Cinnolines. Part XVII.[1] Reactions of 4-Chlorocinnoline-3-carbonitrile and Preparation of 2,3-Dihydro-3-imino-1*H*-pyrazolo[4,3-*c*]cinnolines

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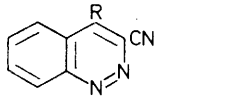
Reaction of 3-bromo-4(1*H*)-cinnoline with copper(I) cyanide in pyridine yields 1,4-dihydro-4-oxocinnoline-3-carbonitrile, which is converted into 4-chlorocinnoline-3-carbonitrile by treatment with phosphoryl chloride. Catalytic hydrogenation of the chloro-compound in the presence of base gives 4,4'-bicinnolyl-3,3'-dicarbonitrile. Condensation reactions of the chloro-compound yield 1,4-dihydro-4-thioxocinnoline-3-carbonitrile (with thiourea), 3-cyanocinnolin-4-ylmalononitrile and similar products (with carbanions), methyl 2,3-dihydro-3-iminothieno[3,2-*c*]cinnoline-2-carboxylate (with methyl thioglycolate), and 2,3-dihydro-3-imino-1*H*-pyrazolo[4,3-*c*]cinnoline and related compounds (with hydrazine and substituted hydrazines).

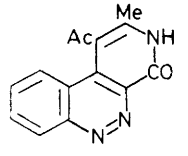
THE action of copper(I) cyanide in *NN*-dimethylformamide on 3-bromo-6,7-methylenedioxy-4(1*H*)-cinnolone gives 1,4-dihydro-6,7-methylenedioxy-4-oxocinnoline-3-carbonitrile.[2] 1,4-Dihydro-4-oxocinnoline-3-carbonitrile has now been prepared similarly from 3-bromo-4(1*H*)-cinnolone; pyridine was a more satisfactory solvent in this case. Alkaline hydrolysis of the product gave 1,4-dihydro-4-oxocinnoline-3-carboxylic acid. The cyanocinnolone reacted with phosphoryl chloride to form 4-chlorocinnoline-3-carbonitrile (Ia), previously prepared from 1,4-dihydro-4-oxocinnoline-3-carboxamide.[3] We report here some reactions of the chloro-nitrile (Ia) for the preparation of 3,4-disubstituted cinnolines, including compounds with a heterocyclic ring fused at the 3- and 4-positions.

Catalytic hydrogenation of the chloro-nitrile (Ia) in the presence of base yielded 4,4'-bicinnolyl-3,3'-dicarbonitrile, which gave 4,4'-bicinnolyl on hydrolysis and decarboxylation.[4] 1,4-Dihydro-4-thioxocinnoline-3-carbonitrile was prepared by the reaction of the chloro-nitrile (Ia) with methanolic thiourea and by the action of phosphorus pentasulphide on 1,4-dihydro-4-oxocinnoline-3-carbonitrile.[5] Methylation of the thione gave 4-methylthiocinnoline-3-carbonitrile (Ib), but attempts to prepare 4-methylsulphonylcinnoline-3-carbonitrile by oxidation were unsuccessful. In each case, 1,4-dihydro-4-oxocinnoline-3-carbonitrile was obtained, presumably by displacement of the good leaving group ($MeSO_2^-$) by water—the activation of the 4-substituent in the cinnoline ring [6] being enhanced by the effect of the 3-cyano-group.

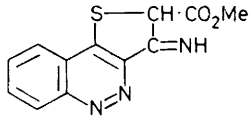
4-Chlorocinnolines condense readily with carbanions; [7] the chloronitrile (Ia) reacted similarly with acetylacetone, phenylacetonitrile, ethyl cyanoacetate, and malononitrile (by use of sodium hydride in 1,2-dimethoxyethane). Several other ' reactive methylene ' compounds gave no condensation product under these conditions (*cf.* refs. 7*a*—*c*). Oxidation of 4-(1-acetylacetonyl)cinnoline-3-carbonitrile (Ic) with potassium permanganate or alkaline hydrogen peroxide gave 1-acetyl-2-methylpyrido[3,4-*c*]cinnolin-4(3*H*)-one (II). This structure was indicated by the absence of the C≡N i.r. band and by the appearance of the methyl signals as two separate peaks at δ 2.42 and 2.30 in the ^{1}H n.m.r. spectrum; in the case of the diketone (Ic) the methyl groups are equivalent



