

Oxidation of 1,10-Phenanthroline by Tetraoxomanganate(VI) and (VII). Preparation, Structure and Properties of 1*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dipyridine-2,5-dione

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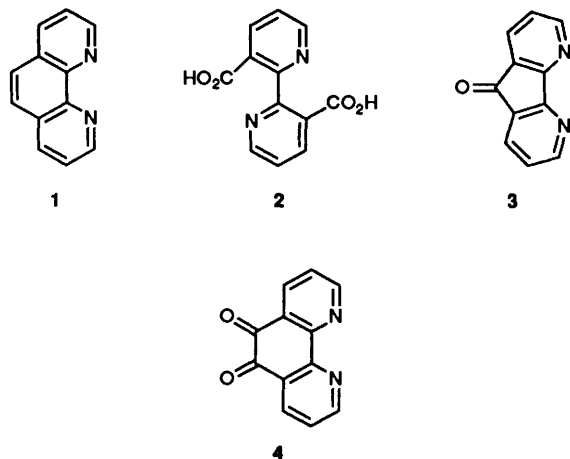
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Oxidation of 1,10-phenanthroline with tetraoxomanganate(VI) gave good yields of ketone **3** and the previously unknown dione **5**, formed by the unusual further oxidation of **3** at the 2 position of a pyridine ring. In contrast, use of the tetraoxomanganate(VII) gave the bipyridine diacid **2** (69%), ketone **3** (20%) and only a trace of the dione **5**. The X-ray crystal structure of the anion of **5** indicates that the negative charge is located mainly on the 2-O rather than 5-O atom, with some delocalisation into the pyridine ring.

The synthesis of 1,10-phenanthroline, **1**, was first reported by Blau¹ who also described the oxidation of the compound by alkaline tetraoxomanganate(VII) to give 2,2'-bipyridine-3,3'-dicarboxylic acid, **2**. The details of this oxidation were defined



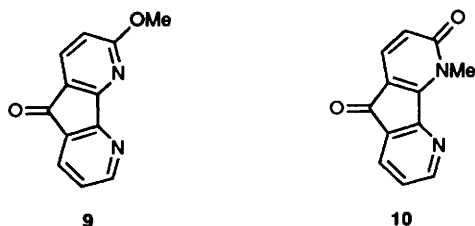
many years later.² Reinvestigation of the reaction³ revealed the presence of the cyclopentadipyridinone **3**, (4,5-diazafluorenone), as a minor product. Formation of 1,10-phenanthroline-5,6-dione, **4**, as an intermediate which undergoes a benzylic acid-type rearrangement in this reaction was presumed. In the course of work⁴ on 3,3'-disubstituted 2,2'-bipyridines, we needed to make the aforementioned dicarboxylic acid, **2**, on several occasions. We noticed that the aqueous filtrate obtained after the oxidation was complete, was bright orange in colour. Previous workers have described methods for the removal of the coloured by-product by absorption onto charcoal, but it has never been either isolated or characterised. We now report the isolation and identification of this by-product. This has led to a study of the oxidation of 1,10-phenanthroline which clarifies the roles of the tetraoxomanganate(VII), MnO_4^- , and tetraoxomanganate(VI), MnO_4^{2-} , ions and of alkalinity in the reaction.

Results and Discussion

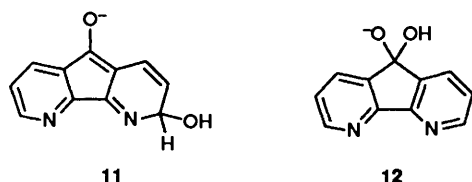
The yellow crystalline minor product of the tetraoxomanganate(VII) oxidation of 1,10-phenanthroline is shown to be the dione **5**, by microanalysis, spectroscopic measurements and the X-ray crystal structure of its sodium salt. In particular, the

