

Stereochemistry of the Tetrahydroquinolines from the Condensation of Methylaniline and Glycolaldehyde

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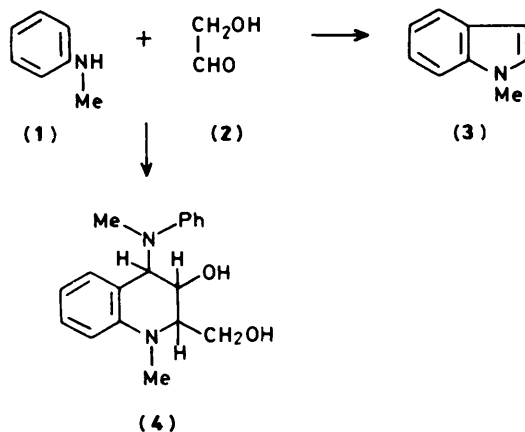
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N-Methylaniline reacts with hydroxyethanal in ethanol at 20 °C to give 3 α -hydroxy-2 α -hydroxymethyl-1-methyl-4 β -(*N*-methylanilino)-1,2,3,4-tetrahydroquinoline (**6**), the structure of which has been established by *X*-ray crystal structure analysis. The heterocyclic ring adopts a C₃-sofa conformation in which the methylanilino residue and the hydroxy group are equatorial and the hydroxymethyl group is axial. The diol (**6**) readily undergoes thermal or acid-catalysed elimination of methylaniline to give the bridged tetrahydroquinoline (**9**).

Formation of *N*-methylindole (**3**) from methylaniline (**1**) and hydroxyethanal (**2**) in hot aqueous ethanol was first reported by Harley-Mason.¹ It was subsequently shown that the indole was not formed when the reaction was carried out at room temperature,² instead, a dimeric diol was obtained in 45% yield. The tetrahydroquinoline structure (**4**; without stereochemistry) was assigned² to this diol by analogy with related Doebner-Miller intermediates (**5**) isolated by Zalukaev and Spitsina^{3,4} from the reaction of ethanal with aniline derivatives. Spectral data, particularly the proton n.m.r. spectra, were in accord with the structure (**4**), but did not allow complete determination of the stereochemistry of the substituents in the heterocyclic ring. We now report the crystal structure analysis of this diol which reveals the stereochemistry depicted in formula (**6**).



The structure analysis of the diol (**6**) was carried out by *X*-ray diffraction and the relevant crystal data are reported in the Experimental section. The molecular structure is shown in Figure 1 and the atomic co-ordinates are listed in Table 1. The bond lengths, valency angles and torsion angles are given in Tables 2–4. Two intermolecular hydrogen bonds are present in the crystal and details are given in Table 5.

The heterocyclic ring has a slightly distorted sofa conformation in which the hydroxymethyl group at C-2(α) is axial, the hydroxy group at C-3(α) is equatorial, and the methylanilino residue at C-4(β) is also equatorial. The diol (**6**) gives a diacetate (**7**) upon acetylation with acetic anhydride in pyridine. Its ¹H n.m.r. spectrum (Figure 2) shows a 5-proton aliphatic

