a golden-yellow compound:



The final product of oxidation by ferric chloride is dinaphthanthraquinone (IX), a yellow substance of very high melting point (389° corr.), which is sharply characterised by the magnificent colour and fluorescence of its solution in concentrated sulphuric acid. When chromic acid is employed for the oxidation of α -tetrahydrodinaphthanthracene, a mixture of dinaphthanthraquinone (IX) and the original dinaphthanthradiquinone (V) results.

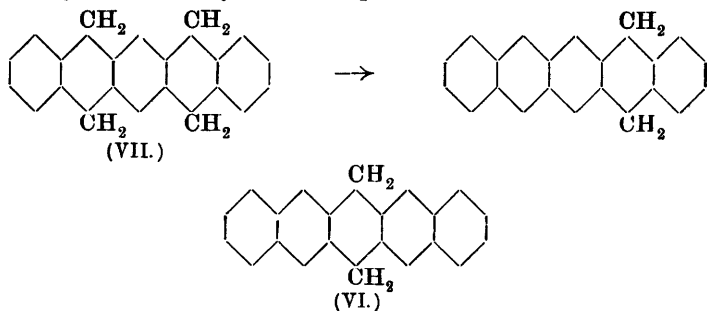
The behaviour of β -tetrahydrodinaphthanthracene on oxidation is very similar. Ferric chloride gives as the first product dihydrodinaphthanthracene (VI), and as the final product dinaphthanthraquinone, whilst chromic acid oxidises it to a mixture of dinaphthanthraquinone and dinaphthanthradiquinone.

The key to the constitution of these oxidation products is the constitution of dinaphthanthraquinone, and this could be readily determined, for, on fusion with sodium hydroxide, the quinone was resolved into two molecules of β -naphthoic acid, and this—in con-

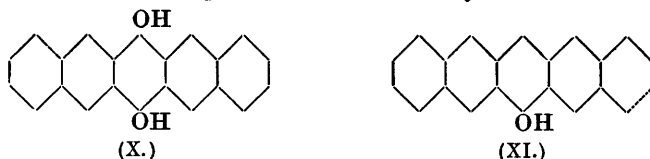


junction with its method of formation—is a conclusive proof that its constitution is correctly represented by formula IX. Further, the position of the oxygen atom in dinaphthanthrone must correspond with that of the oxygen atoms in dinaphthanthraquinone; dinaphthanthrone must accordingly possess the constitution VIII. Finally, the position of the methylene group in dinaphthanthrone must correspond with that of the methylene groups in dihydrodinaphthanthracene, which will thus have the formula VI.

As regards the relationship between the two tetrahydrodinaphthanthracenes, they are certainly not crystallographic modifications, for they differ considerably in stability, and we have not been able to bring about their interconversion. They have the same molecular weight, and since stereoisomerism seems in this case most highly improbable, it is to be concluded that they are structurally isomeric. Unfortunately, their behaviour on oxidation is so similar as scarcely to afford a basis for conclusions as to their constitution. It is, however, probable that one of the two isomerides must have the formula VII (corresponding with that of the diquinone from which they are formed), although the production from it of symmetrical dihydrodinaphthanthracene on oxidation would necessitate the assumption of intramolecular transformation of the primarily formed unsymmetrical product:



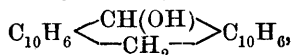
It is of some interest that dinaphthanthraquinone is sharply differentiated from anthraquinone and naphthacenequinone, in that it gives no coloration with sodium hydroxide and zinc dust; that is to say, it is not converted into dinaphthoxanthranol (X) under conditions under which the corresponding change is readily brought about in the case of anthraquinone and naphthacenequinone. Moreover, dinaphthanthrone, unlike anthrone, is neither converted into dinaphthanthranol (XI) by alkalis, nor does it yield the acetyl derivative of that compound with acetic anhydride:



These facts appear to indicate that considerable resistance is opposed to the passage of dihydrodinaphthanthracene derivatives into compounds containing the true dinaphthanthracene nucleus, and the difference between dihydroanthracene and dihydrodinaphthanthracene as regards the readiness with which they can be con-

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verted into their parent hydrocarbons is probably due to this cause, dihydroanthranol, $C_6H_4 \left\langle \begin{array}{c} CH(OH) \\ -CH_2- \end{array} \right\rangle C_6H_4$ (which is to be regarded as the primary oxidation product of dihydroanthracene), undergoing dehydration much more rapidly than it can be oxidised to anthrone, whilst in dihydrodinaphthanthranol,



the tendency to lose the elements of water is so small that the further oxidation product, dinaphthanthrone, alone can be isolated.

