597. *Monomethiodides of Some 3-Substituted 4 : 7-Phenanthrolines.*

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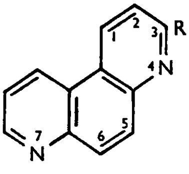
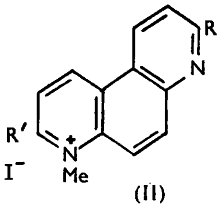
The directly prepared monomethiodides of 3-carboxy-, 3-chloro-, 3-ethoxycarbonyl-, 3-methoxy-, and 3-methyl-4 : 7-phenanthroline are shown to be all 7-methiodides by identifying the dihydro-*N*-methyl-oxo-derivatives obtained from them by oxidation.

Only one monoquaternary salt of a simple 3-substituted 4 : 7-phenanthroline has been described hitherto, namely, the methiodide prepared [1] by the action of methyl iodide on 3-methoxy-4 : 7-phenanthroline (I; R = OMe) in boiling methanol. This product was held to be a 4-methiodide (II; R = H, R′ = OMe) by Karrer and Pletscher.[1] However, if any hindrance were exerted by the 3-substituent, the nitrogen atom in position 7 would be expected to be the first quaternised, as in 5-substituted 4 : 7-phenanthrolines,[2] to produce (II; R = OMe, R′ = H). Evidence was sought, therefore, establishing the structures of any directly preparable monomethiodides of several 3-substituted 4 : 7-phenanthrolines including the 3-methoxy-derivative; the other bases examined were the known 3-chloro- and 3-methyl-4 : 7-phenanthroline, and the newly prepared 3-carboxylic acid and its ethyl ester.



(I)



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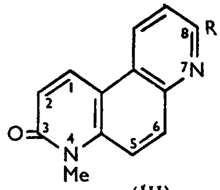

(III)

3-Chloro-4 : 7-phenanthroline [1,3] was converted to the 3-methoxy-compound by sodium methoxide in refluxing methanol as described by Karrer and Pletscher.[1] Willgerodt and Jablonski [4] have prepared 3-methyl-4 : 7-phenanthroline by decarboxylation of 3-methyl-4 : 7-phenanthroline-1-carboxylic acid, but preparation of the latter involves the costly pyruvic acid in a Döbner synthesis with paraldehyde and 6-aminoquinoline.

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[1] Karrer and Pletscher, *Helv. Chim. Acta*, 1948, **31**, 786.
[2] Sykes, *J.*, 1953, 3543.
[3] Douglas, Jacomb, and Kermack, *J.*, 1947, 1659.
[4] Willgerodt and Jablonski, *Ber.*, 1900, **33**, 2918.

Lindner [5] obtained the methylphenanthroline by a Döbner–von Miller reaction performed on 6-aminoquinoline, but only isolated it in poor yield; by using a different method of working up the crude product, we have substantially improved the yield. Tribromination of 3-methyl-4 : 7-phenanthroline, followed by hydrolysis, yielded 4 : 7-phenanthroline-3-carboxylic acid, in analogy with Hammick's preparation [6] of quinaldinic acid from quinaldine. The acid showed marked isoelectric insolubility which greatly facilitated its isolation; it was also obtained, although not consistently, by nitric acid oxidation of 3-benzylidene-4 : 7-phenanthroline. Attempts to prepare the acid from 4 : 7-phenanthroline itself by the Reissert reaction [7] were unsuccessful.

When 4 : 7-phenanthroline-3-carboxylic acid was heated for as long as 8 hours at 100° with an excess of methyl iodide, it was only partly converted into its monomethiodide, as shown by yellowing of the insoluble acid. On the other hand, when heated at 100° with an excess of methyl iodide in methanol, the acid slowly dissolved, giving a monomethiodide of the methyl ester in good yield, though formation of iodine and gaseous products gave evidence of decomposition. Use of dimethyl sulphate or methyl toluene-*p*-sulphonate led to decomposition and no products were identified.

Ethyl 4 : 7-phenanthroline-3-carboxylate was converted in good yield into a monomethiodide simply by heating it with an excess of methyl iodide in methanol solution at 100° for 30 minutes, and so were 3-chloro-, 3-methoxy-, and 3-methyl-4 : 7-phenanthroline.

