# 713. *Unsymmetrical Polynuclear Cinnoline Derivatives. Part I. Cyclisation of Some Cyclohexane-1,2-dione 1-Arylhydrazones.*

By R. S. W. Braithwaite and G. K. Robinson.

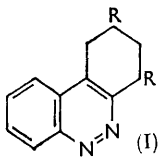
It is shown that unsymmetrical hydrogenated polynuclear cinnolines can be prepared by cyclising cyclohexane-1,2-dione 1-arylhydrazones, and can be dehydrogenated to the fully aromatic cinnolines. The properties of these cinnoline derivatives are described, including the oxidation of two of the new hydrogenated cinnolines to cyclic ketones.

Infrared studies of a number of the hydrazones show that they are tautomeric, some occurring in the azo-form in the solid state.

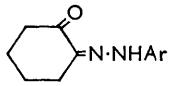
Certain polynuclear cinnolines unsymmetrical about the N:N bond are of interest as *K*-region nitrogen analogues of carcinogenic hydrocarbons.[1]

Polynuclear cinnolines have usually been prepared [2,3] by the reduction of 2,2′-dinitrobiaryls, prepared from *o*-halogenonitroarenes by the Ullmann reaction, or from *o*-aminonitroarenes by the Gattermann reaction. These methods involve joining two similar moieties to give symmetrical biaryls, from which symmetrical polynuclear cinnolines are obtainable. Unsymmetrical 2,2′-dinitrobiaryls, from which unsymmetrical polynuclear cinnolines have been obtained,[4] can be prepared, *e.g.*, by mixed Ullmann reactions, but yields are in general poor, and the products are contaminated with symmetrical biaryls which are difficult to remove.

An inherently unsymmetrical synthesis of polynuclear cinnolines was described by Moore [5] who showed that 1,2,3,4-tetrahydrobenzo[*c*]cinnoline (I; R = H) and its 2,4-dimethyl derivative (I; R = Me) could be prepared by the cyclisation of the relevant cyclohexane-1,2-dione 1-phenylhydrazone with concentrated sulphuric acid.



(I)



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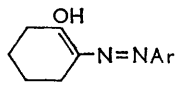


(III)

We find that this method can be used to prepare other hydrogenated polynuclear cinnolines, which can be readily dehydrogenated to the corresponding fully aromatic compounds.

Cyclohexane-1,2-dione 1-phenylhydrazone,[6] 1-(5,6,7,8-tetrahydro-2-naphthyl)hydrazone, 1-(4-nitro-1-naphthyl)hydrazone, and 1-acenaphthen-5′-ylhydrazone were prepared by coupling the relevant diazonium salt with potassium 2-oxocyclohexanecarboxylate. Cyclohexane-1,2-dione 1-1′-naphthylhydrazone and 1-2′-naphthylhydrazone were prepared by this method [6] and also by coupling the relevant diazonium salt with 2-sodioformylcyclohexanone (cf. Coffey [7]). The latter method is more convenient for large-scale work and involves cheaper reagents, while the former, which uses a storable reagent, is more convenient for rapid, small-scale experiments.

The products of these reactions have always been regarded as cyclohexane-1,2-dione 1-arylhydrazones (II), but they can also exist as the tautomeric 2-arylazocyclohex-1-enols (III).

The infrared absorption spectra, in Nujol and hexachlorobutadiene mull, of the

[1] Braithwaite and Holt, *J.*, 1959, 3025.
[2] Taube, *Ber.*, 1891, **24**, 3081.
[3] Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.
[4] Corbett and Holt, *J.*, 1960, 3646.
[5] Moore, *Nature*, 1949, **163**, 918.
[6] Lions, *J. Proc. Roy. Soc. New South Wales*, 1932, **66**, 516.
[7] Coffey, *Rec. Trav. chim.*, 1923, **42**, 528.

