215. *Nitroxide Radicals. Part I. The Chemistry of Azo-1-pyrroline 1-Oxides.*

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Oxidation of the cyclic hydroxylamine (I; $R^1 = R^2 = Me$, $R^3 = R^4 = H$) and related bases gives the corresponding azo-1-pyrroline 1-oxides (II) but the lower homologue (I; $R^1 = Me$, $R^2 = R^3 = R^4 = H$) undergoes ring fission forming the keto-nitrile (XII) and nitrogen. The azo-1-pyrroline 1-oxide (II) forms a copper(I) complex, is reduced by hydrochloric and hydrobromic acids, and can be converted into the blue radical-ion (VIII) in several ways.

Fremy's salt, which in aqueous solution dissociates to the relatively stable nitroxide radical $(KO_3S)_2NO^{\bullet}$, is a valuable reagent for the oxidation of phenols to quinones.[1] However it has a number of disadvantages and since, on occasion, it is ineffective, we were led to examine other nitroxide radicals in a search for alternative oxidising agents.* Of the compounds tested,[2] the stable radical porphyrexide (VI)[3] has shown most of the promising activity; this is difficult and tedious to prepare but it was considered that a potentially useful radical of similar structure could be obtained by oxidation of the readily available base (I). In the event this gave a dimeric product. We describe below the properties of this compound, including the formation of a new nitroxide radical-ion.[4]

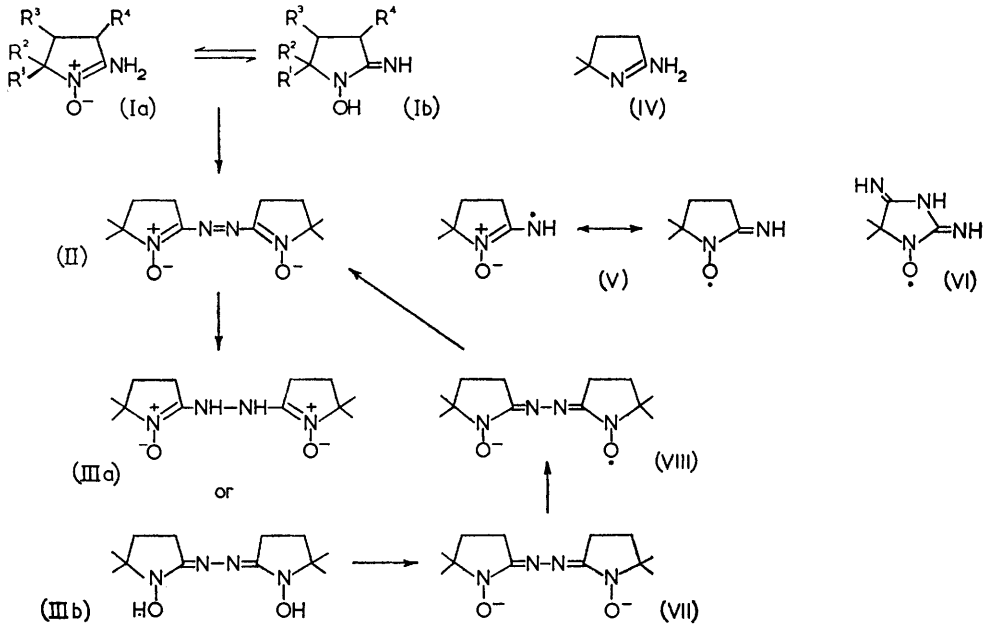
The tautomeric base (Ia $\rightleftharpoons$ Ib; $R^1 = R^2 = Me$, $R^3 = R^4 = H$) exists in chloroform solution as the pyrroline 1-oxide (Ia)[5] but gives derivatives mainly of the other form (Ib).[6] On oxidation with alkaline ferricyanide or neutral permanganate it afforded an orange-red compound to which we assign structure (II) in accordance with its molecular formula, infrared (no absorption above 3000 $cm.^{-1}$) and nuclear magnetic resonance spectra. When hydrogenated over platinum oxide it rapidly absorbed one mol. of hydrogen with loss of colour, the colour being rapidly restored on exposure to air. The leuco-compound, which may have either the hydrazo (IIIa) or the tautomeric azine (IIIb) structure, was isolated as the dihydrochloride and dihydrobromide, picrate, and oxalate. Over Raney nickel, the azo-compound slowly absorbed four mols. of hydrogen giving the cyclic amidine (IV),[5]

* We are indebted to Mr. W. Moser who originally suggested this enquiry.

