LXVIII.—*The Dihydrocyanides of Benzil and Phenanthraquinone. Second Notice.**

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ALTHOUGH the dihydrocyanides of α -diketones are most generally formulated as tartronitriles, no strict proof that they possess this constitution has hitherto been given, with the exception of the hydrolysis of Zinin's benzildihydrocyanide, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CN} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CN}' \end{matrix}$ to diphenyltartramide (Burton, *Ber.*, 1883, **16**, 2232). Indeed, owing to the ease with which these compounds break up into α -diketone and hydrocyanic acid, some writers have preferred to represent them as molecular combinations.

We have obtained conclusive evidence of the tartronitrile constitution of these compounds by preparing their *diacetyl* derivatives. The dihydrocyanides which we have studied in this direction are: (1) benzildihydrocyanide; (2) the phenanthraquinonedihydrocyanide obtained by Japp and Miller; and (3) a stereoisomeric phenanthraquinonedihydrocyanide described in the present paper.

By treatment with concentrated sulphuric acid in the cold, benzildihydrocyanide is converted into *diphenylacetamide*. In order to account for this reaction it is necessary to assume that, as a first stage, a pinacolone migration occurs:

the resulting compound then undergoing hydrolytic fission with formation of diphenylacetamide, $(\text{C}_6\text{H}_5)_2\text{CH} \cdot \text{CONH}_2$, and possibly oxalic acid.

By the interaction of phenanthraquinone with 30 per cent. aqueous hydrocyanic acid in the cold, Japp and Miller (*Trans.*, 1887, **51**, 32) obtained a phenanthraquinonedihydrocyanide crystallising in slender needles. We find that a stronger solution of hydrocyanic acid is practically without action on phenanthraquinone in the cold, but that, on heating the mixture at 50° , a *stereoisomeric phenanthraquinonedihydrocyanide*, crystallising in laminae, is formed. The laminar crystals have a higher decomposing point than the acicular. On the other hand, the diacetyl derivative of the laminar compound melts lower than that of the acicular compound. The best yield of the laminar compound is obtained by employing anhydrous hydrocyanic acid.

* See Japp and Miller, *Trans.*, 1887, **51**, 29.

The reactions of the two phenanthraquinonedihydrocyanides show that both have the structural formula $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CN} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CN} \end{array}$. They must therefore be stereoisomerides, the one being the racemic, the other the meso-form, although it is at present impossible to assign to each its specific configuration.

By hydrolysing acicular phenanthraquinonedihydrocyanide, not previously freed from adhering hydrocyanic acid, with fuming hydrochloric acid in the cold, Japp and Miller (*loc. cit.*) obtained two compounds, $\text{C}_{15}\text{H}_9\text{ON}$ (m. p. 241°) and $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}$ (m. p. 183°), both of which yield salts with bases, the former compound taking up water in the process, so that its dehydrated sodium salt, for example, has the formula $\text{C}_{15}\text{H}_{10}\text{O}_2\text{NNa}$; but it again parts with water when liberated from its salts, yielding the original compound, $\text{C}_{15}\text{H}_9\text{ON}$ (compare Japp and Miller). From a study of the reactions of these compounds we assign to them the constitutional formulæ

Both compounds are capable of interacting also in the tautomeric form, and we are unable to say whether the free substances are lactams, as here represented, or the corresponding lactims. The metallic salts formed from phenanthranil are salts of the unstable phenanthranilic acid, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH}_2 \end{array}$, which, as just mentioned, when liberated from its salts, parts with water, regenerating phenanthranil. Phenanthranil yields a *monacetyl* derivative, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{C}_2\text{H}_5\text{O} \end{array}$. Two esters correspond with it: one is *ethyl phenanthranilate*,

and the other is the *lactim ester** of phenanthranil, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C} \cdot \text{OC}_2\text{H}_5 \\ | \quad | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \end{array}$.

Both esters, when hydrolysed with sodium hydroxide, yield *sodium phenanthranilate*; but a portion of the lactim ester is transformed, at the same time, into the non-hydrolysable *hydroxyethylhydrophen-*

* We would suggest that compounds of this type should be called *esters* rather than *ethers*. Thus, in the complex $\text{C}(\text{NH})\text{OAlk}$ of the so-called *imido-ethers*, the imido-group has, structurally, the same function as the doubly-linked oxygen in the complex COOAlk of the ordinary esters, and the name *imido-ester* would indicate more clearly this analogy.

anthranil, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \text{---} \text{N} \cdot \text{C}_2\text{H}_5 \end{array}$, the ethyl group migrating in the process.

Hydroxydihydrophenanthranil, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \text{---} \text{NH} \end{array}$, dissolves in sodium carbonate, yielding a sodium salt which is probably

but was not obtained in a condition suitable for analysis (compare Japp and Miller, *loc. cit.*, p. 35) and which, when its aqueous solution is digested for some time on the water-bath, decomposes, depositing a brown amorphous substance. Acetylated in the cold with acetic anhydride to which a little concentrated sulphuric acid has been added, hydroxydihydrophenanthranil yields a *monacetyl* derivative,

insoluble in sodium carbonate. Treated with sodium ethoxide and ethyl iodide, hydroxydihydrophenanthranil yields the above-mentioned

hydroxyethylidihydrophenanthranil, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \text{---} \text{N} \cdot \text{C}_2\text{H}_5 \end{array}$, in which the

ethyl is doubtless attached to nitrogen, as the compound is not hydrolysed by warming it with alcoholic potassium hydroxide and is moreover insoluble in aqueous caustic alkalis, showing that the labile hydrogen atom has been replaced by ethyl; this ethyl derivative

yields a *monacetyl* derivative, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5\text{O}) \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \text{---} \text{N} \cdot \text{C}_2\text{H}_5 \end{array}$. Warmed

with benzaldehyde, hydroxydihydrophenanthranil is converted into a *benzylidene* derivative, probably derived from the lactim form and

having the constitution, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \dot{\text{C}} \text{---} \dot{\text{C}} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \end{array}$; it would thus be an analogue of chloralide; it is insoluble in caustic alkalis. The foregoing ethyl derivative of hydroxydihydrophenanthranil, as might be expected from its constitution, does not interact with benzaldehyde.

