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TRANSACTIONS.

I.—*Ethylic Phenanthroxylyene-acetoacetate.*

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IN a paper entitled "Condensations of Glyoxal with Ethylic Malonate and Ethylic Acetoacetate," by Max Polonowsky (*Annalen*, **246**, 1), it is stated as a reason for undertaking the investigation that only the condensations of these esters with *monaldehydes* and *monoketones* have hitherto been studied. Polonowsky has evidently overlooked the fact that the condensation of a diketone—phenanthraquinone—with ethylic acetoacetate has been described by Japp and Streatfeild (*Trans.*, 1883, 27).*

* The paper by Japp and Streatfeild was also sent—unfortunately, in English—to the *Berichte*, where a translation of it appeared (*Ber.*, **16**, 275); but this translation, which was published without being previously submitted to the authors for approval, was so disfigured by blunders (see list of errata, *Ber.*, **16**, 819), that the authors were compelled to withdraw it and to refer intending readers to the English original in the Transactions (*cf.* *Ber.*, **16**, 726). As a specimen of these blunders, we may mention that, in the description of the preparation of the so-called ethylic α -phenanthroxylyene-isocrotonate, the words of the English manuscript, "by warming the acetic acid and zinc-dust," were transformed by the Berlin translator into "durch Erhitzen mit Zinkstaub" ("by heating with zinc-dust"), by which expression every reader would of course understand that the substance had been distilled with zinc-dust. Considering that the compound formed in this reaction was the ethyl salt of a carboxylic acid, it is not going too far to say that such a statement was calculated to raise doubts as to either the sanity or the *bona fides* of the investigators. We mention this case more particularly because, in spite of the withdrawal of the German paper, this erroneous statement as to the heating with zinc-dust has passed into the *Jahresbericht* (1883, 1011) and into Fehling's *Handwörterbuch* (**4**, 1222).

In the present paper, we describe the further investigation of ethylic phenanthroxylene-acetoacetate,

the condensation product obtained by the action of caustic potash on a mixture of phenanthraquinone and ethylic acetoacetate. In spite, however, of the large amount of experimental material which we have accumulated, we must reserve the detailed discussion of our results until the relation of the various compounds to one another has been more fully cleared up. For the present, we may say that the majority of these compounds appear to be derived from a compound,

isomeric with the original condensation product, and formed from it by heating it with certain acids (concentrated formic acid, dilute sulphuric acid). This isomeride may provisionally be named *ethylic isophenanthroxylene-acetoacetate*. The above constitutional formula, which we give with reserve, represents the compound as formed by internal aldol-condensation, and accounts for the formation of a monoacetyl derivative and a monohydrazone, as well as for the fact that the compound can be hydrolysed with alkalis, yielding a monobasic acid. On the other hand, the stability of this acid speaks against the formula, since a γ -ketonic acid would, in all probability, readily part with carbon dioxide, whereas this acid does not decompose below its melting point (267—269°). Moreover, the hydrazone of a γ -ketonic ester ought, under appropriate conditions, to part with alcohol, yielding a pyrazolone; but it was not found possible to effect any such transformation in the case of the hydrazone of the foregoing isocompound.

Another result of our work is to show that two of the compounds described by Japp and Streatfeild (*loc. cit.*), namely, the so-called *ethylic α -phenanthroxylene-isocrotonate*, $\text{C}_{20}\text{H}_{16}\text{O}_3$, and the dibasic acid, $\text{C}_{18}\text{H}_{14}\text{O}_4$, are not, as was supposed, derived from the original condensation product, but, with certain modifications, from the isocompound, and that the constitutional formulæ assigned to these compounds must, therefore, be abandoned.

By subliming the dibasic acid, $\text{C}_{18}\text{H}_{14}\text{O}_4$, Japp and Streatfeild obtained in very small quantity a compound melting at 213°, of which a single combustion, made with less than 0.07 gram, gave figures agreeing with the formula $\text{C}_{14}\text{H}_{10}\text{O}$. By employing a different method, we have obtained a better yield of this compound, and we find, both

from its mode of formation and as the result of analysis, that it has the formula $C_{17}H_{12}O$.

Ethylic phenanthroxylene-acetoacetate, when heated with certain acids, undergoes a variety of chemical changes. The first observation in this direction was made in the course of an attempt to recrystallise the compound from hot glacial acetic acid, when it was noticed that an insoluble compound separated from the hot liquid in colourless, silky needles, the quantity of which increased on further boiling. This led us to examine the action of other acids, both organic and inorganic, and it was found that different acids gave different results. The action in the case of acetic acid is complex, and will be better understood when that with formic acid has first been described.

In the meantime, however, we may mention that although ethylic phenanthroxylene-acetoacetate is acted on by hot glacial acetic acid, it may be dissolved unchanged in this solvent in the cold, and we have thus been able to determine its molecular weight by Raoult's method. The result points to the formula $C_{20}H_{16}O_4$.

Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Mol. wt.	
				Found.	$C_{20}H_{16}O_4$. Calc. for
I. 0.1716	22.35	0.7678	0.103°	290	320
II. 0.2354	25.933	0.9077	0.125	283	„

(Molecular depression of acetic acid = 39).

Action of Formic Acid on Ethylic Phenanthroxylene-acetoacetate.

The substance was heated with excess of concentrated formic acid (sp. gr. 1.22) in a sealed tube at 130° for an hour. On cooling, the greater part of the new substance was deposited in small, brownish crystals, whilst a further quantity could be precipitated from the mother liquor by the addition of water. Alcohol, benzene, light petroleum, and, finally, ethylic acetate were employed as solvents, the last-mentioned giving the best result, and depositing the compound in colourless, triclinic prisms melting at 177° . For ordinary purposes, benzene may be used as a solvent; it deposits the substance in needles, which, however, obstinately retain a trace of a pink colouring matter. This colouring matter is also formed in various other reactions here described, and greatly interferes with the purification of the products. In the case of the present compound, however, the colouring matter can be readily removed by recrystallising the substance from hot alcoholic hydrogen chloride.

Analysis gave figures which lead to the formula $C_{20}H_{16}O_4$, showing that the compound is isomeric with the original condensation product.

	Substance.	CO ₂ .	H ₂ O.
I.....	0·2389	0·6580	0·1075
II.....	0·2378	0·6549	0·1097

	Calculated for		Found.	
	C ₂₀ H ₁₆ O ₄ .		I.	II.
C ₂₀	240	75·00	75·11	75·11
H ₁₆	16	5·00	5·00	5·12
O ₄	64	20·00	—	—
	<hr/>	<hr/>		
	320	100·00		

This compound may receive the provisional name *ethyl isophenanthroxylene-acetoacetate*, but we shall also refer to it, for shortness, as the "iso-compound." We have already given the constitutional formula which we incline to assign to it.