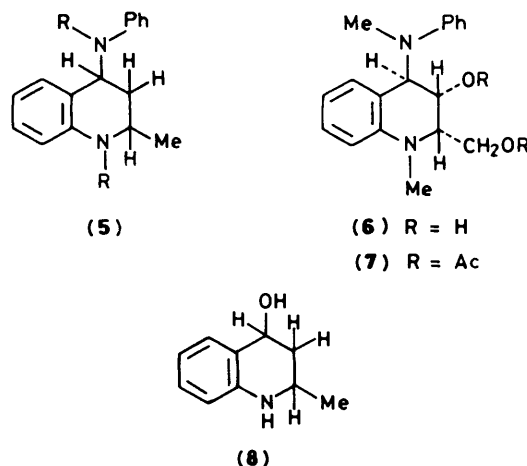


Table 1. Fractional atomic co-ordinates (10^4) with e.s.d.s

N(1)	8 010(3)	0 387(6)	2 292(2)
C(2)	6 956(4)	1 844(7)	2 080(2)
C(3)	7 238(4)	3 615(7)	2 588(2)
C(4)	7 624(4)	2 569(7)	3 243(2)
C(4A)	8 810(4)	1 304(7)	3 419(2)
C(5)	9 743(5)	1 125(8)	4 046(2)
C(6)	10 809(5)	-0 025(10)	4 207(3)
C(7)	10 940(5)	-1 034(9)	3 731(3)
C(8)	10 033(4)	-0 910(8)	3 097(3)
C(8A)	8 938(4)	0 255(7)	2 924(2)
C(9)	8 060(7)	-0 985(10)	1 802(3)
C(10)	5 728(5)	0 655(8)	1 867(2)
O(11)	5 713(3)	-0 686(5)	2 352(2)
O(12)	6 205(3)	5 012(5)	2 380(2)
N(13)	7 712(3)	4 071(6)	3 732(2)
C(14)	8 518(7)	5 929(10)	3 856(3)
C(15)	7 189(4)	3 651(7)	4 123(2)
C(16)	7 255(5)	5 183(10)	4 578(3)
C(17)	6 689(7)	4 835(14)	4 952(3)
C(18)	6 045(5)	2 984(14)	4 904(3)
C(19)	5 980(5)	1 443(11)	4 469(3)
C(20)	6 546(5)	1 749(8)	4 093(2)

system with the benzylic proton (C-4) as a doublet ($J = 11$ Hz) at δ 5.30, the acetoxymethine proton (C-3) as a double doublet ($J = 11$ and 5 Hz) at δ 5.60, the C-2 proton as a multiplet at δ

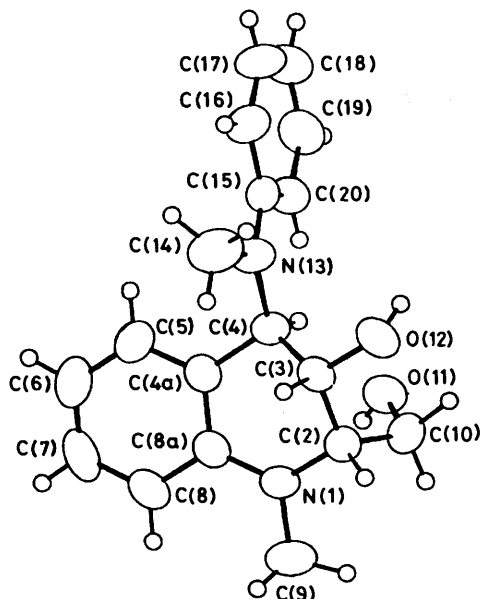


Figure 1. The atomic arrangement in the diol (6)

Table 2. Bond lengths (Å) with e.s.d.s

N(1)–C(2)	1.451(6)	C(6)–C(7)	1.359(9)
N(1)–C(8A)	1.380(5)	C(7)–C(8)	1.376(8)
N(1)–C(9)	1.461(7)	C(8)–C(8A)	1.395(6)
C(2)–C(3)	1.543(6)	C(10)–O(11)	1.423(6)
C(2)–C(10)	1.522(7)	N(13)–C(14)	1.453(7)
C(3)–C(4)	1.531(6)	N(13)–C(15)	1.369(5)
C(3)–O(12)	1.410(5)	C(15)–C(16)	1.409(7)
C(4)–C(4A)	1.517(6)	C(15)–C(20)	1.402(7)
C(4)–N(13)	1.449(6)	C(16)–C(17)	1.367(9)
C(4A)–C(5)	1.376(6)	C(17)–C(18)	1.368(12)
C(4A)–C(8A)	1.409(6)	C(18)–C(19)	1.379(10)
C(5)–C(6)	1.367(8)	C(19)–C(20)	1.368(8)
C(2)–H(2)	0.993(47)	C(10)–H(10B)	1.081(47)
C(3)–H(3)	1.026(44)	O(11)–H(11)	0.837(66)
C(4)–H(4)	0.956(45)	O(12)–H(12)	0.922(40)
C(5)–H(5)	0.937(46)	C(14)–H(14A)	1.027(61)
C(6)–H(6)	0.915(44)	C(14)–H(14B)	0.991(58)
C(7)–H(7)	0.903(48)	C(14)–H(14C)	0.888(64)
C(8)–H(8)	0.963(43)	C(16)–H(16)	0.853(49)
C(9)–H(9A)	1.015(58)	C(17)–H(17)	0.901(48)
C(9)–H(9B)	1.047(56)	C(18)–H(18)	0.922(45)
C(9)–H(9C)	0.862(64)	C(19)–H(19)	0.962(50)
C(10)–H(10A)	0.975(45)	C(20)–H(20)	0.911(46)

3.69, and the methylene protons as a distinct and well-separated double AB system centred at δ 4.38. Restricted rotation of the acetoxymethyl group in this highly hindered molecule is evident in molecular models. Decoupling experiments leading to the above assignments are reproduced in Figure 2.