On the other hand, we must point out that sodium phenanthranilate and ethyl phenanthranilate, although, as above formulated, they contain an amino-group, do not interact with benzaldehyde.

At first we were inclined to regard the compound (m. p. 183°), which we have formulated as hydroxydihydrophenanthranil, as phenanthranilic (10-aminophenanthrene-9-carboxylic) acid. This view is, however, untenable, as it would involve the identity of the totally

distinct sodium salts and ethyl esters of the unstable phenanthranilic acid from phenanthranil with those of hydroxydihydrophenanthranil. Besides, there would be no reason why the closed side chain of phenanthranil, when once opened, should spontaneously close again. Nor would such a formula for hydroxydihydrophenanthranil explain the insolubility of the benzylidene and acetyl derivatives of this compound in alkalis, as also the fact that its ethyl derivative is not only insoluble in, but not hydrolysable by, alkalis. It would be necessary, at all events, to assume that phenanthranil and hydroxydihydrophenanthranil contain different hydrocarbon nuclei: that in one of them, possibly the well-known change to the diphenylenemethane nucleus, as in the formation of diphenyleneglycollic acid from phenanthraquinone, has taken place; and, that this is not the case, is shown by the following experiments:

If hydroxydihydrophenanthranil is heated in a sealed tube with fuming hydrochloric acid it yields 9-hydroxyphenanthrene,

together with the corresponding 9-phenanthryl oxide,

and tetraphenylenefurfuran, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} - \text{C} \cdot \text{C}_6\text{H}_4 \\ | \quad \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \quad \text{C} \cdot \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$, the two last-mentioned

compounds being formed from the first (compare Japp and Findlay, *Trans.*, 1897, 71, 1115). If phenanthranil is treated in the same way, it undergoes the same changes, except that a higher temperature is required owing to the greater stability of the compound. As we were compelled to employ a smaller quantity of phenanthranil for the reaction, we contented ourselves with isolating the primary product—which is also the chief product—9-hydroxyphenanthrene.

Both phenanthranil and hydroxydihydrophenanthranil therefore contain the phenanthrene nucleus.

The mechanism of the decomposition may, in the case of phenanthranil, be formulated as follows:

then

(Japp and Findlay, *loc. cit.*, p. 1117).

We studied the conditions of the hydrolysis of acicular phenanthra-

quinonedihydrocyanide much more thoroughly than had been done by Japp and Miller. A product of the hydrolysis which had been overlooked by them is *diphenylenetartramide*, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CONH}_2 \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CONH}_2 \end{matrix}$.

Our attempts to hydrolyse the laminar phenanthraquinone dihydrocyanide were only partially successful, as the reaction does not occur except at a temperature at which the greater part of the substance is resinified. *Phenanthranil* and *hydroxydihydrophenanthranil* were isolated from the product.

EXPERIMENTAL.

Benzildihydrocyanide.

Acetylation of Benzildihydrocyanide.—The benzildihydrocyanide used in this and the following experiments was prepared by Zinin's method as modified by Japp and Miller (Trans., 1887, 51, 31).

In acetylating the compound, a mixture of 15 grams of acetic anhydride and 4 drops of concentrated sulphuric acid was added to 7 grams of finely-powdered benzildihydrocyanide, and the whole was allowed to stand in the cold for three weeks. The solid was separated by filtration and recrystallised from boiling glacial acetic acid. The yield of recrystallised substance was 6 grams. It crystallised in six-sided plates, or long pointed needles, both of which showed straight extinction, and melted, when rapidly heated, with decomposition at 242°.

Analysis gave figures agreeing with the formula of *diacetylbenzildihydrocyanide*, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5\text{O}) \cdot \text{CN} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5\text{O}) \cdot \text{CN} \end{matrix}$

0.2079 gave 0.5242 CO₂ and 0.0881 H₂O. C = 68.76; H = 4.70.

0.2834 „ 20.05 c.c. moist nitrogen at 8° and 741 mm. N = 8.32.

C₂₀H₁₆O₄N₂ requires C = 68.96; H = 4.59; N = 8.04 per cent.

Action of Concentrated Sulphuric Acid on Benzildihydrocyanide: Formation of Diphenylacetamide, (C₆H₅)₂CH·CONH₂.—Forty grams of finely-powdered benzildihydrocyanide were sifted into 400 grams of concentrated sulphuric acid, whilst the mixture was constantly stirred. The whole was allowed to stand for 40 hours, after which it was poured on to pounded ice. The solid substance was separated by filtration and the acid solution was evaporated on the water-bath.

The solid substance was digested with sodium carbonate, which extracted a yellow acid, but in quantity too small for further investigation. The solid residue remaining after this treatment was thoroughly washed with ether, to remove resinous matters. (If the washing with ether has not been sufficient, the residue cannot be induced to crystallise.) The washed residue was recrystallised first

from alcohol, and afterwards from benzene. It was somewhat difficult to purify, but was ultimately obtained in pointed, or obliquely truncated, flat prisms, with an extinction angle of $44-45^\circ$ from the long axis, and melting at $167.5-168^\circ$.

The above-mentioned acid solution yielded, on evaporation, an oil, which solidified on standing. It was boiled with sodium carbonate, and the residue, recrystallised from the foregoing solvents, yielded a further quantity of the substance melting at $167.5-168^\circ$. The substance thus obtained was free from resin and was much easier to purify than the original solid residue.

0.2081 gave 0.6048 CO_2 and 0.1181 H_2O . $\text{C} = 79.26$; $\text{H} = 6.30$.

0.2079 „ 0.6041 CO_2 „ 0.1195 H_2O . $\text{C} = 79.24$; $\text{H} = 6.38$.

0.1002 „ 5.95 c.c. moist nitrogen at 20.5° and 759 mm. $\text{N} = 6.76$.