For the following crystallographical examination of the compound we are indebted to Mr. A. E. Tutton:—

"The crystals are perfectly colourless and very highly refractive when purified by several recrystallisations from acetic ether. The reflections obtained were generally excellent; but, owing to longitudinal striation, and occasionally to the presence of twin lamellæ, recognisable by the polariscope, the prism faces often gave several images. On this account a large number of crystals were measured. They vary in size from 2 to 4 mm. in length, and from 0.5 to about 1.5 mm. in thickness.

"System: triclinic. Habit: prismatic.

"Elements. Axial angles: $\alpha = 78^{\circ} 6'$, $\beta = 72^{\circ} 0'$, $\gamma = 83^{\circ} 18'$.

Ratio of axes: $a : b : c = 0.9640 : 1 : 0.5069$.

"Forms present: $a, \{100\}, \infty\bar{P}\infty$; $b, \{010\}, \infty\check{P}\infty$; $c, \{001\}, oP$.

$$p, \{110\}, \infty P'; p', \{1\bar{1}0\}, \infty' P; q, \{0\bar{1}1\}, \check{P}, \infty.$$

“ Fig. 1 represents the usual appearance of the crystals drawn to scale, and Fig. 2 is the spherical projection.

FIG. 1.

FIG. 2.

"Parallel faces b are generally the best developed, sometimes so much so that the crystals become converted into thin, tabular plates. All the individuals examined showed the whole six forms. Following is a table of measurements of the principal angles, together with the values obtained by calculation from the elements.

	No. of measurements.	Limits.	Mean observed angles.	Calculated angles.
$b : p, 010 : 110 \dots$	20	$41^\circ 38' - 40^\circ 18'$	$40^\circ 57'$	*
$p : a, 110 : 100 \dots$	20	$38 30 - 37 14$	$37 53$	*
$a : p', 100 : 1\bar{1}0 \dots$	20	$49 41 - 47 33$	$48 32$	$48^\circ 19'$
$p' : b, 1\bar{1}0 : 0\bar{1}0 \dots$	20	$53 51 - 51 35$	$52 38$	$52 51$
$b : c, 010 : 001 \dots$	35	$75 34 - 74 54$	$75 9$	*
$c : q, 001 : 0\bar{1}1 \dots$	33	$28 28 - 27 58$	$28 11$	$28 11$
$q : b, 0\bar{1}1 : 0\bar{1}0 \dots$	33	$77 0 - 76 17$	$76 40$	*
$p : c, 110 : 001 \dots$	13	$67 29 - 66 45$	$67 8$	$67 3$
$p : q, 110 : 0\bar{1}1 \dots$	10	$89 6 - 88 17$	$88 45$	$88 39$
$a : c, 100 : 001 \dots$	14	$70 23 - 69 41$	$69 57$	*
$a : q, 100 : 0\bar{1}1 \dots$	11	$75 45 - 75 1$	$75 28$	$75 31$
$p' : c, 1\bar{1}0 : 001 \dots$	11	$85 26 - 84 44$	$85 8$	$85 13$
$p' : q, 1\bar{1}0 : 0\bar{1}1 \dots$	11	$67 50 - 67 16$	$67 35$	$67 45$

"The angles marked with an asterisk were used for the calculation of the elements. The mean temperature during the measurements was 14.8°C. , the limits being $13.8-16.5^\circ$.

"There are two well-developed cleavages, one parallel to the basal plane c , and another parallel to the brachypinakoid b .

"Twins are occasionally found of the form indicated in Fig. 3.

FIG. 3.

They are produced by rotation of one individual (the front one) 180° about the vertical axis.

"The twin plane is consequently the prism zone plane, the plane of the spherical projection. The upper termination exhibits re-entrant

angles, while the lower end shows apparently four pyramid faces. Measurements indicate that, as expected, the angles of the prism zone remain the same, the face $b(0\bar{1}0)$ of the front and $b(010)$ of the back crystal forming one plane in the twin. The angle made by this plane with c of the back crystal is $75^\circ 9'$, and with q of the front crystal $76^\circ 40'$. The twinning is occasionally repeated, the individuals appearing as twin lamellæ.

"As regards the optical properties, the extinctions upon all the faces are oblique to the crystallographic axes and facial edges. The extinction upon face b occurs at an angle of 48° to the prism edges; upon face p , 36° ; upon a , 50° ; and upon c , as seen through a cleavage plate, about 10° with the trace of b .

"In convergent light, looking through a cleavage plate parallel to c (001), one optic axis with its brush and rings is visible, emerging on the side nearest the edge ac , and making an apparent angle of about 46° with the normal to the plate.

"Through $b(010)$ another brush is visible, the axis being apparently just beyond the edge bp . This axis is distinctly seen with its rings on looking through face $p(110)$ near the edge bp . The rings are very close together even in the thinnest sections; hence the double refraction is very strong."

The same compound can be readily obtained by boiling ethylic phenanthroxyline-acetoacetate with sulphuric acid diluted with twice its weight of water. The substance cakes together to a crust, which should be broken up with a glass rod during the operation. The product was powdered under water, thoroughly washed with water, and purified as in the case of the substance obtained with formic acid. It crystallised from ethylic acetate in the prismatic forms of the iso-compound, melting, like the latter, at 177° . Analysis gave C, 74.90; H, 5.03 per cent. Calculated for $C_{20}H_{16}O_4$: C, 75.00; H, 5.00 per cent.

The crude product obtained in the foregoing reaction is yellow instead of pink, the colouring matter which gave so much trouble in preparing the compound by the action of formic acid not being formed, and the substance is consequently easier to purify.

In our first experiment with dilute sulphuric acid we obtained a practically quantitative yield of the iso-compound; but in subsequent experiments a small quantity of a substance insoluble in benzene and acetic acid was formed at the same time. This proved to be the compound $C_{20}H_{14}O_3$, more readily obtained by the action of glacial acetic acid on ethylic phenanthroxyline-acetoacetate (*vide infra*), and formed from this latter compound by elimination of a molecule of water. Possibly its formation in the present case might be avoided by the use of a more dilute sulphuric acid.

Action of Acetic Anhydride on Ethylic Isophenanthroxylene-acetate.—The iso-compound was heated with excess of acetic anhydride for three hours at 150°. As the solution, which was of a pink colour, deposited nothing on cooling, it was boiled with alcohol to destroy the excess of anhydride, and then concentrated. On cooling, large, well-shaped crystals separated, resembling in form those of copper sulphate, and melting indistinctly at 165–170°. It crystallises from benzene in thick needles. Analysis showed that a monacetyl derivative, $C_{20}H_{15}(C_2H_3O)_4$, had been formed.

