Preparation and the Acid- and Base-catalysed Isomerisation of 5,5-Dimethyl-3-phenyl-1-pyrroline 1-Oxide (5,5-Dimethyl-3-phenyl-4,5-dihydro-3*H*-pyrrole 1-Oxide):† Unprecedented Acid-catalysed 1,3-Oxygen Migration[1]

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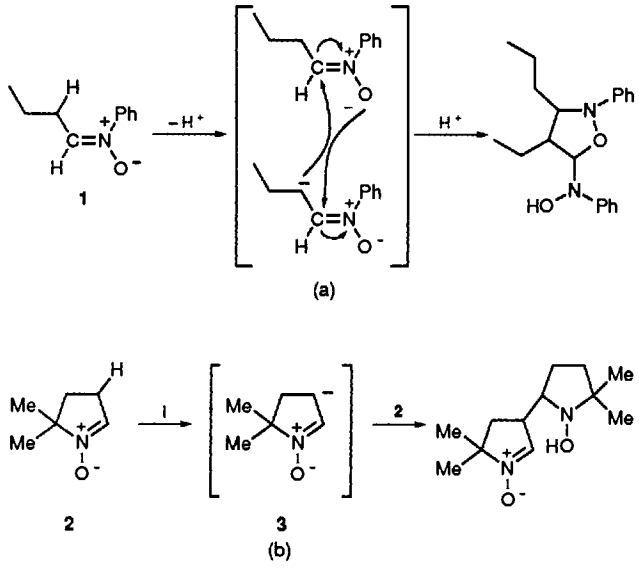
5,5-Dimethyl-3-phenyl-1-pyrroline 1-oxide undergoes acid-catalysed isomerisation to a 3-hydroxy-1-pyrroline in aqueous solution and base-catalysed isomerisation in non-aqueous solution to a pyrrolidin-2-one.

The high polarity of the nitrone functionality increases the acidity of protons β to the C=N⁺(O⁻) bond. Some non-cyclic nitrones such as *C*-propyl-*N*-phenylnitrone **1** spontaneously form isoxazolidines[2] under neutral conditions following an aldol-type dimerisation and subsequent cyclisation [Scheme 1(a)]. This spontaneous dimerisation[3] is rare in the case of cyclic nitrones and with 5,5-dimethyl-1-pyrroline 1-oxide† (DMPO) **2** can only be effected by the removal of a proton at C-3 by a strong base such as sodamide or triphenylmethylsodium to form the carbanion **3** [Scheme 1(b)] which reacts to give 2,3′ coupled aldol-type adducts.[4] In such reactions the nitrone is acting as both nucleophile and electrophile. 1-Pyrroline 1-oxides such as DMPO **2** also undergo deuterium exchange at C-3 when treated with NaOD–D_2O.[5] In this instance the nitrone is the nucleophile while D_2O is the electrophile.

In the course of work[1] designed to functionalise the 3-position of 5,5-dimethyl-1-pyrroline 1-oxide (DMPO), 5,5-dimethyl-3-phenyl-1-pyrroline 1-oxide (DM_3PPO) became an important synthetic target and its synthesis was attempted according to Scheme 2.