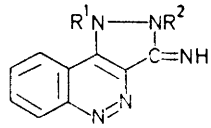
(I) a; R = Cl
b; R = SMe
c; R = $CHAc_2$
d; R = NPh·NHPh
e; R = $\overset{+}{N}Me_2 \cdot NH_2, OH^-$



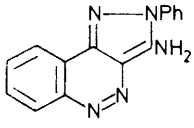
(II)



(III)



(IV) a; $R^1 = R^2 = H$
b; R^1 = Me, R^2 = H
c; R^1 = H, R^2 = Ph
d; R^1 = H, $R^2 = SO_2 \cdot C_6H_4Me$-*p*



(V)

(δ 1.85). The product is presumably formed by hydrolysis of the cyano-group to amide and condensation with an acetyl group.

4-Chloropyrimidine-5-carbonitrile reacts with thioglycolate esters to form thienopyrimidines; [8] 4 chlorocinnoline-3-carbonitrile reacted similarly to give methyl 2,3-dihydro-3-iminothieno[3,2-*c*]cinnoline-2-carboxylate (III) in good yield. This structure is assigned, rather than the alternative aminothiophen form, because the n.m.r. spectrum includes peaks at δ 3.9 (C*H*·CO_2Me) and 7.4 (NH, exchanging with D_2O).

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[2] W. A. White, G.P., 2 005 104/1971.
[3] N. H. Kurihara, U.S.P., 3 657 241/1972.
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[5] *Cf.* R. N. Castle, H. Ward, N. White, and K. Adachi, *J. Org. Chem.*, 1960, **25**, 570.
[6] *Cf.* G. W. Barlin and W. V. Brown, *J. Chem. Soc.* (*B*), 1967, 736; *J. Chem. Soc.* (*C*), 1967, 2473.
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Pyrazolopyrimidines, prepared from chlorocyanopyrimidines and hydrazines, show various pharmacological effects.[9] 2,3-Dihydro-3-imino-1*H*-pyrazolo-[4,3-*c*]cinnoline (IVa) was prepared by the reaction of 4-chlorocinnoline-3-carbonitrile with hydrazine in ethanol. Formulation as the imino-form (IVa) rather than the amino-tautomer is based on i.r. maxima at 3 300br (NH) and 1 640 cm^{-1} (C=N). Attempts to hydrolyse or diazotise this product gave unsatisfactory results. Hinman [10] has shown that, although substitution of an alkyl group for a hydrogen atom in hydrazine is accompanied by a decrease in basic strength, the ease of alkylation increases as successive alkyl groups are introduced. According to Hinman, the positive charge which develops in the transition state is better stabilised on the nitrogen bearing the larger number of alkyl groups so that further alkylation occurs at the alkylated nitrogen atom. Thus 2-chloropyridine and methylhydrazine give only *N*-methyl-*N*-(2-pyridyl)hydrazine [11] and chloro-nitriles [9b] and chloro-esters [12] react so that the halogen is displaced by the α-nitrogen atom of alkylhydrazines but by the β-nitrogen atom of arylhydrazines. The products of reaction of 4-chlorocinnoline-3-carbonitrile with methylhydrazine and phenylhydrazine are therefore formulated as (IVb and c) respectively. The u.v. spectra of the products (IVa—c) were similar (Table), consistent with

U.v. spectra of pyrazolocinnolines (IV) (in ethanol)

	$\lambda_{max.}$/nm	ε	$\lambda_{max.}$/nm	ε	$\lambda_{max.}$/nm	ε
(IVa)	234	24 500	287	4 500	343	1 500
(IVb)	234	17 500	290	5 500	348	2 000
(IVc)	231	18 500	294	16 500	352	3 000

the structures assigned, and confirmed the presence of the imino-group; in the case of (IVc) the only possible amino-tautomer (V) would be quinonoid. A cyclic product (IVd) was also obtained from 4-chlorocinnoline-3-carbonitrile and *p*-tolylsulphonylhydrazine, but *NN'*-diphenylhydrazine gave a nitrile (Id) and *NN*-dimethylhydrazine formed a quaternary compound, isolated as the hydroxide (Ie) the i.r. red spectrum of which showed C≡N and NH_2 absorptions.