electron impact mass spectrum of dione **5** shows a molecular ion at m/z 198 ($I = 100\%$) and the IR spectrum of a sublimed thin film contains two strong absorptions (ν/cm^{-1} 1715, 1650) assigned to the carbonyl groups. The $\nu(\text{CO})$ absorption in cyclopentadipyridone **3** is observed at ν/cm^{-1} 1718, so that the lower frequency absorption (ν/cm^{-1} 1650) in compound **5** may be assigned to the pyridone carbonyl group. This is to be compared with the band at ν/cm^{-1} 1656 in 2-pyridone.⁵ The intensity of this absorption in compound **5** is rather lower (0.29) than that at ν/cm^{-1} 1715. The weak absorption at ν/cm^{-1} 3415 is assigned to $\nu(\text{N-H})$ in compound **5** which is comparable to that (ν/cm^{-1} 3398) in 2-pyridone.⁵ The $^1\text{H NMR}$ spectrum of compound **5** consists of an ABC system due to the protons 8-H (δ 8.66, $^3J_{7,8}$ 5.2, $^4J_{6,8}$ 1.6 Hz), 7-H (δ 7.47, $^3J_{7,8}$ 5.2, $^3J_{6,7}$ 7.4 Hz) and 6-H (δ 7.93, $^4J_{6,8}$ 1.4, $^3J_{6,7}$ 7.4 Hz) of the unsubstituted pyridine ring and an AB doublet of doublets [δ 7.72 (2J 9.3), 6.44 (2J 9.1 Hz)] due to the two protons of the monosubstituted ring. The $^{13}\text{C NMR}$ spectrum indicates the presence of eleven carbon atoms, of which six are quaternary. These are readily assigned by comparison with the $^{13}\text{C NMR}$ spectra of **3** and of 4,5-diazafluorene. The dione **5** is readily deprotonated and the sodium and tetrabutylammonium salts **6** and **7** were isolated. The latter is soluble in hot benzene.

Unambiguous evidence for the identity of dione **5** was obtained from the X-ray crystal structure of the hydrated sodium salt **6**. A structural measurement on the anion was chosen to investigate whether the negative charge was shared by the 5-O atom by delocalisation through the π system. Compound **6** was prepared by treating dione **5** with sodium hydrogen carbonate: it was characterised by spectroscopy. The structure and bond lengths of the anion are given in Fig. 1, the bond angles in Table 1, and fractional atomic coordinates in Table 2. Comparison of corresponding bond lengths in the two pyridine rings reveals that the presence of O^- in the 2-position leads to some degree of bond localisation in the sequence C(2)–C(3)–C(4)–C(4A)–C(5): C(2)–C(3) and C(4)–C(4A) are longer than C(7)–C(8) and C(6)–C(5A) (by 0.054 and 0.022 Å respectively) and C(3)–C(4) and C(4A)–C(5) are shorter than C(6)–C(7) and C(5)–C(5A) (by 0.028 and 0.033 Å). This strongly suggests some delocalisation of charge towards the 5-O atom from the 2- O^- , which can be regarded in valence bond terms as a contribution to the structure from the canonical form **8**. However this contribution is not large since the C(2)–O(2) bond is substantially longer than C(5)–O(5), and the latter is a quite reasonable length for a ketone group. The anion is twisted