	Substance.	CO ₂ .	H ₂ O.
I.	0.1964	0.5285	0.0892
II.	0.2444	0.6562	0.1113

	Calculated for $C_{20}H_{15}(C_2H_3O)_4$.		Found.	
			I.	II.
C ₂₂	264	72.93	73.38	73.22
H ₁₈	18	4.97	5.04	5.06
O ₅	80	22.10	—	—
	362	100.00		

The compound is identical with one of those described later, obtained by heating ethylic phenanthroxylene-acetoacetate with glacial acetic acid. On the other hand, the iso-compound does not yield this acetyl derivative when heated with glacial acetic acid, even at 150°.

Some further reactions of this acetyl derivative will be described in connection with its preparation by the second method just referred to.

Action of Phenylhydrazine on Ethylic Isophenanthroxylene-acetoacetate.—The iso-compound was heated with phenylhydrazine in alcoholic solution for an hour at 130–140°. As nothing was deposited on cooling, sufficient water was added to cause a slight turbidity, and on standing the hydrazone separated in aggregates of flat, yellow needles. The substance was recrystallised from a mixture of benzene and light petroleum, and was thus obtained as a yellow, crystalline powder. Heated in a capillary tube, it began to change colour at 140°, was quite black at 200°, and melted with strong decomposition at 210–212°. It dissolves in concentrated sulphuric acid with a deep blue colour.

Analysis of the substance dried at 100° showed that a monohydrazone, $C_{20}H_{16}O_3(N_2HC_6H_5)$, had been formed:—

- I. 0.1515 gram gave 0.4245 CO₂ and 0.0737 H₂O.
 II. 0.1046 „ 9.02 c.c. dry nitrogen at 16.5°, and under 522 mm. pressure. Nitric oxide absent.

	Calculated for $C_{26}H_{22}N_2O_3$		Found.	
	I.	II.	I.	II.
C_{26}	312	76·10	76·41	—
H_{22}	22	5·36	5·40	—
N_2	28	6·83	—	7·01
O_3	48	11·71	—	—
	410	100·00		

The iso-compound was then heated with phenylhydrazine in alcoholic solution for two hours at 190° , in the hope that the hydrazone might split off water yielding a pyrazolone; but only the hydrazone was obtained as before.

Ethyl phenanthroxylene-acetoacetate, on the other hand, does not appear to react with phenylhydrazine under ordinary conditions: thus no action took place when the two substances were heated together in alcoholic solution for one hour at 100° . The reaction has yet to be tried at a higher temperature.

Action of Bromine on Ethyl Isophenanthroxylene-acetoacetate.—Two grams of the iso-compound were dissolved in dry chloroform, and 1 gram of bromine (also dissolved in chloroform) was added. As the colour of the bromine did not disappear, the solution was allowed to stand in a desiccator over solid paraffin. After standing for a few hours, the colour of the liquid had changed to a light yellow, and fumes of hydrobromic acid were evolved, whilst well-shaped crystals, sometimes prismatic, sometimes tabular, had separated; these were washed with chloroform and air-dried in the dark. Precisely similar crystals were obtained by further spontaneous evaporation of the mother liquors. Heated in a capillary tube, both specimens began to blacken at 195 – 200° , and melted with decomposition at 217° . Analysis gave results which showed that a monobromo-derivative, $C_{20}H_{15}BrO_4$, had been formed; but the carbon was found too high and the bromine too low. Calculated for $C_{20}H_{15}BrO_4$: C, 60·15; H, 3·76; Br, 20·05. Found: C, 61·27; H, 4·09; Br, 19·13. It, therefore, appeared that, in spite of its homogeneous appearance, the bromine compound was contaminated with unchanged substance.

As it was clear from the foregoing that an additive compound was not formed, we did not pursue the subject further.

Reduction of Ethyl Isophenanthroxylene-acetoacetate with Zinc and Hydrochloric Acid.—The iso-compound was dissolved in alcohol on the water-bath, and a little alcoholic hydrochloric acid and zinc filings added from time to time. After continuing the reduction for several hours, the solution was poured into water. The precipitated oily substance solidified after standing for some days, and was recrystallised from a

mixture of benzene and light petroleum. The first crop of crystals melted about 165—170°, and appeared to be unchanged substance. The mother liquor deposited a substance of lower melting point: this was recrystallised from ethyl acetate, and was thus obtained in well-shaped, colourless crystals of prismatic habit, melting at 123°, and identical with the compound of the formula $C_{20}H_{16}O_3$ (m. p. 124) prepared by Japp and Streatfeild (Trans., 1883, 29) by warming the original condensation compound with hydriodic acid and amorphous phosphorus. The smallness of the yield made further purification impracticable: the compound was therefore analysed, and gave a result which, although not good, left no doubt as to the formula:—

0.1180 gram gave 0.3380 CO_2 and 0.0562 H_2O .

	Calculated for $C_{20}H_{16}O_3$.		Found.
C_{20}	240	78.95	78.12
H_{16}	16	5.26	5.29
O_3	48	15.79	—
	304	100.00	

The foregoing mode of formation shows that the compound cannot well have the constitution ascribed to it by Japp and Streatfeild.

In preparing the compound by Japp and Streatfeild's method, we found it better to omit the addition of amorphous phosphorus. Ethylic phenanthroxylene-acetoacetate was boiled for a short time with fuming hydriodic acid; the product was washed with water, freed from iodine by boiling with a solution of hydrogen sodium sulphite, and recrystallised from alcohol or from a mixture of benzene and petroleum. By working in this way, the red colouring matter which gave so much trouble in the original method of preparation does not appear to be formed.

When this compound is heated with phenylhydrazine in alcoholic solution in a sealed tube at 100°, it forms a hydrazone, which separates from the hot solution as a yellow, crystalline powder, readily soluble in hot benzene, sparingly soluble in hot alcohol. For analysis it was recrystallised from a mixture of benzene and petroleum, but the recrystallisation was attended with loss, and the substance looked less pure than when merely boiled out with a little alcohol. It blackens about 190°, and is totally decomposed at 195°. A nitrogen determination showed that a monohydrazone, $C_{20}H_{16}O_2(N_2HC_6H_5)$, had been formed.

