Equilibria in Complexes of N-Heterocyclic Molecules. Part 30.[1] Reaction of 5-Nitro-1,10-phenanthroline with Aqueous Bases

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In water and in dimethyl sulphoxide, hydroxide anion adds reversibly to position 6 of 5-nitro-1,10-phenanthroline to give an anion whose equilibrium constant of formation (in water) at 20 °C is 1.2 ± 0.1 dm^3 mol^{-1}. When heated in aqueous media, this anion rearranges to the anion of the mono-oxime of 1,10-phenanthroline-5,6-quinone. A further reaction then affords ammonia in high yield and whose nitrogen atom is derived entirely from the nitro-group of the nitrophenanthroline, and 4,5-diazafluoren-9-one as the major organic product.

DURING studies on the effects of metal ions on the reactions of 1,10-phenanthroline and some of its derivatives, Gillard and Hill[2] observed that hot solutions of salts of tris chelates (these being of unknown isomeric composition, facial or meridional or both) of 5-nitro-1,10-phenanthroline (1) with ruthenium(II) in aqueous sodium hydroxide rapidly evolved ammonia. To account for this interesting observation and to extend our studies of the formation of pseudo-bases by attack of nucleophiles on N-heterocyclic compounds, we have studied the effect of aqueous bases on 5-nitrophenanthroline both in chelated and non-chelated forms. In Part 25 of this series[3] we described the action of cold aqueous bases on iron(II) and ruthenium(II) tris chelates of the nitro-compound (finding distinctions between the initial site of attack and the final product at equilibrium), and in this paper we describe the action of aqueous bases on the free nitro-compound.

RESULTS AND DISCUSSION

The nitro-compound (1) is sparingly soluble in water, and the solution shows a strong absorption band at 265 nm with a weaker but broader band at 323 nm. Successive addition of small amounts of aqueous sodium hydroxide causes (a) an increase in the intensity of the latter band, (b) a decrease in the intensity of the former band, and (c) the formation of an isosbestic point at 286 nm. (This last fact, of course, signifies no more than that the concentrations of all absorbing species present are linearly related, but the proton-resonance evidence supports our analysis in terms of a simple equilibrium between only two species.) These changes,

(1)   (2a) R = H
         (2b) R = Me
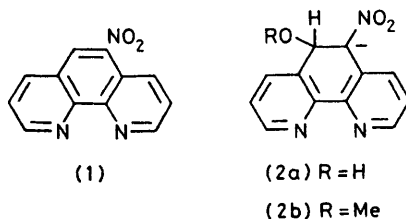
which are reversed by the addition of acid, have previously been reported by Burgess and Prince,[4] who suggested that they were due to removal of the proton at position 6. However, we consider that they arise

from addition of hydroxide anion to the 5-nitrophenanthroline to give an anion to which we assign the structure (2a).

This assignment is made on the basis of the [1]H n.m.r. spectrum obtained when a solution of 5-nitrophenanthroline in [²H₆]dimethyl sulphoxide is treated with Na[OD] in deuterium oxide. The spectrum is essentially the same as that reported by Anderson et al.[5] (since the work described here was completed) for the addition of methoxide anion to the nitro-compound, and which is consistent with attack at carbon 6. The anion (2a) should be the most stable of those that might be produced by the addition of hydroxide anion, for it alone contains two isolated and fully aromatic ring systems. Since dimethyl sulphoxide is a poor solvent for OH$^-$, (2a) seems also to be the kinetically controlled adduct for unco-ordinated 5-nitrophenanthroline, so it is likely to be the initial adduct in aqueous solution. When the

Observed and calculated absorbance at 325 nm of aqueous 5-nitro-1,10-phenanthroline (initially 1.6×10^{-4} mol dm^{-3}) as a function of the concentration of hydroxide ion introduced by means of aliquots of Na[OH] (aq)

[OH$^-$]/mol dm^{-3}	Absorbance	
	obs.	calc.
ca. 4×10^{-5} [a]	0.370	(0.370)
0.011	0.375	0.379
0.056	0.400	0.413
0.275 [b]	0.510	0.528
0.537 [b]	0.615	0.609
1.02 [b]	0.675	0.681

[a] Calculated from K_b of 5-nitro-1,10-phenanthroline. [b] Corrected for volume of added Na[OH] (aq).

nitro-compound is co-ordinated to ruthenium(II), initial addition of OH$^-$ occurs at carbon 7 (or 2); the co-ordinated anion then rearranges fairly readily to give co-ordinated (2a) which is[3] the more stable form.