each portion of aqueous MnO_4^- solution to the reaction mixture and the need for alkaline conditions suggested that tetraoxomanganate(vi), MnO_4^{2-} is the effective oxidant. Indeed, when compound **3** is treated with alkaline solutions of K_2MnO_4 the isolated yield of dione **5** increases to 70% under optimal conditions. The yield of this reaction is sensitive to hydroxide ion concentration. At $[\text{OH}^-] < 0.6 \text{ mol dm}^{-3}$, tetraoxomanganate(vi) disproportionates so that the yield of compound **5** is correspondingly variable and lower (<50%); at $[\text{OH}^-] > 5 \text{ mol dm}^{-3}$, no dione **5** is formed. The highest yield of dione **5** is achieved when the oxidation of ketone **3** is performed in the presence of moderate hydroxide ion concentration, $0.6 < [\text{OH}^-] < 1.5 \text{ mol dm}^{-3}$. The specificity of this oxidation may be judged by the fact that under identical conditions ($[\text{OH}^-] = 0.6 \text{ mol dm}^{-3}$) neither 4,5-diazafluorene nor 2,2'-bipyridine are oxidised by MnO_4^{2-} to the corresponding 2-pyridones. This suggests that the presence of the carbonyl group in compound **3** plays a crucial role in facilitating the oxidation of the pyridine ring probably by promoting nucleophilic addition of MnO_4^{2-} to the 2-position followed by loss of manganese dioxide and hydroxide. The electronic absorption of ketone **3** in aqueous solution [$\lambda_{\text{max}}/\text{nm}$ (log ϵ) 340 (3.079), 317 (3.851), 310sh (3.748), 303 (3.813), 244 (3.531)] is changed irreversibly by the addition of hydroxide ion to form a species with a single broad absorption ($\lambda_{\text{max}}/\text{nm}$ 273). The identity of the new species has not been established but either (or both) of the species **11** or **12** may be involved. Heating a solution of ketone **3** in NaOH-NaOD (0.8 mol dm^{-3}) for 7 h did not result in H/D exchange detectable by ^1H NMR spectroscopy. Interestingly, the MnO_4^{2-} oxidation of compound **3** stops at the 2-position; no 2,8-disubstituted product was isolated. This is presumably because deprotonation of compound **5** under alkaline conditions would inhibit further nucleophilic addition of MnO_4^{2-} (structure **8**).



Oxidation of 1,10-phenanthroline **1**, with K_2MnO_4 in alkaline solution produces both compounds **3** and **5** in a combined yield of 55–60%; only trace amounts of compound **2** were isolated. The yields of compounds **3** and **5** are more than double the combined yield of these products (22–24%) when KMnO_4 is used as oxidant under similar conditions. 1,10-Phenanthroline-5,6-dione, **4**, (or the 5,6-diol) is the most likely intermediate between compounds **1** and **3**: compound **4** is known to readily undergo benzylic acid-type rearrangement in refluxing aqueous alkali.^{6,7} The fact that treatment of compound **1** with alkaline K_2MnO_4 produces ketone **3** with only traces of diacid **2**, whereas alkaline KMnO_4 produces diacid **2** (70–80% yield) rather than ketone **3** (20% yield), strongly suggests that manganese (vi) oxidises compound **1** to the intermediate dione **4**, and that manganese(vii) is responsible for

oxidising the intermediate dione, **4**, to diacid **2**. Indeed, we find that neutral aqueous MnO_4^- oxidises the dione, **4**, to diacid **2**, in 44% yield. Therefore manganese(vi) and manganese(vii) have to be present simultaneously in solution in order to oxidise compound **1** to compound **2**.

The direct synthesis of a 2-pyridone from a pyridine is unusual. Other examples include the synthesis of 2-pyridone in low yield by passing⁸ pyridine vapour over molten KOH at 300–320 °C, the conversion of quinolinic acid to 6-hydroxyquinolinic acid,⁹ the oxidative hydroxylation of 4,5-dihydroxypyridine-2-carboxylic acid to 4,5,6-trihydroxypyridine-2-carboxylic acid which is mediated by tetraoxomanganate(vii) in acid solution¹⁰ and the oxidation of 8-nitroquinoline to the corresponding 3,4-epoxy-2-pyridone by 3-chloroperbenzoic acid.¹¹

Experimental

1,10-Phenanthroline was purchased from Aldrich. Potassium tetraoxomanganate(vii) was purchased from BDH. Potassium tetraoxomanganate(vi), K_2MnO_4 , was prepared from KMnO_4 by a standard method.¹² IR spectra of materials as sublimed thin films on KBr discs were recorded on a Mattson Alpha Centauri FTIR instrument interfaced with an AT&T UNIX PC. ^1H and ^{13}C NMR spectra were measured using a JEOL GX270 FT spectrometer at 270 MHz for ^1H and 67.80 MHz for ^{13}C resonances; δ values relative to internal $(\text{CH}_3)_4\text{Si}$, J values in Hz. Electronic absorption spectra were recorded using a Shimadzu UV 240 GraphiCORD spectrometer and silica cells.