The structures of the monomethiodides were elucidated by the reactions with alkaline potassium ferricyanide. In no case was the product 3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline (III; R = H), which would be obtained from a 3-substituted 4-methiodide (II; R = H) if the substituent were displaced, as occurs when *N*-methyl-5-nitrocarbostyril is obtained from 5-nitroquinaldine methiodide.[8] Moreover, all the products contained hydrogen in proportions close to those expected for dihydro-*N*-methyl-oxo-derivatives (III), not quaternary ammonium hydroxides (a difference of 2 H); the products isolated from the methiodides of 3-methoxycarbonyl- and 3-ethoxycarbonyl-4 : 7-phenanthroline were both the same as that from the methiodide of 4 : 7-phenanthroline-3-carboxylic acid, namely, the dihydro-*N*-methyl-oxo-acid (III; R = CO_2H).

The individual oxidation products were confirmed as being dihydro-*N*-methyl-oxo-derivatives by the following transformations: (*a*) The oxidation product obtained from the methiodide of 3-chloro-4 : 7-phenanthroline was converted in good yield by sodium methoxide in boiling methanol into the 3-methoxy-compound obtained also by oxidation of the 3-methoxy-4 : 7-phenanthroline methiodide. Further, hydrazine hydrate converted the chloro-compound into the hydrazino-compound (III; R = $NH{\cdot}NH_2$) and this decomposed to the known 3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline when boiled with copper sulphate solution.

(*b*) The dihydro-*N*-methyl-oxo-derivative of 3-methyl-4 : 7-phenanthroline (III; R = Me) was prepared, although in poor yield, by a Döbner–von Miller reaction from 6-amino-*N*-methylcarbostyril, and was identical with the ferricyanide oxidation product of 3-methyl-4 : 7-phenanthroline methiodide.

(*c*) The dihydro-*N*-methyl-oxo-derivative of 4 : 7-phenanthroline-3-carboxylic acid (III; R = CO_2H) (obtained from the methiodide of the acid or from either of the two ester methiodides) decomposed at about 260°, to carbon dioxide and 3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline. Similar decarboxylation of 4 : 7-phenanthroline-3-carboxylic acid yielded 4 : 7-phenanthroline.

In order to have been precursors of the oxidation products thus described, the purified quaternary salts must all have been 7-methiodides of the 3-substituted 4 : 7-phenanthrolines (II; R′ = H, R = OMe, etc.); no evidence was found, from their iodine contents or decomposition points, to indicate that the crude quaternary salts contained any considerable proportion of other substances.

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[5] Lindner, *Monatsh.*, 1921, **42**, 421.
[6] Hammick, *J.*, 1923, 2882.
[7] Reissert, *Ber.*, 1905, **38**, 1603.
[8] Decker and Remfry, *Ber.*, 1905, **38**, 2773.

EXPERIMENTAL

3-*Chloro*-7-*methyl*-4 : 7-*phenanthrolinium Iodide* (II; R = Cl, R′ = H).—Chlorophenanthroline (2·0 g.) was heated with methanolic methyl iodide (8 c.c. of 40% w/v solution) in a sealed tube on a boiling-water bath for 30 min. The yellow *methiodide* (2·8 g.) was separated from the the cooled mixture, washed with ether, and dried; it recrystallised from water as yellow needles, m. p. 288° (decomp.) with previous darkening (Found : I, 35·5. $C_{13}H_{10}N_2ClI$ requires I, 35·6%).

8-*Chloro*-3 : 4-*dihydro*-4-*methyl*-3-*oxo*-4 : 7-*phenanthroline* (III; R = Cl).—The above methiodide (2·8 g.), in hot water, was added gradually with stirring to a mixture of 10% w/v potassium ferricyanide solution (70 c.c.) with 10% sodium hydroxide solution. The yellow precipitate (2 g.) which began to appear immediately was collected, dried, and extracted with alcohol for several hours. Deeply pigmented *dihydro*-N-*methyl-oxo-compound* (0·9 g.) separated from the alcohol during the extraction and on cooling, and recrystallised (charcoal) from alcohol or formamide as very pale yellow needles, m. p. 268—269° (Found: C, 63·4; H, 3·7. $C_{13}H_9ON_2Cl$ requires C, 63·8; H, 3·6%).