One striking feature about the formation of the anion (2a) is the ease with which it occurs. Indeed, a graphical analysis of the u.v. spectral results (shown in the Table) shows that the equilibrium constant $\{K_{PB} = [(2a)]/[(1)][OH^-]\}$ for the formation of the anion from 5-nitrophenanthroline and hydroxide anion in water at 20 °C has the remarkably high value of 1.2 ± 0.1 dm^3 mol^{-1}. Presumably the value of K_{PB}, which is almost the same as that (2.7 dm^3 mol^{-1}) reported[6,7] for the

formation of the ' Meisenheimer ' anion (3) from 1,3,5-trinitrobenzene and hydroxide in water at 25 °C, is higher still in dimethyl sulphoxide because of the poor solvating properties mentioned above. Evidently, carbon 6 of 5-nitrophenanthroline is a highly electrophilic centre (see also below).

Using the calculated value of the equilibrium constant in water, the absorption coefficient of the anion (2a) at 325 nm was found to be 1.32×10^4 dm^3 mol^{-1} cm^{-1}. The absorbances of the solutions, calculated from K_{PB} and the absorption coefficient, are given in the Table to

(3)
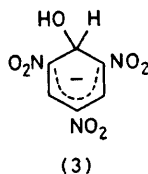
indicate the degree of self-consistency of the derived constants.

When 5-nitrophenanthroline was heated with aqueous sodium hydroxide (2 mol dm^{-3}) a yellowish brown solution was formed which rapidly evolved small amounts of ammonia and deposited a green sodium salt. Using as base hot aqueous tetraethylammonium hydroxide, the yellowish brown solution initially produced soon darkened to a greenish brown but remained clear. Addition of saturated aqueous sodium sulphate to the clear solution caused the precipitation of the same green sodium salt as had been obtained by the direct action of sodium hydroxide, while the addition of tetraphenylarsonium chloride afforded the corresponding tetraphenylarsonium salt in the form of green plates. Elemental analysis of the sodium and tetraphenylarsonium salts indicated that the gegenion present was an isomer of the anion (2a); this was confirmed when acidification of the sodium salt gave a pale yellow solid which was shown by analysis and spectra to be isomeric with the starting 5-nitrophenanthroline and to be the α-keto-


(4)
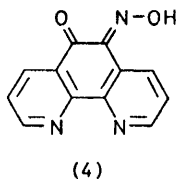
oxime (4). An alternative preparation of this oxime has been briefly reported in abstract form,[8] but as no physical properties were described (and we have been unable to obtain the parent article) we cannot confirm that our compound is identical with that reported in the abstract.

When heated with aqueous tetraethylammonium hydroxide the quinoline analogue (5b) gave a solution of a tetraethylammonium salt which on acidification afforded the α-keto-oxime (6b). Presumably, in solution both the keto-oximes (4) and (6b) are in equilibrium with

the corresponding tautomeric nitrosophenol, and therefore in both cases the solids isolated were probably mixtures of two tautomers.

The rearrangement of the nitro-compounds (1) and

(5)   (6)

(a) X = CH

(b) X = N
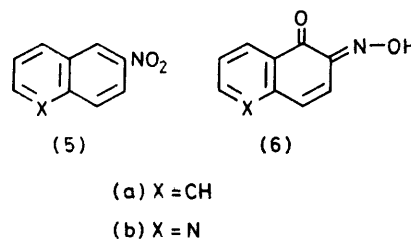
(5b) under the influence of hot aqueous base (see Scheme 1 for plausible mechanism) is directly analogous to that first described by Friedlaender [9] (for a derivative of 1-nitronaphthalene) and to those subsequently studied in detail by Meisenheimer who found, for example, that heating 2-nitronaphthalene (5a) for 4—5 h with aqueous potassium hydroxide followed by neutralisation gave the isomeric o-quinone monoxime (6a).[10] However, the rearrangements reported by these workers occur
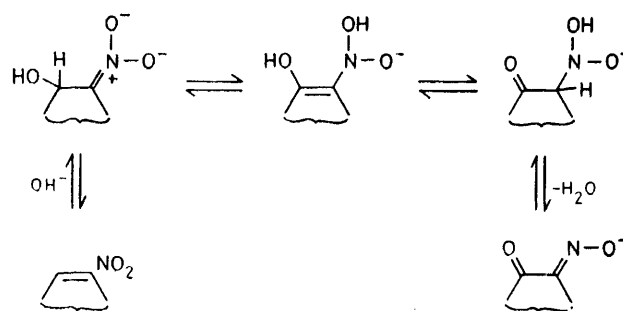
SCHEME 1