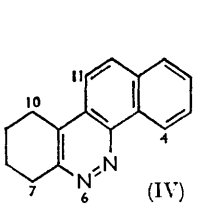
hydrazones described above fall into two groups. Those of the 1-phenyl-, 1-(5,6,7,8-tetrahydro-2-naphthyl)-, and 1-2′-naphthyl-hydrazone show what appears to be an NH stretching frequency near 3300 cm.$^{-1}$ and a carbonyl stretching frequency near 1660 cm.$^{-1}$. Those of the 1-1′-naphthyl-, 1-(4-nitro-1-naphthyl)- and 1-acenaphthen-5′-yl-hydrazone show neither of these absorptions. The absence of clear bands near 3500 cm.$^{-1}$ is known to be a peculiarity of *o*-hydroxyazo-compounds.[8,9]

The infrared spectrum of one member of each group [the 1-(5,6,7,8-tetrahydro-2-naphthyl)- and the 1-1′-naphthyl-hydrazone] was determined for carbon tetrachloride solution at various concentrations. Both compounds show almost identical spectra, which are similar to those of the second group in mulls, except that the " missing " OH stretching frequency appears as a very strong and rather broad band centred near 3400 cm.$^{-1}$, not altered in any way by varying the dilution. There is no absorption at 1660 cm.$^{-1}$.

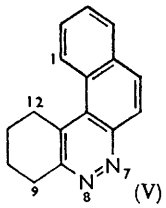
The ultraviolet spectrum of the 1-1′-naphthylhydrazone in carbon tetrachloride solution shows a broad absorption centred near 400 mμ, which does not distinguish clearly between the tautomers.

These results suggest that the second group of hydrazones exist as the 2-arylazocyclohex-1-enols (III) in the crystalline state, and that cyclohexane-1,2-dione 1-(5,6,7,8-tetrahydro-2-naphthyl)hydrazone tautomerises in carbon tetrachloride solution to the cyclohex-1-enol.

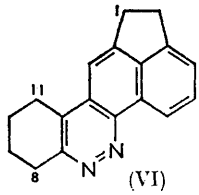
The action of cold sulphuric acid of various concentrations on the hydrazones described above has been investigated. The 1-phenylhydrazone gave a low yield of 1,2,3,4-tetrahydrobenzo[*c*]cinnoline (I; R = H).[5,10] The 1-1′-naphthyl-, 1-2′-naphthyl-, and 1-acenaphthen-5′-yl-hydrazones gave the new cinnolines (IV), (V), and (VI), respectively. The 1-(5,6,7,8-tetrahydro-2-naphthyl)hydrazone dissolved in sulphuric acid, but was recovered unchanged after several days; warm sulphuric acid appeared to cause sulphonation.



(IV)



(V)



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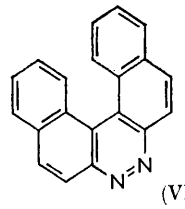


(VII)

When sulphuric acid acts on a cyclohexane-1,2-dione 1-arylhydrazone, side reactions such as Fischer indole cyclisation, sulphonation, and hydrolysis compete with cinnoline formation. In order to achieve an efficient cinnoline synthesis, the reaction conditions must be chosen so as to minimise these side reactions. In particular, heating should be avoided.

Compounds (IV) and (V) are smoothly dehydrogenated with palladium–charcoal in boiling naphthalene, to give the cinnolines which have been prepared from the 2,2′-dinitrobiaryls [4] and by oxidation of the 2,2′-diaminobiaryls.[11,12]

The tetrahydrocinnolines (IV) and (V) form stable monopicrates.

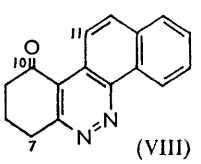
Polynuclear cinnolines give mono-*N*-oxides with hydrogen peroxide in acetic acid,[1,4] and monoquaternary salts with alkyl halides in alcohol [1,13] or nitromethane; [4] the compound (VII) gives a methotri-iodide with excess of methyl iodide in alcohol.[1] Corbett and Holt [4] showed that naphtho[2,1-*c*]cinnoline [cf. (V)], in which co-ordination to the