Oxidation of 1,10-Phenanthroline Using Potassium Tetraoxomanganate(vii).—Following the method of Eckhard and Summers,³ a boiling aqueous solution of KMnO_4 (0.39 mol dm^{-3} , 400 cm^3 , 0.158 mol) was added in portions (25 cm^3) to a boiling, stirred solution of 1,10-phenanthroline (10 g , 0.055 mol) and potassium hydroxide (5 g , 0.089 mol) in water (750 cm^3) over 20 min. Each portion of boiling KMnO_4 was added only after the colour resulting from the previous aliquot had been discharged. The mixture was filtered, and the orange filtrate washed with chloroform ($2 \times 300 \text{ cm}^3$). The pH of the aqueous phase was adjusted by the dropwise addition of concentrated hydrochloric acid. At neutrality the orange colour of the solution was suddenly discharged, and after standing at pH 5 for 5 h a fine yellow precipitate was collected by filtration, dried and purified by sublimation ($185\text{--}200 \text{ }^\circ\text{C}/0.5 \text{ Torr}^*$) to yield 1H-cyclopenta[2,1-b:3,4-b']dipyridine-2,5-dione, **5** (0.31 g , 3%), m.p. $> 300 \text{ }^\circ\text{C}$ (from nitromethane) (Found: C, 66.4; H, 2.6; N, 14.2. $\text{C}_{11}\text{H}_6\text{N}_2\text{O}_2$ requires C, 66.7; H, 3.1; N, 14.1%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3415, 3065, 1715, 1650, 1603, 1570 and 1559; $\delta_{\text{H}}([\text{}^2\text{H}_6\text{]}\text{-DMSO}; 90 \text{ }^\circ\text{C})$ 8.66 (1 H, dd, 8-H, J 5.2, 1.6), 7.93 (1 H, dd, 6-H, J 7.4, 1.4), 7.72 (1 H, d, 4-H, J 9.3), 7.47 (1 H, dd, 7-H, J 7.4, 5.2) and 6.41 (1 H, d, 3-H, J 9.1); $\delta_{\text{C}}([\text{}^2\text{H}_6\text{]}\text{-DMSO}; 90 \text{ }^\circ\text{C})$ 185.9 (C-5), 164.1 (C-2), 158.36 and 158.44 (C-9a, -9b), 152.1 (C-8), 133.1 and 129.7 (C-4, -6), 129.0 and 114.1 (C-4a, -5a) and 124.9 and 117.8 (C-3, -7); $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ (log ϵ) 414 (3.114), 356 (4.176), 340 (4.209), 328 (4.033) and 239 (4.190); m/z (%) 198 (M^+ , 100), 170 (56) and 149 (20); compound **5** exhibits poor solubility in most organic solvents. Treatment of the acidified aqueous filtrate according to the method of Gillard¹³ produces 2,2'-bipyridine-3,3'-dicarboxylic acid, **2**, (9.4 g , 69%). Evaporation of the chloroform extracts yielded compound **3** (2.0 g , 20%).

Sodium Salt of Dione 5.—Solid compound **5** (22 mg , 0.113 mmol) and sodium hydrogen carbonate (9.5 mg , 0.113 mmol) were mixed in water (6 cm^3) and then boiled until all the organic material had dissolved. The solution was left to evaporate at

* 1 Torr = 133.322 Pa.

30 °C over several days to give orange platelets of compound **6** which dehydrate on drying at 100 °C; $\delta_{\text{H}}(\text{D}_2\text{O})$ 8.07 (1 H, dd, 8-H, *J* 5.2, 1.4), 7.19 (1 H, dd, 6-H, *J* 7.4, 1.6), 7.05 (1 H, d, 4-H, *J* 8.8), 6.94 (1 H, dd, 7-H, *J* 7.4, 5.2) and 5.89 (1 H, d, 3-H, *J* 8.8); $\delta_{\text{C}}(\text{D}_2\text{O})$ 190.0 (C-5), 176.8 (C-2), 166.4 and 161.8 (C-9a, -9b), 151.9 (C-8), 133.6 and 130.3 (C-4, -6), 131.0 (C-5a), 124.9 (C-7), 115.6 (C-4a) and 115.2 (C-3); $\lambda_{\text{max}}(\text{H}_2\text{O})/\text{nm}$ (log ϵ) 430 (3.342), 353 (4.021), 340 (3.991), 282 (4.082), 274 (4.079) and 330 (4.336).