much less rapidly than those of (1) and (5b). This is undoubtedly a direct result of the much lower extent to which the benzenoid systems examined earlier undergo addition of hydroxide, i.e. the first stage of the rearrangement, compared with their heterocyclic analogues.

As mentioned above, in addition to the green sodium salt the initial action of hot, aqueous, sodium hydroxide on 5-nitrophenanthroline also gave small amounts of ammonia. Other products of the reaction were 4,5-diazafluoren-9-one (7), which was extracted from the reaction mixture after the sodium salt had been filtered

(7)
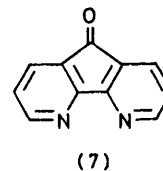
off, and an unidentified yellow solid whose i.r. spectrum suggested the presence of CO$_2$H and CONH$_2$ groups. The formation of both diazafluorenone and ammonia suggested that the nitrogen atom in the latter compound

was that originally in the nitro-group of the nitro-phenanthroline, rather than one of those in the pyridine rings, and that both the ketone and the ammonia were being formed together either in a side reaction or in a further reaction of the green sodium salt. These suggestions were confirmed when it was found that use of 5-nitrophenanthroline labelled with ^{15}N specifically in the nitro-group [2] gave ammonia which contained virtually all the label, and that further action of hot, aqueous, sodium hydroxide on the sodium salt gave higher yields (up to 84% based on one available nitrogen atom) of ammonia; these higher yields were associated with higher yields (up to 62%) of diazafluorenone.

Initially, it seemed possible that hydrolysis of the α-keto-oxime was yielding 1,10-phenanthroline-5,6-quinone (known [2] to form diazafluorenone by a benzil-benzilic acid route readily in alkaline solution) and hydroxylamine, from which ammonia would form by disproportionation. However, the present yield of ammonia is too high, and further the disproportionation of hydroxylamine to ammonia, dinitrogen, and small amounts of NO is slow: according to Wilson and Bremner [11] only 10.3% of a 0.1N solution of hydroxylamine in 0.1 mol dm^{-3} sodium hydroxide, after 4 h at

(7) + NH$_3$
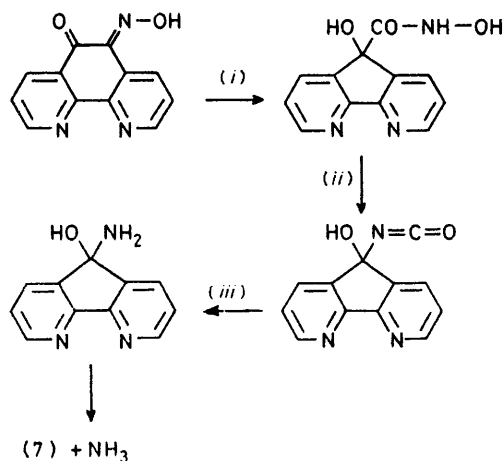
SCHEME 2 (i) OH$^-$, benzil–benzilic acid rearrangement; (ii) OH$^-$, Lossen rearrangement; (iii) H$_2$O, $-CO_2$

reflux, has decomposed. Moreover, direct qualitative tests for hydroxylamine failed.

Another appealing mechanism is that indicated in Scheme 2. Since both rearrangement steps here are prompted by alkali, this seems entirely reasonable.