Substance.		v.	t.	p.
0.1027	{ dry N + NO	9.02 c.c.	17°	536 mm.
	{ „ N	9.02 „	17	526 „

	Calculated for $C_{20}H_{16}O_2(N_2HC_6H_5)$.	Found.
N in 100 parts	7.10	7.25

Reduction of Ethylic Isophenanthroxylene-acetoacetate with Hydriodic Acid.—The finely powdered iso-compound was heated with excess of fuming hydriodic acid in a sealed tube at 100° for 20 minutes. There was strong pressure in the tube on opening. The product was treated with water, boiled with hydrogen sodium sulphite to remove iodine, again washed, and recrystallised from boiling alcohol. It was deposited in slender, flat needles, with a brownish tinge, melting, not very sharply, at 215° . It can be obtained in *white* needles by sublimation. Analysis gave figures agreeing with the formula $C_{17}H_{12}O$:—

	Substance.	CO_2 .	H_2O .
I.	0.0946	0.3056	0.0452
II.	0.1055	0.3397	0.0515

	Calculated for $C_{17}H_{12}O$.		Found.	
			I.	II.
C_{17}	204	87.93	88.10	87.81
H_{12}	12	5.17	5.30	5.42
O	16	6.90	—	—
	<hr/>	<hr/>		
	232	100.00		

The substance is formed from the iso-compound according to the equation

The reaction may be represented as occurring in three stages: in the first, the iso-compound is reduced to the compound $C_{20}H_{16}O_3$ (m. p. 124°) :—

in the second, this compound is hydrolysed, yielding a monobasic acid :—

which latter then parts with carbon dioxide :—

This compound is identical with that melting at 213° obtained by Japp and Streatfeild (*Trans.*, 1883, 33) by heating the dibasic acid $C_{18}H_{14}O_4$. On the strength of a combustion made with less than 0.07

gram they assigned to it, as already mentioned, the formula $C_{14}H_{10}O$. We have again prepared the substance by heating the dibasic acid, and find that it is indistinguishable in its physical properties from the foregoing compound obtained by the action of hydriodic acid on the iso-compound. Analysis also gave figures agreeing with the formula $C_{17}H_{12}O$, which formula, moreover, better accounts for the formation of this compound from the dibasic acid than that formerly given :—

In the formation of the dibasic acid from the compound $C_{20}H_{16}O_3$ (m. p. 124°) by the action of caustic alkalis, a closed chain (probably a penta-carbon ring) is opened; in the formation of the compound $C_{17}H_{12}O$ from the dibasic acid, this ring is closed again. The compound $C_{17}H_{12}O$ is probably a ketone containing the carbonyl group in a penta-carbon ring; but its constitution has yet to be studied.

Hydrolysis of Ethylic Isophenanthroxylene-acetoacetate with Caustic Alkali.—The iso-compound dissolves readily in hot aqueous caustic soda, and from the solution hydrochloric acid precipitates the new acid as a white, crystalline powder. The yield is quantitative. It may be purified by recrystallisation either from alcohol, which deposits it in flat, satiny needles, or from glacial acetic acid, from which it separates in slender needles. It softens at 265° , and melts with decomposition at 267 – 269° .

Analysis gave figures agreeing with the expected formula $C_{18}H_{12}O_4$:—

0.2213 gram gave 0.6001 CO_2 and 0.0832 H_2O .

	Calculated for $C_{18}H_{12}O_4$.		Found.
C_{18}	216	73.97	73.95
H_{12}	12	4.11	4.17
O_4	64	21.92	—
	<hr/> 292	<hr/> 100.00	

The acid has been formed by the hydrolysis of the ethyl salt, and may therefore be called *isophenanthroxylene-acetoacetic acid*.

It dissolves readily in ammonia, and from the solution barium chloride and calcium chloride precipitate gelatinous barium and calcium salts. In like manner, the silver salt was obtained as a white, apparently crystalline precipitate; it was washed with water, dried over sulphuric acid, and analysed. Different preparations did not give concordant results; but the figures left no doubt that the acid was monobasic. Calculated for $C_{18}H_{11}O_4Ag$: Ag, 27.06 per cent.

Found: 27.23 and 26.05 per cent. The carbon in both preparations was found too low, so that the salt is evidently difficult to obtain pure.

The copper salt, prepared in the same way, formed a light-green powder. For analysis it was air-dried at ordinary temperatures.

0.1562 gram, when heated at 120°, lost 0.0315 gram H_2O .

	Calculated for $(\text{C}_{18}\text{H}_{11}\text{O}_4)_2\text{Cu} + 9\text{H}_2\text{O}$.	Found.
H_2O in 100 parts	20.7	20.16

0.1227 gram anhydrous copper salt gave on ignition 0.0144 CuO .

	Calculated for $(\text{C}_{18}\text{H}_{11}\text{O}_4)_2\text{Cu}$.	Found.
Cu in 100 parts	9.77	9.35

The carbon in this specimen was 1 per cent. too high (67.94, instead of 66.93), so that this salt was also impure.

Action of Caustic Potash on Isophenanthroxylylene-acetoacetic Acid.—As some of the compounds obtained from ethylic phenanthroxylylene-acetoacetate are converted, by the action of caustic alkali, into salts of dibasic acids, we made an experiment for the purpose of ascertaining whether any such change could be effected in the case of isophenanthroxylylene-acetoacetic acid. The reaction, however, took a wholly different course.

The acid was heated with excess of strong aqueous potash in a sealed tube at 150° for two hours. There was no pressure on opening the tube, and a solid substance had separated. The contents of the tube were poured into water, and the solid substance was separated by filtration, washed, and dried. As it was insoluble in the ordinary organic solvents of low boiling point, it was dissolved in boiling phenol, and the solution poured into hot alcohol, which caused the substance to separate almost immediately as a pale-yellow, crystalline powder. It was washed with boiling alcohol and dried for analysis. It did not melt even at 300—310°. An analysis, which had to be made with a very small quantity of substance, gave figures which agreed, although not well, with the formula $\text{C}_{17}\text{H}_{10}\text{O}$. The same substance may, however, be obtained in greater quantity by the action of acetic anhydride on isophenanthroxylylene-acetoacetic acid (*vide infra*). Analyses of the substance from this source are given later on.

0.0793 gram gave 0.2563 CO_2 and 0.0348 H_2O .

	Calculated for $C_{17}H_{10}O$.		Found.
C_{17}	204	88·70	88·14
H_{10}	10	4·35	4·87
O	16	6·95	—
	230	100·00	

The substance is formed according to the equation

Action of Acetic Anhydride on Isophenanthroxylene-acetoacetic Acid.—The acid was heated with acetic anhydride in a sealed tube for one hour at 150° . There was a slight pressure in the tube on opening. A substance crystallising in long, pale-yellow needles had separated; these were filtered off and thoroughly boiled with alcohol, in which they are quite insoluble. After this treatment they were washed with boiling alcohol, dried, and analysed. The compound has the formula $C_{17}H_{10}O$, and is identical with the foregoing obtained by the action of caustic potash.