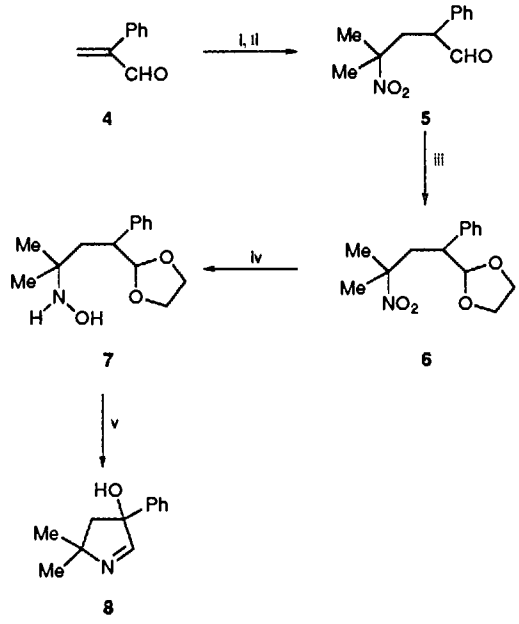


Scheme 1 (b) i, $Ph_3C^-Na^+$ or $NH_2^-Na^+$

Results and Discussion

In the event, attempts to deprotect the hydroxyaminodioxolane **7** with 2 mol dm^{-3} HCl for 16 h did not give the expected 1-pyrroline 1-oxide **9** but rather the isomeric 3-hydroxy-1-pyrroline **8**. The IR spectrum of **8** shows absorption at 3156 (hydroxy) and 1630.1 cm^{-1} (imine). The presence of the imine functionality was confirmed by the ^{13}C NMR spectrum which revealed that C-2 has a shift of 165.3 ppm which is at considerably lower field than expected for an aldo 1-pyrroline 1-oxide[1] and that C-3, with a shift of 88.36 ppm, is bonded to oxygen while the 3/4 π spectrum reveals that C-3 is quaternary. The presence of the hydroxy functionality was confirmed by the ^1H NMR spectrum which showed a broad signal corresponding to one proton which exchanges in D_2O. The ^1H NMR spectrum also shows an AB quartet for the C-4 methylene group and a singlet for the proton on C-2, the lack of couplings to proton on C-3 confirming that this carbon is quaternary. 5,5-Dimethyl-3-phenyl-1-pyrroline 1-oxide **9** was subsequently prepared in low yield by the Zn–NH_4Cl reduction of the γ-nitro aldehyde **5**. The IR spectrum of this compound showed prominent absorption at 1572.2 cm^{-1} from the C=N⁺(O⁻) bond which is characteristic of aldo 1-pyrroline 1-oxides[1] while the ^{13}C NMR spectrum shows an equally characteristic[1]

† Although in the earlier sections of this paper the compounds are, for convenience, described as 1-pyrrolines, the IUPAC-approved names are given in the Experimental section.



Scheme 2 i, Me_2CHNO_2, EtO^-Na^+; ii, HCl_g; iii, ethylene glycol, *p*-TSA, C_6H_6, reflux; iv, Zn, NH_4OAc; v, 0.1 mol dm^{-3} HCl, 16 h

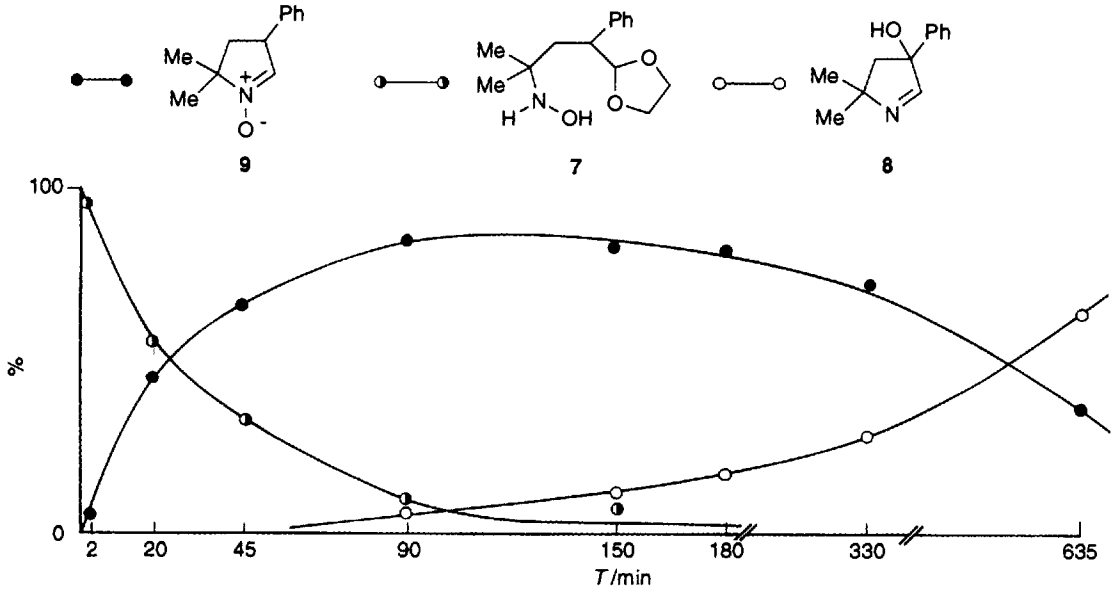
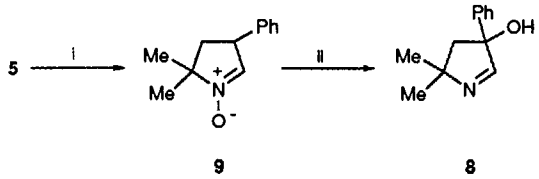