EXPERIMENTAL

Evaporations were carried out under reduced pressure; petrol refers to light petroleum (b.p. 60—80°). ^{1}H N.m.r. spectra were measured on a Perkin-Elmer R10 spectrometer at 60 MHz. U.v. spectra were recorded on a Perkin-Elmer 402 spectrophotometer with ethanol as solvent.

1,4-Dihydro-4-oxocinnoline-3-carbonitrile.— 3-Bromo-4(1*H*)-cinnolone [13] (11 g) and copper(I) cyanide (7.7 g) in dry pyridine (100 ml) were boiled under reflux for 16 h and the cooled mixture was added to a solution of iron(III) chloride (18 g) in 4M-hydrochloric acid (300 ml). Filtration and crystallisation from ethanol gave the *nitrile* (7.75 g, 92%), m.p. 260—261° (Found: C, 63.0; H, 2.9; N, 24.4. $C_9H_5N_3O$ requires C, 63.2; H, 2.9; N, 24.6%), $\nu_{max.}$ 2 240 cm^{-1} (C≡N).

4-Chlorocinnoline-3-carbonitrile.—A suspension of the nitrile (0.5 g) in phosphoryl chloride (3 ml) was heated (bath at 140 °C for 2 min and then 110 °C for 8 min), cooled, and poured onto ice. Basification and isolation with ethyl acetate gave the chloro-nitrile (0.3 g, 50%), m.p. 179—181° (from benzene), $\nu_{max.}$ 2 230 cm^{-1} (lit.,[3] m.p. 177—178.5°). Hydrolysis of the nitrile (0.25 g) by boiling with 4M-sodium hydroxide for 2.5 h, acidification, filtration, and crystallisation from aqueous ethanol gave 1,4-dihydro-4-oxocinnoline-3-carboxylic acid (0.16 g), m.p. 266—267° (lit.,[14] 268—268.5°).

4,4'-Bicinnolyl-3,3'-dicarbonitrile.— 4-Chlorocinnoline-3-carbonitrile (0.5 g) in ethanol (75 ml) and triethylamine (3 ml) was hydrogenated over palladium–barium sulphate (0.2 g, 10%). Filtration, evaporation, and crystallisation from methanol gave the *bicinnolyl* (0.16 g, 39%), m.p. 296—297° (Found: C, 69.9; H, 2.7; N, 27.2. $C_{18}H_8N_6$ requires C, 70.1; H, 2.6; N, 27.3%), $\nu_{max.}$ 2 250 cm^{-1} (C≡N); $\lambda_{max.}$ 253 and 315 nm (ε 20 000 and 4 000). A solution of the dinitrile (0.2 g) in ethanol (5 ml) and 2M-sodium hydroxide (10 ml) was boiled under reflux for 5 h. Removal of ethanol and acidification with concentrated hydrochloric acid precipitated the crude dicarboxylic acid which was collected and dried and then heated (bath 240 °C) for 1 h. Crystallisation of the residue from benzene gave 4,4'-bicinnolyl, m.p. and mixed m.p. 228—230°.[4]

1,4-Dihydro-4-thioxocinnoline-3-carbonitrile.—(*a*) A solution of 4-chlorocinnoline-3-carbonitrile (1.65 g) and thiourea (1.5 g) in methanol (15 ml) was heated under reflux for 10 min. On cooling, the product separated and, after crystallisation from benzene–methanol, the *thione* (1.4 g) was obtained as orange crystals, m.p. 292—293° (Found: C, 57.4; H, 2.7; N, 22.4. $C_9H_5N_3S$ requires C, 57.7; H, 2.7; N, 22.5%); $\nu_{max.}$ 2 230 cm^{-1} (C≡N), $\lambda_{max.}$ 237 and 470 nm (ε 23 500 and 1 300).