	Substance.	CO_2 .	H_2O .
I.....	0·2353	0·7654	0·0927
II.....	0·1165	0·3776	0·0460

	Calculated for $C_{17}H_{10}O$.		Found.	
			I.	II.
C_{17}	204	88·70	88·71	88·39
H_{10}	10	4·35	4·37	4·38
O	16	6·95	—	—
	230	100·00		

The acetic anhydride mother liquor from these crystals was boiled with alcohol for some time and allowed to stand. It deposited light-brown crystals, which were purified by recrystallisation from ethylic acetate, and then formed small, transparent, pale-yellow, oblique plates melting constantly at 224 — 226° . At this temperature there is no decomposition, but gas is evolved on heating to 235 — 240° .

This compound is much more readily obtained by merely boiling isophenanthroxylene-acetoacetic acid with acetic anhydride until the insoluble compound $C_{17}H_{10}O$ begins to separate, which occurs after from 20 to 30 minutes. Alcohol is then added, and the solution is filtered hot; the filtrate deposits the new compound, which is then purified as already described. Acetic acid may also be used as a

solvent, and deposits the substance in small, shining plates of the foregoing melting point.

Analysis gave figures agreeing best with the formula $C_{19}H_{14}O_4$, although the formation of a compound $C_{19}H_{16}O_4$ could be more readily accounted for.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.1828	0.4954	0.0815
II.....	0.1842	0.5012	0.0842
III.....	0.2145	0.5846	0.0910
IV.....	0.2068	0.5634	0.0843

	Calc. for $C_{19}H_{14}O_4$.	Calc. for $C_{19}H_{16}O_4$.	Found.			
			I.	II.	III.	IV.
C.....	74.51	74.02	73.91	74.20	74.32	74.30
H.....	4.58	5.20	4.95	5.07	4.71	4.52
O.....	20.91	20.78	—	—	—	—
	<hr/> 100.00	<hr/> 100.00				

Analyses I and II were made with substance recrystallised from ethyl acetate, III and IV with substance recrystallised from acetic acid.

We must leave the formula of this compound undecided for the present.

Action of Acetic Acid on Ethylic Phenanthroxylylene-acetoacetate.

Three compounds are formed in this reaction.

When ethylic phenanthroxylylene-acetoacetate is dissolved in glacial acetic acid and the solution boiled, slender, colourless needles speedily begin to separate from the boiling liquid. As the presence of this solid substance produced bumping, it was found more convenient to heat the ethylic phenanthroxylylene-acetoacetate with acetic acid in a sealed tube at 130—140°. In this way we obtained from 5 grams of the condensation compound 1.5 grams of the new product. The mother liquor was pink-coloured.

The new compound was separated by filtration, washed with boiling acetic acid, and dried for analysis. It is practically insoluble in the ordinary organic solvents of low boiling point, but dissolves in high boiling solvents, such as phenol and ethyl benzoate, and may be precipitated in a crystalline form from these solutions by the addition of alcohol. When heated in a capillary tube it decomposes, apparently without melting, at about 285°.

It gave figures agreeing with the formula $C_{20}H_{14}O_3$, showing that it

had been formed from the condensation product by the abstraction of 1 mol. of water.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.1897	0.5533	0.0822
II.....	0.1895	0.5517	0.0827

	Calculated for C ₂₀ H ₁₄ O ₃ .		Found.	
			I.	II.
C ₂₀	240	79.47	79.55	79.40
H ₁₄	14	4.64	4.81	4.84
O ₃	48	15.89	—	—
	302	100.00		

The same compound is formed, as already mentioned, along with ethylic isophenanthroxylene-acetoacetate by the dehydrating action of sulphuric acid on ethylic phenanthroxylene-acetoacetate.

Strange to say, this abstraction of water could not be effected by boiling ethylic phenanthroxylene-acetoacetate with acetic anhydride; but by heating it in a sealed tube with the anhydride for one hour at 150°, the compound C₂₀H₁₄O₃, together with the compound C₂₂H₁₈O₅ (also formed in the acetic acid reaction, *v. infra*), was formed. A similar observation has been made by Zincke (*Ber.*, **10**, 1475), who found that water could be eliminated from benzpinacone by heating the latter with glacial acetic acid, but not with acetic anhydride.

The relation of the compound C₂₀H₁₄O₃ to the compound C₁₇H₁₀O is, perhaps, expressed by the formula C₁₇H₅O(COOC₂H₅); but this point requires further study. The compound is not hydrolysed by strong aqueous potash.

The acetic acid mother liquor resulting from the preparation of the compound C₂₀H₁₄O₃ was poured into water. A dark-red, soft substance separated which soon solidified; this was dried and treated with benzene, in which the greater part of it dissolved; the insoluble residue will be described later on. As the benzene solution, even when concentrated, did not deposit the substance in a satisfactory form, the benzene was expelled, and the residue was extracted with hot light petroleum (b. p. 90—120°) which dissolved it only sparingly, but deposited it in well-shaped crystals of a pinkish colour. After a further recrystallisation from alcohol, it was obtained colourless, and melted indistinctly at 165—171°. This substance proved to be identical with the acetyl derivative of ethylic isophenanthroxylene acetoacetate, already described. Calculated for C₂₀H₁₅(C₂H₃O)O₄: C, 72.93; H, 4.97 per cent. Found: C, 73.06; H, 4.91 per cent.

Boiling with aqueous caustic soda readily hydrolysed this com-

pound and yielded a salt of isophenanthroxylene-acetoacetic acid, the acetyl group being estimated in the process. The purified acid melted at 269–270° (softening at 265°), and gave on analysis: C, 74·00; H, 4·38 per cent. Calculated for $C_{18}H_{12}O_4$: C, 73·97; H, 4·11 per cent.

The monacetyl compound was also heated in alcoholic solution with excess of phenylhydrazine at 100°. A yellow, crystalline substance separated, which was purified by dissolving it in hot benzene and pouring the solution into hot light petroleum, when it was deposited in minute, yellow needles. When heated in a capillary tube, it turned dark at about 190° and melted, with complete decomposition, about 207°. It dissolved in concentrated sulphuric acid with a dark-blue colour. It is identical with the hydrazone of ethylic isophenanthroxylene-acetoacetate already described, and is formed from the acetyl derivative with elimination of the acetyl group, doubtless according to the equation

Calculated for $C_{20}H_{16}O_3(N_2H \cdot C_6H_5)$: C, 76·10; H, 5·36 per cent. Found: C, 76·76; H, 5·64 per cent. The formula

which is that of a hydrazone formed from the acetyl compound *without* elimination of the acetyl group, would require only 74·34 per cent. of carbon.