The diol (6) readily loses a molecule of methylaniline when heated to its melting point, but gives a product in which the tetrahydroquinoline structure is retained, in contrast to the behaviour of Zalukaev's intermediates of type (5), which also undergo thermal elimination of aniline but give quinolines and dihydroquinolines⁴ or are converted into 'pseudo-bases' of type (8).⁵ The compound obtained by elimination of methylaniline from the diol (6) is formulated as the bridged alcohol (9). Its n.m.r. spectrum showed 4 aromatic protons, a single *N*-methyl group, and a 5-proton aliphatic system (Figure 3) as in that of the precursor diol (6) but showing much less coupling. Both

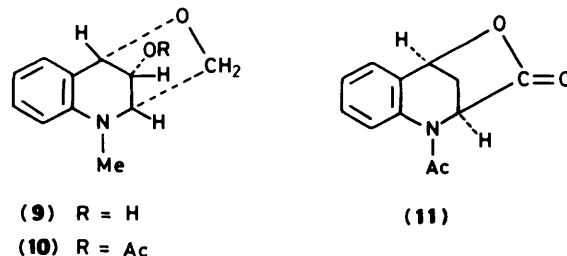


Table 3. Valency angles (°)

C(8A)–N(1)–C(2)	123.0(4)	C(9)–N(1)–C(2)	117.0(4)
C(3)–C(2)–N(1)	110.2(3)	C(10)–C(2)–N(1)	112.1(4)
C(9)–N(1)–C(8A)	120.0(4)	C(4A)–C(8A)–N(1)	120.8(4)
C(8)–C(8A)–N(1)	121.6(4)	C(10)–C(2)–C(3)	115.3(4)
C(4)–C(3)–C(2)	109.1(3)	O(12)–C(3)–C(2)	109.7(3)
O(11)–C(10)–C(2)	113.8(4)	O(12)–C(3)–C(4)	114.2(3)
C(4A)–C(4)–C(3)	107.1(3)	N(13)–C(4)–C(3)	113.5(3)
N(13)–C(4)–C(4A)	114.5(4)	C(5)–C(4A)–C(4)	121.9(4)
C(8A)–C(4A)–C(4)	118.5(4)	C(14)–N(13)–C(4)	117.6(4)
C(15)–N(13)–C(4)	121.9(4)	C(8A)–C(4A)–C(5)	119.6(4)
C(6)–C(5)–C(4A)	122.0(5)	C(8)–C(8A)–C(4A)	117.6(4)
C(7)–C(6)–C(5)	118.6(5)	C(8)–C(7)–C(6)	121.6(5)
C(8A)–C(8)–C(7)	120.6(5)	C(15)–N(13)–C(14)	120.0(4)
C(16)–C(15)–N(13)	120.3(4)	C(20)–C(15)–N(13)	123.5(4)
C(20)–C(15)–C(16)	116.1(4)	C(17)–C(16)–C(15)	121.2(6)
C(19)–C(20)–C(15)	121.6(5)	C(18)–C(17)–C(16)	121.5(7)
C(19)–C(18)–C(17)	118.5(6)	C(20)–C(19)–C(18)	121.0(6)

the benzylic proton (C-4) at δ 4.53 and the hydroxymethine proton (C-5) at δ 4.67 appear as singlets, showing that the hydroxymethine proton is orthogonal to both of the adjacent protons. This is in accord with dihedral angles measured on a Dreiding model of the bridged alcohol. Furthermore, one of the protons of the bridging methylene group is also orthogonal to the C-6 proton. That it was a secondary alcohol was evident from the downfield shift of the one-proton singlet from δ 4.67 to δ 5.60 upon acetylation with acetic anhydride to the monoacetate (10). The chemical shift of the benzylic proton (δ 4.53 in the alcohol and δ 4.73 in the acetate) compares favourably with that reported⁶ for the bridged lactone (11) derived from kynurenic acid (δ 4.85). Other spectral data were in accord with the epoxymethanoquinoline structure (9), with an *exo*-hydroxy group.