[1] Teuber and Rau, *Chem. Ber.*, 1953, **86**, 1036, and later Papers.
[2] Forrester and Thomson, unpublished work.
[3] Piloty and Schwerin, *Ber.*, 1901, **34**, 1870; Piloty and Vogel, *Ber.*, 1903, **36**, 1283.
[4] Forrester and Thomson, *Proc. Chem. Soc.*, 1962, 360.
[5] Forrester and Thomson, *Spectrochim. Acta*, 1963, **19**, 1481.
[6] Forrester and Thomson, *J.*, 1963, 5632.

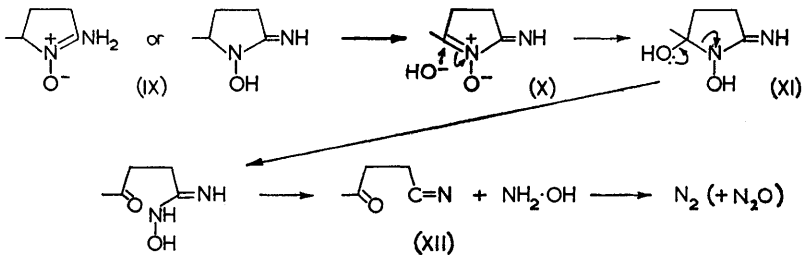
isolated as its picrate. Reduction with hydrazine and Raney nickel, and with sodium borohydride, gave the same result.

The oxidation of the base (I; $R^1 = R^2 = Me$, $R^3 = R^4 = H$) presumably proceeds *via* the radical intermediate (V) which, in contrast to porphyrexide (VI), rapidly dimerises. The ferricyanide oxidation has been extended to the homologous aminopyrroline 1-oxides



(I; $R^1 = R^2 = R^3 = Me$, $R^4 = H$; $R^1 = R^2 = R^4 = Me$, $R^3 = H$; $R^1 = R^2 =$ cyclohexyl, $R^3 = R^4 = H$), all of which formed azo-nitrones. Silver oxide, alkaline hydrogen peroxide, and Fremy's salt failed to effect the oxidation.

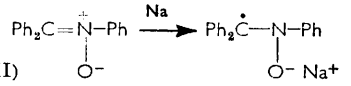
In general, nitroxide radicals can be formed by the oxidation of *NN*-disubstituted hydroxylamines provided that α-hydrogen atoms are absent. This was confirmed in the present series by the oxidation of 2-amino-5-methyl-1-pyrroline 1-oxide (IX) with alkaline ferricyanide which took a completely different course. No azo-compound appeared but nitrogen and a little nitrous oxide were evolved, and lævulinonitrile (XII) was isolated. In this case the initial oxidation probably yields the nitrone (X), which is converted into the amidoxime (XI), followed by elimination of hydroxylamine as shown (or otherwise).



Reactions of the Azopyrroline 1-Oxide (II).—(a) *Radical-ion formation.* (i) Treatment of the leuco-compound (III) or its dihydrochloride with aqueous sodium hydroxide, in the

presence of air, gave a bright blue paramagnetic * solution which gradually changed to red through green and yellow. The azo-compound (II) was isolated quantitatively from this solution. Weak bases (*e.g.*, ammonia) merely gave yellow solutions which slowly turned red. Rapid evaporation of the blue solution *in vacuo* afforded a blue paramagnetic * solid, which was stable indefinitely in the absence of air. We consider the blue compound to be the mesomeric radical-ion (VIII) formed by aerial oxidation of the dianion (VII) with loss of one electron. Further oxidation, with loss of a second electron, then gives a biradical which mesomerises to the diamagnetic azo-compound (II).† Oxidation of the colourless dianion (VII) (prepared by addition of a strong base to a methanolic solution of the leuco-compound under hydrogen) to the radical-ion (VIII) can be accomplished equally well in the absence of air by using potassium ferricyanide.

(ii) In (i) the radical-ion (VIII) was formed by removal of one electron from the dianion (VII). It can also be obtained by addition of one electron to the azo-compound (II) by reaction with sodium in tetrahydrofuran under nitrogen, the solution slowly changing from red to green to blue. The process is analogous to the formation of radical-anions by addition of sodium to azoxybenzene and the nitrone (XIII).[7]



(XIII)

(iii) Russell *et al.*[8] have shown that radical-anions can be formed, under suitable conditions, by electron transfer between an unsaturated compound (π) and the dianion of its dihydro-derivative (πH_2).

$$\pi H_2 \longrightarrow \pi^{2-} \xrightarrow{\pi} 2\pi^{\cdot -}$$

In this way radical-ions were produced from azobenzene–hydrazobenzene, fluorenone–fluorenol, and similar pairs of related compounds, and the method is applicable to the present system. Addition of the azo-compound to an equimolecular amount of the dianion (VII) in dimethyl sulphoxide containing potassium t-butoxide gave an immediate blue solution of the radical-ion (VIII), *i.e.*, (II) + (VII) ⟶ 2(VIII).