Russig, in his paper quoted above, refers to a hydrocarbon having the composition of a dinaphthanthracene, which he obtained by distilling dinaphthanthraquinone with zinc dust, and consequently regarded as $\beta\beta\beta'\beta'$ -dinaphthanthracene (*loc. cit.*, p. 49). This hydrocarbon was further investigated by Hartenstein (*Diss.*, Jena, 1892), who obtained from it by oxidation with chromic acid a quinone having the composition $C_{22}H_{12}O_2$, to which, without further confirmation, he assigned the formula (IX), which we have shown to be that of the dinaphthanthraquinone described in the present communication. From Hartenstein's description, however, his compound is undoubtedly different from ours; its melting point is more than 180° lower, and he describes it as dissolving in sulphuric acid with a purple colour, whereas the colour of the solution of our dinaphthanthraquinone in sulphuric acid is an intense pure blue, with a magnificent crimson fluorescence, which could not possibly escape notice. Moreover, if the hydrocarbon of Russig and Hartenstein were really $\beta\beta\beta'\beta'$ -dinaphthanthracene, it would be expected to give on oxidation with chromic acid our dinaphthanthraquinone, and possibly also dinaphthanthradiquinone. That the product could be a monoquinone different from ours seems so unlikely that the more probable conclusion would appear to be that the hydrocarbon of Russig and Hartenstein was not $\beta\beta\beta'\beta'$ -dinaphthanthracene, but an isomeric hydrocarbon, distillation of the triquinone with zinc dust having brought about some change more profound than simple reduction. It is probable, therefore, that $\beta\beta\beta'\beta'$ -dinaphthanthracene is still unknown.

EXPERIMENTAL.

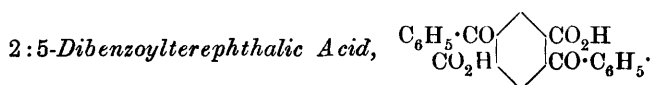
Dibenzoyl-terephthalic and -isophthalic Acids.

Thirty grams of finely ground pyromellitic anhydride are heated with 750 c.c. of benzene and 70 grams of powdered aluminium chloride for three hours in a water-bath at $65-70^\circ$. The mixture is then poured on ice, and, after the addition of concentrated hydro-

chloric acid, is distilled in a current of steam. When the benzene has been completely removed, the acids produced are left in the form of white, granular masses suspended in the hot liquid. These are collected,* washed with water, and dissolved in boiling dilute potassium hydroxide solution. After filtration to remove a little insoluble matter, the acids are reprecipitated with hydrochloric acid.

The weight of the crude mixture of dibenzoyl-terephthalic and *isophthalic* acids thus obtained is approximately equal to that of the pyromellitic anhydride taken, corresponding with a yield of about 60 per cent. of the theoretical.

This product may be used without further purification for conversion into dinaphthanthradiquinone.



When the crude mixture of acids, obtained as described above, is dissolved in the minimum quantity of boiling glacial acetic acid, the solution after cooling gradually deposits this compound in clusters of fine, white needles, in amount equal to rather more than half that of the mixed acids taken. After recrystallisation from glacial acetic acid or dilute alcohol it melts at 319—320°. It crystallises with one molecule of water:

0.4894 (air-dried) lost, at 135°, 0.0214. $\text{H}_2\text{O}=4.4$.

$\text{C}_{22}\text{H}_{14}\text{O}_6, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=4.6$ per cent.

0.3306 † gave 0.8527 CO_2 and 0.1110 H_2O . $\text{C}=70.34$; $\text{H}=3.73$.

$\text{C}_{22}\text{H}_{14}\text{O}_6$ requires $\text{C}=70.59$; $\text{H}=3.74$ per cent.

The acid dissolves readily in acetone, and is rather soluble in alcohol. It is moderately soluble in boiling glacial acetic acid, but almost insoluble in benzene or chloroform. It is characterised by a sparingly soluble *sodium* salt.