[8] Hadži, *J.*, 1956, 2143.
[9] Ueno, *J. Amer. Chem. Soc.*, 1957, **79**, 3066.
[10] Soutter and Tomlinson, *J.*, 1961, 4256.
[11] Badger and Walker, *J.*, 1956, 122.
[12] Corbett and Holt, *J.*, 1961, 3695.
[13] Wohlfahrt, *J. prakt. Chem.*, 1902, **65**, 295.

nitrogen atoms is not hindered, gives a mixture of oxides, and a mixture of methiodides, but that the [1,2-*c*]isomer [cf. (IV)], in which the 4-hydrogen atom hinders co-ordination to the 5-nitrogen atom, gives a single oxide and a single methiodide, presumed to be at the 6-nitrogen atom. We find that compound (IV) gives a single *N*-oxide, and a single methiodide, presumed to be the 6-oxide and 6-methiodide for similar reasons. Compound (V) gives a mixture of *N*-oxides, in which one isomer appears to predominate and can be separated by crystallisation, and a single methiodide. Molecular models show that the hydrogenated ring hinders co-ordination to the 6-nitrogen atom of compound (IV) and the 8-nitrogen atom of the isomer (V) to some extent, though the hindrance is less than that caused by the 4-hydrogen atom of compound (IV). The methiodide of compound (V) is therefore probably the 7-methiodide, and the predominating *N*-oxide the 7-oxide. Methylation of the 8-nitrogen atom is completely hindered, but a certain amount of the 8-oxide is formed because the smaller oxygen atom can be accommodated.

Whereas simple methiodides are formed from these cinnolines with an excess of methyl iodide in nitromethane, an excess of freshly distilled methyl iodide in ordinary ethanol forms methotri-iodides with three of our products, but simple methiodides with three others (cf. refs. 1 and 13); in one case a mixture of methotri-iodides is formed, for the reasons outlined above. The methiodide of compound (V) gives the methotri-iodide with iodine in ethanol or nitromethane, or with methyl iodide in ethanol.

Fully aromatic cinnolines are, in general, stable to oxidation.[1] The hydrogenated cinnolines (IV) and (V) are oxidised to monoketones by chromium trioxide in acetic acid. The former ketone is reconverted into the cinnoline (IV) by Wolff–Kishner (Huang-Minlon modification) reduction,[14] indicating that the ketone is cyclic and that no ring fission has taken place. The ketone forms an oxime, but not a semicarbazone, phenylhydrazone, or 2,4-dinitrophenylhydrazone. The infrared spectrum of the ketone, in Nujol mull, with a sharp absorption at 1678 cm.$^{-1}$, suggests that the carbonyl group is conjugated with the aromatic system and is therefore in the 7- or the 10-position. The oxime is insoluble in carbon disulphide, carbon tetrachloride, and chloroform, so dioxan was used as a solvent for infrared analysis. A 0·42% solution of the oxime in a 0·1 mm. cell showed an OH stretching absorption band as a double peak with maxima at 3640 and 3700 cm.$^{-1}$, whilst a 0·042% solution in a 1 mm. cell gave a single peak at 3510 cm.$^{-1}$. In Nujol mull the OH stretching absorption maximum occurs at 4320 cm.$^{-1}$. The shift of this absorption band to longer wavelengths on dissolution and dilution suggests that the oxime group is not hydrogen-bonded intramolecularly, and that strong intermolecular hydrogen bonding between oxime molecules is replaced by weaker hydrogen bonding between the oxime and the solvent (dioxan). The oxime is therefore not the *syn*-oxime (X) of the 7-ketone, which would be strongly intramolecularly hydrogen bonded, and is more probably an oxime (IX)



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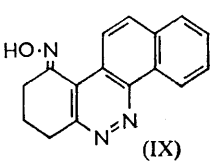

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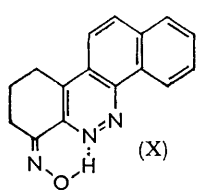

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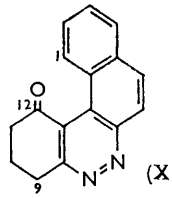