Formation of the bridged tetrahydroquinoline (9) by pyrolysis of the diol (6) is due to participation of the neighbouring primary hydroxy group in the displacement of the methylanilino residue [(12), Figure 4]. The stereochemistry of the diol (6) explains the ready loss of methylaniline, as the oxygen atom of the axial hydroxymethyl group at C-2 is ideally situated to assist in the displacement of the methylaniline residue at C-4. Acid catalysis of the elimination of methylaniline was also observed. Complete conversion to the bridged alcohol (9) was rapid at concentrations of hydrochloric acid down to 5mM, but at 0.5mM the half-life of the diol (6) was approximately 10 min at 20 °C. As a preparative method this was much cleaner than the pyrolysis, as no decomposition occurred.

The formation of both indoles and tetrahydroquinolines from methylaniline and glycolaldehyde can be explained by a mechanism in which the primary adduct (13) undergoes dehydration to the enaminal (14) as depicted in the Scheme. In concentrated solution intermolecular reaction would occur by a nucleophilic attack of the enaminal (14) upon the primary

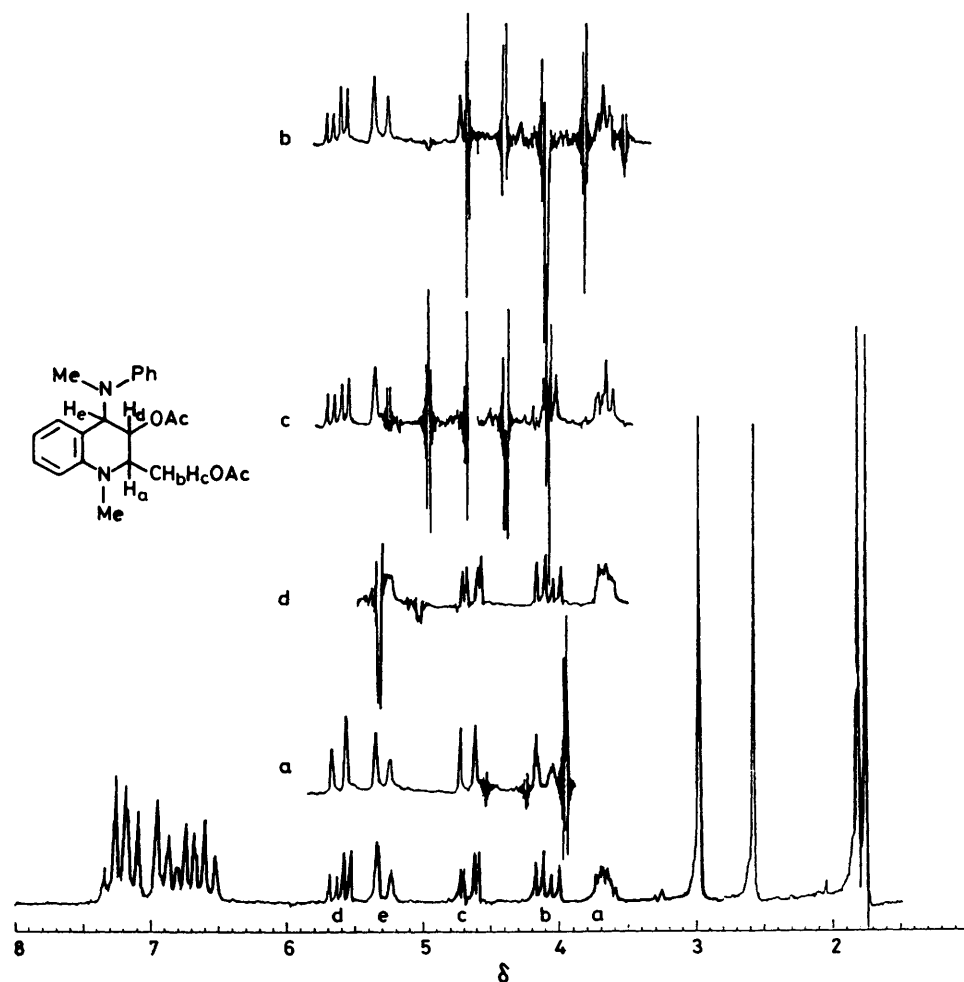


Figure 2. ^1H N.m.r. spectrum of the diacetate (7) with spin decoupling of aliphatic protons