(iv) When alkaline solutions of the azo-compound were warmed in the presence of air, greenish-brown to greenish-blue colours were produced according to the strength of the base used. These solutions gave electron spin resonance spectra identical with that of the radical-ion (VIII), and slowly reverted to red on prolonged exposure. In the absence of air, the azo-compound with excess of potassium t-butoxide in dimethyl sulphoxide solution gave a greenish-blue solution which slowly turned brown during two days, best results being obtained using a 2 : 1 molar ratio of azo-compound to butoxide when the resulting blue solution persisted for seven days. We attribute radical-ion formation here to electron transfer between a carbanion (R^-) and an unsaturated centre (π), exemplified by the

$$R^- + \pi \longrightarrow \pi^{\cdot -} + R^{\cdot}$$

behaviour of alkylated aromatic nitro-compounds in strongly basic media.[9] The latter form carbanions by abstraction of a proton from an α-carbon atom and presumably this occurs at position 3 in the azo-compound (II). The formation of the radical-ion (VIII) can then be represented,

$$(II) \longrightarrow (II)^- \xrightarrow{(II)} (VIII) + (II)^{\cdot}$$

where $(II)^-$ and $(II)^{\cdot}$ represent the anion and radical derived from the azo-compound (II)

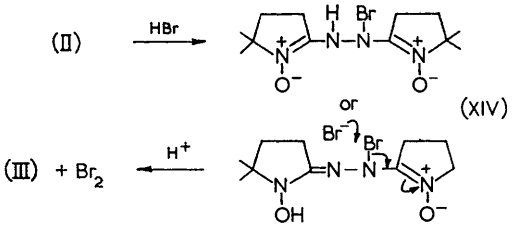
* The electron spin resonance spectra will be reported separately.
† Actually the azo-compound (II) is very weakly paramagnetic in the solid state.

[7] Kauffmann and Hage, *Angew. Chem.*, 1961, **73**, 680.
[8] Russell, Janzen, and Strom, *J. Amer. Chem. Soc.*, 1962, **84**, 4155.
[9] Russell and Janzen, *J. Amer. Chem. Soc.*, 1962, **84**, 4153.

by abstraction of a proton and a hydrogen atom, respectively. The fate of the radical (II)• is not known.

The radical-ion (VIII) inhibits the polymerisation of styrene, is reduced by ascorbic acid and dithionite, and oxidised by iodine and ferricyanide. It dehydrogenates quinol and hydrazobenzene but has no effect on bibenzyl or dihydroanthracene in boiling methanol.

(b) *With acids.* On evaporation of a solution of the azo-nitrone (II) in aqueous hydrochloric or hydrobromic acid, the dihydrohalide of the leuco-compound (III) was obtained and free halogen was evolved. In the case of hydrobromic acid appreciable reaction occurred at room temperature. The reduction of azo-compounds by halogen acids has been noted previously,[10,11] the reaction being accompanied always by nuclear halogenation. The bromination of azobenzene is catalysed by hydrobromic acid and the first step is considered [11] to be a slow addition of the acid to the azo-linkage to give an *N*-bromo-compound which may, *inter alia*, undergo an Orton-type of rearrangement to form 4-bromohydrazobenzene. The evidence is derived from kinetic rather than product studies and neither of the intermediates mentioned have been isolated. The mechanism is probably similar in the present case (see annexed scheme), the reaction being assisted by the electron-withdrawing groups attached to the azo-linkage (cf. the reduction of 1,2-dibenzoylethylene to 1,2-dibenzoylethane by hydrogen bromide in acetic acid [12]).



An attempt to isolate the postulated intermediate (XIV) by treating the azo-nitrone with one mol. of hydrogen bromide in acetic acid afforded a salt which reverted to the azo-compound (II) on treatment with water.