Another possible mechanism for the formation of ammonia and diazafluorenone from the sodium salt (see Scheme 3) involves an ' abnormal ' Beckmann re-arrangement [12] of the parent keto-oxime (4), which presumably * would be present to some extent in aqueous solutions of its sodium salt, to give the cyano-carboxylate anion (9). Addition of hydroxide anion (the
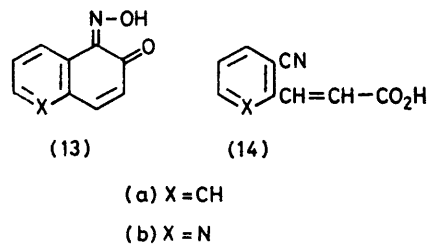
* Values of pK_a for the monoximes of 1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone are, according to E. Havinga and A. Schors (*Rec. Trav. Chim.*, 1950, **69**, 457), 6.21, 8.01, and 9.78 respectively.

initial stage of a base-catalysed ' covalent hydration ' of a pyridine) would afford the carbanion (10) which could then cyclise to the imine (11). Hydrolysis would then afford ammonia and the α-keto-carboxylate anion
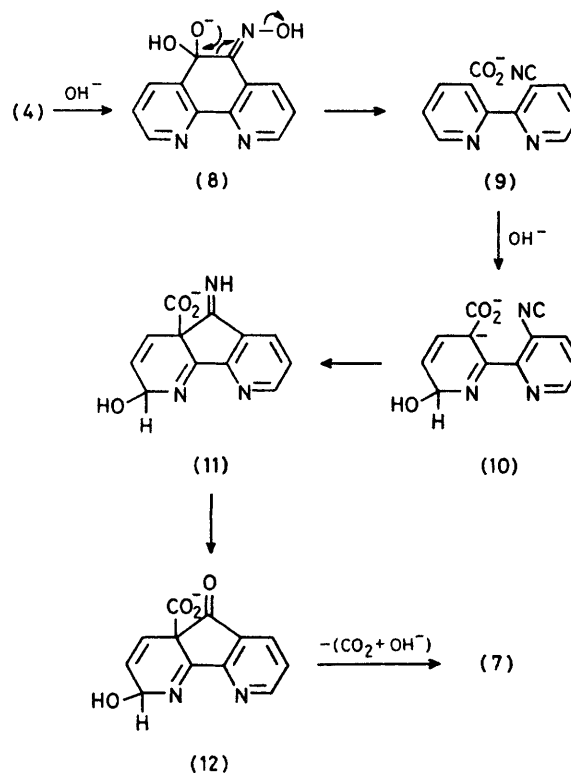
SCHEME 3

(12) which would be expected to decarboxylate rapidly. Loss of hydroxide anion from the resultant carbanion would afford diazafluorenone.

One objection which may be raised to the above mechanism is that the ' abnormal ' Beckmann rearrangement of α-keto-oximes is commonly carried out under conditions which convert the OH group of the oxime function into a good leaving group: for example, the rearrangement of (13b) into the cyano-acid (14b) is carried out by use of benzenesulphonyl chloride and aqueous sodium hydroxide.[13] However, there are reports of this type of rearrangement proceeding under

(a) X = CH

(b) X = N

conditions in which the leaving group is almost certainly an unmodified hydroxide anion, as in the mechanism suggested above. Thus the conversion of the α-mono-oxime of benzil into benzoic acid and benzonitrile readily

proceeds in a solution of potassium cyanide in aqueous ethanol [14] or when the mono-oxime is heated at 200 °C.[15] Particularly relevant to the present work is the observation [16] that the sodium salt of the cyano-acid (14a) can be prepared by heating the sodium salt of the oxime (13a) at 250 °C. Presumably, traces of moisture are essential for the thermal conversion.

A further comment on the first stage of the suggested mechanism is that the carbonyl group of the α-keto-oxime is probably far more reactive towards hydroxide than is that in the analogous phenanthrene system or in the α-mono-oxime of benzil. This is because the carbonyl group and the adjacent 3-pyridyl ring constitute a planar conjugated system, and the positive charge induced on the carbonyl-carbon atom by polarisation of the carbonyl group is delocalised into the ring and shared by the α- and γ-carbon atoms. These atoms are just those which bear the positive charge mesomerically induced in the ring by the electron-withdrawing nitrogen atom. Accordingly, this pyridyl ketone system is less stabilised by resonance than is the corresponding benzenoid system, and hence less resonance energy is lost when the keto-group undergoes nucleophilic addition, e.g. when it adds hydroxide anion to give the species (8). The same situation is present in 3-formyl-pyridine, which although less reactive than the 2 and 4 isomers, is still substantially more reactive than benzaldehyde in nucleophilic additions to the aldehyde group, e.g. in hydrate [17,18] and hemiacetal [19] formation.