Table 4. Torsion angles ($^\circ$) with e.s.d.s

C(8A)-N(1)-C(2)-C(3)	17.5(5)	C(8A)-N(1)-C(2)-C(10)	-112.2(5)
C(9)-N(1)-C(2)-C(3)	162.7(4)	C(9)-N(1)-C(2)-C(10)	67.6(5)
C(2)-N(1)-C(8A)-C(4A)	9.9(6)	C(2)-N(1)-C(8A)-C(8)	-170.0(4)
C(9)-N(1)-C(8A)-C(4A)	-169.9(4)	C(9)-N(1)-C(8A)-C(8)	10.2(7)
N(1)-C(2)-C(3)-C(4)	-53.7(4)	N(1)-C(2)-C(3)-O(12)	-179.5(3)
C(10)-C(2)-C(3)-C(4)	74.4(5)	C(10)-C(2)-C(3)-O(12)	-51.5(5)
N(1)-C(2)-C(10)-O(11)	57.9(5)	C(3)-C(2)-C(10)-O(11)	-69.2(5)
C(2)-C(3)-C(4)-C(4A)	62.1(4)	C(2)-C(3)-C(4)-N(13)	-170.5(3)
O(12)-C(3)-C(4)-C(4A)	-174.7(3)	O(12)-C(3)-C(4)-N(13)	-47.2(5)
C(3)-C(4)-C(4A)-C(5)	145.0(5)	C(3)-C(4)-C(4A)-C(8A)	-36.2(5)
N(13)-C(4)-C(4A)-C(5)	18.2(6)	N(13)-C(4)-C(4A)-C(8A)	-163.1(4)
C(3)-C(4)-N(13)-C(14)	-55.0(5)	C(3)-C(4)-N(13)-C(15)	133.0(4)
C(4A)-C(4)-N(13)-C(14)	68.5(5)	C(4A)-C(4)-N(13)-C(15)	-103.5(5)
C(4)-C(4A)-C(5)-C(6)	179.6(5)	C(8A)-C(4A)-C(5)-C(6)	0.8(7)
C(4)-C(4A)-C(8A)-N(1)	0.5(6)	C(4)-C(4A)-C(8A)-C(8)	-179.6(4)
C(5)-C(4A)-C(8A)-N(1)	179.2(4)	C(5)-C(4A)-C(8A)-C(8)	-0.9(6)
C(4A)-C(5)-C(6)-C(7)	-0.6(8)	C(5)-C(6)-C(7)-C(8)	0.4(9)
C(6)-C(7)-C(8)-C(8A)	-0.5(8)	C(7)-C(8)-C(8A)-N(1)	-179.4(5)
C(7)-C(8)-C(8A)-C(4A)	0.7(7)	C(4)-N(13)-C(15)-C(16)	-177.7(4)
C(4)-N(13)-C(15)-C(20)	0.9(6)	C(14)-N(13)-C(15)-C(16)	10.5(7)
C(14)-N(13)-C(15)-C(20)	-170.9(5)	N(13)-C(15)-C(16)-C(17)	176.9(5)
C(20)-C(15)-C(16)-C(17)	-1.8(8)	N(13)-C(15)-C(20)-C(19)	-176.4(5)
C(16)-C(15)-C(20)-C(19)	2.3(7)	C(15)-C(16)-C(17)-C(18)	0.5(10)
C(16)-C(17)-C(18)-C(19)	0.4(11)	C(17)-C(18)-C(19)-C(20)	0.1(10)
C(18)-C(19)-C(20)-C(15)	-1.4(9)		

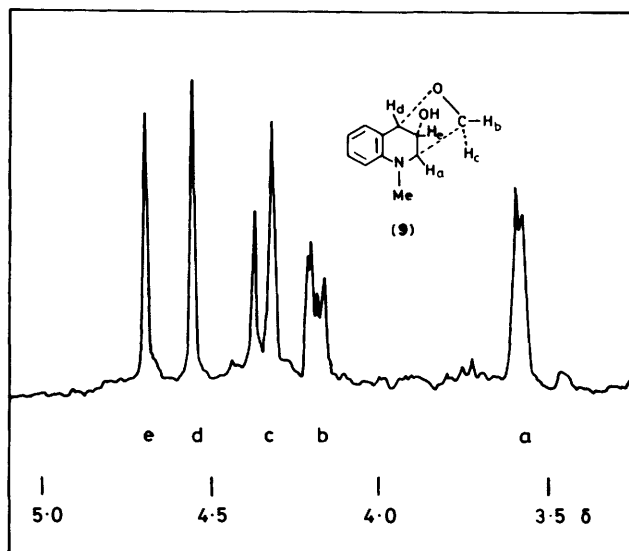


Figure 3.