$\text{C}_{14}\text{H}_{13}\text{ON}$ requires $\text{C} = 79.62$; $\text{H} = 6.16$; $\text{N} = 6.63$ per cent.

The compound is *diphenylacetamide*, $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{CONH}_2$. It was further identified by comparison with a specimen of this substance prepared by heating ammonium diphenylacetate in a sealed tube at 230° (Neure, *Annalen*, 1888, 250, 141). The melting points, mixture melting point, crystalline form and optical properties of the two preparations were identical. Both Neure, and Anschütz and Römig (*Annalen*, 1886, 233) give the melting point of diphenylacetamide at $165-166^\circ$; but we confirmed the somewhat higher melting point of $167.5-168^\circ$, above given, by a determination with a normal thermometer.

The action of hydrochloric acid on benzildihydrocyanide was also studied, but did not yield results of interest. By heating the substance in a sealed tube with fuming aqueous hydrochloric acid the only products obtained were benzoic acid and an uncrystallisable oil. By allowing benzildihydrocyanide to stand with alcoholic hydrogen chloride in the cold, only a hydrochloride of the dihydrocyanide was formed.

*Isomeric Phenanthraquinonedihydrocyanides.**

Acicular Phenanthraquinonedihydrocyanide.—In preparing this compound one of the methods devised by Japp and Miller (*loc. cit.*, p. 33) was employed. Finely powdered phenanthraquinone was allowed to stand for 4—5 days in a strong corked flask with a considerable excess of 30 per cent. aqueous hydrocyanic acid, and the mixture was shaken from time to time. At the end of this time the orange-coloured

* In preparing these compounds, it is essential to employ a phenanthraquinone that has been purified by means of its hydrogen sodium sulphite compound, as otherwise the anthraquinone which is invariably present in specimens of phenanthraquinone which have been purified merely by recrystallisation will contaminate the products.

particles of the phenanthraquinone had disappeared and the flask contained a magma of white, needle-shaped crystals. The substance was freed from the adhering liquid by means of a filter-pump, and then dried in a vacuum desiccator over sulphuric acid. It turns reddish-brown on drying, owing to a partial regeneration of phenanthraquinone.

Japp and Miller purified the substance for analysis by washing it with chloroform, which readily dissolves the phenanthraquinone but in which the dihydrocyanide is practically insoluble. We found, however, that the dihydrocyanide can be recrystallised from hot benzene, provided that too long boiling is avoided. It was deposited in colourless needles, which, when heated in a capillary tube, decompose and turn red at a temperature below 100° .

0.1662 gave 15.1 c.c. moist nitrogen at 13° and 746 mm. $N = 10.53$.

$C_{16}H_{10}O_2N_2$ requires $N = 10.69$ per cent.

Sometimes the hot benzene solution deposited at first colourless six-sided plates and afterwards needles. We were at first inclined to think that these plates were the stereoisomeric laminar phenanthraquinonedihydrocyanide (to be described later on). On separating some of these plates, however, we found that they showed the same decomposing point as the needles, whereas the laminar form does not decompose until $160-170^{\circ}$, and that their diacetyl derivative melted at $255-256^{\circ}$, the melting point of the diacetyl derivative of the needles, and showed no depression when mixed with a specimen of the latter substance. The difference was, therefore, doubtless nothing more than a difference in crystalline habit.

The following experiments on the loss of weight which acicular phenanthraquinonedihydrocyanide, purified by recrystallisation from benzene, suffers on heating, are of interest. The substance was heated at the respective temperatures until the weight remained constant.

0.6374 lost, on heating at 100° for 2 hours, $0.1314 = 20.61$ per cent.

$C_{16}H_{10}O_2N_2 - 2HCN$ requires a loss $= 20.61$ per cent.

The substance which remained was phenanthraquinone.

0.2102 lost, on heating at 70° for 11 hours (weight constant), $0.0217 = 10.32$ per cent.

$C_{16}H_{10}O_2N_2 - HCN$ requires a loss $= 10.30$ per cent.

The substance which remained in the latter case was a scarlet powder and was doubtless *phenanthraquinonemonohydrocyanide*. Its solution in hot benzene deposited scarlet crystals, but a portion of it was decomposed in the process into phenanthraquinone and hydrocyanic acid.

The experiment just described shows that phenanthraquinonedihydrocyanide, when heated for a long time, shows a much lower decomposing point than that (a little under 100°) indicated by its behaviour when quickly heated in a melting-point tube.

Acetylation of Acicular Phenanthraquinonedihydrocyanide.—Twenty grams of acetic anhydride containing 5 drops of concentrated sulphuric acid were added to 10 grams of powdered acicular phenanthraquinonedihydrocyanide. There was a slight rise of temperature on mixing, and the flask was therefore cooled with water. The dihydrocyanide dissolved completely, and in less than an hour crystals began to form. After two days the contents of the flask had almost solidified to a mass of colourless crystals. After recrystallisation from boiling glacial acetic acid, the substance was obtained in colourless, flat, pointed needles, showing straight extinction and melting, with decomposition, at 255—256°. The yield was 7 grams, and more could be obtained by diluting the acetic anhydride mother liquor with water.

The substance is extraordinarily difficult to burn, and we preferred to determine the carbon and hydrogen in separate portions, using lead chromate for the former and copper oxide for the latter.

0.1838 gave 0.4662 CO₂. C = 69.17.

0.1970 „ 0.4988 CO₂. C = 69.05.

0.1623 „ 0.0617 H₂O. H = 4.22.

0.1568 „ 0.0584 H₂O. H = 4.13.

0.2290 „ 16 c.c. moist nitrogen at 11° and 742.4 mm. N = 8.13.

C₂₀H₁₄O₄N₂ requires C = 69.36; H = 4.04; N = 8.08 per cent.