(XI)

of the 10-ketone (VIII) than the 7-*anti*-oxime. The oxime was purified by boiling it with ethanol and water, and allowing the product to crystallise; thus, if it were a 7-oxime it would probably be in the more stable form (X) which is stabilised by hydrogen bonding, rather than in the unbonded *anti*-form. On this basis the ketone will be the 10-ketone (VIII). Oxidation of compound (V) gave a ketone with an infrared spectrum similar to that of the ketone from (IV); this failed to form an oxime or a phenylhydrazone. This

[14] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

ketone is presumed by analogy to be the 12-oxo-compound (XI). The reluctance of the ketones (VIII) and (XI) to form derivatives is ascribed to steric hindrance. Hindrance by the 11-hydrogen atom of the former is less than that by the 1-hydrogen atom of the latter and permits introduction of the small oxime group.

## Experimental

*Cyclohexane-1,2-dione 1-Arylhydrazones from Potassium 2-Oxocyclohexanecarboxylate.*—Cyclohexane-1,2-dione 1-phenylhydrazone and 1-(2-naphthyl)hydrazone, and 2-1′-naphthylazocyclohex-1-enol were prepared by coupling the relevant diazotised amine with potassium 2-oxocyclohexanecarboxylate.[6] 5,6,7,8-Tetrahydro-2-naphthylamine hydrochloride (3·7 g.), diazotised in dilute hydrochloric acid, was added in one portion at 0° to a stirred solution of potassium 2-oxocyclohexanecarboxylate prepared from the ethyl ester (3·5 g.). Sodium acetate (5 g.) was added, and stirring continued until evolution of gas ceased. The resulting precipitate, recrystallised from ethanol, gave *cyclohexane-1,2-dione 1-(5,6,7,8-tetrahydro-2-naphthyl)hydrazone* as yellow needles (3·0 g.), m. p. 148—150°. A sample, recrystallised to constant m. p., had m. p. 153° (Found: C, 74·9; H, 7·9; N, 10·9. $C_{16}H_{20}N_2O$ requires C, 74·7; H, 7·9; N, 11·2%). *2-(4-Nitro-1-naphthylazo)cyclohex-1-enol*, prepared as described above from 4-nitro-1-naphthylamine hydrochloride (0·6 g.), formed orange-brown needles (from ethanol) (0·5 g.), m. p. 166° (Found: C, 64·8; H, 5·2; N, 14·1. $C_{16}H_{15}N_3O_3$ requires C, 64·6; H, 5·1; N, 14·1%). *2-Acenaphthen-5′-ylazocyclohex-1-enol*, prepared in a similar manner from 5-aminoacenaphthene (32 g.), formed brown crystals (from ethanol) (21 g.), m. p. 158—160° (Found: C, 77·5; H, 6·4; N, 10·1. $C_{18}H_{18}N_2O$ requires C, 77·7; H, 6·5; N, 10·1%).

*Cyclohexane-1,2-dione 1-Arylhydrazones from 2-Sodioformylcyclohexanone.*—1-Naphthylamine (100 g.) was diazotised in the presence of hydrochloric acid, and the solution was filtered and treated with sodium acetate (290 g.). An aqueous solution of 2-sodioformylcyclohexanone, prepared from cyclohexanone [15] (20 g.), was neutralised to Congo Red with acetic acid at 0° and slowly added to the diazonium salt solution with stirring. After 2 hr. the mixture was filtered and the precipitate recrystallised from ethanol, to give 2-(1-naphthylazo)cyclohex-1-enol (60 g.), m. p. 130° (lit.,[7] m. p. 133°). Cyclohexane-1,2-dione 1-2′-naphthylhydrazone (38·6 g.), m. p. 170° (lit.,[7] m. p. 173°), was prepared in the same way from 2-naphthylamine hydrochloride (135 g.).

*1,2,3,4-Tetrahydrobenzo[c]cinnoline.*—1,2,3,4-Tetrahydrobenzo[*c*]cinnoline was formed in low yield when a solution of cyclohexane-1,2-dione 1-phenylhydrazone in sulphuric acid was kept at room temperature for several hours or at 0° for several days. The product, isolated by pouring the solution on ice, making it alkaline with sodium hydroxide, and extracting the precipitate with boiling light petroleum (b. p. 100—120°), formed yellow crystals, m. p. 98° (from light petroleum) (lit.,[5] m. p. 98°), giving a pale yellow solution in concentrated sulphuric acid.