(*b*) 1,4-Dihydro-4-oxocinnoline-3-carbonitrile (1 g), phosphorus pentasulphide (0.7 g), and sodium hydrogen carbonate (50 mg) in acetonitrile (25 ml) were boiled under reflux for 20 h. After evaporation, the residue was warmed at 40 °C with 4M-potassium hydroxide (50 ml) for 30 min. Filtration, acidification of the filtrate, and recrystallisations of the precipitate from benzene–methanol gave the thione (0.6 g, 55%), m.p. and mixed m.p. 292—293°. Attempts to isolate the thione by chromatography in benzene on alumina (type 0) gave a red *aluminium hydroxide complex*, m.p. 300° [Found: C, 40.3; H, 2.6; N, 15.3. $C_9H_5N_3S,Al(OH)_3$ requires C, 40.7; H, 3.0; N, 15.7%].

4-Methylthiocinnoline-3-carbonitrile.— 1,4-Dihydro-4-thioxocinnoline-3-carbonitrile (0.5 g) was dissolved in butan-2-one (25 ml) and anhydrous potassium carbonate (1 g) and methyl iodide (0.6 g) were added. The mixture was stirred and boiled under reflux for 2 h, and filtered; addition of water and acidification with acetic acid gave a brown precipitate. This was collected and purified by chromatography on alumina (type 0) in benzene–chloroform to give *4-methylthiocinnoline-3-carbonitrile* (0.34 g, 64%) as yellow cubes, m.p. 133—134° (Found: C, 59.7; H, 3.3;

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N, 20.9. $C_{10}H_7N_3S$ requires C, 59.7; H, 3.5; N, 20.9%); $\nu_{max.}$ 2 230 cm^{-1} (C≡N) and 1 310 cm^{-1} (SMe).

4-(1-Acetylacetonyl)cinnoline-3-carbonitrile.— Acetylacetone (0.3 g) was added to a suspension of sodium hydride (0.1 g, 50%) in 1,2-dimethoxyethane (30 ml) and the mixture was stirred for 20 min. 4-Chlorocinnoline-3-carbonitrile (0.5 g) in 1,2-dimethoxyethane (20 ml) was added gradually and the mixture was stirred and boiled under reflux for 4 h. Evaporation and addition of 0.1M-acetic acid (100 ml) gave a solid which was collected and crystallised from benzene–methanol to yield the pale yellow *dioxonitrile* (0.28 g), m.p. 243—244° (Found: C, 66.8; H, 4.4; N, 16.7. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%); $\nu_{max.}$ 2 240 (C≡N) and 1 610 cm^{-1}; $\lambda_{max.}$ 243 and 288 nm (ε 58 000 and 23 500); δ [$(CD_3)_2SO$] 1.85 (6 H, s, 2 Me) and 7.9—8.2 (4 H, m, ArH).

The following compounds were prepared similarly: *3-cyanocinnolin-4-ylmalononitrile* (68%), m.p. 265—266° (from benzene–ethyl acetate) (Found: C, 65.7; H, 2.7; N, 31.7. $C_{12}H_5N_5$ requires C, 65.7; H, 2.3; N, 32.0%), $\nu_{max.}$ 2 220 and 2 210 cm^{-1} (C≡N); *ethyl α-cyano-α-(3-cyanocinnolin-4-yl)acetate* (hemihydrate; 54%), red plates, decomp. above 195° (Found: C, 61.8; H, 3.7; N, 20.7. $C_{14}H_{10}N_4O_2,0.5H_2O$ requires C, 61.1; H, 3.9; N, 20.4%), $\nu_{max.}$ 2 240 and 2 210 (C≡N), and 1 710 cm^{-1} (CO_2Et), $\lambda_{max.}$ 240 and 408 nm (ε 59 000 and 500); *α-(3-cyanocinnolin-4-yl)-α-phenylacetonitrile* (hemihydrate; 41%), yellow crystals, m.p. 194—195° (from benzene–ethyl acetate) (Found: C, 73.6; H, 3.9; N, 20.3. $C_{17}H_{10}N_4,0.5H_2O$ requires C, 73.2; H, 3.9; N, 20.1%), $\nu_{max.}$ 2 210 and 2 200 cm^{-1} (C≡N), $\lambda_{max.}$ 232, 282, and 410 nm (ε 50 000, 14 000, and 24 000).