3-*Methoxy*-7-*methyl*-4 : 7-*phenanthrolinium Iodide* (II; R = OMe, R′ = H).—3-Methoxy-4 : 7-phenanthroline (1·0 g.), prepared from 3-chloro-4 : 7-phenanthroline by Karrer and Pletscher's method,[1] was converted into its methiodide (1·5 g.) as above. This recrystallised from water as orange or yellow needles, m. p. 244° (decomp.) with previous darkening and softening (Karrer and Pletscher[1] give m. p. 243—245°) (Found : I, 35·7. Calc. for $C_{14}H_{13}ON_2I$: I, 36·0%).

3 : 4-*Dihydro*-8-*methoxy*-4-*methyl*-3-*oxo*-4 : 7-*phenanthroline* (III; R = OMe).—(*a*) The above methiodide (1·0 g.) was oxidised with alkaline potassium ferricyanide as for the chloro-analogue. The crude *dihydro*-N-*methyl-oxo-compound* which was precipitated on strong basification of the mixture was dried and crystallised from formamide (charcoal), to yield very pale yellow needles (0·4 g.), m. p. about 174°, improved to 176° by further crystallisations (Found : C, 69·1; H, 5·0. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%). To free the product from the last traces of formamide it was best to transfer the crystals to cold water, a hydrate being formed which was filtered off and washed with water; it lost its water of hydration at 100°, and was then stable at this temperature for at least several hours.

(*b*) 8-Chloro-3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline (0·5 g.) was refluxed for 12 hr. with methanol in which sodium (0·1 g.) had been dissolved. The residue left after evaporation, when treated with water and dried at 100°, consisted of the 8-methoxy-derivative (0·4 g.) which after crystallisation from formamide had m. p. 177—178°, changed only to m. p. 176—177° by admixture with the above product.

8-*Hydrazino*-3 : 4-*dihydro*-4-*methyl*-3-*oxo*-4 : 7-*phenanthroline* (III; R = $NH{\cdot}NH_2$).—8-Chloro-3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline (1·0 g.) was refluxed with hydrazine hydrate for 1 hr., during which the chloro-compound gradually dissolved and the *hydrazino-compound* was precipitated. This was separated from the cooled mixture, washed sparingly with water, and dried at 100° (0·7 g.); it crystallised from absolute ethanol as yellow needles, m. p. about 248° with previous softening (Found: C, 64·8; H, 5·2. $C_{13}H_{12}ON_4$ requires C, 65·0; H, 5·0%). The *acetone hydrazone* separated when the hydrazino-compound in hot water was allowed to stand in admixture with acetone, and crystallised from alcohol as yellow needles, m. p. 258° with previous softening (Found: C, 68·2; H, 5·8. $C_{16}H_{16}ON_4$ requires C, 68·5; H, 5·8%). On admixture, it depressed the m. p. of the hydrazino-compound.

Adding 10% w/v copper sulphate solution (10 c.c.) gradually to the hydrazino-compound (0·3 g.) in boiling water caused an exothermic reaction. The solution was filtered, excess of copper sulphate removed by sodium carbonate solution, and the cooled filtrate was strongly basified with 40% w/v sodium hydroxide solution. The precipitate was separated, dried, and crystallised from chlorobenzene (charcoal), to yield pale yellow needles (0·1 g.), m. p. and mixed m. p. 239—240°, of 3 : 4-dihydro-4-methyl-3-oxo-4 : 7-phenanthroline.

6-*Aminoquinoline*.—6-Nitroquinoline (87 g.) was boiled gently, under reflux, with ammonium sulphide solution (1 l.; about 7% w/v of H_2S) for 1 hr. The mixture was then made acid cautiously with concentrated hydrochloric acid, and filtered hot after treatment with charcoal. The filtrate was made strongly alkaline with 40% w/v sodium hydroxide solution, with ice-cooling. 6-Aminoquinoline was filtered off, washed sparingly with water (soluble), and dried at 100°, where it partly melted, then solidified. The dry product was distilled at about 2 cm., to yield a pale yellow distillate, m. p. 116° (about 50 g.).