This lower stability (and resultant higher reactivity towards nucleophiles) of heterocyclic systems that contain an electrophilic carbon at the 3 position of a pyridyl (or 2,2'-bipyridyl group) is also demonstrated by the ease with which hydroxide anion adds to carbon 6 of 5-nitrophenanthroline as described earlier. The remarkable rapidity with which 1,10-phenanthroline-5,6-quinone [(4) if NOH is replaced by O] undergoes the benzilic acid rearrangement [2] can be explained similarly. With all such systems the high reactivity towards nucleophilic attack will be increased still further when the pyridine nitrogen(s) is protonated, quaternised, or co-ordinated with a metal cation, for these processes increase the size of the positive charge at the α and γ positions of the heterocyclic ring(s); in some cases these positions may be attacked preferentially by the nucleophile. Thus, while the equilibrium constant for the addition of hydroxide anion to 5-nitrophenanthroline is 1.2 dm^3 mol^{-1} in water at 20 °C (this paper), chelation of three molecules of the phenanthroline to ruthenium(II) or quaternisation of both nitrogens by means of a bimethylene bridge raises the corresponding equilibrium constants to **33.0** and 1.6 × 10^4 respectively; with both modifications, the addition of the hydroxide anion is kinetically controlled and initially occurs at carbon 7, rather than at carbon 6.[3]

EXPERIMENTAL

Ultraviolet spectra were obtained with a Pye Unicam SP 800 spectrophotometer, i.r. spectra were run as Nujol mulls on a Perkin-Elmer 257 instrument, and n.m.r. spectra were measured at 35 °C on a Perkin-Elmer R32 (90 MHz) spectrometer. Mass spectra were determined with a Varian CH5D instrument at 70 eV.*

5-Nitro-1,10-phenanthroline was prepared by the method of Smith and Cagle.[20] Acidic impurities were removed by dissolving the crude material in chloroform and extracting the solution with aqueous sodium hydroxide. Crystallisation from ethanol afforded the pure compound, m.p. 203—206 °C (lit.,[21] 202 °C) (Found: C, 64.2; H, 3.30; N, 18.7. Calc. for $C_{12}H_7N_3O_2$: C, 64.0; H, 3.15; N, 18.65%). A sample isotopically labelled with ^{15}N in the nitro-group was conveniently prepared as described by Gillard and Hill,[2] by the remarkably rapid nitration of bis(ethylenediamine)(phenanthroline)cobalt(III) perchlorate with nitric acid containing 30.5% of $H^{15}NO_3$, followed by treatment of the resultant complex with ethylenediaminetetra-acetate.

6-Nitroquinoline supplied by R. N. Emanuel Ltd. was recrystallised from ethanol and then had m.p. 152 °C (lit.,[22] 150 °C).

Ultraviolet Spectra of Basic Aqueous Solutions of 5-Nitro-1,10-phenanthroline.—A sample (1.90 cm^3) of a stock solution of the nitro-compound (0.90 mg, 4.0 mol) in water (25.0 cm^3) was placed in a silica u.v. cell (path length 5.0 mm) and its absorption spectrum vs. water obtained in the range 225—450 nm. The spectrum showed a broad band, $\lambda_{max.}$ 325 nm ($\varepsilon = 4.64 \times 10^3$ dm^3 mol^{-1} cm^{-1}), and a stronger band near 265 nm. To this sample were added successive measured volumes (2.0, 8.0, 40.0, 50.0, and 100 μl) of a solution of Na[OH] (4.30 g) in water (10.0 cm^3) by means of a microlitre syringe. A spectrum was obtained after each addition. The absorbance at 325 nm increased in each successive spectrum (see Table), the peak shifting to slightly greater wavelength. A concomitant decrease in intensity of the peak in the region of 265 nm occurred with an isosbestic point at 285 nm (the trace of the final spectrum passed near but not through this point).

These changes could be reversed by adding concentrated H_2SO_4 from a glass micropipette (in 5-μl aliquots) to a mixture of the stock solution of the nitro-compound (1.80 cm^3) and the sodium hydroxide solution (100 μl). The isosbestic point occurred at 287 nm, and a slight residual absorption (ca. 0.01 absorbance units) between 400 and 450 nm was seen, possibly due to reaction at the higher base concentrations.