Fig. 1 The course of the acid-catalysed hydrolysis of 4-(dioxolan-2-yl)-2-methyl-4-phenyl-2-hydroxyaminobutane **7** as determined by the ^{1}H NMR analysis of the products of the reaction at various time invervals between 2 and 635 min

signal at 134.0 ppm for C-2. The ^{1}H NMR spectrum shows an AMX spin system for the three protons on C-3 and C-4 and no exchange protons.

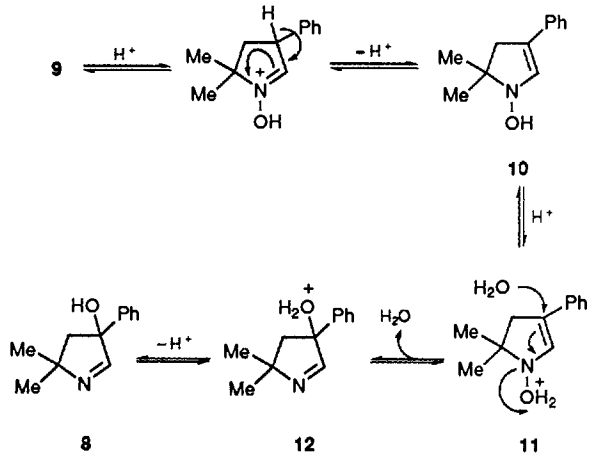
The large differences in the chemical shifts of the *gem*-methyl groups of compounds **7**, **8** and **9** allowed measurement of their concentrations in solutions containing all three. Thus, a solution of hydroxyaminodioxolane **7** in 2 mol dm^{-3} HCl was quenched after various time intervals by the addition of hydrogen carbonate whereupon the ^{1}H NMR spectrum of the product mixture was measured. The data obtained are displayed in Fig. 1 and show that, as expected, the 1-pyrroline 1-oxide **9** is the first product formed from the acid-catalysed hydrolysis of **7** and that there is a subsequent, slower isomerisation of the 1-pyrroline 1-oxide to the 1-pyrroline **8**. This finding was confirmed preparatively by treating the 1-pyrroline 1-oxide **9** with 2 mol dm^{-3} HCl for 16 h whereupon the hydroxypyrroline **8** was isolated in moderate yield (Scheme 3).



Scheme 3 i, Zn, NH_4OAc; ii, 0.1 mol dm^{-3} HCl, 16 h

The acid catalysed isomerisation of a 1-pyrroline 1-oxide to the corresponding 3-hydroxy-1-pyrroline is without precedent and is clearly due to the influence of the phenyl ring in the 3-position. Scheme 4 shows a possible mechanism for the rearrangement.

The tautomerisation of nitrone **9** to the *N*-hydroxy enamine **10** is analogous to keto–enol tautomerisation and can be followed by ^{1}H NMR spectroscopy. Thus, when the 1-pyrroline 1-oxide **9** is treated with D_2O–DCl the signals from the protons attached to C-2, C-3 and C-4 slowly diminish while signals which can be assigned to the pyrroline **8** and to the intermediate *N*-hydroxy enamine **10** increase in intensity over the same period. The spectrum then remains constant suggesting that an equilibrium has been established (Fig. 2). This is confirmed by the observation that the same spectrum is obtained when the hydroxypyrroline **8** is treated with D_2O–DCl (Fig. 2b). Since the *N*-hydroxy enamine **10** is essentially planar the C-4



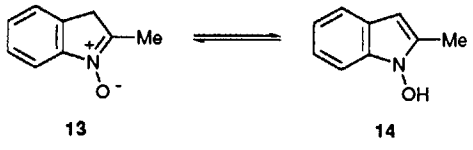
Scheme 4

methylene protons appear as a singlet. Despite the apparent stability of this species at low pH, it was not isolated on basic work-up and, therefore, the equilibrium shown in Scheme 4 appears to move fully to the right as the pH is raised.