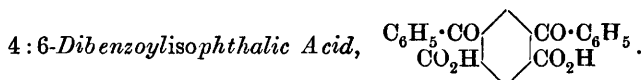
Half a gram of the acid was fused for three hours with 10 grams of potassium hydroxide at 275°. The fusion was then dissolved in water and acidified with dilute sulphuric acid, when an acid was precipitated which on heating sublimed without previous fusion, and was identified as terephthalic acid by conversion (through the chloride) into its methyl ester. This melted at 140°, both alone and when mixed with pure methyl terephthalate prepared in the usual manner from *p*-toluidine. The filtrate from the terephthalic

* The filtrate deposits during the course of two or three days the greater part of the pyromellitic acid which has escaped condensation.

† Dried at 135°.

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acid on extraction with ether yielded 0.25 gram of an acid readily identified as benzoic acid.



After the separation of the sparingly soluble dibenzoylterephthalic acid from the acetic acid solution of the crude mixture of dibenzoylphthalic acids, the mother liquor is diluted with an equal volume of water. 4:6-*Dibenzoylisophthalic acid* then separates gradually in well-formed crystals in the course of a few days.

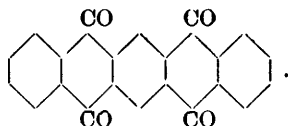
After purification by recrystallisation from dilute acetic acid or dilute alcohol, it melts at 277—278°:

0.3801 gave 0.5368 CO₂ and 0.0716 H₂O. C = 70.7; H = 3.8.

C₂₂H₁₄O₆ requires C = 70.6; H = 3.7 per cent.

The acid dissolves very readily in acetone, alcohol, glacial acetic acid, or ether. In benzene or chloroform it is practically insoluble. It crystallises far less readily than the isomeric acid, and tends to separate as an oil.

One gram of the acid was fused for two and three-quarter hours with 18 grams of potassium hydroxide, the temperature being kept as nearly as possible at 275°. The fusion was dissolved in water, and the solution, after filtration, acidified and extracted with ether. The residue after evaporation of the ether weighed 1.05 grams. It was boiled twice with 8 c.c. water, and the undissolved portion was crystallised twice from dilute alcohol. An acid was thus obtained crystallising in very fine needles, which melted at 328—329°, and then sublimed. A specimen of *isophthalic acid* melted at the same temperature, as did also the mixture of the two substances. As a confirmation, the acid was converted into its methyl ester by warming with methyl-alcoholic hydrogen chloride. The ester melted at 65—66°, and its melting point was not depressed by the addition of methyl *isophthalate*. Pure benzoic acid was separated from the portions which had dissolved in boiling water by sublimation in a vacuum at 100°.

5 : 7 : 12 : 14-*Dinaphthanthradiquinone*,

The mixture of dibenzoyl-*isophthalic* and -*terephthalic* acids, obtained as described above, is dissolved in concentrated sulphuric

acid in the proportion of 8 c.c. to each gram of the mixed acids, and the resulting deep yellowish-brown liquid is heated in a boiling-water-bath for four to five hours. On keeping—sometimes even during the heating—the mixture sets to a mass of excessively fine, long, yellow, flexible, silky needles, which are so asbestos-like that filtration can be effected on a filter disk, without using filter paper, the substance forming its own filter. After having been collected, the quinone is washed with glacial acetic acid, finally with water, and then dried. A further quantity can be obtained by pouring the sulphuric acid mother liquor into 10 volumes of water, and adding excess of sodium hydroxide. The finely divided yellow precipitate thus produced is allowed to settle, the supernatant liquid is syphoned off, and the quinone collected and washed. The total yield is about 95 per cent. of the theoretical.

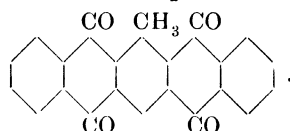
Dinaphthanthradiquinone is very sparingly soluble in most organic media, even at the boiling temperature. It can be best recrystallised from boiling nitrobenzene or pyridine, separating in bright yellow needles. The melting point is 408° (corr.),* the substance being apparently quite stable up to this temperature. Small quantities can readily be sublimed:

0.1971 gave 0.5652 CO_2 and 0.0547 H_2O . $\text{C}=78.2$; $\text{H}=3.0$.