Conversion of 5-Nitro-1,10-phenanthroline into Salts of the Keto-oxime (4).—(a) The nitro-compound (500 mg) was heated with 2 mol dm^{-3} sodium hydroxide solution (30 cm^3) at 90—100 °C. After 10 min, the solid had dissolved to give a yellowish brown solution which smelt strongly of ammonia. After 20 min, the mixture was cooled: filtration then gave a green solid and a filtrate (A). The solid was washed successively with cold aqueous 2 mol dm^{-3} sodium hydroxide, ice-cold water, and ethanol to leave the *sodium salt* (380 mg, 60%) of the α-keto-oxime (4) as a green dihydrate, $\nu_{max.}$ at 3 340s, br, 1 630vs, 1 305, 1 275, 1 241br, 1 172, 1 107, 912, 815, 803, and 743 cm^{-1} (Found: C, 48.9; H, 2.50; N, 15.0. $C_{12}H_{10}N_3NaO_4$ requires C, 50.9; H, 3.55; N, 14.8%). Although the figure found for the content of carbon appears unacceptably low, the discrepancy is accounted for by one carbon atom per two sodium atoms being retained as $Na_2[CO_3]$ during the combustion. On this basis the required figure for carbon

* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

is 48.7%. Thermogravimetric analysis showed a 6% weight loss (of water) near 100 °C followed by extensive decomposition; the weight of the residue ($Na_2[CO_3]$) at 900 °C indicated that the sodium salt had a sodium content of 8.0% compared with a calculated value of 8.1%.

A solution of the sodium salt (100 mg) in water (50 cm³) was brought to pH 7 by the addition of 1 mol dm⁻³ sulphuric acid. Filtration gave the α-keto-oxime (4) as a pale yellow powder (75 mg), m.p. *ca.* 240 °C (decomp.), $\nu_{max.}$ 2 600m, vbr, 1 855m, vbr, 1 680s, br, 1 580, 1 560, 1 312s, br, 1 090, 1 060, 1 034s, br, 982s, br, 900s, 808s, 744s, 733, and 725 cm⁻¹. Proton n.m.r. spectrum [in $S(CD_3)_2O$ relative to $SiMe_4$]: 7.7 (unresolved, 2 H), 8.5 (br d, 1 H), 8.9 (br, 1 H), 9.1 (br, 1 H), and 9.3 (br d, 1 H). The mass spectrum showed the molecular ion at $m/e = 225$ (calc. 225).

The filtrate (A) obtained from the original reaction mixture was extracted with dichloromethane to give 4,5-diazafluoren-9-one (7) (120 mg, 30%), m.p. 212 °C (light petroleum, b.p. 120 °C) (lit.,[23] m.p. 212—213 °C) (Found: C, 72.7; H, 2.7; N, 14.1. Calc. for $C_{11}H_6N_2O$: C, 72.9; H, 3.3; N, 15.5%). The mass-spectral results were in accord with the literature,[2] and the i.r. spectrum was identical with that of an authentic sample.

When the nitro-compound was heated with aqueous sodium hydroxide for longer (55 min) the yield of the diaza-fluorenone was 250 mg (62%).

(*b*) A mixture of the nitro-compound (2.25 g), sodium hydroxide (6.0 g), and water (150 cm³) was heated under reflux for 20 h, and then extracted continuously with diethyl ether for 24 h. The ether extract was evaporated to leave 4,5-diazafluoren-9-one (309 mg, 17%) which was identical with the sample described above. The aqueous material was treated with acetic acid (9 cm³) and then filtered to remove a brown solid (502 mg) which was not identified. The filtrate was treated with more acetic acid (15 cm³) and then extracted continuously with ether for 24 h to give a very pale yellow solid (115 mg), $\nu_{max.}$ at 1 705, 1 650, and 1 560 cm⁻¹.