The compound is therefore the *diacetyl* derivative of acicular phenanthraquinonedihydrocyanide:

Laminar Phenanthraquinonedihydrocyanide.—In the course of an attempt to prepare Japp and Miller's acicular phenanthraquinonedihydrocyanide we employed a much stronger hydrocyanic acid than the 30 per cent. aqueous solution prescribed by them. As very little reaction took place in the cold we heated the mixture of phenanthraquinone and hydrocyanic acid in a stout, corked flask. Most of the phenanthraquinone dissolved, and the solution, on cooling, deposited laminae, quite different in appearance from the needles of Japp and Miller's compound, and having a much higher decomposing point. The filtrate from the laminae, as it gave off hydrocyanic acid by exposure to the air, deposited a large quantity of the acicular compound. After various experiments we found that the laminar modification could be best prepared by the following method.

Five grams of finely-powdered phenanthraquinone and 5 grams of anhydrous hydrocyanic acid were heated for 5 hours at 60° in a strong glass tube, of test-tube form and closed by an india-rubber stopper tightly wired. The tube was clamped upright so that only the extreme lower end dipped into a beaker of water heated to the required temperature. In this way a circulation and reflux distillation of the liquid was kept up, and the phenanthraquinone went into solution. On cooling, the liquid deposited colourless, elongated, six-sided laminae, with bevelled edges, also thick short prisms, of the new compound. After standing for six days in the cold the liquid was decanted from the crystals, which were then washed with 85 per cent. hydrocyanic acid and dried in a vacuum desiccator over sulphuric acid. As the crystals turned brownish on the surface in drying they were washed with chloroform to remove the regenerated phenanthraquinone. The powdered substance dissolved, although with greater difficulty than the acicular modification, in hot benzene, and was deposited in slender, oblique prisms, showing straight extinction. The elongated, six-sided laminae extinguish at an angle of about 25° from the long axis. When heated, the substance did not decompose until $160\text{--}170^{\circ}$ (very much higher than the acicular modification), turning red and giving off gas, and finally melting at 200° , the melting point of phenanthraquinone. The original laminae and thick, short prisms, on the one hand, and the slender prisms from benzene on the other, showed an absolutely identical behaviour in this respect, and all gave the same diacetyl derivative (see next section).

Analysis showed that the compound had the composition of a phenanthraquinonedihydrocyanide, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CN}$
 $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CN}$. It is stereo-isomeric with the acicular modification.

0.1559 gave 0.4162 CO_2 and 0.0554 H_2O . $\text{C} = 72.81$; $\text{H} = 3.94$.

0.1842 „ 16.4 c.c. moist nitrogen at 10° and 762 mm. $\text{N} = 10.69$.

0.1850 „ 17 c.c. moist nitrogen at 14° and 750 mm. $\text{N} = 10.66$.

$\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C} = 73.28$; $\text{H} = 3.82$; $\text{N} = 10.69$ per cent.

Analyses I and II were made with the original substance merely washed with chloroform; analysis III with the substance purified by recrystallisation from benzene.

Both the phenanthraquinonedihydrocyanides are slowly decomposed by the moisture of the air and rapidly on boiling with water or with alcohol. The latter solvent readily dissolves them with evolution of hydrocyanic acid and formation of phenanthraquinone. This decomposition, however, does not occur if the water or the alcohol contains hydrochloric acid.

Acetylation of Laminar Phenanthraquinonedihydrocyanide.—The re-

action was carried out as in the case of the acicular compound (*vide supra*) using the same quantities. The yield of uncrystallised substance was 11 grams. It was deposited from hot glacial acetic acid in long, flat, pointed needles, showing straight extinction, and melting, with decomposition, at 235—237°. It is difficult to burn, and the carbon was determined separately by combustion of the substance in a current of moist oxygen. The figures agreed with the formula of a diacetyl derivative, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \cdot \text{CN}$

0.1549 gave 0.3946 CO_2 . $\text{C} = 69.47$.

0.1664 „ 0.0628 H_2O . $\text{H} = 4.19$.

0.2032 „ 14 c.c. moist nitrogen at 9° and 760.5 mm. $\text{N} = 8.23$.

$\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{C} = 69.36$; $\text{H} = 4.04$; $\text{N} = 8.08$ per cent.

The diacetyl derivatives of acicular and laminar phenanthraquinone-dihydrocyanide are indistinguishable in appearance and optical properties, so far at least as a rough examination in polarised light is able to decide; but the former melts at 255—256°, the latter at 235—237°, and the mixture of the two at about 220°—in every case with decomposition.

Hydrolysis of the Phenanthraquinonedihydrocyanides.

Hydrolysis of Acicular Phenanthraquinonedihydrocyanide.—Japp and Miller (*loc. cit.*) showed that carbon dioxide is evolved during the formation of phenanthranil and hydroxydihydrophenanthranil by the hydrolysis of acicular phenanthraquinonedihydrocyanide with cold, fuming hydrochloric acid:—

and

As, therefore, the evolution of carbon dioxide may be utilised as an index of the progress of the reaction, we attached, in the majority of the experiments which we made, a delivery tube to the flask in which the hydrolysis was carried out, and collected the carbon dioxide from time to time.

In our first hydrolysis experiment the acicular phenanthraquinone-dihydrocyanide, prepared as already described and dried over sulphuric acid, was mixed with an excess of the strongest hydrochloric acid and allowed to stand at the ordinary temperature for a fortnight. No gas was given off, and the substance in the flask, freed from hydro-

chloric acid, proved to be unchanged dihydrocyanide. We therefore reverted to Japp and Miller's method, which we describe in detail, inasmuch as the results which we obtained differed somewhat from theirs.