The ^{1}H NMR spectra of 1-pyrroline-1-oxides do not usually show signals arising from *N*-hydroxy enamines.[7] The ^{1}H NMR spectrum of DMPO **2** remains unaltered after several days exposure to D_2O–DCl. The stability of the *N*-hydroxy enamine **10** can be attributed to the extended conjugation of the double bond by the phenyl ring. A similar effect has been cited[8] to explain the tautomerisation of the indolenine *N*-oxide **13** to the *N*-hydroxy form **14**; in neutral solution the proportion of **14** increases with solvent polarity.[9]

The exact mechanism by which the nitrone oxygen migrates fron N-1 to give the 3-hydroxy-1-pyrroline **8** is unclear. The reaction possibly proceeds by *O*-protonation of **10** to give the cation **11** which loses water with either synchronous or non-synchronous reaction with water at C-3 to give **12**. The 1-pyrroline 1-oxide **9** is degraded extremely rapidly by the action of aqueous base so that very low yields of **9** were obtained when the acid-catalysed hydrolysis of the hydroxyaminodioxolane **7** was quenched by adding sodium hydroxide to the reaction mixture to bring it to pH 13–14. Good yields were only obtained

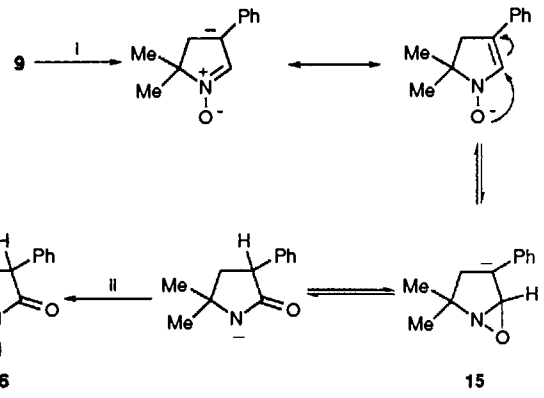
Fig. 2 (a) The ^{1}H NMR spectrum of the 1-pyrroline 1-oxide **9** in D_2O–DCl. (b) The ^{1}H NMR spectrum of the 1-pyrroline **8** in D_2O–DCl.



13 **14**

upon mild basicification by the addition of a slight excess of hydrogen carbonate. The destruction of **9** by the action of aqueous base was too rapid to follow by ^{1}H NMR in D_2O–NaOD nor were any of the products of this degradation identified. However, when the 1-pyrroline 1-oxide **9** was treated with base in non-aqueous solution in order to effect dimerisation as shown in Scheme 1, the sole product isolated was the pyrrolidin-2-one **16**. The IR spectrum of **16** showed strong absorption at 1693 cm^{-1}, consistent with the carbonyl stretch of a γ-lactam. The ^{13}C NMR spectrum showed signals from six non-phenyl carbons including the amide carbon at 169 ppm and the ^{1}H NMR spectrum showed an AMX pattern for the protons attached to C-3 and C-4.

The rearrangement of nitrones to amides is well known and can be effected with electrophiles such as acid anhydrides,[10] acyl halides[11] and sulfonyl chlorides[12] as well as with nucleophiles such as alkoxide anions.[13] The trityl anion is a poor nucleophile but is a strong base capable of removing a proton from C-3 of 1-pyrroline 1-oxides.[4] Removal of this proton from **9** gives the anion of the *N*-hydroxy enamine **10** (Scheme 5) which appears to undergo oxygen migration, possibly *via* the oxaziridine intermediate **15**. No dimeric product was formed, probably for steric reasons. The pyrrolidin-2-one **16** was also isolated in low yield during the basic (hydrogen carbonate) work-up of 1-pyrroline 1-oxide **9**, suggesting that the isomerisation of **9** to **16** is one of the degradation pathways when **9** is treated with aqueous base

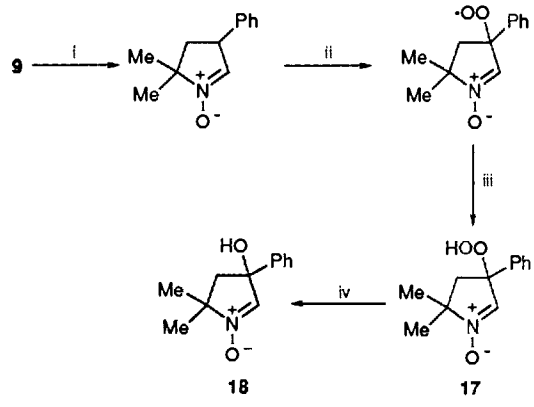


Scheme 5 i, $Ph_3C^-Na^+$; ii, H_2O

although the lactam was never isolated when **9** was degraded with strong aqueous base.