Attempts to acylate the azo-nitrone resulted in slow loss of colour but no identifiable product was isolated, and all efforts to acylate the leuco-compound (III) failed owing to rapid oxidation to the azo-compound, even in the absence of air. No reduction products of the acylating agents could be found. The leuco-compound readily reduced *p*-benzoquinone to quinhydrone but had no effect on benzaldehyde or stilbene.

(c) *With copper*(I) *chloride.* When an aqueous solution of the azo-compound was shaken with copper(I) chloride it formed a violet solution from which a dark blue crystalline solid could be isolated by chloroform extraction. The same product was obtained by reaction of the leuco-compound with copper(II) chloride, but there was no reaction between the azo-compound and copper(II) chloride nor between the leuco-compound and copper(I) chloride. Analysis indicated the formula $C_{12}H_{21}Cl_2CuN_4O_2$, *i.e.*, (II),CuCl,HCl. Its aqueous solution was slightly acidic and gave a precipitate with silver nitrate; dilute nitric acid and dilute alkali regenerated the azo-compound. As the compound gave no e.s.r. signal it appears to be a Cu^{I} rather than a Cu^{II} complex. Chelate formation by aromatic azo-compounds with copper(II) salts is well known [13] but copper(I)–azo-complexes are rare. The only well authenticated example is the azomethane–copper(I) chloride complex [14] (formed by reaction of hydrazomethane with copper(II) sulphate, followed by acidification with hydrochloric acid) in which each nitrogen atom is co-ordinated to a molecule of

[10] Colonna, Risaliti, and Serra, *Gazzetta*, 1955, **85**, 1508; Colonna and Risaliti, *ibid.*, 1956, **86**, 288.
[11] Robertson, Hitchings, and Will, *J.*, 1950, 808.
[12] Kobayashi, *J. Chem. Soc. Japan*, 1953, **74**, 968 (*Chem. Abs.*, 1955, **49**, 2989).
[13] Zollinger, " Azo and Diazo Chemistry," Interscience, New York, 1961, p. 338—360.
[14] Brown and Dunitz, *Acta Cryst.*, 1960, **13**, 28.

copper(I) chloride, the copper having a co-ordination number of three. The azopyrroline 1-oxide complex may be a hydrochloride of this type. Alternatively, as complex formation by heterocyclic *N*-oxides has been demonstrated,[15] the copper may be linked to oxygen and an azo-nitrogen atom. Such a structure would resemble an *o*-hydroxyazo-complex but would seem to be less likely as no complex is formed in this case with copper(II) chloride. Clearly the structural problem can only be settled by crystallographic analysis.

Treatment of the azo-nitrone (II) with iron(II) chloride gave a dark green solution whose colour could not be extracted into organic solvents.

Experimental

2-Methyl-3-nitrobutyl Cyanide.—A mixture of allyl cyanide (13 g.), nitroethane (15 g.), aqueous tetraethylammonium hydroxide (10 ml., 30%), and ethanol (100 ml.) was refluxed for 20 hr., the solution made just acid to Congo Red with dilute sulphuric acid, shaken with barium carbonate to remove excess of acid, filtered, and fractionated to give the *nitrocyanide* (15 g., 54%) as a colourless oil, b. p. 80—81°/0·2 mm. (Found: C, 50·4; H, 6·8; N, 19·8. $C_6H_{10}N_2O_2$ requires C, 50·7; H, 7·0; N, 19·7%); $\nu_{max.}$ (film) 2250, 1555, 1395 cm.$^{-1}$.

Preparation of 2-Amino-1-pyrroline 1-Oxides.—General method. The nitrocyanide [16] (0·1 mole) was dissolved in methanol (50 ml.) and hydrogenated over Raney nickel until absorption of 2 mol. of hydrogen was complete. The solution was filtered, taken to dryness *in vacuo*, and the residue treated with dry acetone to give the aminopyrroline 1-oxide. Concentration of the mother-liquors produced a second crop. Yields were in the range 60—75%. The extremely hygroscopic nature of some of these compounds gave rise to rather low carbon percentages. The following are new: *2-amino-4,5,5-trimethyl-1-pyrroline 1-oxide*, needles (from chloroform–acetone), m. p. 171—172° (Found: C, 58·8; H, 9·7; N, 19·6. $C_7H_{14}N_2O$ requires C, 59·15; H, 9·9; N, 19·7%); *2-amino-4,5-dimethyl-1-pyrroline 1-oxide*, hygroscopic needles (from chloroform–acetone), m. p. 219—220 (Found: C, 55·5; H, 9·4; N, 21·5. $C_6H_{12}N_2O$ requires C, 56·25; H, 9·4; N, 21·9%); *2-amino-3,5,5-trimethyl-1-pyrroline 1-oxide*, extremely hygroscopic needles (from chloroform–ether), m. p. 142—144° (Found: C, 58·5; H, 10·3; N, 19·5. $C_7H_{14}N_2O$ requires C, 59·15; H, 9·9; N, 19·7%). The infrared spectra (in Nujol) of these aminopyrrolines all have a broad NH absorption band above 3000 cm.$^{-1}$ and a C=N stretching vibration near 1700 cm.$^{-1}$. A strong peak near 1200 cm.$^{-1}$ is assigned to the $N^+–O^-$ stretching frequency.