The third compound formed by the action of acetic acid on ethylic phenanthroxylene-acetoacetate is that which is left undissolved when the substance precipitated with water is extracted with benzene. This compound is formed only in small quantity, and it was necessary to unite the products of several preparations in order to obtain enough for analysis. It was purified by recrystallisation, first from hot glacial acetic acid, afterwards from ethyl acetate, the latter solvent giving the best results. It was thus obtained in transparent, yellow, rectangular plates melting at 227°. Analysis gave figures agreeing with the formula $C_{44}H_{34}O_9$, which is that of a compound formed from 2 mols. of the foregoing monacetyl compound with elimination of 1 mol. of water:—

This higher molecular weight is in keeping with the more sparing solubility of the compound.

0·2857 gram gave 0·7816 CO_2 and 0·1283 H_2O .

	Calculated for $C_{40}H_{28}(C_3H_5O)_2O_7$.		Found.
C ₄₄	528	74.79	74.61
H ₃₄	34	4.82	4.98
O ₉	144	20.39	—
	706	100.00	

It is to be noted that ethylic isophenanthroxylene-acetoacetate may be heated with glacial acetic acid, even at 150°, without yielding any of these compounds.

Action of Propionic Acid on Ethylic Phenanthroxylene-acetoacetate.

The action of propionic acid closely resembles that of acetic acid, except that no compound corresponding with $C_{44}H_{34}O_9$ was isolated—possibly because the reaction was conducted on too small a scale.

Ethylic phenanthroxylene-acetoacetate was heated with propionic acid in a sealed tube for one hour at 140°. There was no pressure on opening the tube, which contained a crystalline compound and a pink liquid. The crystalline compound was separated by filtration; it consisted of slender, silky needles, insoluble in the ordinary organic solvents of low boiling point, and was identical with the compound $C_{20}H_{14}O_3$, already referred to, obtained by the action of glacial acetic acid on ethylic phenanthroxylene-acetoacetate.

The pink-coloured mother liquor was poured into water, and the precipitated substance was dried and dissolved in light petroleum (b. p. 90—120°). After standing for some days, the petroleum solution deposited tufts of red crystals; these were then twice recrystallised from alcohol, after which they melted constantly at 134°. The crystals were well shaped, but still retained their red colour, which was, of course, due to the impurity already mentioned. Analysis (*v. infra*) gave figures agreeing with the formula $C_{23}H_{20}O_5$.

We then prepared the same compound by heating ethylic isophenanthroxylene-acetoacetate with propionic anhydride for three hours at 150°. It resembled in every respect the foregoing. The compound has, therefore, the formula $C_{20}H_{16}(C_3H_5O)_4$.

Substance.	CO ₂ .	H ₂ O.
I. 0.1915	0.5164	0.0924
II. 0.2159	0.5808	0.1024

	Calculated for $C_{20}H_{15}(C_3H_5O)O_4$		Found.	
	I.	II.	I.	II.
C_{23}	276	73·40	73·54	73·36
H_{20}	20	5·32	5·36	5·27
O_5	80	21·28	—	—
	376	100·00		

Analysis I was made with substance prepared from propionic acid and ethylic phenanthroxylene-acetoacetate; II, with substance from the iso-compound and propionic anhydride.

Action of Sulphuric Acid and Alcohol on Ethylic Phenanthroxylene-acetoacetate.

The results obtained in this reaction differ greatly, according to the relative proportions of alcohol and sulphuric acid employed.

Action of Alcohol containing a few drops of Sulphuric Acid.—Ethylic phenanthroxylene-acetoacetate was dissolved in a slight excess of hot absolute alcohol, a small quantity of concentrated sulphuric acid (3 drops for every 5 grams of the condensation product) was added, and the whole was heated on the water-bath for three hours. After standing over night, the solution was filtered from a little impure substance which had separated, after which it was precipitated with water. The precipitated substance was twice recrystallised from alcohol, and was thus obtained in pinkish, tabular, rectangular crystals, melting constantly at 143—144°. The pink colouring matter was partially removed by recrystallisation from light petroleum.

Analysis agreed with the formula $C_{22}H_{20}O_4$:—

	Substance.	CO_2 .	H_2O .
I.	0·1803	0·5012	0·0941
II	0·1894	0·5279	0·0997

	Calculated for $C_{22}H_{20}O_4$		Found.	
	I.	II.	I.	II.
C_{22}	264	75·86	75·81	76·01
H_{20}	20	5·75	5·79	5·84
O_4	64	18·39	—	—
	348	100·00		

Different preparations were analysed.

The compound is formed according to the equation—

The formula $C_{22}H_{20}O_4$ may be expanded into

The behaviour of this compound towards phenylhydrazine and caustic alkalis shows that it is closely related to the hydriodic acid reduction compound, $C_{20}H_{16}O_3$ (m. p. 124°), the formula of which may be written $C_{17}H_{11}O(COOC_2H_5)$. The compound $C_{22}H_{20}O_4$ is thus the ethoxy-derivative of the reduction compound. Both these compounds form hydrazones, showing that they contain a carbonyl group; and both are hydrolysed by caustic alkalis with simultaneous assumption of the elements of water, yielding dibasic acids; the carbonyl group being converted in this process into a carboxyl group:—

This conversion of the carbonyl into the carboxyl group must be accompanied by the opening up of the closed chain containing the carbonyl group.

Ethylic isophenanthroxylene-acetoacetate may be formulated $C_{17}H_{10}O(OH)(COOC_2H_5)$, and it might, therefore, appear that the foregoing ethoxy-compound was derived from it by the substitution of ethyl for the hydrogen of the alcoholic hydroxyl group. We do not consider, however, that this view is tenable. The iso-compound, when treated with alkali, is merely hydrolysed, yielding a *monobasic* acid; whereas if it had a constitution analogous to that of the ethoxy-compound or of the reduction compound, it ought to yield a *dibasic* acid, since a hydroxyl group attached to a closed chain would probably render that closed chain more susceptible to the attack of alkalis than would an ethoxy-group, and certainly more than a hydrogen atom. It seems, therefore, necessary to assume that the closed chain contained in the iso-compound and its derivatives has a different constitution from that contained in the ethoxy-compound and in the reduction compound; and as the reduction can be obtained from the iso-compound, we must further assume that this change in constitution occurs during the reduction. Further experiment will be necessary to enable us to decide wherein this difference of constitution consists.

A further argument against the view that the ethoxy-compound is a direct derivative of the iso-compound is to be found in the fact that the latter compound is not etherified when treated in the foregoing manner with alcohol and sulphuric acid.