(*c*) The nitro-compound was treated with an excess of aqueous tetraethylammonium hydroxide (2 mol dm⁻³) at 65 °C to give a yellowish brown solution which darkened to brownish green on further heating. Treatment of a portion of the solution with saturated sodium sulphate gave the green sodium salt of the α-keto-monoxime (4) which was identical (i.r.) with the sample described above. Treatment of the remainder of the solution with aqueous tetraphenylarsonium chloride resulted in the deposition of the corresponding *tetraphenylarsonium salt* which crystallised from hot water as the tetrahydrate. This lost water readily when heated and showed $\nu_{max.}$ at 3 300s, vbr, 1 650m (sh), *1 610*s, 1 585, *1 572*, 1 550, 1 435, 1 350, 1 295, 1 230vs, br, 1 160vs, 1 099, 1 080, 997, 906vs, sharp, 811, *745*br, poorly resolved, and *690* cm⁻¹ (the i.r. spectrum of [AsPh$_4$]Cl·2H$_2$O contains bands at or near the italicised bands) (Found: C, 63.7; H, 4.35; N, 6.10. $C_{36}H_{34}AsN_3O_6$ requires C, 63.6; H, 5.05; N, 6.20%). The low figure found for H is due to water loss in the preheating stage of the analysis (another determination gave: C, 63.5; H, 4.05; N, 6.10%); such loss of 3H$_2$O would give apparent H, 4.15%.

Formation of Ammonia from 5-Nitro-1,10-phenanthroline and from the Sodium Salt of the Keto-oxime (4).—(*a*) The nitro-compound (115 mg, 0.51 mmol) containing 30.5% of ¹⁵N in the nitro-group was heated with a boiling solution

of Na[OH] (1 g) in water (20 cm³) in a distillation apparatus fitted with an anti-splash head and a U-tube receiver (containing sulphuric acid) which was cooled in liquid nitrogen. The acidified distillate was analysed for ¹⁵NH$_4$⁺ content by ¹H n.m.r. as previously described;[24] this was found to be 28.5 ± 1.5% of the total ammonium-ion content.

(*b*) The sodium salt (350 mg, 12.4 mmol) was placed together with aqueous Na[OH] (*ca.* 1 mol dm⁻³, 50 cm³) in a flask fitted with a reflux condenser and an inlet tube. The condenser was connected to a Drechsel bottle containing 0.05 mol dm⁻³ H$_2$SO$_4$ (50 cm³), and a slow stream of nitrogen was passed through the gently boiling basic solution so that any ammonia evolved would be caught in the sulphuric acid trap. Refluxing was continued for 60 h. The ammonia content of the solution in the trap (one drop of which gave a strong positive reaction with freshly prepared Nessler's reagent) was then estimated according to Vogel's indirect method[25] (using a known excess of 0.1N H$_2$SO$_4$ and back-titrating with 0.1N aqueous Na[OH]), and found to correspond to a yield of 82%.

Reaction of 6-Nitroquinoline with Aqueous Tetraethyl-ammonium Hydroxide.—A mixture of the nitro-compound (1.1 g, 6.3 mmol) and the aqueous base (2 mol dm⁻³, 20 cm³) was warmed on a steam-bath to give a deep yellow solution which turned dark brown on further heating. The mixture was cooled in ice and then filtered to remove unchanged nitro-compound, further traces of which were extracted from the filtrate with chloroform. The pH of the aqueous material was raised to 7 by the addition of dilute sulphuric acid and filtered to give the α-keto-oxime (6b) as a primrose-yellow solid (540 mg, 49%) which showed $\nu_{max.}$ at 2 600s, vbr, 1 835m, vbr, 1 677s, 1 603, 1 580, 1 560, 1 435, 1 425, 1 311, 1 135, 1 105, 1 071, 1 054, 936, 920vs, 818, 787, 700m, v. sharp, and 678 cm⁻¹. The n.m.r. spectrum in $S(CD_3)_2O$ consisted of an ABX system arising from the protons on the pyridine ring, and an AB quartet arising from those at positions 7 and 8 on the carbocyclic ring: δ 8.91 (q, 1 H), 8.43 (br, 1 H), 7.58 (q, 1 H), 7.46 and 7.12 (AB q, 2 H). The mass spectrum showed the molecular ion to be at $m/e = 174$ (Found: C, 61.95; H, 3.30; N, 16.1. $C_9H_6N_2O_2$ requires C, 62.1; H, 3.45; N, 16.1%). The compound gave with aqueous cobalt chloride a wine-red colour very similar to that given by 1-nitroso-2-naphthol and 2-nitroso-1-naphthol [the tautomeric forms of (13a) and (6a) respectively].

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