$\text{C}_{22}\text{H}_{10}\text{O}_4$ requires $\text{C}=78.1$; $\text{H}=3.0$ per cent.

It gives a golden-yellow solution in concentrated sulphuric acid. When heated with sodium hydroxide solution and zinc dust a deep brownish-red colour is developed, which disappears on shaking with air. When boiled with glacial acetic acid, tin, and a drop of concentrated hydrochloric acid, a bluish-mauve solution is produced.

13-Methyl-5:7:12:14-dinaphthanthradiquinone,



Anhydrous *s*-dibenzoylglutic acid (Mills and Easterfield, *Trans.*, 1902, **81**, 1321) is dissolved in concentrated sulphuric acid (4 c.c. for every gram), and heated for six to seven hours in a boiling-water bath. The deep golden-yellow solution gradually becomes dark brown. After cooling, it is poured on ice, rendered alkaline with sodium hydroxide (the production of an alkaline reaction is marked by the appearance of a slight blue coloration), and the mixture

* The determinations of the melting points of this compound and of dinaphthanthraquinone were determined in a bath composed of an equimolecular mixture of sodium and potassium nitrates.

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heated for twelve hours on a water-bath. The supernatant liquid can then be readily syphoned off, the precipitate washed once by decantation, collected, and washed.

This compound is very sparingly soluble in the usual solvents at the boiling temperature. It can be recrystallised from nitrobenzene, from which it separates in yellow needles showing no sharp melting point, but decomposing between 298° and 304°:

0.1218 gave 0.3495 CO₂ and 0.0397 H₂O. C=78.3; H=3.3.

C₂₈H₁₂O₄ requires C=78.4; H=3.4 per cent.

A deep brownish-red colour is produced when the substance is heated with zinc dust and sodium hydroxide solution.

α- and β-Tetrahydrodinaphthantracene.

A mixture of two parts of dinaphthantracenediquinone with one part of red phosphorus is heated in sealed tubes for forty-eight hours with hydriodic acid (D 1.9) to 120–130°, 3 grams of the mixture and 10 c.c. of hydriodic acid being placed in each tube. After opening the tubes, water is added, and the solid products are collected and well washed with water, and, if necessary, with sulphurous acid. If the reduction has been carried out at 115–120°, an appreciable quantity of an intermediate product of red colour will be present, which, since it has phenolic properties, is best removed by boiling out once or twice with a mixture of equal volumes of alcohol and a 20 per cent. aqueous solution of sodium hydroxide, which dissolves it, forming a greenish-blue solution. On acidification of this solution the red compound is recovered, and can be fully reduced by a second heating with phosphorus and hydriodic acid. Reduction at temperatures above 135°, on the other hand, leads to loss through the formation of more highly reduced products. The residue left after the removal of the above-mentioned red compound is almost colourless. It is dried and crystallised from boiling benzene, which removes the higher reduction products. The substance obtained in this way is manifestly a mixture, melting between 237° and 250°. Attempts to effect a separation by fractional crystallisation from various solvents were fruitless. It was found, however, that on boiling with a quantity of amyl alcohol insufficient for complete solution (30 c.c. of amyl alcohol for each gram of substance) and filtering hot, the compound of higher melting point was concentrated in the residue, and that of lower melting point crystallised from the filtrate almost pure. By one or two repetitions of this process, the mixture can be resolved into two substances, one crystallising in lustrous platelets melting at

240—241°, the other in needles melting at 270° with some decomposition (turning pink from about 240° upwards).

The relative quantities of the two substances depend on the temperature employed in the reduction—the lower this temperature the larger the proportion of the compound melting at 270°; but this always forms the smaller part of the product, and if the reduction is carried out at 135° or over, none of it can be isolated.

The substance melting at 240—241° is *α-tetrahydrodinaphthanthracene*:

0·2034 gave 0·6995 CO₂ and 0·1148 H₂O. C=93·8; H=6·3.

C₂₂H₁₈ requires C=93·6; H=6·4 per cent.

The compound of higher melting point is the isomeric *β-tetrahydrodinaphthanthracene*:

0·1842 gave 0·6296 CO₂ and 0·1027 H₂O. C=93·2; H=6·5.

C₂₂H₁₈ requires C=93·6; H=6·4 per cent.