Preparation of Azo-pyrroline 1-Oxides.—(i) *By oxidation with alkaline ferricyanide.* 2-Amino-5,5-dimethyl-1-pyrroline 1-oxide (64 g.) in water (150 ml.) cooled to 0°, was added to a cold solution of potassium ferricyanide (362 g.) and sodium hydroxide (44 g.) in water (1 l.). The bright red solution produced was stirred for a few minutes and then left for 1 hr. The solid which separated and the solution were extracted with chloroform, the extracts were washed with water, dried ($CaCl_2$) evaporated to dryness *in vacuo*, and the residue crystallised from alcohol giving *5,5:5′,5′-tetramethyl-2,2′-azo-1,1′-pyrroline 1,1′-dioxide* (19·6 g., 31%) as red needles, m. p. 203—204° (decomp.) (Found: C, 57·2; H, 8·1; N, 22·2%; *M* (mass spectrum), 252. $C_{12}H_{20}N_4O_2$ requires C, 57·1; H, 7·9; N, 22·2%; *M*, 252); $\lambda_{max.}$ (in ethanol) 240, 435, 590 mμ (log ε 3·68, 4·50, 3·22); the n.m.r. spectrum measured at 60 Mc./sec. (in $CDCl_3$) showed peaks at τ = 8·48 (CH_3, singlet, 12 protons), *ca.* 7·84 (CH_2, sextuplet, 4 protons), *ca.* 6·92 (CH_2, sextuplet, 4 protons). It showed no activity in any of the tests for antibacterials, anthelmintics, or anti-arthritics.

(ii) *By oxidation with permanganate.* 2-Amino-5,5-dimethyl-1-pyrroline 1-oxide (1·28 g.) in water (10 ml.) was treated with potassium permanganate (1·2 g.) in water (30 ml.). The solution was warmed at 60—70° for a few minutes, cooled, and extracted with chloroform. Treatment of the chloroform extracts as before gave the azo-nitrone (II) (0·18 g., 14%), m. p., mixed m. p., and infrared spectrum identical with that obtained in (i).

The following azo-compounds were prepared by method (i): *4,5,5,4′,5′,5′-hexamethyl-2,2′-azo-1,1′-pyrroline 1,1′-dioxide*, red needles (from ethanol), m. p. 204—205° (decomp.) (Found: C, 59·7; H, 8·5; N, 19·8. $C_{14}H_{24}N_4O_2$ requires C, 60·0; H, 8·6; N, 20·0%); *3,5,5,3′,5′,5′-hexamethyl-2,2′-azo-1,1′-pyrroline 1,1′-dioxide*, red needles (from benzene–light petroleum (b. p.

[15] Carlin, *J. Amer. Chem. Soc.*, 1961, **83**, 3773; Quagliano, Fujita, Franz, Phillips, Walmsley, and Tyree, *ibid.*, 1961, **83**, 3770; Harris, Kokot, Lenzer, and Lockyer, *Chem. and Ind.*, 1962, 651.

[16] Buckley and Elliot, *J.*, 1947, 1508.

60—80°)), m. p. 204—205° (decomp.) (Found: C, 60·3; H, 8·8; N, 19·6. $C_{14}H_{24}N_4O_2$ requires C, 60·0; H, 8·6; N, 20·0%); *5,5:5′,5′-dispirocyclohexyl-2,2′-azo-1,1′-pyrroline 1,1′-dioxide*, orange needles (from methanol), m. p. 207—208° (decomp.) (Found: C, 64·7; H, 8·6; N, 16·7. $C_{18}H_{28}N_4O_2$ requires C, 65·0; H, 8·4; N, 16·9%). The infrared spectra (in KBr) of these azo-nitrones showed no C=N absorption in the 6 μ region but were characterised by absorption bands near 1260, 1220, and 720 cm.$^{-1}$.