The freshly-prepared hydrocyanide, freed as far as possible from adhering aqueous hydrocyanic acid by means of the filter-pump, *but still moist with this liquid*, was mixed with a large excess of the strongest hydrochloric acid (the ordinary fuming acid into which hydrogen chloride had been passed to complete saturation) in a flask fitted with a delivery tube. Carbon dioxide was evolved and was collected over mercury in a tube containing a little water so as to absorb any hydrogen chloride. Japp and Miller state that the evolution of carbon dioxide ceases "after some days." This is incorrect. The evolution became much slower after about a week, but did not entirely cease until $3\frac{1}{2}$ months had elapsed. The contents of the flask were then diluted with water, and the solid matter was separated by filtration, digested several times on the water-bath with sodium carbonate, and filtered hot. (Too long digestion is to be avoided, as otherwise the sodium salt of hydroxydihydrophenanthranil is decomposed with separation of a brown substance.) After the treatment with sodium carbonate, there was only a small residue which proved to be *diphenylenetartramide* (*vide infra*), whereas Japp and Miller found a large insoluble residue of phenanthraquinone, which must have been regenerated by the action of the hot aqueous carbonate solution on the acicular phenanthraquinonedihydrocyanide that had escaped hydrolysis owing to the shortness of the time during which the experiment was allowed to proceed.*

The united sodium carbonate extracts yielded, on acidification, a copious precipitate, which, after recrystallisation from boiling benzene, was obtained in tufts of slender needles of *hydroxydihydrophenanthranil*,

$\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO}$
 $\text{C}_6\text{H}_4 \cdot \text{CH} - \text{NH}$ melting at 183° . A small quantity of

phenanthranil, $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO}$
 $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH}$ (m. p. 241°), was obtained from the

benzene mother liquor and was freed from any hydroxydihydrophenanthranil with which it was mixed by dissolving it in sodium carbonate and digesting the solution for some days on the water-bath, by which treatment the salt of hydroxydihydrophenanthranil is destroyed with separation of a brown insoluble substance. The filtrate then gives, on acidifying, a precipitate of pure phenanthranil (compare Japp and Miller, *loc. cit.*, p. 36).

Although acicular phenanthraquinonedihydrocyanide that has been

* This residue is not referred to in the original paper.—F. R. J.

previously dried is not hydrolysed by hydrochloric acid in the cold, the reaction readily takes place at a higher temperature.

Seven grams of dry acicular phenanthraquinonedihydrocyanide and 150 c.c. of ordinary fuming hydrochloric acid were heated for 40 hours at 80–90° in a flask fitted with an air condensing tube. The product of the reaction was treated precisely as in the previous experiment; but in the present case phenanthranil was the chief product. It separated in a state of purity from the benzene solution, whilst hydroxydihydrophenanthranil, mixed with phenanthranil, was obtained from the mother liquor.

In this way, by varying the temperature at which the hydrolysis is conducted, one can obtain either phenanthranil or hydroxydihydrophenanthranil as chief product.

Japp and Miller state that phenanthranil and hydroxydihydrophenanthranil are of about equal solubility in benzene. We find, however, that the latter is the more soluble.

We also studied the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide and obtained, in addition to the foregoing compounds, the ethyl ester of phenanthranilic acid and an ethyl derivative of hydroxydihydrophenanthranil.

Twenty-four grams of dry acicular phenanthraquinonedihydrocyanide were mixed with 300 grams of saturated alcoholic hydrogen chloride, and the mixture was allowed to stand for 3 months in a flask fitted with a mercury safety valve. It was noticed that less carbon dioxide was evolved than when aqueous hydrochloric acid was used. The solid substance was separated by filtration, and the alcoholic filtrate was diluted with an equal bulk of water. The solid was treated with water to remove ammonium chloride, and the residue was treated several times with boiling benzene, which extracted phenanthranil mixed with a little hydroxydihydrophenanthranil. The residue from the extraction with benzene was recrystallised from boiling glacial acetic acid, in which it readily dissolved; the crystals were again extracted with benzene, and the residue again recrystallised from glacial acetic acid. The substance was thus obtained in slender transparent prisms melting with decomposition at 274°. It proved to be *diphenylenetartramide* combined with a molecule of acetic acid, the latter being present either as solvent of crystallisation or as salt-forming acid, but probably the former, owing to the ease with which the acetic acid was expelled on heating the compound, and also owing to the fact that the diphenylenetartramide was not found combined with hydrochloric acid in the process in which it was formed. The yield was 0.8 gram. The compound was analysed before we discovered that it contained acetic acid.

0.2040 gave 0.4512 CO₂ and 0.0924 H₂O. C = 60.32; H = 5.03.

0.2118 „ 13.65 c.c. moist nitrogen at 9° and 764.5 mm. N = 7.79.
C₁₆H₁₄O₄N₂·C₂H₄O₂ requires C = 60.33; H = 5.02; N = 7.82 per cent.

The compound was heated at 110° until its weight was constant. It lost 1 mol. proportion of acetic acid.

0.3222 lost, at 110°, 0.0546. Acetic acid = 16.94.

C₁₆H₁₄O₄N₂·C₂H₄O₂ requires acetic acid = 16.76 per cent.

The residue melted with decomposition at 274°, like the original substance, as the latter had of course parted with its acetic acid of crystallisation far below this temperature. It was analysed.

0.1342 gave 0.3164 CO₂ and 0.0570 H₂O. C = 64.30; H = 4.71.

0.1241 „ 10.05 c.c. moist nitrogen at 7.5° and 746 mm. N = 9.62.

C₁₆H₁₄O₄N₂ requires C = 64.42; H = 4.69; N = 9.39 per cent.

The compound is, therefore, *diphenylenetartramide*,

It is identical with the product obtained by the action of cold fuming hydrochloric acid on acicular phenanthraquinonedihydrocyanide (*vide supra*), as was proved by a comparison of the two specimens and by the mixture melting-point test.

Diphenylenetartramide is not chemically altered by heating with fuming hydrochloric acid at 190—200°, as it merely dissolves in the hot acid and crystallises out again on cooling. It is therefore evident that it cannot be an intermediate product in the formation of phenanthranil and hydroxydihydrophenanthranil.

The phenanthranil obtained by the extraction of the original residue with benzene was freed from hydroxydihydrophenanthranil by destroying the latter compound by digesting the mixture with sodium carbonate for several days on the water-bath as described in the case of the product of the hydrolysis with aqueous hydrochloric acid. It gave the correct melting point of 241°, and was further identified by the mixture melting-point test.