Since the formation of bimolecular products is not uncommon in the reduction of substances containing the carbonyl group, and the difference in composition between a tetrahydro- and a bistrhydro-derivative lies not far without the limits of analytical error, it seemed desirable to satisfy ourselves that these substances were really isomeric by determining their molecular weight.

The molecular weight of *α-tetrahydrodinaphthanthracene* was determined by the ebullioscopic method:

0·0745 in 6·4 c.c. benzene gave E=0·13. M.W.=287.

0·0708 „ 5·63 „ „ „ E=0·16. M.W.=258.

0·0716 „ 6·1 „ „ „ E=0·145. M.W.=270.

0·0721 „ 5·1 „ „ „ E=0·16. M.W.=289.

C₂₂H₁₈ requires M.W. 282.

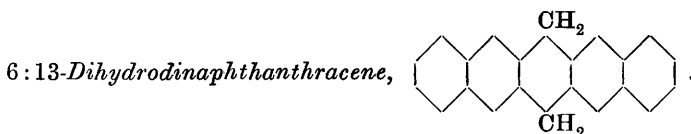
β-Tetrahydrodinaphthanthracene was found to be too sparingly soluble in boiling benzene to give accurate results by this method. Its molecular weight was accordingly determined cryoscopically in naphthalene:

0·1007 in 17·9 naphthalene gave $\Delta t = -0·142$. M.W.=273.

0·2049 „ 17·9 „ „ „ $\Delta t = -0·279$. M.W.=283.

C₂₂H₁₈ requires M.W. 282.

Both compounds with concentrated sulphuric acid containing a trace of nitrosylsulphuric acid give an amethyst-purple coloration, which slowly passes into olive-green.



The production of this compound by oxidation of tetrahydrodinaphthanthracene is most successfully carried out in small quantities.

To a boiling solution of 0.4 gram of α -tetrahydrodinaphthanthracene in 200 c.c. of glacial acetic acid, a solution of 0.7 gram of anhydrous ferric chloride in 70 c.c. of glacial acetic acid is added drop by drop during the course of three-quarters of an hour. The boiling is continued two hours after the addition of the ferric chloride is complete, and crystals of the sparingly soluble product frequently separate during the heating. The crude substance contains much unoxidised tetrahydrodinaphthanthracene, which is removed by extracting twice with 25 c.c. of boiling glacial acetic acid. Since the tetrahydrodinaphthanthracene is deposited almost quantitatively from the filtrate and can be treated again with ferric chloride, the final yield is satisfactory. By recrystallising twice from pyridine the new hydrocarbon is obtained in a state of purity. It separates in small crystals, which form a colourless, lustrous, felted mass on the filter. It decomposes in the neighbourhood of its melting point, beginning to turn pink at 295° , and melting between 300° and 310° , the exact temperature depending on the rate of heating:

0.2232 gave 0.7706 CO_2 and 0.1167 H_2O . $\text{C}=94.2$; $\text{H}=5.8$.

$\text{C}_{22}\text{H}_{18}$ requires $\text{C}=94.3$; $\text{H}=5.7$ per cent.

This compound is much less soluble in boiling benzene and boiling acetic acid than are the tetrahydrodinaphthanthracenes, and on protracted boiling with solvents like amyl alcohol and xylene, in which it is more soluble, it turns mauve. It is readily recrystallised from pyridine. It can be sublimed in small quantities, but becomes thereby partly transformed into a purple substance. It dissolves in concentrated sulphuric acid, giving a solution of a pale yellow colour, gradually deepening to orange-brown, and finally becoming green. In concentrated sulphuric acid containing a trace of nitrosylsulphuric acid it gives the same coloration as the tetrahydro-compounds, namely, an amethyst-purple, which passes slowly into green.

Dihydrodinaphthanthracene is also obtained when β -tetrahydrodinaphthanthracene is oxidised with ferric chloride in acetic acid solution in the manner described above.

Production of Dihydrodinaphthanthracene from Dinaphthanthraquinone by Reduction with Zinc Dust in Alkaline Suspension.

To 5 grams of the diquinone suspended in 250 c.c. of 20 per cent. sodium hydroxide solution was added a zinc-copper couple, prepared by grinding zinc dust (10 grams) with a little concentrated ammonia, and adding gradually an ammoniacal solution of basic cupric chloride.