X-Ray Crystal Structure of Compound 6.—Crystal data. $\text{C}_{11}\text{H}_5\text{N}_2\text{O}_2 \cdot \text{Na}(\text{H}_2\text{O})_{3.5}$, $M = 283.2$, monoclinic, $a = 33.639(2)$, $b = 6.186(2)$, $c = 12.181(2)$ Å, $\beta = 103.24(1)^\circ$, $V = 2467.4$ Å³, space group $C2/c$, $Z = 8$, $D_c = 1.52$ g cm⁻³; $\lambda = 0.71069$ Å, $\mu = 1.4$ cm⁻¹, $F(000) = 1176$, $T = 293$ K, $R = 0.039$ for 2281 observed reflections. Hydrogen atom fractional coordinates and isotropic displacement parameters, and non-hydrogen atom anisotropic displacement parameters have been deposited at the CCDC.*

Experimental details. Data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo-K α X radiation by ω - 2θ scans to a maximum $\sin\theta/\lambda$ of 0.62 Å⁻¹, on a needle crystal of **6** with dimensions 0.20 × 0.25 × 0.80 mm; 2700 reflections measured, 2282 unique with $R_{\text{int}} = 0.02$, counted as observed [$I \geq 2.5\sigma(I)$]; no significant decay. Structure solved by direct methods (SHELXS-86)¹⁴ and refined on F by full-matrix least squares methods including anisotropic displacement parameters for non-hydrogen atoms (SHELX 76).¹⁵ All H atoms were located and their coordinates refined with a fixed isotropic displacement parameter; 213 parameters refined. With weights $w = [\sigma^2(F) + 0.0002 F^2]^{-1}$ the refinement converged with $R = 0.039$, $R_w = 0.41$; max Δ/σ in final cycle for positional parameters: non-H, 0.1; H, 0.3; for displacement parameters: 0.07. Maximum and minimum residual electron density in final difference Fourier map: +0.20 e Å⁻³ and -0.26 e Å⁻³. Molecular illustration and geometric calculations were performed using PLUTON-91 and PLATON-91.¹⁶

Tetrabutylammonium Salt of Dione 5.—Aqueous tetrabutylammonium hydroxide (20% w/v, Aldrich) was added dropwise to a stirred suspension of dione **5** (45.6 mg) in hot (85–90 °C) water (5 cm³) until all the suspended solid had just dissolved. The orange-red alkaline (pH ca. 8) solution was extracted with chloroform (6 × 5 cm³), the organic extracts were combined, dried (MgSO₄), and evaporated to provide a sticky red solid which was washed with diethyl ether and dried. Recrystallisation from benzene yielded tetrabutylammonium 5-oxo-5H-cyclopenta[2,1-b:3,4-b']dipyridin-2-oate **7** as red needles (74 mg, 73%) which are soluble in alcohols, THF, chloroform and acetone (Found: C, 73.7; H, 9.5; N, 9.5. $\text{C}_{27}\text{H}_{41}\text{N}_3\text{O}_2$ requires C, 73.8; H, 9.4; N, 9.6%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.63 (1 H, dd, 8-H, *J* 5.2, 1.4), 7.67 (1 H, dd, 6-H, *J* 7.4, 1.6), 7.47 (1 H, d, 4-H, *J* 8.8), 7.07 (1 H, dd, 7-H, *J* 7.4, 5.2) and 6.09 (1 H, d, 3-H, *J* 8.8); $\delta_{\text{C}}(\text{CDCl}_3)$ 187.3 (C-5), 177.4 (C-2), 168.8 and 164.7 (C-9a, 9b), 150.8 (C-8), 131.6 and 128.1 (C-4, -6), 133.4 (C-5a), 123.1 (C-7), 113.2 (C-4a) and 115.7 (C-3); $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ (log ϵ), 452 (3.544), 374 (3.929), 356 (4.107), 340 (3.982), 285 (4.021), 276 (4.009), 253 (4.184); (H_2O) 422 (3.278), 352 (4.170), 337 (4.152), 283 (4.012), 273 (4.045), 227 (4.444); (C_6H_6) 448 (4.535), 380 (4.945), 360 (5.055) and 343 (4.902).