3-Hydroxy-5,5-dimethyl-3-phenyl-1-pyrroline 1-oxide **18** was also isolated in very low yield from the liquors from the recrystallisation of the nitrone **9**. The IR spectrum of **18** showed strong absorption at 3127 (hydroxy) and 1583.8 cm^{-1} [C=N$^+$(O$^-$), aldo 1-pyrroline 1-oxide]. The ^{1}H NMR spectrum showed an AB quartet for the C-4 methylene and a singlet for the proton on C-2 showing that C-3 was quaternary. There was also a broad, exchangeable signal integrating for one proton from the hydroxy group. The ^{13}C NMR spectrum showed a signal at 136.7 ppm which is characteristic of an aldo 1-pyrroline 1-oxide.[1] The 3/4 π spectrum showed that C-3 was quaternary while a chemical shift of 77.89 ppm for this carbon is consistent with an attached oxygen.

The hydroxy nitrone **18** is probably formed *via* the minor autoxidation of the nitrone **9** with subsequent base-catalysed reduction of the intermediate hydroperoxide **17** to the alcohol. The possibility that the product was the hydroperoxide **17** is



Scheme 6 i, oxidation; ii, O_2; iii, reduction, H^+; iv, base

discounted by the electron impact mass spectrum which shows a weak mass ion at *m/z* 205, while the NH_3 chemical ionisation mass spectrum shows a strong M + 1 peak at *m/z* 206. *C*-Benzyl nitrones have been shown to undergo autoxidation at the benzyl carbon[14] while a 2,3-diphenyl-1-pyrroline undergoes autoxidation to the stable 3-hydroperoxide during recrystallisation from oxygenated hexane.[15] Attempts to prepare the hydroxy nitrone **18** by treating the nitrone **9** with oxygen in aqueous methanol in the presence of the cupprammonium ion were unsuccessful.

In conclusion, it has been shown that 5,5-dimethyl-3-phenyl-1-pyrroline 1-oxide **9** displays a very different pattern of reactivity when compared with 5,5-dimethyl-1-pyrroline 1-oxide **2**. Activation at C-3 by the phenyl ring renders the 1-pyrroline 1-oxide ring system liable to degradation in aqueous

base and leads to isomerisation by oxygen migration in both aqueous acid and non-aqueous base.

Experimental

For details concerning instrumentation see previous paper in this series.[1]

4-Methyl-4-nitro-2-phenylpentanal **5**.—To a vigorously stirred solution of sodium (0.80 g, 35 mmol) and 2-nitropropane (7.99 g, 90 mmol) in absolute alcohol (100 cm^3) was added, with vigorous stirring over 45 min, 2-phenylpropenol[6] (9.87 g, 75 mmol) in absolute alcohol (50 cm^3). After completion of the addition, glacial acetic acid (3 cm^3) was added to the solution which was then concentrated under reduced pressure to give a semisolid mass. This was treated with a mixture of hexane–ether (50:50; 50 cm^3) with shaking and the insoluble sodium acetate was collected. The filtrate was concentrated to an oil which was distilled to give the title aldehyde **5** (14.61 g, 88%) as an orange oil, b.p. 156–160 °C at 1.0 mmHg (Found: M + NH_4, 239.1396. $C_{12}H_{19}N_2O_3$ requires M + NH_4, 239.1396) [m.p. of 2,4-dinitrophenylhydrazone (from EtOH) 172–173 °C (Found: C, 53.9; H, 4.6; N, 17.5. $C_{18}H_{19}N_5O_6$ requires C, 53.9; H, 4.8; N, 17.4%)]; ν_{max}/cm^{-1} 2720, 1725, 1539, 1454 and 702; δ_H 1.53, 1.56 (both 3 H, s, 2 × CH_3), 2.29 (1 H, dd, J 15.0 and 6.0, 3-H), 2.99 (1 H, dd, J 15.0 and 6.0, 3′-H), 3.65 (1 H, td, J 6.0, 6.0 and 1.1, 2-H), 7.28–7.42 (5 H, m, Ph) and 9.59 (1 H, d, J 1.1, 1-H); δ_C 26.02q, 27.76q (2 × CH_3), 39.19d (C-2), 55.00t (C-3), 87.47s (C-4), 128.1d, 128.6d, 129.3d, 135.3s (Ph) and 197.8d (CO); m/z (EI) 175 (M − NO_2, 6%), 131 (23), 105 (100), 91 (68) and 77 (58); m/z (NH_3 chemical ionisation) 239 (M^+ + 18, 75%) and 161 (100).