Oxidation of 2-Amino-5-methyl-1-pyrroline 1-Oxide.—(i) *With alkaline ferricyanide.* The base (1·14 g.) in chloroform (25 ml.) was shaken for 16 hr. with a solution of potassium ferricyanide (7·2 g.) and sodium hydroxide (0·88 g.) in water (25 ml.), gas evolution occurring. The organic layer was separated, the aqueous layer extracted with chloroform (25 ml.) and the combined chloroform fractions dried (Na_2SO_4) and distilled to give a yellow oil (0·6 g.), b. p. 76—84°/0·5 mm.; $\nu_{max.}$ (film) 2280 (C≡N) and 1720 cm.$^{-1}$ (C=O). The 2,4-dinitrophenylhydrazone separated from alcohol in orange leaflets, m. p. 147°, identical (mixed m. p. and infrared spectrum) with authentic lævulinonitrile 2,4-dinitrophenylhydrazone. Mass spectrometry of the gas evolved during the oxidation gave the following percentage composition: N_2, 97·8; N_2O, 2·1; O_2, 0·015; H_2, 0·027; unidentified products 0·05%.

(ii) *With potassium permanganate.* The base (1·14 g.) in chloroform (25 ml.) was shaken for 16 hr. with a solution of potassium permanganate (1·2 g.) in water (25 ml.). The organic layer was separated and the aqueous layer extracted with chloroform (25 ml.). The chloroform extracts were treated as described in (i) giving lævulinonitrile 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 147°.

Reduction of the Azopyrroline 1-Oxide (II; $R^1 = R^2 = Me$, $R^3 = R^4 = H$).—(i) *Hydrogenation over platinum oxide.* The azo-nitrone (II) (0·252 g., 0·001 mole) in methanol (50 ml.) was shaken with platinum oxide (0·1 g.) in an atmosphere of hydrogen until 22·4 ml. (0·001 mole) were absorbed. The colourless solution was filtered in air, and evaporated to dryness. The residual orange solid, on further exposure to air, gave the original azo-nitrone quantitatively. When the hydrogenation solution was filtered under nitrogen, and then treated with hydrochloric acid and evaporated to dryness, the *dihydrochloride* of the leuco-compound (III) was obtained. It formed hygroscopic needles (from ethanol–chloroform), m. p. 203° (Found: C, 43·7; H, 7·6; Cl, 21·4; N, 17·4. $C_{12}H_{24}Cl_2N_4O_2$ requires C, 44·0; H, 7·3; Cl, 21·7; N, 17·1%). The solid lost hydrogen chloride when dried above 40°. Addition of oxalic acid (0·2 g.) to the hydrogenation solution gave the *oxalate* which formed needles (from ethanol–ether), m. p. 170—171° (Found: C, 49·2; H, 7·0; N, 16·3. $C_{14}H_{24}N_4O_6$ requires C, 48·8; H, 7·0; N, 16·3%). Similarly picric acid (0·24 g.) gave the *monopicrate*, yellow needles (from ethanol), m. p. 159—160° (Found: C, 44·7; H, 5·4; N, 20·3. $C_{18}H_{25}N_7O_9$ requires C, 44·7; H, 5·2; N, 20·3%).

(ii) *Hydrogenation over Raney nickel.* The azo-nitrone (II) (2·52 g., 0·01 mole) in methanol (100 ml.) was shaken with freshly prepared Raney nickel (*ca.* 2 g.) in an atmosphere of hydrogen until 900 ml. (0·04 mole) were absorbed. After an initial rapid uptake of 224 ml. the subsequent 676 ml. were absorbed very slowly (36 hr.). The resulting greenish-brown solution was filtered, boiled with a saturated solution of picric acid and left to crystallise. The yellow needles which separated (2·9 g.) had m. p. 204° (after recrystallisation from aqueous ethanol) not depressed on admixture with an authentic specimen of the picrate of 2-amino-5,5-dimethylpyrroline.[16] A further quantity (1·3 g.) was obtained by evaporation of the mother-liquors (Found: C, 42·1; H, 4·4; N, 20·2. Calc. for $C_{12}H_{15}N_5O_7$: C, 42·2; H, 4·4; N, 20·5%).

(iii) *With Raney nickel and hydrazine.* To the azo-compound (II) (0·252 g.) in methanol (25 ml.) at 50°, Raney nickel (*ca.* 2 g.) and hydrazine hydrate (2 ml., 60% w/w) were added. The solution was refluxed for 24 hr., filtered, and the hot filtrate treated with picric acid (0·5 g.) and left to crystallise. The picrate of 2-amino-5,5-dimethyl-1-pyrroline separated as yellow needles (0·2 g.), m. p., mixed m. p., and infrared spectrum identical with that of an authentic specimen.