The mixture was heated for thirty-six hours in a water-bath, contact with air being prevented by a mercury valve, and four or five further quantities of zinc-copper couple, each prepared from 5 grams of zinc dust, were added in ammoniacal suspension through a tap funnel.

The deep reddish-brown colour, which appears at first, gradually fades, and the solution finally becomes nearly colourless. It must be filtered as far as possible with exclusion of air, since it contains a substance rapidly oxidised by atmospheric oxygen with the formation of a dark blue precipitate. To remove any of the latter which may have been produced during the filtration the solid residue is again heated with sodium hydroxide solution, when the blue compound is reduced to its phenolic precursor by the excess of zinc dust present. The solid is then collected, the zinc and zinc hydroxide dissolved with hydrochloric acid, and the dried residue extracted with 300 c.c. of benzene. The substance left on evaporation of the benzene after crystallisation from pyridine should be colourless. If, however, the above-mentioned oxidation product has been incompletely removed, the crystals will have a red colour. This impurity can be removed by cautious washing with concentrated sulphuric acid. The hydrocarbon thus obtained was found on comparison to be identical with the dihydrodinaphthanthracene produced by oxidation of the α - and β -tetrahydro-compounds. The yield barely exceeded 10 per cent. of the theoretical.

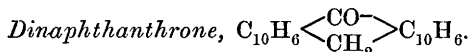
The blue insoluble substance formed by atmospheric oxidation of the colourless intermediate product was also examined. On acidification it gave reddish-purple flocks, which seemed to undergo alterations on heating with organic solvents. It was therefore acetylated, 2 grams being heated with 30 c.c. of acetic anhydride and a few drops of sulphuric acid for one hour in an oil-bath at 140°. The solution became yellow, and the orange-yellow acetyl derivative crystallised on cooling. After several recrystallisations from glacial acetic acid, it was obtained in aggregates of rather short, reddish-orange needles, melting not very sharply at 255°. The analysis corresponded with a compound of the formula $C_{22}H_{14}O_2(C_2H_3O)_2$:

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0.2004 gave 0.5326 CO₂ and 0.0739 H₂O. C = 73.0; H = 4.1.

C₂₂H₁₆O₆ requires C = 73.2; H = 4.2 per cent.

It thus appears to be the diacetyl derivative of a dihydroxytetrahydrodinaphthanthraquinone.



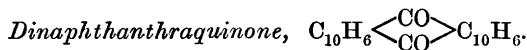
A solution of five parts of anhydrous ferric chloride in acetic acid and a little water is allowed to drop during the course of two hours into a boiling solution of one part of α -tetrahydrodinaphthanthracene in 1000 parts of glacial acetic acid. Crystals of the sparingly soluble dihydrodinaphthanthracene usually separate during the addition of the ferric chloride, but redissolve as the oxidation proceeds. The heating is continued for one and a-quarter hours after the whole of the ferric chloride has been added. From the cold solution brown crystals are slowly deposited, which are collected after two or three days, and purified by repeated crystallisation from pyridine.

Dinaphthanthrone is obtained in this way in golden-yellow, highly lustrous platelets, which melt at 271—273°. It is rather more soluble in the common solvents at their boiling points than dinaphthanthraquinone:

0.1787 gave 0.5869 CO₂ and 0.0759 H₂O. C = 89.6; H = 4.7.

C₂₂H₁₄O requires C = 89.8; H = 4.8 per cent.

The behaviour of the substance towards sulphuric acid is characteristic. On the addition of sulphuric acid containing a trace of nitrosylsulphuric acid, the crystals turn brown, and slowly dissolve to form a brown solution, which on warming becomes green. If water is now cautiously added, the green passes over into a beautiful deep blue.



A solution of twenty-two parts of anhydrous ferric chloride in eight to ten times its weight of acetic acid containing a little water is added slowly drop by drop to a boiling solution of one part of α -tetrahydrodinaphthanthracene in 500 parts of glacial acetic acid. Crystals of dihydrodinaphthanthracene appear after a short time, but gradually redissolve. The boiling is continued for two hours after the addition of the ferric chloride is complete, and the crystals which separate slowly from the cold solution are collected after twelve to twenty-four hours. Their weight is approximately equal to that of the tetrahydrodinaphthanthracene taken. After having been two or three times recrystallised from pyridine, the quinone is obtained pure in flattish, yellow needles, which melt at 388—389°

(corr.), and are very sparingly soluble in the common solvents. It can be sublimed in small quantities:

0·1246 gave 0·3925 CO₂ and 0·0471 H₂O. C=85·9; H=4·2.