The alcoholic hydrogen chloride filtrate, diluted as already mentioned with water, deposited a solid substance. This was separated by filtration, washed with water, and extracted with hot sodium carbonate, which removed a quantity of hydroxydihydrophenanthranil, which on reprecipitation and recrystallisation from benzene melted at 183°, and was further identified by the mixture melting-point test.

The residue from the foregoing sodium carbonate extraction, recrystallised from benzene, formed very slender white needles melting at 207°. The yield was 0.7 gram.

0.1666 gave 0.4680 CO₂ and 0.0854 H₂O. C = 76.61; H = 5.69.

0.2048 „ 9.05 c.c. moist nitrogen at 6° and 741 mm. N = 5.24.

C₁₇H₁₅O₂N requires C = 76.98; H = 5.66; N = 5.28 per cent.

The synthesis of this compound, to be described later on, from the sodium salt of hydroxydihydrophenanthranil and ethyl iodide, and the fact that it is not hydrolysed by boiling it with alcoholic potassium hydroxide, lead us to regard it as a *hydroxyethyl-dihydrophenanthranil*, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO}$
 $\text{C}_6\text{H}_4 \cdot \text{CH} - \text{N} \cdot \text{C}_2\text{H}_5$, in which the ethyl group is attached to nitrogen.

Possibly the sodium salt of hydroxydihydrophenanthranil is derived from the tautomeric form and has the formula, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{ONa}$
 $\text{C}_6\text{H}_4 \cdot \text{CH} - \text{N}$, or possibly the side chain opens in the formation of this salt, as in the case of the metallic salts of phenanthranil. Japp and Miller were unable to obtain the metallic salts of hydroxydihydrophenanthranil sufficiently pure to decide with certainty on their composition.

The dilute alcoholic hydrochloric acid filtrate, from which the foregoing substance had been separated by filtration, was allowed to evaporate spontaneously. As the alcohol was given off, a brownish solid was deposited; this was boiled with benzene, which did not dissolve it, but left it white. This white substance proved to be the hydrochloride of a weak base; it was found that, by digesting it with water on the water-bath for half an hour, the whole of the hydrochloric acid could be removed. The basic product resulting from this treatment was recrystallised first from alcohol and afterwards from benzene; from the latter solvent it is deposited in slender needles with a yellowish tinge, melting at 185°, with decomposition, to a red liquid which resolidifies and then does not melt even at 290°.

0.1485 gave 0.4171 CO₂ and 0.0742 H₂O. C = 76.60; H = 5.55.

0.1868 „ 8.45 c.c. moist nitrogen at 9° and 733 mm. N = 5.24.

C₁₇H₁₅O₂N requires C = 76.98; H = 5.66; N = 5.28 per cent.

We regard this compound as *ethyl phenanthranilate* (10-aminophenanthrene-9-carboxylate), $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO}_2\text{C}_2\text{H}_5$
 $\text{C}_6\text{H}_4 \cdot \text{CH} - \text{N} \cdot \text{H}_2$, although we must point out that the fact that the substance does not interact with benzaldehyde, even at the boiling point of the latter, is not in keeping with this formula.

When the foregoing ester (m. p. 185°) is heated with aqueous caustic soda, it dissolves, and on acidifying the solution, phenanthranil is precipitated, the liberated phenanthranilic acid parting with water and yielding this compound. The phenanthranil thus obtained was recrystallised from benzene. It showed the correct melting point of 241° and was further identified by the mixture melting-point test.

By treating the foregoing ester (m. p. 185°) in the cold with excess of acetic anhydride containing a little concentrated sulphuric acid (1 drop per 5 grams), a crystalline substance was obtained, insoluble in the ordinary organic menstrua, melting at 218—219°, and yielding, on analysis, C=76·55, H=4·47, N=5·05. These figures do not appear to lead to any formula that can be accounted for. Possibly the carbon is too low, but we had not sufficient substance for further analysis.

An attempt to synthesise the foregoing ester (m. p. 185°) from sodium phenanthranilate and ethyl iodide yielded, instead, *phenanthranil ethyl ester*, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C} \cdot \text{OC}_2\text{H}_5 \\ | \quad | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \end{array}$ (m. p. 110°), derived from the lactim form of phenanthranil (*vide infra*).

Hydrolysis of Laminar Phenanthraquinonedihydrocyanide.—In the case of this substance only the hydrolysis with aqueous hydrochloric acid was studied. At the ordinary temperature fuming hydrochloric acid had no action whatever. It was necessary to heat the finely-powdered substance with the fuming acid at 100° in order to obtain any result. Only a small quantity of *phenanthranil* and *hydroxydihydrophenanthranil* could be isolated from the product. Dark-coloured, resinous matters, insoluble in sodium carbonate, were formed in considerable amount.

Hydroxydihydrophenanthranil,

190—192°, with decomposition).—One gram of hydroxydihydrophenanthranil, 6 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to interact in the cold for 3 weeks. The solid was filtered off, washed with a little cold glacial acetic acid, and recrystallised from boiling alcohol. It forms small white needles melting at 190—192° with decomposition. The yield was almost 1 gram.

0·1826 gave 0·4904 CO₂ and 0·0792 H₂O. C=73·24; H=4·81.

0·1460 „ 6·2 c.c. moist nitrogen at 6° and 751 mm. N=5·10.

C₁₇H₁₃O₃N requires C=73·11; H=4·65; N=5·01 per cent.

The compound is therefore a *monacetyl* derivative of hydroxydihydrophenanthranil. The acetyl group replaces the labile hydrogen atom, as the compound does not dissolve in sodium carbonate. On long digestion with sodium carbonate solution on the water-bath, however, it is decomposed with separation of the brown amorphous substance which hydroxydihydrophenanthranil yields under similar

circumstances, the decomposition being, in the present case, doubtless preceded by the hydrolysis of the acetyl derivative.