*7,8,9,10-Tetrahydronaphtho[1,2-c]cinnoline.*—A solution of 2-1′-naphthylazocyclohex-1-enol (54 g.) in sulphuric acid (500 ml.) was kept at 0° for 2 days. The solution was poured on ice, the tarry green precipitate removed, and the filtrate made alkaline with sodium hydroxide. The resulting precipitate was washed with water and recrystallised from light petroleum (b. p. 100—120°), to give straw-coloured needles of *7,8,9,10-tetrahydronaphtho[1,2-c]cinnoline* (11·4 g.), m. p. 159—161°. The tarry green precipitate was extracted with hot 5N-hydrochloric acid (2 × 150 ml.), the solution made alkaline with ammonia, and the resulting solid recrystallised from light petroleum to give more of the same product (2·6 g., total 27%), m. p. 161—162°. A sample, recrystallised to constant m. p., had m. p. 162—163° (Found: C, 81·8; H, 6·2; N, 11·8. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%). The compound gives a bright red solution in concentrated sulphuric acid. The *monopicrate*, prepared in ethanol solution, formed golden-yellow crystals, m. p. 216° (decomp.) (Found: C, 57·4; H, 3·4; N, 15·0. $C_{22}H_{17}N_5O_7$ requires C, 57·0; H, 3·7; N, 15·1%).

*9,10,11,12-Tetrahydronaphtho[2,1-c]cinnoline.*—A solution of cyclohexane-1,2-dione 1-2′-naphthylhydrazone (36 g.) in 90% sulphuric acid (1 l.) was kept at 0° for 2 days, poured on ice, and made alkaline with sodium hydroxide. The tarry precipitate was extracted with boiling light petroleum (b. p. 100—120°), and the extracts were concentrated to give *9,10,11,12-tetrahydronaphtho[2,1-c]cinnoline* as yellow needles (15 g., 45%), m. p. 129—130° (Found: C, 82·0;

[15] Borsche, *Annalen*, 1910, **377**, 84.

H, 6·2; N, 12·1. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%), giving an orange-red solution in concentrated sulphuric acid. The *monopicrate* formed yellow needles (from ethanol), m. p. 210° (decomp.) (Found: C, 57·5; H, 3·7; N, 15·3. $C_{22}H_{17}N_5O_7$ requires C, 57·0; H, 3·7; N, 15·1%).

1,2,8,9,10,11-*Hexahydroacenaphtho*[5,4-c]*cinnoline*.—A solution of 2-acenaphthen-5′-ylazocyclohex-1-enol (10 g.) in 75% sulphuric acid (250 ml.) was kept at 0° for 24 hr., poured on ice, and made alkaline with sodium hydroxide. The precipitate, extracted with light petroleum (b. p. 100—120°), gave a low yield of 1,2,8,9,10,11-*hexahydroacenaphtho*[5,4-c]*cinnoline* as yellow needles, m. p. 195—197° (Found: C, 83·2; H, 6·4; N, 10·7. $C_{18}H_{16}N_2$ requires C, 83·0; H, 6·2; N, 10·8%), giving a cherry-red solution in concentrated sulphuric acid.

*Action of Sulphuric Acid on Cyclohexane-1,2-dione* 1-(5,6,7,8-*Tetrahydro-2-naphthyl*)*hydrazone*.—Solutions of the hydrazone in sulphuric acid were set aside. The product was isolated by making the reaction mixture alkaline with sodium hydroxide, and was identified by its m. p. and mixed m. p. The hydrazone was recovered after 6 days in sulphuric acid of strength up to 98% at 15°, but no solid was recovered from a solution in 98% acid at 60° after 45 min.