4-(Dioxolan-2-yl)-2-methyl-2-nitro-4-phenylbutane **6**.—A solution of the pentanal **5** (69.71 g, 0.315 mol) in benzene (150 cm^3) was washed with water (50 cm^3) then dried ($MgSO_4$) and filtered. Ethylene glycol (22.0 g, 0.35 mol) and toluene-*p*-sulfonic acid (1.0 g) were added to the filtrate and the mixture was heated at reflux with the continual removal of water under Dean–Stark conditions. Once formation of water had ceased the cooled reaction mixture was washed successively with saturated aqueous sodium hydrogen carbonate (50 cm^3) and water (50 cm^3) and then dried ($MgSO_4$) and concentrated to a dark oil which was distilled to give the title dioxolane **6** (50.98 g, 61%) as a colourless oil, b.p. 120–127 °C at 0.2 mmHg (Found: C, 63.8; H, 7.2; N, 5.0. $C_{14}H_{19}NO_4$ requires C, 63.4; H, 7.2; N, 5.3%) (Found: M^+ + 1, 266.1392. $C_{14}H_{20}NO_4$ requires M + 1, 266.1392); ν_{max}/cm^{-1} 1541, 1127 and 702; δ_H 1.44, 1.47 (both 3 H, s, 2 × CH_3), 2.44 (1 H, dd, J 14.7 and 10.0, 3-H), 2.58 (1 H, dd, J 14.7 and 2.8, 3′-H), 2.92 (1 H, ddd, J 14.7, 2.8 and 4.0, 4-H), 3.80–3.93 (4 H, m, OCH_2CH_2O), 4.93 (1 H, d, J 4.0, O-CH-O) and 7.26–7.37 (5 H, m, ArH); δ_C 25.84q, 26.88q (2 × CH_3), 40.06t (C-3), 46.07d (C-4), 65.04t, 65.14t (OCH_2CH_2O), 87.96s (C-2), 106.3d (O-C-O) and 127.2d, 128.4d, 128.9d and 139.2s (ArH); m/z (EI) 219 (M^+ − NO_2, 10%) and 73 (100); m/z (NH_3 chemical ionisation) 283 (M^+ + NH_4, 45%), 266 (M^+ + 1, 15%), 219 (95) and 73 (100).