245—246° with decomposition).—Half a gram of hydroxydihydrophenanthranil was boiled for 3 minutes in a test-tube with 2 grams of benzaldehyde. Water was given off. Alcohol was then added and the mixture digested for some time. The crystalline substance which separated was recrystallised from boiling glacial acetic acid, from which it was deposited in clusters of very slender white needles melting at 245—246° with decomposition, evolving gas and turning yellow. It is very sparingly soluble in alcohol and in benzene, and does not dissolve in sodium carbonate or sodium hydroxide even on long heating.

0.1702 gave 0.5018 CO_2 and 0.0728 H_2O . $\text{C} = 80.40$; $\text{H} = 4.75$.

0.2585 „ 9.35 c.c. moist nitrogen at 7° and 756 mm. $\text{N} = 4.36$.

$\text{C}_{22}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 81.23$; $\text{H} = 4.61$; $\text{N} = 4.30$ per cent.

The compound is thus the *benzylidene* derivative of hydroxydihydrophenanthranil.

Phenanthranil, on the contrary, is not acted on by benzaldehyde at the boiling point of the latter.

Synthesis of Hydroxyethylidihydrophenanthranil,

(m. p. 207°).—As the salts of hydroxydihydrophenanthranil are very unstable, we thought it better, instead of attempting to prepare its sodium salt and acting on this with ethyl iodide, to employ the method of alkylation devised by Japp and Klingemann (*Trans.*, 1888, 53, 526—527) to meet such cases.

One and a half grams of hydroxydihydrophenanthranil and 4.8 grams of ethyl iodide were dissolved in absolute ethyl alcohol, the solution was boiled in a flask fitted with a reflux condenser, and a solution of 0.7 gram of sodium in absolute alcohol was allowed to fall drop by drop into the boiling liquid. The boiling was continued for $3\frac{1}{2}$ hours. The solution was cooled, diluted with water, and extracted with ether. The ethereal extract was freed from a small quantity of unchanged hydroxydihydrophenanthranil by shaking it with sodium carbonate solution, and a further quantity of the same compound was precipitated on acidifying the extracted aqueous alcoholic solution, 0.4 gram of unchanged substance in all being thus recovered. The ethereal extract yielded, on evaporation, *hydroxy-*

ethylidihydrophenanthranil, which crystallised from boiling benzene in slender, white needles melting at 207° . It was proved by the mixture melting-point test to be identical with the substance of the same melting point obtained by the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide.

0.2000 gave 0.5633 CO_2 and 0.1029 H_2O . $\text{C} = 76.77$; $\text{H} = 5.71$.

$\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C} = 76.98$; $\text{H} = 5.66$.

As already mentioned, the compound is not hydrolysed by boiling it with alcoholic potassium hydroxide. We also ascertained that boiling benzaldehyde is without action on it.

Acetyl Derivative of Hydroxyethylidihydrophenanthranil,

(m. p. $148-149^{\circ}$).—One gram of hydroxyethylidihydrophenanthranil (m. p. 207°), 10 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to stand in the cold. At first the substance dissolved, but afterwards the liquid became filled with crystals. At the end of a fortnight the solid was separated by filtration; the filtrate, diluted with water, yielded a further quantity of the same product, the total yield being 0.8 gram. The substance was purified by dissolving it in benzene and adding light petroleum, when it separates in very slender, silky needles melting constantly at $148-149^{\circ}$.

0.1674 gave 0.4548 CO_2 and 0.0847 H_2O . $\text{C} = 74.09$; $\text{H} = 5.62$.

0.2544 „ 10.00 c.c. moist nitrogen at 15.5° and 756 mm. $\text{N} = 4.56$.

$\text{C}_{19}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 74.26$; $\text{H} = 5.53$; $\text{N} = 4.56$ per cent.

Hydrolysis of Hydroxyethylidihydrophenanthranil with Fuming Hydrochloric Acid.—Three sealed tubes, each containing 2 grams of hydroxydihydrophenanthranil with 50 c.c. of fuming hydrochloric acid, were heated for 6 hours at 130° . There was pressure in the tubes on opening. The fused mass of organic substance was powdered and extracted with ether. The ethereal solution was shaken with dilute sodium hydroxide, and the sodium hydroxide solution, heated to expel ether and then filtered, was saturated with carbon dioxide. A phenolic substance was thus precipitated which, after recrystallisation from hot benzene, formed brownish needles melting at $151-153^{\circ}$. The

properties were those of 9-hydroxyphenanthrene, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{OH} \end{array}$, and its melting point was not altered by mixing it with a specimen of this compound prepared by Japp and Klingemann (Trans., 1893, 63, 770) by the partial reduction of phenanthraquinone with hydriodic acid.

0.1601 gave 0.5051 CO_2 and 0.0751 H_2O . $\text{C} = 86.04$; $\text{H} = 5.21$.

$\text{C}_{14}\text{H}_{10}\text{O}$ requires $\text{C} = 86.60$, $\text{H} = 5.16$ per cent.

It was further identified by mixing its hot benzene solution with a similar solution of phenanthraquinone. The mixed solution deposited, on cooling, ruby-red, lozenge-shaped crystals of the compound $\text{C}_{28}\text{H}_{18}\text{O}_3$, melting at 155° (compare Japp and Findlay, 1897, 71, 1121).

The ethereal solution from which the 9-hydroxyphenanthrene had been removed by sodium hydroxide yielded, on evaporation, a substance, which, after recrystallisation from benzene, formed crystals melting at 209° . This proved to be 9-phenanthryl oxide,

(m. p. 210°).

It was identified by a comparison, including the mixture melting-point test, with the original specimen of this substance prepared by Japp and Findlay (*loc. cit.*, p. 1119). Examined microscopically, both specimens appeared as rhomboidal plates with an acute angle of about 66° and with extinction parallel to the diagonal.

The residue, which remained after the extraction of the original product of hydrolysis with ether, was recrystallised from boiling coal oil (b. p. $170-190^\circ$). It was thus obtained in clusters of colourless slender needles melting at 305° and was identified as *tetraphenylene-furfuran*,

and by the colour reaction with concentrated sulphuric acid and sodium nitrite (compare Japp and Findlay, *loc. cit.*, p. 1120).