Action of Phenylhydrazine on the Ethoxy-compound.—When the ethoxy-compound is heated with phenylhydrazine in alcoholic solution at 100° , it forms a yellow hydrazone, very similar to that obtained from the iso-compound, and, like the latter, giving a blue coloration with concentrated sulphuric acid, but distinguished from it by its insolubility in benzene. It melts very indistinctly, with decomposition, at about 220° . A nitrogen determination agreed with the formula $C_{17}H_{10}(N_2H \cdot C_6H_5)(OC_2H_5)(COOC_2H_5)$.

0.1609 gram gave 13.50 c.c. dry nitrogen at 16° and under 482 mm. pressure. Nitric oxide absent.

	Calculated for $C_{28}H_{26}N_2O_3$.	Found.
N in 100 parts	6.39	6.31

Action of Caustic Potash on the Ethoxy-compound.—The ethoxy-compound, when boiled with aqueous caustic potash, yielded a pale yellow solution, from which hydrochloric acid precipitated the organic acid as a reddish oil, which solidified on cooling. The substance was purified by dissolving it in ethylic acetate, adding light petroleum to the hot solution until a slight turbidity was produced, and filtering from the first impure portion which separated. The filtrate deposited tufts of crystals. These were again treated in the same way, and were thus obtained colourless. They melted, with decomposition, at 203° . Benzene may also be employed as a solvent; the hot solution, on cooling, deposits nearly the whole of the substance in minute, colourless needles. Analysis gave figures agreeing with the formula $C_{16}H_{11}(OC_2H_5)(COOH)_2$:—

	Substance.	CO_2 .	H_2O .
I.	0.2009	0.5250	0.0984
II.	0.2429	0.6339	0.1198

	Calculated for $C_{20}H_{18}O_5$.		Found.	
			I.	II.
C_{20}	240	71.01	71.27	71.17
H_{18}	18	5.32	5.44	5.48
O_5	80	23.67	—	—
	338	100.00		

The mode of formation of this acid has already been discussed.

The acid readily dissolves in aqueous ammonia, and the neutral solution of the ammonia salt gives white precipitates with silver nitrate and lead acetate and a bluish-green precipitate with copper sulphate. The silver salt was prepared for analysis. It was washed

with hot and then with cold water, and dried in a vacuum. In spite of this it contained, according to analysis, a molecule of water of crystallisation; but this water was not determined directly:—

Substance.	CO ₂ .	H ₂ O.	Ag.
I. 0·2722	0·4214	0·0798	9·1030
II. 0·2740	0·4246	0·0773	0·1035

	Calculated for C ₂₀ H ₁₆ Ag ₂ O ₅ ,H ₂ O.		Found.	
			I.	II.
C ₂₀	240	42·11	42·22	42·26
H ₁₆	18	3·16	3·25	3·13
Ag ₂	216	37·89	37·84	37·77
O ₆	96	16·84	—	—
	570	100·00		

The methyl ester was also prepared. For this purpose, 3 grams of the acid were heated in a sealed tube with 15 grams of methyl alcohol and 10 grams of concentrated sulphuric acid for three hours at 100°. There was a strong pressure (of methyl oxide) on opening the tube. The turbid solution was precipitated with water and the precipitate recrystallised from boiling methyl alcohol. The ester was thus obtained in slender, colourless needles melting at 125°.

Analysis gave figures agreeing with the formula

0·1216 gram gave 0·3215 CO₂ and 0·0655 H₂O.

	Calculated for C ₂₂ H ₂₂ O ₅ .		Found.
C ₂₂	264	72·13	72·10
H ₂₂	22	6·01	5·98
O ₅	80	21·86	—
	366	100·00	

The ester was insoluble in carbonates. Caustic alkali hydrolysed it, and the regenerated dibasic acid melted at 202°.

Along with the foregoing ester there was formed a crystalline substance, insoluble in methyl alcohol, melting, with evolution of gas, at 243°; but the quantity was too small for further examination.

Action of Alcohol, with a Large Proportion of Sulphuric Acid, on Ethylic Phenanthroxylene-acetoacetate.—Five grams of ethylic phenanthroxylene-acetoacetate were heated with a mixture of 12 grams

of concentrated sulphuric acid and 15 grams of absolute alcohol, in a sealed tube, at 100° , for one hour. A solid substance had separated, and there was considerable pressure in the tube. The contents of the tube were poured into water, and the precipitate thus obtained was filtered off and boiled with alcohol, which separated it into a soluble and an insoluble portion. The soluble portion, after purification, proved to be identical with the compound $C_{22}H_{20}O_4$ (m. p. 144°), already described, obtained by boiling the condensation product with alcohol containing a few drops of sulphuric acid. The portion insoluble in alcohol was dissolved in boiling phenol and reprecipitated by pouring the solutions into boiling alcohol, when it separated at once in yellow, glistening, microscopic, six-sided plates. It melted with decomposition, but without blackening, at $276-277^{\circ}$. The yield was very small, only 0.17 gram being obtained from 5 grams of the condensation product. Analysis led to the formula $C_{17}H_{12}O_2$.

0.1523 gram gave 0.4596 CO_2 and 0.0666 H_2O .

	Calculated for $C_{17}H_{12}O_2$		Found.
C_{17}	204	82.26	82.30
H_{12}	12	4.84	4.86
O_2	32	12.90	—
	248	100.00	

The compound is formed according to the equation

and, therefore, the alcohol used in its preparation merely acts as a solvent and diluent.

*Action of Alcoholic Hydrogen Chloride on Ethylic
Phenanthroxylene-acetoacetate.*

20 grams of ethylic phenanthroxylene-acetoacetate were dissolved in boiling absolute alcohol, and twice the volume of saturated alcoholic hydrogen chloride was added to the hot solution. After standing over night, 12 grams of a compound containing chlorine had separated. It proved to be somewhat difficult to purify, but by repeated recrystallisation, both from alcohol and from a mixture of benzene and light petroleum, it was obtained in flat, lustrous needles melting at $145-146^{\circ}$. A faint, brownish tinge could not be removed. The substance is readily soluble in hot alcohol and hot benzene, less soluble in hot light petroleum.