4-(Dioxolan-2-yl)-2-hydroxyamino-2-methyl-4-phenylbutane **7**.—A mixture of the nitrodioxolane **6** (22.63 g, 0.085 mol), THF (150 cm^3), ammonium chloride (9.3 g) and water (50 cm^3) was cooled to 0 °C. Zinc dust (33.0 g, 0.50 mol) was added slowly with vigorous stirring over 2 h to the reaction mixture so that its temperature did not exceed 5 °C; stirring was then continued for a further 2 h. The zinc salts were collected and washed with warm THF (50 °C; 2 × 50 cm^3) and the combined filtrate and washings were reduced to 100 cm^3 and diluted with chloroform (80 cm^3) to give a precipitate which was collected. The aqueous phase of the filtrate was separated and extracted with chloroform (2 × 50 cm^3). The combined organic phases were dried ($MgSO_4$) and reduced to afford an oil which was shaken with dry ether (15 cm^3) and cooled overnight to −20 °C to afford crystals which were collected. This process was repeated twice and the crude product was recrystallised from hexane to give the title hydroxylamine **7** (7.06 g, 33%) as microcrystals, m.p. 85.5–86.0 °C (Found: C, 66.9; H, 8.7; N, 5.7. $C_{14}H_{21}NO_3$ requires C, 66.9; H, 8.4; N, 5.6%) (Found: M^+ + 1, 252.1600. $C_{14}H_{22}NO_3$ requires M + 1, 252.1600); ν_{max}/cm^{-1} 1603, 1495, 1451 and 700; δ_H 0.96, 1.03 (both 3 H, s, 2 × CH_3), 1.89 (1 H, dd, J 14.5 and 8.8, 3-H), 2.13 (1 H, dd, J 14.5 and 2.7, 3′-H), 3.10 (1 H, ddd, J 8.8, 2.7 and 4.6), 3.81–3.97 (4 H, m, OCH_2CH_2O), 3.96 (1 H, d, J 4.6 O-CH-O), 5.08 (2 H, br s, NH. OH) and 7.21–7.34 (5 H, m, ArH); δ_C 24.49q, 25.38q (2 × CH_3), 37.79t (C-3), 45.34d (C-4), 57.54 (C-2), 65.01t, 65.06t (OCH_2CH_2O), 107.3d (O-CH-O) and 126.7d, 128.3d, 138.0d and 141.9s (ArH); m/z (EI) 252 (M^+ + 1, 2%), 178 (35) and 73 (100); m/z (NH_3 chemical ionisation) 252 (M^+ + 1, 100%).

5,5-Dimethyl-3-phenyl-4,5-dihydro-3H-pyrrole 1-Oxide **9**.—(i) *By reduction of the γ-nitro aldehyde* **5**. A mixture of the γ-nitro aldehyde **5** (10.78 g, 48 mmol) THF (40 cm^3), water (12 cm^3) and ammonium chloride (2.1 g) was treated with zinc dust (15.0 g, 230 mmol) as for the nitrodioxolane **6**. The crude product was an orange gum which when shaken with ether (5 cm^3) gave the title nitrone **9** (0.70 g, 8%) as microcrystals, recrystallised from ether, m.p. 99–100 °C (Found: M^+ + 1, 190.123. $C_{12}H_{16}NO$ requires M + 1, 190.123); ν_{max}/cm^{-1} 1572, 1227, 764 and 702; δ_H 1.51, 1.53 (both 3 H, s, 2 × CH_3), 2.02 (1 H, dd, J 13.0 and 8.2, 4-H), 2.69 (1 H, dd, J 13.0 and 8.8, 4′-H), 4.13 (1 H, 1 H, m, J 8.2, 8.8, 2.4, 3-H), 6.90 (1 H, d, J 2.4, 2-H) and 7.21–7.41 (5 H, m, ArH); δ_C 24.86t, 26.02t, (2 × CH_3), 42.64d (C-3), 44.53t (C-4), 74.16s (C-5), 126.8d, 127.7d, 128.7d, 140.5s (ArH) and 134.0d (C-2); m/z (EI) 191 (M^+ + 2, 7%), 190 (M^+ + 1, 56%), 189 (M^+, 20%), 159 (88), 117 (82), 104 (89) and 103 (100); m/z (NH_3 chemical ionisation) 190 (M^+ + 1, 100%).

(ii) *By acid-catalysed hydrolysis of the γ-hydroxyaminodioxolane* **7**. A solution of the hydroxyaminobutane **7** (0.354 g, 1.45 mmol) in hydrochloric acid (2 mol dm^{-3}; 14.5 cm^3) was neutralised after 110 min with sodium hydrogen carbonate and the solution was immediately extracted with chloroform (2 × 30 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to afford a solid which gave the title nitrone **9** (0.170 g, 62%) as needles from ether.