Phenanthranil,

Acetylphenanthranil, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{C}_2\text{H}_5\text{O} \end{array}$ (m. p. 145°).—The acetyla-

tion was carried out with acetic anhydride containing a small quantity of concentrated sulphuric acid, exactly as in the acetylation of hydroxydihydrophenanthranil (*vide supra*) and using the same proportions. The product was crystallised from hot alcohol, in which it is readily soluble. It formed clusters of slender, silky needles melting at 145° . It does not dissolve in sodium carbonate solution, even at 100° . Analysis showed that a *monacetyl* derivative had been formed.

0.1634 gave 0.4660 CO₂ and 0.0624 H₂O. C = 77.77; H = 4.24.

0.1716 „ 0.4930 CO₂ „ 0.0666 H₂O. C = 78.35; H = 4.31.

0.2186 „ 9.05 c.c. moist nitrogen at 6° and 759 mm. N = 5.03.

C₁₇H₁₁O₂N requires C = 78.16; H = 4.21; N = 5.36 per cent.

Lactim Ester of Phenanthranil (Phenanthranil Ethyl Ester),

(m. p. 110°).—Sodium phenanthranilate, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO}_2\text{Na} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH}_2 \end{array}$, 4H₂O, was prepared by dissolving phenanthranil in a hot solution of sodium carbonate; on cooling, the liquid deposited laminae of the salt. It was dried at 110° to expel water of crystallisation. The dried salt, together with an excess of ethyl iodide, was dissolved in absolute alcohol, and the mixture was boiled for 3½ hours. Dilution with water precipitated a white substance; this was filtered off and digested with warm sodium carbonate, which removed a little phenanthranil. The residue was recrystallised, first from alcohol and afterwards from light petroleum (sp. gr. 0.71—0.72). It was thus obtained in slender needles melting at 110°. It is very soluble both in alcohol and in benzene.

0.1342 gave 0.4064 CO₂ and 0.0662 H₂O. C = 82.59; H = 5.48.

0.2256 „ 11.25 c.c. moist nitrogen at 11.5° and 758 mm. N = 5.92.

C₁₇H₁₃ON requires C = 82.59; H = 5.26; N = 5.66 per cent.

An attempt to acetylate the compound with acetic anhydride containing a little sulphuric acid gave no result.

A portion of the compound was digested on the water-bath in a silver basin with a 20 per cent. solution of potassium hydroxide in absolute alcohol, renewing the alcohol as required. The alcohol was then expelled, water was added, and the mixture was digested and filtered hot from the insoluble residue. The hot filtrate was acidified and the precipitate recrystallised from benzene. Needles of *phenanthranil* (m. p. 241°) were thus obtained. The insoluble residue, separated by filtration from the potassium hydroxide solution, was crystallised from benzene; it was thus obtained in slender needles melting at 207°, and was identical with the *hydroxyethylidihydrophenanthranil*, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} - \text{N} \cdot \text{C}_2\text{H}_5 \end{array}$, already described, as was proved by the mixture melting-point test. The lactim ester of phenanthranil is thus partly hydrolysed to phenanthranil, and partly transformed by migration of the ethyl group and assumption of the elements of water into hydroxyethylidihydrophenanthranil.

The latter result was so surprising that we repeated the entire

experiment, preparing the lactim ester of phenanthranil from a specimen of phenanthranil which had been purified by digesting it for several days on the water-bath with a solution of sodium carbonate and from which, consequently, every trace of hydroxydihydrophenanthranil must have been removed by the destruction of this compound. The result, however, was the same as before.

The only alternative, so far as we can see, to assuming a migration of the ethyl group from carbon to nitrogen in a portion of the lactim ester is to suppose that the latter substance is in reality a mixture of the *O*-ethyl and *N*-ethyl derivatives of phenanthranil, the former being hydrolysed by the caustic alkali to phenanthranil, and the latter taking up the elements of water to form the hydroxyethyl-dihydrophenanthranil. The lactim ester of phenanthranil, however, shows no sign of being other than a perfectly homogeneous substance.

We also digested a specimen of hydroxyethyl-dihydrophenanthranil (m. p. 207°), prepared from hydroxydihydrophenanthranil, ethyl iodide, and sodium ethoxide (*vide supra*), for $3\frac{1}{2}$ hours with 20 per cent. alcoholic potassium hydroxide on the water-bath. The hydroxyethyl-dihydrophenanthranil was recovered unchanged, and the potash solution, treated as in the experiment just described, gave no precipitate on acidifying.

Hydrolysis of Phenanthranil with Fuming Hydrochloric Acid.—Unlike hydroxydihydrophenanthranil, phenanthranil is not acted on by fuming hydrochloric acid at 130° . At a temperature of 160 – 170° , however, 9-hydroxyphenanthrene was formed, and was identified by its properties and by the mixture melting-point test. As the quantity of phenanthranil which we could spare for the experiment was small, we did not search for the other products obtained from hydroxydihydrophenanthranil.

The production of 9-hydroxyphenanthrene, both from phenanthranil and from hydroxydihydrophenanthranil, is of importance, inasmuch as it proves, as already pointed out, that both these compounds contain the phenanthrene nucleus.

Distinction between Phenanthranil (m. p. 241°) *and Hydroxydihydrophenanthranil* (m. p. 183°).—Both phenanthranil and hydroxydihydrophenanthranil crystallise from benzene in slender needles, the former being the less soluble. The two substances are very similar in appearance. In addition to the melting points, the following differences may be noted. In polarised light the needles of phenanthranil show straight extinction; those of hydroxydihydrophenanthranil oblique extinction at an angle of about 13° from the long axis. Phenanthranil does not dissolve in cold concentrated sulphuric acid, but, on warm-

ing, dissolves slowly, yielding a grass-green solution. Hydroxy-dihydrophenanthranil dissolves in cold concentrated sulphuric acid giving a light yellow solution which is unaltered on warming.

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