3-*Methyl*-4 : 7-*phenanthroline* (I; R = Me).—6-Aminoquinoline (50 g.) and paraldehyde

(75 c.c.) in hot concentrated hydrochloric acid (125 c.c.) were heated on a water-bath for 1 hr., then cooled and poured into ice-water. Basification with 40% w/v sodium hydroxide solution precipitated a semi-solid tar which, after it had been freed from moisture as thoroughly as possible, was distilled. The orange syrupy distillate was dissolved in a similar volume of alcohol and the solution was gradually diluted with water to permanent turbidity; methylphenanthroline hydrate then crystallised. The hydrate, freed as completely as possible from the contaminating oil, was dissolved in hot, dilute nitric acid from which, when it was further acidified with concentrated nitric acid and cooled, the nitrate of the base crystallised. The nitrate, in hot water (charcoal), was partly cooled and then basified with dilute ammonia solution to precipitate the purified hydrate; this was dried at 100° (partly melted), and the residue of anhydrous methylphenanthroline was distilled, to yield 17—23 g. of yellow distillate, m. p. about 110°. Further purification by recrystallising the nitrate and distilling the reliberated base produced a very pale yellow, markedly hygroscopic product, m. p. 114°, b. p. 352°/744 mm. Lindner[5] gives m. p. 115°, and m. p. 84—85° for the hydrate. Willgerodt and Jablonski[4] give only m. p. 88°, presumably for the hydrate. The *dinitrate* crystallised from water as pale yellow prismatic needles, m. p. about 167° (decomp.) (Found: equiv., 163. $C_{13}H_{10}N_2,2HNO_3$ requires equiv., 160).

3 : 7-*Dimethyl*-4 : 7-*phenanthroline Iodide* (II; R = Me, R′ = H).—3-Methyl-4 : 7-phenanthroline (10 g.) was converted into its *methiodide* (13 g.) as for the chloro-analogue, but with a smaller excess of methyl iodide. The methiodide crystallised from water and from methanol as yellow needles, m. p. 267° (decomp.) with previous darkening (Found: I, 37·3. $C_{14}H_{13}N_2I$ requires I, 37·9%).

3 : 4-*Dihydro*-4 : 8-*dimethyl*-3-*oxo*-4 : 7-*phenanthroline* (III; R = Me).—(*a*) The above methiodide (13 g.) was oxidised with alkaline potassium ferricyanide as for the chloro-analogue. The material precipitated by strong basification was dried and extracted with benzene (Soxhlet) to yield about 6 g. of crude product. This *dihydro*-N-*methyl-oxo-compound* recrystallised from ethyl acetate (charcoal) as very pale yellow needles, m. p. 188° (Found: C, 74·7; H, 5·4. $C_{14}H_{12}ON_2$ requires C, 75·0; H, 5·4%).

(*b*) 6-Amino-*N*-methylcarbostyril (2 g.) in hot concentrated hydrochloric acid (5 c.c.) was heated with paraldehyde (3 c.c.) under reflux on a water-bath for 1 hr., then poured into water and adjusted to faint alkalinity; a tarry deposit was separated with the aid of charcoal. The supernatant liquid was then strongly basified, yielding a precipitate which was dried in a desiccator and extracted with benzene; 0·2 g. of a product of m. p. 184—185° crystallised from the extract after it had been treated with charcoal and concentrated. This product, after recrystallisation from ethyl acetate, had m. p. 187—188°, not depressed by admixture with the above dihydro-*N*-methyl-oxo-compound.

3-*Styryl*-4 : 7-*phenanthroline* (I; R = CHPh:CH).—3-Methyl-4 : 7-phenanthroline (10 g.), benzaldehyde (6 g.), and zinc chloride (2 g.) were heated at 140—150° for 4 hr. The product was dissolved in a large volume of hot, dilute hydrochloric acid (charcoal) and reprecipitated by ammonia. The *styrylphenanthroline* (12 g.) recrystallised from alcohol (charcoal) as needles, m. p. 166° (Found: C, 85·1; H, 5·1. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0%).

3-*Tribromomethyl*-4 : 7-*phenanthroline* (I; R = CBr_3).—3-Methyl-4 : 7-phenanthroline (20 g.) and sodium acetate (50 g.) were dissolved in hot glacial acetic acid (100 c.c.). To the solution at about 70° was added, in portions with shaking, bromine (48 g.) in acetic acid (100 c.c.). When the mixture was heated to the b. p., a brief, brisk reaction ensued and all the bromine disappeared. The mixture was poured into cold water, *tribromomethylphenanthroline* separating. This crystallised with poor recovery from acetic acid or chlorobenzene as needles which darkened and softened above about 180° (Found: C, 35·8; H, 1·8; Br, 55·5. $C_{13}H_7N_2Br_3$ requires C, 36·2; H, 1·6; Br, 55·6%). The last trace of colour was removed only with difficulty.