3-Hydroxy-5,5-dimethyl-3-phenyl-4,5-dihydro-3H-pyrrole **8**.—A solution of the hydroxyaminobutane **7** (0.595 g, 2.37 mmol) was treated with HCl as for the nitrone **9** except that the reaction time was 16 h and the product was recrystallised from hexane to give the title compound (0.323 g, 72%) as microcrystals, m.p. 113–113.5 °C (Found: C, 75.9; H, 8.0; N, 7.6. $C_{12}H_{15}NO$ requires C, 76.2; H, 8.0; N, 7.6%) (Found M^+ + 1, 190.1232. $C_{12}H_{16}NO$ requires M + 1, 190.1232); ν_{max}/cm^{-1} 3156, 1630, 756 and 696; δ_H 1.27, 1.35 (both 3 H, s, 2 × CH_3), 2.03 (1 H, d, J 14.0, 4-H), 2.16 (1 H, d, J 14.0, 4′-H), 4.65 (1 H, br s, OH), 7.24–7.40 (5 H, m, ArH) and 7.26 (1 H, s, 2-H); δ_C 29.90q, 29.18q (2 × CH_3), 53.14t (C-4), 73.78s (C-5), 88.36s (C-3), 124.8d, 127.8d, 128.5d, 144.1s (ArH) and 165.3d (C-2); m/z (EI) 162 (60%), 147 (100), 105 (40) and 77 (42); m/z (NH_3 chemical ionisation) 190 (M^+ + 1, 100%).

5,5-Dimethyl-3-phenylpyrrolidin-2-one **16**.—To triphenylmethyl chloride (0.965 g, 3.46 mmol) in dry ether (20 cm^3) was added butyllithium (2.5 mol dm^{-3}; 1.0 cm^3, 2.5 mmol) with stirring under nitrogen. The temperature was allowed to rise to room temperature whereupon a deep red colour developed. The

1-pyrroline 1-oxide **9** (0.473 g, 2.50 mmol) in ether (20 cm^3) was added dropwise over 15 min to the mixture which then, over a period of 1.5 h, became colourless. The reaction mixture was concentrated and subjected to preparative TLC [silica, $CHCl_3$–MeOH (1 : 1) as eluent] to give the title compound which was recrystallised from ether to afford plates, m.p. 167–169 °C (Found: C, 76.6; H, 8.1; N, 7.6. $C_{12}H_{15}NO$ requires C, 76.2; H, 8.0; N, 7.4%); ν_{max}/cm^{-1} 3432, 1694 and 743; δ_H 1.22, 1.25 (both 3 H, s, 2 × CH_3), 1.81 (1 H, dd, *J* 12.8 and 9.3, 4-H), 2.34 (1 H, dd, *J* 12.8 and 9.3, 4'-H), 3.66 (1 H, t, *J* 9.3, 3-H) and 7.14–7.29 (5 H, m, ArH); δ_C 24.15q, 26.72q (2 × CH_3), 41.34t (C-4), 43.95d (C-3), 59.78s (C-5), 127.1d, 127.9d, 128.7d, 139.3s (ArH) and 169.5d (C=O); *m/z* (EI) 125 (2%), 81 (38) and 77 (100); *m/z* (NH_3 chemical ionisation) 207 ($M^+ + NH_4$, 100%), 190 ($M^+ + 1$0%) and 143 (98).

3-Hydroxy-5,5-dimethyl-3-phenyl-4,5-dihydro-3H-pyrrole 1-Oxide **18**.—This nitrone was isolated in very low yield from the liquors of recrystallisation of the 1-pyrroline 1-oxide **9**, m.p. 150–151 °C (Found: $M^+ + 1$, 206.1181. $C_{12}H_{16}NO_2$ requires $M + 1$, 206.1181); ν_{max}/cm^{-1} 3395, 3127, 1584, 764 and 702; δ_H 1.33, 1.49 (both 3 H, s, 2 × CH_3), 2.28 (1 H, d, *J* 12.1, 4-H), 2.52 (1 H, d, *J* 12.1, 4'-H), 4.79 (1 H, br s, OH), 6.88 (1 H, s, 2-H) and 7.20–7.34 (5 H, m, ArH); δ_C 26.49q, 26.55q (2 × CH_3), 52.12t (C-4), 74.76s (C-5), 77.89s (C-3), 124.7d, 127.8d, 128.6d, 144.1s (ArH) and 136.7d (C-2); *m/z* (EI) 206 ($M^+ + 1$, 2%), 190 (17), 175 (28), 105 (100), 91 (25) and 77 (60); *m/z* (NH_3 chemical ionisation) 206 ($M^+ + 1$, 100%), 190 (38) and 187 (35).

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