*Naphtho*[1,2-c]*cinnoline*.—A solution of 7,8,9,10-tetrahydronaphtho[1,2-*c*]cinnoline (10 g.) in naphthalene was refluxed for 27 hr. in the presence of 5% palladium–charcoal catalyst (6 g.). The molten mixture was extracted several times with hot concentrated hydrochloric acid, and the extracts were made alkaline with aqueous ammonia. The precipitate recrystallised from acetone as yellow needles of naphtho[1,2-*c*]cinnoline (6·7 g.), m. p. 182—184°. A sample, recrystallised to constant m. p., had m. p. 195—196° (lit.,[4] m. p. 190°) (Found: C, 83·2; H, 4·7; N, 11·9. Calc. for $C_{16}H_{10}N_2$: C, 83·4; H, 4·4; N, 12·2%) and gave a yellow-orange solution in concentrated sulphuric acid. The monopicrate had m. p. 215° (decomp.) [lit.,[4] m. p. 216° (decomp.)].

*Naphtho*[2,1-c]*cinnoline*.—9,10,11,12-Tetrahydronaphtho[2,1-*c*]cinnoline (10 g.), dehydrogenated in the presence of palladium–charcoal as described above, gave naphtho[2,1-*c*]cinnoline, yellow blades (from acetone) (7·0 g.), m. p. 154—156°. A sample, recrystallised to m. p. 159° (lit., m. p. 156·5—157·5°,[11] 157°[4]) (Found: C, 83·2; H, 4·6; N, 12·0. Calc. for $C_{16}H_{10}N_2$: C, 83·4; H, 4·4; N, 12·2%), gave a dark brown solution in concentrated sulphuric acid. The monopicrate had m. p. 187° (decomp.) [lit.,[4] m. p. 188° (decomp.)].

7,8,9,10-*Tetrahydronaphtho*[1,2-c]*cinnoline* 6-*Oxide*.—7,8,9,10-Tetrahydronaphtho[1,2-*c*]cinnoline (120 mg.) in acetic acid (80 ml.) was treated with 80% w/v aqueous hydrogen peroxide (12 ml.), left at room temperature overnight, and poured into water, and the mixture was made alkaline with aqueous ammonia. The precipitate, recrystallised from ethanol, gave 7,8,9,10-*tetrahydronaphtho*[1,2-c]*cinnoline* 6-*oxide* (100 mg.), m. p. 230—231° (Found: C, 76·8; H, 5·5; N, 11·2. $C_{16}H_{14}N_2O$ requires C, 76·8; H, 5·6; N, 11·2%), which gives a pale orange solution in concentrated sulphuric acid.

9,10,11,12-*Tetrahydronaphtho*[2,1-c]*cinnoline* 7-*Oxide*.—9,10,11,12-Tetrahydronaphtho[2,1-*c*]cinnoline (100 mg.), oxidised as above, gave a yellow solid, which on crystallisation from ethanol had m. p. 163—166° (58 mg.). Two more recrystallisations produced pale yellow needles of the 7-*oxide*, m. p. 182—184° (Found: C, 77·0; H, 5·8; N, 11·0. $C_{16}H_{14}N_2O$ requires C, 76·8; H, 5·6; N, 11·2%), which give an orange solution in concentrated sulphuric acid.

*Quaternary Salts of Polynuclear Cinnoline Derivatives*.—(*a*) *Quaternisation in nitromethane*. 9,10,11,12-Tetrahydronaphtho[2,1-*c*]cinnoline (0·2 g.) was refluxed in nitromethane (20 ml.) with freshly distilled methyl iodide (12 ml.) for 4 hr., then the solution was concentrated and allowed to cool. 9,10,11,12-*Tetrahydronaphtho*[2,1-c]*cinnoline* 7-*methiodide* separated as golden-yellow needles, m. p. 230—231°, raised to 234—235° on recrystallisation from nitromethane (Found: C, 54·3; H, 4·5; N, 7·3; I, 33·9. $C_{17}H_{17}N_2I$ requires C, 54·3; H, 4·6; N, 7·4; I, 33·7%).