4 : 7-*Phenanthroline*-3-*carboxylic Acid* (I; R = CO_2H).—(*a*) The crude tribromo-derivative obtained from methylphenanthroline (20 g.) was boiled under reflux with 10% dilute sulphuric acid (200 c.c.) for 3 hr. The hot solution was treated with charcoal, made alkaline with ammonia solution (*d* 0·88), filtered, and taken back to pH *ca.* 4 with glacial acetic acid. Deposition of *phenanthrolinecarboxylic acid* ensued, facilitated by scratching. (Precipitation from cold solution gave a gelatinous product which was harder to filter and wash.) The crude yield was 6—14 g., generally about 11 g. The acid was purified by reprecipitation with acetic acid from a solution in ammonia (charcoal) as threads, m. p. about 255° (decomp.) (Found: C, 69·0; H, 3·7. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6%). No satisfactory crystallising solvent was found for the acid. It was readily soluble in dilute ammonia or sodium hydroxide solution but the sodium salt was precipitated on strongly basifying the solution in sodium hydroxide.

The respective salts crystallised on cooling of hot saturated solutions of the acid in mineral acids and were hydrolysed in water.

When the phenanthrolinecarboxylic acid (2 g.) was heated it decomposed with evolution of carbon dioxide and on further heating yielded 1 g. of distillate, m. p. 168—170° which was changed only to 169—170° by admixture with authentic 4 : 7-phenanthroline, m. p. 171°.

(*b*) 3-Styryl-4 : 7-phenanthroline (5 g.) in dilute nitric acid (25 c.c. of nitric acid, *d* 1·4; 25 c.c. of water) was refluxed for 5 hr. and the solution was then concentrated under reduced pressure. The residue was dissolved in hot water and basified with ammonia solution to produce a precipitate, largely of unchanged styrylphenanthroline (variable amount), which was filtered off. When the filtrate, after treatment with charcoal, was adjusted to pH *ca.* 4 with acetic acid and set aside, phenanthrolinecarboxylic acid separated in very variable amount which did not appear to be directly related to the purity of the starting material. The best yield, obtained once only, was 2¾ g., but in other trials the yield was between a trace and about 1 g. Phenanthrolinecarboxylic acid itself was stable in the conditions of the oxidation.

3-*Carboxy*-7-*methyl*-4 : 7-*phenanthrolinium Iodide* (II; R = CO_2H, R′ = H).—Powdered 4 : 7-phenanthroline-3-carboxylic acid (1·0 g.) was heated with an excess of methyl iodide in a sealed tube in a boiling-water bath for 8 hr. The yellow solid was separated from the cooled mixture, washed with ether, and dried (1·2 g.) before extraction of the *methiodide* from it with boiling water, leaving a large residue of unchanged acid. The hot solution was treated with charcoal, concentrated, and allowed to cool, the methiodide crystallising (0·3 g.); this crystallised from water as yellow needles, apparently of a hydrate, which lost water at 100° and became orange, m. p. about 257° (decomp.) with previous darkening and softening; it lost all the water at 100° over phosphoric oxide *in vacuo* (Found : I, 34·2. $C_{14}H_{11}O_2N_2I$ requires I, 34·7%). An aqueous solution of the methiodide was acid (pH *ca.* 3).

3-*Methoxycarbonyl*-7-*methyl*-4 : 7-*phenanthrolinium Iodide* (II; R = CO_2Me, R′ = H).—Powdered 4 : 7-phenanthroline-3-carboxylic acid (1·0 g.) was heated with 40% methanolic methyl iodide (5 c.c.) at 100° for 4 hr. forming slowly a dark brown solution and orange crystals. The solid product was separated, washed with ether, and dried (1·4 g.). Contaminating iodine was removed by boiling acetone, before recrystallisation from methanol as golden-yellow needles; the *methiodide* had m. p. about 231° (decomp.) with previous darkening and softening (Found : I, 32·9. $C_{15}H_{13}O_2N_2I$ requires I, 33·4%). An aqueous solution was only faintly acid (pH *ca.* 5).