1-Acetyl-2-methylpyrido[3,4-c]cinnolin-4(3H)-one.— 4-(1-Acetylacetonyl)cinnoline-3-carbonitrile (1 g) was dissolved in 0.5M-sodium hydroxide (75 ml) and potassium permangate (1.25 g) was added. The mixture was heated at 100 °C for 2 h and filtered (Celite) with thorough washing of the solid with warm 0.1M-sodium hydroxide. The filtrates were neutralised with 2M-hydrochloric acid and evaporated to dryness. Repeated extraction of the residue with methanol and evaporation gave the *pyridocinnoline* (0.38 g), pale yellow needles, m.p. 294—295° (from methanol) (Found: C, 66.5; H, 4.6; N, 16.6. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%); $\nu_{max.}$ 3 310 (NH) and 1 660 cm^{-1} (C=O); $\lambda_{max.}$ 244 and 363 nm (ε 17 000 and 5 000); δ [$(CD_3)_2SO$] 2.3 (3 H, s, Ac), 2.4 (3 H, s, CH_3), and 7.8—8.6 (4 H, m, ArH).

Methyl 2,3-Dihydro-3-iminothieno[3,2-c]cinnoline-2-carboxylate.—4-Chlorocinnoline-3-carbonitrile (0.5 g), methyl thioglycolate (0.35 g), and anhydrous sodium carbonate (0.3 g) in absolute ethanol (25 ml) were stirred and boiled under reflux for 4 h. Evaporation, addition of water (75 ml), filtration, and crystallisations from benzene–methanol yielded the *product* (0.62 g), yellow plates, m.p. 219—220° (Found: C, 55.8; H, 3.6; N, 16.0. $C_{12}H_9N_3O_2S$ requires C, 55.6; H, 3.5; N, 16.2%); $\nu_{max.}$ 3 460, 3 310 (NH), and 1 680 cm^{-1} (CO_2Me); $\lambda_{max.}$ 242, 252, 258infl, 317, and 355infl nm (ε 17 500, 19 000, 18 500, 15 500, and 3 000); δ [$(CD_3)_2SO$] 3.35 (3 H, s, Me), 3.9 (1 H, s, 2-H), 7.4 (1 H, s, NH, exchanges with D_2O), and 7.8—8.7 (4 H, m, ArH).

Reactions of 4-Chlorocinnoline-3-carbonitrile with Hydrazines.—A solution of the chloro-compound (0.5 g) and hydrazine hydrate (0.75 ml) in ethanol (30 ml) was boiled under reflux for 2 h. After evaporation, the residue was washed with water and then crystallised from benzene–methanol to give *2,3-dihydro-3-imino-1H-pyrazolo[4,3-c]cinnoline* (0.31 g), yellow needles, m.p. 292—293° (Found: C, 58.2; H, 3.8; N, 37.8. $C_9H_7N_5$ requires C, 58.4; H, 3.8; N, 37.8%); $\nu_{max.}$ 3 300 (NH) and 1 640 cm^{-1} (C=N); δ [$(CD_3)_2SO$] 6.2br (2 H, s, 2NH, exchange with D_2O) and 7.75—8.6 (4 H, m, ArH). Treatment with ethanolic hydrogen chloride gave the *hydrochloride*, red cubes, m.p. 287—288° (decomp.) (Found: C, 49.0; H, 3.8; N, 31.7. $C_9H_7N_5$,HCl requires C, 48.8; H, 3.6; N, 31.6%).