0·2063 „ 0·6458 CO₂ „ 0·0729 H₂O. C=85·4; H=3·9.

C₂₂H₁₂O₂ requires C=85·7; H=3·9 per cent.

This compound remains unchanged when heated with sodium hydroxide solution and zinc dust. Its most characteristic property is that of dissolving in concentrated sulphuric acid with the formation of a solution of most striking appearance; intensely blue by transmitted light, crimson by reflected light, the true colour of the solution being in the latter case masked by the powerful red fluorescence. The absorption spectrum of this solution contains two bands in the visible region; one in the yellowish-green, the other in the red, the approximate boundaries of which in dilute solutions are wave-lengths 5610—5820 and 6120—6420 respectively. The band in the red is the more persistent and sharply defined. The fluorescent spectrum consists of a single red band, extending approximately from wave-length 6210 to 6740, and accordingly overlapping the lower two-thirds of the absorption band in the red. The fluorescence is excited chiefly by the part of the spectrum which lies between the outer limits of the two absorption bands and most powerfully by the region of the band in the red. Blue or violet light produces no visible effect.

On the addition of a little water the blue solution becomes cherry-red, and the fluorescence disappears.

The scission of dinaphthanthraquinone into two molecules of β -naphthoic acid was carried out as follows: The finely-powdered substance was added to molten potassium hydroxide heated to 275°, and the mixture kept at this temperature for one hour. A certain quantity of naphthalene was produced, the odour of naphthalene being perceptible, especially towards the commencement of the operation.* After cooling, the chocolate-brown fusion was dissolved in water, and sulphuric acid gradually added. When the solution was nearly neutral a dark, flocculent substance was precipitated. After removal of this, the liquid on acidification deposited an acid which, having been recrystallised from dilute acetic acid, melted at 181—182°, the melting point of β -naphthoic acid.

A mixture of the acid and β -naphthoic acid melted also at this temperature:

0·1706 was neutralised by 9·96 c.c. *N*/10-sodium hydroxide solution.

C₁₀H₇·CO₂H requires 9·92 c.c.

* Dinaphthanthraquinone is easily converted into naphthalene by heating with soda-lime in a small ignition tube.

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It was further converted into its methyl ester by heating with methyl alcohol and sulphuric acid. In appearance, odour, and melting point (77°) the ester agreed exactly with a specimen of methyl β -naphthoate prepared for comparison. The mixed melting point was also 77° .

Oxidation of Tetrahydrodinaphthanthracene with Chromic Acid.

To a boiling solution of one part of α -tetrahydrodinaphthanthracene in 350 parts of glacial acetic acid was added drop by drop during one and three-quarter hours a solution of 1.9 parts of chromium trioxide in a little water and 100 parts of acetic acid, and the mixture was then boiled for ten minutes longer. On cooling, bright yellow crystals separated, the weight of which was 80–85 per cent. of the hydrocarbon taken. These crystals were a mixture of dinaphthanthraquinone and dinaphthanthradiquinone, the former of which was isolated by boiling the mixture with sodium hydroxide solution and zinc dust, when the diquinone passed into solution as the red sodium salt of the oxanthranol-like reduction product, and the monoquinone was left undissolved, whilst the diquinone was obtained in a state of purity by repeatedly extracting the mixture with small quantities of boiling acetic acid (which removed most of the monoquinone), and crystallising the residue from pyridine. Analysis showed that the product was a dinaphthanthradiquinone:

0.1748 gave 0.4994 CO_2 and 0.0488 H_2O . $\text{C}=77.9$; $\text{H}=3.1$.

$\text{C}_{22}\text{H}_{10}\text{O}_4$ requires $\text{C}=78.1$; $\text{H}=3.0$ per cent.

The melting point and mixed melting point, 408° (corr.), conclusively proved its identity with the original diquinone.

The oxidation of β -tetrahydrodinaphthanthracene was carried out in the same manner with similar results.

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NORTHERN POLYTECHNIC INSTITUTE,
LONDON, N.