(*b*) *Quaternisation in ethanol*. The cinnoline (50 mg.) was heated under reflux with methyl iodide (5 ml.) in commercial ethanol (50 ml.) for 2½ hr. The solution was concentrated, the salt separating on cooling. 7,8,9,10-Tetrahydronaphtho[1,2-*c*]cinnoline gave the 6-*methiodide*, yellow needles, m. p. 230° (Found: C, 54·5; H, 4·6; N, 7·1; I, 33·5. $C_{17}H_{17}N_2I$ requires C, 54·3; H, 4·6; N, 7·4; I, 33·7%). 9,10,11,12-Tetrahydronaphtho[2,1-*c*]cinnoline gave the 7-*methotri-iodide*, brown needles, m. p. 196—197° (from ethanol) (Found: C, 32·7; H, 3·0; N, 4·5; I, 60·5. $C_{17}H_{17}N_2I_3$ requires C, 32·4; H, 2·7; N, 4·4; I, 60·4%). Naphtho[1,2-*c*]cinnoline gave the 6-methiodide, reddish-brown needles (60 mg.), m. p. 220° (lit.,[4] m. p. 215°) (from ethanol). Naphtho[2,1-*c*]cinnoline gave a mixture of the methotri-iodides, m. p. 190—200° (from ethanol) (Found: C, 32·9; H, 2·3; N, 4·6; I, 60·6%).

(*c*) 9,10,11,12-*Tetrahydronaphtho*[2,1-c]*cinnoline 7-methotri-iodide from the 7-methiodide.* The 7-methiodide (0·1 g.), refluxed in ethanol or nitromethane with iodine (0·1 g.), gave the 7-methotri-iodide, m. p. and mixed m. p. 196—197°, in both cases. The 7-methiodide, refluxed in ethanol with an excess of freshly distilled methyl iodide, gave the 7-methotri-iodide, m. p. 195—196°, mixed m. p. 196—197°.

7,8,9,10-*Tetrahydro*-10-*oxonaphtho*[1,2-c]*cinnoline.* — 7,8,9,10-Tetrahydronaphtho[1,2-*c*]-cinnoline (0·4 g.) in acetic acid (40 ml.) was treated with chromium trioxide (0·8 g.) in acetic acid (40 ml.) at 100°. After 20 min. the mixture was poured into water, and made alkaline with ammonia. The precipitate, recrystallised from light petroleum (b. p. 100—120°), gave the *ketone* as yellow plates (100 mg.), m. p. 132·5—133·5° (Found: C, 77·8; H, 4·7; N, 11·1. $C_{16}H_{12}N_2O$ requires C, 77·4; H, 4·8; N, 11·3%), giving a yellow solution in concentrated sulphuric acid. The *oxime* was prepared by boiling the ketone with hydroxylamine hydrochloride in ethanol in the presence of pyridine, and recrystallised from boiling aqueous ethanol as needles, m. p. 290° (decomp.) (Found: C, 73·1; H, 5·2; N, 15·7. $C_{16}H_{13}N_3O$ requires C, 73·0; H, 5·0; N, 16·0%).

9,10,11,12-*Tetrahydro*-12(?)-*oxonaphtho*[2,1-c]*cinnoline.*—9,10,11,12-Tetrahydronaphtho[2,1-*c*]cinnoline (0·4 g.), oxidised as above with chromium trioxide in acetic acid, gave the *ketone* (92 mg.), m. p. 173—174° (from aqueous acetone) (Found: C, 77·2; H, 4·8; N, 11·7%), which gives an orange solution in concentrated sulphuric acid.

*Wolff–Kishner Reduction.*—A mixture of the 10-ketone (50 mg.), sodium hydroxide (50 mg.), diethylene glycol (2 ml.), and 90% aqueous hydrazine hydrate (0·1 ml.) was heated under reflux 4 hr., cooled, and diluted with water. The tarry precipitate was extracted with boiling light petroleum (b. p. 100—120°), and the solid which separated on cooling recrystallised to give yellow needles of 7,8,9,10-tetrahydronaphtho[1,2-*c*]cinnoline, m. p. 159—160°, which did not depress the melting point of an authentic sample, m. p. 162—163°.

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