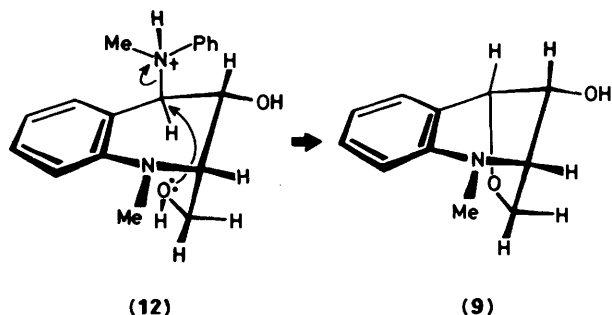
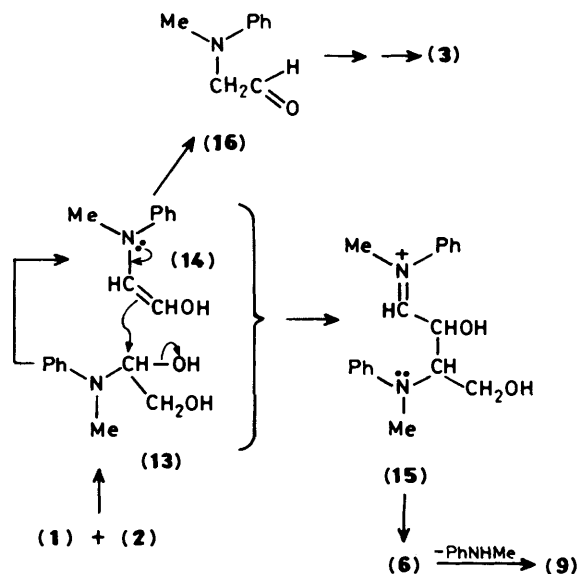


Figure 4.

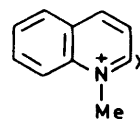


Scheme.

adduct (13) to give the dimeric intermediate (15), which would cyclise readily to the tetrahydroquinoline (6). The enamine mechanism for the linkage of the two hydroxyethanol units could be a general one for the formation of quinoline derivatives

by reaction of anilines with saturated aldehydes and ketones, so that these reactions need not involve the once commonly-invoked 'dimerisation' of the carbonyl component to an α,β -unsaturated aldehyde or ketone prior to nucleophilic attack by the aromatic amine.^{7,8} In more dilute solution there would be more time for the enaminol (14) to tautomerise to the aldehyde (16), a likely precursor of the *N*-methylindole (3) obtained by Harley-Mason.¹

In the mass spectra of these bridged tetrahydroquinolines the parent ions are generally weak, and the spectra are dominated by the base peak at m/z 144. This corresponds to the quaternary



(17) X = H

(18) X = CH₂OAc

methylquinolinium ion (17), which probably arises by loss of formaldehyde followed by loss of the hydroxyl radical. In the bridged compounds the ($M^+ - 1$) ions are the only other significant fragments. The mass spectrum of the diol (6) is also dominated by the m/z 144 ion, together with ions at m/z 191, 107, and 106, indicative of a combination of electronic effects along with the thermal process already described. The base peak in the mass spectrum of the diacetate (7) occurs at m/z 216, and corresponds to the quaternary quinolinium ion (18) resulting from loss of acetic acid and the methylanilino residue. This diacetate (7) distils unchanged at 180 °C/0.2 mmHg, confirming hydroxy group participation in the fragmentation of the diol (6).