Methylhydrazine similarly gave *2,3-dihydro-3-imino-1-methyl-1H-pyrazolo[4,3-c]cinnoline* (53%), yellow crystals, m.p. 317—318° (Found: C, 60.2; H, 4.8; N, 35.1. $C_{10}H_9N_5$ requires C, 60.3; H, 4.6; N, 35.2%); $\nu_{max.}$ 3 300 and 3 200 (NH), and 1 630 cm^{-1} (C=N); δ [$(CD_3)_2SO$] 3.45 (3 H, s, Me) and 7.6—8.5 (4 H, m, ArH). Phenylhydrazine gave 2,3-dihydro-3-imino-2-phenyl-1*H*-pyrazolo[4,3-*c*]cinnoline (49%), orange needles, m.p. 236—237° (decomp.), which could not be obtained analytically pure (Found: C, 68.1; H, 3.8; N, 26.0. Calc. for $C_{15}H_{11}N_5$: C, 69.0; H, 4.2; N, 26.8%); $\nu_{max.}$ 3 320, 3 190 (NH), and 1 660 cm^{-1} (C=N); δ [$(CD_3)_2SO$] 7.2br (2 H, s, 2NH), 7.5—8.5 (9 H, m, ArH). The *hydrochloride*, red needles from benzene–methanol, had m.p. 250—251° (decomp.) (Found: C, 60.2; H, 4.1; N, 23.4. $C_{15}H_{11}N_5$,HCl requires C, 60.5; H, 4.1; N, 23.5%). *NN'*-Diphenylhydrazine gave *1-(3-cyanocinnolin-4-yl)-1,2-diphenylhydrazine* (20%), yellow needles, m.p. 240—242° (from benzene) (Found: C, 74.5; H, 4.4; N, 20.6. $C_{21}H_{15}N_5$ requires C, 74.8; H, 4.5; N, 20.8%), $\nu_{max.}$ 3 240 (NH) and 2 230 cm^{-1} (C≡N). *NN*-Dimethylhydrazine gave (after heating for 5 h) *1-(3-cyanocinnolin-4-yl)-1,1-dimethylhydrazinium hydroxide* (39%), m.p. 204—205°, orange crystals from ethyl acetate (Found: C, 57.8; H, 5.2; N, 30.0. $C_{11}H_{13}N_5O$ requires C, 57.5; H, 5.3; N, 30.4%), $\nu_{max.}$ 3 290 and 3 260 (NH), and 2 200 cm^{-1} (C≡N). *p*-Tolylsulphonylhydrazine (3 g) and 4-chlorocinnoline-3-carbonitrile (1 g) in chloroform (150 ml) were left at room temperature for 7 days. The red precipitate was collected and recrystallised from benzene–methanol to give *2,3-dihydro-3-imino-2-p-toylsulphonyl-1H-pyrazolo[4,3-c]cinnoline* (1.2 g), red plates, m.p. 271—272° (Found: C, 56.6; H, 3.5; N, 20.6; S, 9.3. $C_{16}H_{13}N_5O_2S$ requires C, 56.6; H, 3.8; N, 20.7; S, 9.4%); $\nu_{max.}$ 3 400 (NH) and 1 650 cm^{-1} (C=N).

Acetylation of 2,3-Dihydro-3-imino-1H-pyrazolo[4,3-c]cinnoline.—The base (0.3 g) and acetic anhydride (1.0 g) in pyridine (20 ml) were boiled under reflux for 60 h. Evaporation, addition of water, isolation with chloroform, and chromatography on alumina (20 g; type 0) in benzene–ethanol (1 : 3) gave an *acetyl derivative* (0.21 g), yellow needles, m.p. 210—211° (from benzene) (Found: C, 57.9; H, 3.7; N, 30.8. $C_{11}H_9N_5O$ requires C, 58.1; H, 4.0; N, 30.8%); $\nu_{max.}$ 3 190br (NH) and 1 690 cm^{-1} (AcN); δ [$(CD_3)_2SO$] 2.2 (3 H, s, COMe), and 7.9—8.8 (4 H, m, ArH).

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