(iv) *With sodium borohydride.* The azo-compound (II) (0·252 g.) in ethanol (10 ml.) and water (20 ml.) was shaken with sodium borohydride (1·0 g.) for 2 hr. The solution was left overnight, then made alkaline, and extracted with ether. The extract was evaporated to a yellow oil which formed a salt when treated with oxalic acid in acetone. It crystallised from ethanol–ether giving the *2-amino-5,5-dimethyl-1-pyrroline oxalate* as hygroscopic needles, m. p. 154—155° (Found: C, 47·6; H, 6·8; N, 14·0. $C_8H_{14}N_2O_4$ requires C, 47·5; H, 6·9; N, 13·9%).

Reactions of the Azopyrroline 1-Oxide (II; $R^1 = R^2 = Me$, $R^3 = R^4 = H$).—(a) *Radical-ion formation.* (i) The dihydrochloride of the leuco-compound (III) (0·325 g.) in methanol (10 ml.)

was treated with aqueous N-sodium hydroxide (4 ml.) giving a blue solution which was evaporated *in vacuo* to give the radical-ion (VIII) as a deep blue residue. Many attempts to purify the product by crystallisation resulted in rapid oxidation (even under nitrogen) to the azo-compound (II). The solid turned red within 12 hr. when exposed to air but *in vacuo* it was stable indefinitely. On heating in a sealed tube it became red above 100° and decomposed at 180—190°.

(ii) The azo-nitrone (II) (1·26 g.) in dry tetrahydrofuran (150 ml.) was refluxed under a stream of nitrogen for 1 hr. Finely dispersed sodium (0·115 g.) in dry tetrahydrofuran (10 ml.) was added in small quantities, with rapid stirring, during 1 hr. The solution was stirred and refluxed until it turned blue (8—15 hr.), filtered, and evaporated *in vacuo* giving a blue solid whose e.s.r. spectrum was identical with that of the solid prepared in (i), the infrared spectrum being very similar; $\nu_{max.}$ (in Nujol) 1600br, 1180br, and 720 cm.$^{-1}$. The use of glyme as solvent, and ultrasonically dispersed sodium, offered no advantages.

(iii) A colourless solution of the dianion of the leuco-compound (III) was prepared by hydrogenating the azo-nitrone (II) (0·252 g.) in dimethyl sulphoxide (30 ml.) containing 0·1N-potassium t-butoxide in t-butyl alcohol (5 ml.) over platinum oxide (0·1 g.). After removing the catalyst under nitrogen, the solution was treated with an equimolecular quantity of the azo-compound (0·252 g.) when the blue radical-ion (VIII) was formed in solution immediately.

(iv) Thoroughly degassed solutions of the azo-compound (0·126 g.) in dimethyl sulphoxide (15 ml.) and 0·1N-potassium t-butoxide in t-butyl alcohol (2·5 ml.) were mixed *in vacuo* giving a greenish-blue colour which changed to blue on warming. The e.s.r. spectrum of this solution was identical with that of the radical-ion (VIII) produced in (i)—(iii).

(b) *With acids.* (i) The azo-nitrone (II) (1 g.) in 2N-hydrochloric acid (50 ml.) was evaporated to dryness below 50°. The colourless residue obtained gave, on crystallisation from methanol–ether, the dihydrochloride of the leuco-compound (III) as needles, m. p. 203° not depressed on admixture with an authentic sample.

(ii) Hydrogen bromide (10 ml., 48% w/w) was added dropwise to a suspension of the azo-compound (2·52 g.) in water (5 ml.). The solution rapidly became colourless and bromine was evolved. Water (30 ml.) was added and the solution evaporated to dryness below 50°. The residue was crystallised from methanol–ether giving the *dihydrobromide* of the leuco-compound as hygroscopic needles, m. p. 203° (Found: Br, 38·6; N, 13·1. $C_{12}H_{24}Br_2N_4O_2$ requires Br, 38·5; N, 13·5%).

(iii) The azo-nitrone (II) (0·252 g.) in acetic acid (10 ml.) was treated with a solution of hydrogen bromide (0·16 g., 48% w/w) in acetic acid (5 ml.) at room temperature and left for 24 hr. The pale yellow needles which separated were crystallised from acetic acid to give the *azo-nitrone dihydrobromide* (0·13 g.), m. p. 203—204° (Found: C, 34·6; H, 5·6; Br, 38·5; N, 13·5. $C_{12}H_{22}Br_2N_4O_2$ requires C, 34·8; H, 5·3; Br, 38·6; N, 13·5%).