Methylation of Dione 5.—Excess ethereal diazomethane azeotrope (25 cm³, approx. 8 mmol) was added to a stirred suspension of finely powdered **5** (0.167 g, 0.84 mmol) in THF (10

cm³) which had been cooled to -5 °C. The cold mixture was stirred for 6 h. The stirring continued at 0 °C for a further 6 h during which time the yellow colour of the suspended solid became orange-brown. The solvent was evaporated in a stream of air at ambient temperatures and the residue sublimed (125–140 °C/0.5 Torr) to give an orange-yellow solid. Chromatography of the sublimate (neutral alumina, Brockman grade 1) with 16% v/v acetonitrile-dichloromethane gave two coloured fractions. Evaporation of the less polar pale yellow fraction and sublimation of the residue at 130 °C/0.05 Torr yielded yellow 2-methoxycyclopenta[2,1-b:3,4-b']dipyridin-5-one, **9** (0.022 g, 12%), m.p. 204–205 °C (Found: C, 68.3; H, 4.0; N, 12.7. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ requires C, 67.9; H, 3.8; N, 13.2%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3402, 3085, 3066, 1713 (CO), 1597, 1582 and 1570; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.73 (1 H, dd, 8-H, *J* 5.1, 1.5), 7.91 (1 H, dd, 6-H, *J* 7.4, 1.6), 7.87 (1 H, d, 4-H, *J* 8.2), 7.30 (1 H, dd, 7-H, *J* 7.4, 5.2), 6.75 (1 H, d, 3-H, *J* 8.5) and 4.18 (3 H, s, CH₃); $\delta_{\text{C}}(\text{CDCl}_3)$ 188.8 (C-5), 169.5 (C-2), 164.4 and 162.9 (C-9a, -9b), 154.1 (C-8), 133.9 and 130.8 (C-4, -6), 130.2 and 123.3 (C-4a, 5a), 124.4 (C-7), 112.4 (C-3) and 54.9; $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ (log ϵ) 383 (3.079), 359 (3.230), 332 (4.097), 324 (3.924), 318 (3.964), 260sh (4.223) and 245 (4.336); m/z 212 (M^+ , 23%), 211 (20), 183 (58), 182 (46), 154 (100), 153 (37), 141 (31), 128 (28), 127 (37), 126 (21), 114 (53), 103 (30), 101 (16), 100 (26) and 99 (26). The more polar orange band was eluted with 20% v/v methanol-chloroform, evaporated and sublimed at 140 °C/0.5 Torr to yield orange 1-methylcyclopenta[2,1-b:3,4-b']dipyridine-2,5-dione **10** (0.142 g, 79%), m.p. 239–240.5 °C (Found: C, 68.2; H, 3.6; N, 13.3. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ requires C, 67.9; H, 3.8; N, 13.2%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3048, 1716 (CO), 1684 (CO), 1600, 1568 and 1538; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.60 (1 H, dd, 8-H, *J* 5.2, 1.6), 7.87 (1 H, dd, 6-H, *J* 7.4, 1.6), 7.67 (1 H, d, 4-H, *J* 9.1), 7.32 (1 H, dd, 7-H, *J* 7.4, 5.2), 6.55 (1 H, d, 3-H, *J* 9.1) and 4.24 (3 H, s, CH₃); $\delta_{\text{C}}(\text{CDCl}_3)$ 186.0 (C-5), 163.9 (C-2), 159.7 and 156.3 (C-9a, -9b), 151.8 (C-8), 132.5 and 130.5 (C-4, -6), 130.1 (C-5a), 124.7 and 119.3 (C-3, -7), 114.2 (C-4a) and 32.3 (CH₃); $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ (log ϵ) 426 (3.176), 357 (4.250), 341 (4.230), 327sh (3.996), 258 (4.176) and 243 (4.245); m/z 212 (M^+ , 56%), 183 (100), 155 (16) and 128 (16).