Analysis gave figures agreeing with the formula $C_{20}H_{15}ClO_3$. In the combustions a silver spiral was employed to absorb the chlorine.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.1992	0.5198	0.0811
II.....	0.1928	0.5026	0.0809

III. 0.4045 gram gave 0.1667 gram AgCl (Carius).

	Calculated for $C_{20}H_{15}ClO_3$.		Found.		
			I.	II.	III.
C ₂₀	240.0	70.90	71.16	71.19	—
H ₁₅	15.0	4.43	4.52	4.66	—
Cl.....	35.5	10.49	—	—	10.19
O ₃	48.0	14.18	—	—	—
	338.5	100.00			

The compound has been formed according to the equation

Action of Ammonia on the Compound $C_{20}H_{15}ClO_3$.—When the compound $C_{20}H_{15}ClO_3$ is dissolved in hot alcohol, and an excess of alcoholic ammonia is added, the solution assumes a deep-red colour, and, on standing, deposits small, yellowish crystals, whilst the colour of the liquid becomes gradually fainter, and at last disappears almost entirely. It is advantageous to work with a dilute solution, as in this way the substance is deposited at once in an almost pure condition; and this is of importance, as it cannot easily be purified by recrystallisation. It dissolves readily in acetic acid, but does not separate again from the solution. Alcohol dissolves it on prolonged boiling, but does not deposit it in a crystalline form. Ethyl acetate dissolves it only slightly, and deposits it in minute crystals. It melts, with decomposition, at 267°. It does not contain chlorine.

For analysis, the substance was not recrystallised, but merely boiled out with ethyl acetate, and dried at 100°. It gave figures agreeing with the formula $C_{40}H_{31}NO_6$.

	Substance.	CO ₂ .	H ₂ O.
I.....	0.2217	0.6260	0.1039
II.....	0.2336	0.6613	0.1100

Substance.	v.	t.	p.
III. 0.1173 { dry N + NO	9.02 c.c.	19°	206 mm.
{ „ N.....	9.02 „	19	203 „
IV. 0.1548 { dry N + NO	9.02 „	19	259 „
{ „ N.....	9.02 „	19	253 „

	Calculated for		Found.			
	$C_{40}H_{31}NO_6$		I.	II.	III.	IV.
C ₄₀	480	77·30	77·00	77·20	—	—
H ₃₁	31	4·99	5·20	5·23	—	—
N.....	14	2·25	—	—	2·42	2·30
O ₆	96	15·46	—	—	—	—
	621	100·00				

The formula $C_{40}H_{31}NO_6$ may possibly be resolvable into $(C_{20}H_{15}O_3)_2NH$. The compound is formed according to the equation

Action of Alcoholic Potash on Ethylic Phenanthroxyene-acetoacetate.

Ethylic phenanthroxyene-acetoacetate was dissolved in hot methyl alcohol, the solution was cooled quickly, and before anything had time to separate, a cold solution of caustic potash in methyl alcohol was added, and the mixture was allowed to stand in a corked flask for two days. A small quantity of a dark-brown powder, which had separated, was filtered off, but nothing was obtained from this. The filtrate was poured into excess of water, which caused a slight separation of an amorphous substance, and the diluted liquid was allowed to stand in a shallow basin for two days, in order to get rid of the methyl alcohol. This occasioned a further separation of amorphous substance, which was removed by filtration. On acidifying the filtrate with hydrochloric acid, a flocculent, yellow precipitate of an organic acid was obtained. When freshly precipitated, this acid redissolves in alkaline carbonates, but becomes insoluble by keeping. The acid, separated by filtration, and pressed to free it from excess of moisture, was at once dissolved in alcohol in the cold. Heating with alcohol prevents it from dissolving; and if the solution, prepared in the cold, is heated, insoluble matter separates. A portion of the alcoholic solution was allowed to stand, but this yielded chiefly oily products, and all attempts to purify this unstable acid failed. Another portion of the alcoholic solution was heated in a sealed tube at 100° , when almost immediately a separation of minute, glistening, yellow crystals was observed. As the quantity of this substance did not appear to increase after half an hour's heating, the tube was allowed to cool, which occasioned the separation of an oily substance. No pressure was observed on opening the tube. The substance was collected on a filter and washed with boiling alcohol, which removed the oily matter. The crystalline substance was insoluble in the ordinary organic solvents of low boiling point. It was purified by

dissolving it in hot phenol and pouring the solution into boiling alcohol, when it separated immediately as a yellow, crystalline powder, which, under the microscope, was seen to consist of minute needles, generally grouped in stars or crosses; no six-sided plates could be observed. It melted, with decomposition, at 259° . The yield was very small.

Analysis gave figures agreeing with the formula $C_{17}H_{12}O_2$.

0.1000 gram gave 0.3024 CO_2 and 0.0423 H_2O .

	Calculated for $C_{17}H_{12}O_2$.		Found.
C_{17}	204	82.26	82.47
H_{12}	12	4.84	4.70
O_2	32	12.90	—
	248	100.00	

This would make it isomeric with the compound obtained by heating ethylic phenanthroxylene-acetoacetate with a mixture of alcohol and concentrated sulphuric acid. As this latter compound, however, only differs from it in its somewhat higher melting point (277°), and in being precipitated from its solution in phenol in the shape of minute, six-sided plates, instead of in needles, we would not lay too much stress on this supposed isomerism, especially as we were dealing with such small quantities of substance. The two compounds may be identical.

Action of Ammonia on Ethylic Phenanthroxylene-acetoacetate.

Ethylic phenanthroxylene-acetoacetate was heated with excess of alcoholic ammonia in a sealed tube at 100° for an hour and a half. On allowing the solution thus obtained to stand, a substance crystallising in groups of lustrous, yellow laminæ was deposited. By recrystallisation from benzene it was obtained in small tufts melting, with decomposition, at 168° .

Analysis does not decide between the two formulæ $C_{40}H_{38}N_4O_5$ and $C_{40}H_{40}N_4O_5$.

Substance.		CO ₂ .	H ₂ O.
I.....	0.2069	0.5514	0.1140
II.....	0.2175	0.5792	0.1177

Substance.		<i>v.</i>	<i>t.</i>	<i>p.</i>
III. 0.1282	{ dry N + NO	13.50 c.c.	16.5°	503 mm.
	{ „ N.....	13.50 „	16.5	484 „
IV. 0.1453	{ dry N + NO	13.50 „	15.2	592 „
	{ „ N.....	13.50 „	15.2	572 „

	Calc. for $C_{40}H_{38}N_4O_5$	Calc. for $C_{40}H_{40}N_4O_5$	Found.			
			I.	II.	III.	IV.
C.....	73·40	73·17	72·68	72·62	—	—
H.....	5·81	6·09	6·12	6·01	—	—
N.....	8·56	8·53	—	—	8·09	8·46
O.....	12·23	12·21	—	—	—	—
	<hr/> 100·00	<hr/> 100·00				

A compound of the formula $C_{40}H_{38}N_4O_5$ would be formed according to the equation

whilst the formation of a compound $C_{40}H_{40}N_4O_5$ would involve a simultaneous process of reduction.

As already mentioned, we must reserve a fuller discussion of the constitution of the various compounds described in this paper until more experimental material has been collected.

We have also obtained a condensation compound from benzil and ethylic acetoacetate. It belongs to a different class from the phenanthraquinone compound, and will be described later.

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