(c) *With copper(I) chloride.* The azo-nitrone (II) (1 g.) suspended in water (70 ml.) was shaken with copper(I) chloride (3 g.) for 30 min. The violet solution so formed was filtered, thoroughly extracted with chloroform and the combined extracts evaporated to give a deep blue crystalline residue (1·1 g.) which crystallised from chloroform–light petroleum (b. p. 50—60°) in blue needles, m. p. 196—197° (Found: C, 37·1; H, 5·3; Cl, 17·8; Cu, 16·7; N, 14·5. $C_{12}H_{21}Cl_2CuN_4O_2$ requires C, 37·2; H, 5·4; Cl, 18·3; Cu, 16·4; N, 14·45%). The hydrochloride of the leuco-compound (III) (0·65 g.) in water (20 ml.) was treated with a solution of copper(II) chloride (2 g.) in water (20 ml.). The violet solution was extracted with chloroform and the extracts evaporated as before to give the copper(I) complex, m. p., mixed m. p., and infrared spectrum identical with that prepared previously. Copper(I) and copper(II) bromides behaved similarly.

Reactions of the Radical-ion (VIII).—(i) *Inhibition of the polymerisation of styrene.* A mixture of azobisisobutyronitrile (0·16 g.) in methanol (2 ml.) and 0·2N-methanolic sodium ethoxide (2 ml.) contained in a dilatometer tube was thoroughly degassed. Styrene monomer (8·0 ml.) and methanol (8·8 ml.), which had both been previously degassed, were distilled from separate graduated vessels into the dilatometer which was then sealed *in vacuo* and placed in a thermostat at 30°. Polymerisation commenced within 20 min. The experiment was repeated with the addition of a methanolic solution of the dihydrochloride of the leuco-compound (III) (2 ml.; 0·05M) to the initial solution. Polymerisation commenced in the blue solution approximately a month later.

(ii) *With quinol.* A solution of the radical-ion (VIII), prepared from the azo-nitrone (II) (0·504 g.) and sodium (*ca.* 0·046 g.), in tetrahydrofuran (100 ml.) was refluxed for 3 hr. under

nitrogen with quinol (0·11 g.). The solvent was removed *in vacuo* and the residue sublimed giving *p*-benzoquinone (0·03 g.), infrared spectrum identical with that of an authentic specimen.

(iii) *With hydrazobenzene.* A solution of the radical-ion (VIII), from the azo-nitrone (II) (0·252 g.) and sodium (*ca.* 0·023 g.), in tetrahydrofuran (60 ml.) was refluxed with hydrazobenzene (0·092 g.) for 1 hr. under nitrogen. The brownish-green solution formed was made just acid with hydrochloric acid and evaporated to dryness. The residue was extracted with acetone, filtered, and the yellowish-red filtrate chromatographed on alumina in light petroleum (b. p. 50—60°) giving azobenzene (0·038 g.), m. p., mixed m. p., and infrared spectrum identical with that of an authentic sample.

(iv) *With oxidising agents.* A solution of the radical-ion (VIII) prepared from the dihydrochloride of the leuco-compound (III) (0·325 g.), in water (5 ml.) and aqueous N-sodium hydroxide (4 ml.) when treated with either aqueous N-iodine (1 ml.) or N-potassium ferricyanide (1 ml.) immediately turned red and the azo-compound (II) separated.

(v) *With reducing agents.* A solution of the radical-ion (VIII) prepared as in (iv) was treated with aqueous sodium dithionite (1 ml., *ca.* 5%). The colourless solution produced slowly turned blue on prolonged exposure to air. Reduction with aqueous ascorbic acid (1 ml., 5%) gave a similar result.

Reaction of leuco-compound (III) *with* p-*benzoquinone.*—A solution of the leuco-compound (0·564 g.) in chloroform (20 ml.) under nitrogen was treated with *p*-benzoquinone (0·432 g.) in chloroform (5 ml.). The solution was kept for 2 hr. before the quinhydrone (0·4 g.), which had separated as green plates, m. p. and mixed m. p. 171°, was collected. The filtrate was evaporated and the residue crystallised from alcohol to give the azo-nitrone (II) (0·51 g.), m. p. and mixed m. p. 203°.

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