Oxidation of 1,10-Phenanthroline using Dipotassium Tetraoxomanganate(vi).—A freshly prepared solution of K_2MnO_4 (7.0 g, 0.036 mol) in aqueous potassium hydroxide (0.6 mol dm⁻³; 80 cm³) was added in small (ca. 7 cm³) portions to a rapidly stirred refluxing solution of 1,10-phenanthroline (2.0 g, 0.011 mol) in aqueous 0.6 mol dm⁻³ KOH solution (150 cm³). Each portion of K_2MnO_4 was added only after the colour from the previous addition had been completely discharged. The mixture was boiled for a further 5 min, filtered while still hot and the cooled orange filtrate was extracted with chloroform (3 × 80 cm³). The combined organic extracts were dried (MgSO₄), and evaporated under reduced pressure to leave a pale yellow solid (0.975 g) containing unchanged compound **1** (0.708 g) and ketone **3** (0.267 g, 20%). [The former was isolated by complexation with cobalt(II) sulfate heptahydrate.] The orange aqueous filtrate was acidified with aqueous HBF₄ to pH approx. 4 to produce a copious precipitate of dione **5** and KBF₄. After being left to settle overnight the mixture was filtered. Only trace amounts of diacid **2** were isolated on treatment of the filtrate with AgNO₃ and decomplexation of the silver(I) salt of **2** with H₂S. The solid was dried and sublimed (200 °C/0.05 Torr) to yield dione **5** (0.568 g, 40% yield based on compound **1** consumed). The total conversion of compound **1** was 60%. More detailed investigations showed that this could be increased to 75% if the volume of the portions of alkaline K_2MnO_4 solution was reduced to 1 cm³, however, the ratio of the products, **5:3** changed from 2 to 1.3. The product ratio changed to 0.3 (56% yield based on **1** consumed) when the oxidant was added in small portions as a solid.

* For details of the CCDC scheme see, 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, Issue 1, 1992.

Oxidation of 1,10-Phenanthroline-5,6-dione Using Potassium Tetraoxomanganate(VII).—An aqueous solution of KMnO_4 ($0.082 \text{ mol dm}^{-3}$; 25 cm^3) was added in portions (1 cm^3) to a stirred, refluxing suspension of dione **4** (0.32 g , 1.52 mmol) in water (100 cm^3). A pale brown precipitate formed immediately as each portion of KMnO_4 was added to the stirred suspension. The pale brown precipitate slowly dissolved to give a pale yellow solution. When the addition was complete (permanent ink colouration), the mixture was heated at reflux for a further 75 h, filtered, concentrated to *ca.* 15 cm^3 and fluoroboric acid (48% v/v aqueous) added dropwise to adjust the pH to 2.5. A saturated aqueous solution of silver(I) nitrate was added to precipitate a salt which was isolated by filtration, resuspended in water and then treated with gaseous hydrogen sulfide [to precipitate silver(I) sulfide]. Evaporation of the filtrate yielded diacid **2** as a crystalline solid (0.164 g , 44%).

Oxidation of Cyclopenta[2,1-b:3,4-b']dipyridin-5-one using Dipotassium Tetraoxomanganate(VI).—A solution of K_2MnO_4 (1.87 g , 9.5 mmol) in aqueous potassium hydroxide (0.6 mol dm^{-3} ; 80 cm^3) was added in small portions (*ca.* 1.5 cm^3) to a boiling, stirred solution of ketone **3** (2.0 g , 10.9 mmol) in aqueous potassium hydroxide (0.4 mol dm^{-3} ; 200 cm^3). Each portion of oxidant was added after the colour of the preceding addition had been discharged. When the addition was complete, the mixture was boiled for a further 5 min and then the hot mixture was filtered. The filtrate was extracted with chloroform ($3 \times 80 \text{ cm}^3$) to remove unchanged ketone **3** (1.42 g). The aqueous layer was acidified (to pH 4) with concentrated hydrochloric acid, to give a yellow precipitate which was filtered, dried (90°C) and sublimed ($200^\circ\text{C}/0.05 \text{ Torr}$) to give dione **5** (0.44 g , 70% based on compound **3** consumed).

Acknowledgements

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