The pure methiodide (1·0 g.) was heated at 100° with dilute hydriodic acid (sealed tube) for 2 hr. The hot solution was then treated with sodium hydroxide solution (a small excess of the previously determined equivalent of the added hydriodic acid), with care to avoid loss of volatile material. The solution, still markedly acid, was distilled to provide 10 c.c. of aqueous distillate from which a *p*-nitrobenzoate was obtained (Schotten–Baumann). This derivative had m. p. 94—95° (from light petroleum) and did not depress the m. p. of methyl *p*-nitrobenzoate, m. p. 95—96°. The residual solution in the distilling flask was treated with charcoal and allowed to cool; yellow needles of the acid methiodide (II; R = CO_2H, R′ = H) separated, orange on drying (0·6 g.), m. p. about 256° (decomp.) with previous darkening and softening (Found : I, 34·3%).

3-*Ethoxycarbonyl*-4 : 7-*phenanthroline* (I; R = CO_2Et).—Powdered 4 : 7-phenanthroline-3-carboxylic acid (10 g.) was refluxed with absolute ethanol containing a small proportion of concentrated sulphuric acid until dissolved (3—5 hr.). Most of the alcohol was then distilled off and the residual liquid made faintly alkaline with dilute ammonia solution, with cooling. The precipitated ester was washed with water and dried at 100°. A further, smaller, quantity of ester was obtained from a chloroform extract of the combined mother-liquor and washings. The *ester* (total yield 9 g.) crystallised from alcohol (charcoal) as needles, m. p. 163° (Found : C, 71·2; H, 4·8. $C_{15}H_{12}O_2N_2$ requires C, 71·4; H, 4·8%). The same product (2·5 g.) was obtained by refluxing the acid (3 g.) with thionyl chloride (9 c.c.) for 1 hr., distilling off excess of thionyl chloride, refluxing the dry residue with absolute ethanol (20 c.c.), and liberating the ester from the alcohol-insoluble hydrochloride thus prepared.

3-*Ethoxycarbonyl*-7-*methyl*-4 : 7-*phenanthrolinium Iodide* (II; R = CO_2Et, R′ = H).—The above ester (10 g.) was converted into its *methiodide* by the method described for the chloro-analogue. The product (12 g.), separated from the mixture after dilution with ether, crystallised from methanol as golden-yellow needles, m. p. about 225° (decomp.) with previous darkening and softening (Found : I, 31·8. $C_{16}H_{15}O_2N_2I$ requires I, 32·2%). It appeared to form a hydrate on contact with water.

7 : 8-*Dihydro*-7-*methyl*-8-*oxo*-4 : 7-*phenanthroline*-3-*carboxylic Acid* (III; R = CO_2H).—The

above methiodide (11 g.) was oxidised with alkaline potassium ferricyanide as for the chloro-analogue. The mixture was strongly basified, giving the crude sodium salt of the *dihydro*-N-*methyl-oxo-acid.* This salt was dissolved in hot water, and the solution acidified with 90% formic acid (acetic acid was not suitable). The precipitated acid (6 g.) was reprecipitated from solution in dilute ammonia (charcoal) as yellowish needles, m. p. about 256° (decomp.) (Found: C, 65·5; H, 4·2. $C_{14}H_{10}O_3N_2$ requires C, 66·1; H, 4·0%). The *acid* had amphoteric properties.

The same product (identified by its decomp. point and m. p. of its ethyl ester) was obtained in similar yields from both the 3-carboxy- and the 3-methoxycarbonyl-phenanthroline methiodide by alkaline ferricyanide on a smaller scale (order of 1/20).

When the acid (0·5 g.) was heated to its decomposition point, carbon dioxide was evolved (lime-water test). The dark residue was extracted with a small volume of hot chlorobenzene, and the extract was treated with charcoal and allowed to crystallise. It yielded 3 : 4-dihydro-4 methyl-3-oxo-4 : 7-phenanthroline as pale yellow needles (0·1 g.), m. p. and mixed m. p. 239—240°.

The *ethyl ester*, prepared by ethanol–sulphuric acid, and isolated by way of its yellow sulphate, crystallised from alcohol as very pale yellow prismatic needles or from chlorobenzene as prisms, m. p. 234° (Found: C, 68·1; H, 5·1. $C_{16}H_{14}O_3N_2$ requires C, 68·1; H, 5·0%).

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