Experimental

M.p.s were determined on a Kofler block and are uncorrected. I.r. spectra were recorded with a Perkin Elmer 197 spectrophotometer as KBr discs. N.m.r. spectra were determined for solutions in [²H]chloroform on a Varian HA 100 or a Perkin Elmer R34 (220 MHz) spectrometer using tetramethylsilane as an internal reference. Mass spectra were measured on an A.E.I. MS 30 mass spectrometer at 70 eV. Materials and methods have been described previously.⁹

*3 α -Hydroxy-2 α -hydroxymethyl-1-methyl-4 β -(N-methyl-anilino)-1,2,3,4-tetrahydroquinoline (6).**—A mixture of *N*-methylaniline (3.6 g, 0.033 mol) and hydroxyethanal (2.0 g, 0.033 mol) was left at 20 °C for 48 h. Addition of ether gave the diol as colourless needles (2.26 g, 45%), m.p. 128–134 °C, raised, after recrystallisation from ethanol and two further recrystallisations from benzene, to 165–166 °C (Found: C, 72.7; H, 7.3; N, 9.3; NMe, 21.55. C₁₈H₂₂N₂O₂ requires C, 72.5; H, 7.4; N, 9.4; NMe, 22.65%); ν_{\max} . 3 350, 1 600, 1 495, 1 300, 1 240, 1 210, 1 090, 1 005, 955, 930, 860, 745, and 685 cm⁻¹; m/z 298 (M^+ , 1%), 297 (3), 192 (11), 191 (36), 174 (17), 161 (17), 160 (30), 144 (92), 132 (43), 117 (20), 107 (82), 106 (100), and 77 (38).

3 α -Acetoxy-2 α -acetoxymethyl-1-methyl-4 β -(N-methyl-anilino)-1,2,3,4-tetrahydroquinoline (7).—To a solution of the above diol (1.25 g) in dry pyridine (10 ml) was added acetic

* α -Substituents are represented on the structures as dotted bonds, β -substituents by solid bonds.

Table 5. Hydrogen bonding in the crystal

D...A	D...A (Å)	D-H (Å)	H...A (Å)	D-H...A (°)
O(11)-H(11)...O(12) ¹	2.740(5)	0.84(7)	1.96(7)	156(7)
O(12) ⁱⁱ -H(12) ⁱⁱ ...O(11)	2.721(6)	0.92(5)	1.81(5)	169(4)

Co-ordinates transformed by:

$$\begin{array}{l} \text{I} \quad x, y-1, z \\ \text{II} \quad 1-x, -\frac{1}{2}+y, \frac{1}{2}-z \end{array}$$

anhydride (2 ml). After 3 days at 20 °C, water was added and, an hour later, the mixture was evaporated to dryness under reduced pressure. The resulting gum was crystallised from light petroleum (b.p. 40–60 °C)—benzene (4:1) to give the diacetate (1.03 g, 64%) as colourless needles, m.p. 66–68 °C, raised after two recrystallisations to 71–72 °C (Found: C, 69.2; H, 7.0; N, 7.4. C₁₈H₂₂N₂O₂ requires C, 69.1; H, 6.8; N, 7.3%; ν_{\max} 1 750, 1 605, 1 500, 1 370, 1 225, 1 105, 1 040, 750, and 695 cm⁻¹; δ 1.76 (s, OAc), 1.82 (s, OAc), 2.58 (s, NMe), 2.98 (2, NMe), 3.69 (m, 2 β -H), 4.13 (q, *J* 12 and 6 Hz, H of CH₂), 4.62 (q, *J* 12 and 3.5 Hz, H of CH₂), 5.30 (d, *J* = 11 Hz, 4 α -H), 5.60 (dd, *J* 11 and 5 Hz, 3 β -H), and 6.6–7.4 (m, ArH); *m/z* 382 (*M*⁺, 14%), 322 (11), 276 (21), 234 (11), 217 (18), 261 (100), 201 (18), 174 (60), 160 (32), 146 (16), 144 (43), 132 (21), 107 (20), and 106 (21).

3 α -Hydroxy-1-methyl-1,2,3,4-tetrahydro-4 α ,2 α -epoxymethanoquinoline (9).—The diol (6) (200 mg) was heated at 170 °C for 20 min in a cold finger under slightly reduced pressure. Preparative t.l.c. of the black residue on silica gel plates, developing and eluting with ether–benzene (1:1) gave *N*-methylaniline (10 mg), together with a further 20 mg (total yield 42%) isolated from the cold finger and the walls of the air condenser, and the alcohol (9) [45 mg from the residue and 5 mg from the condensate (35%)] as colourless needles, m.p. 79–82 °C, raised upon recrystallisation from ethanol to 89–91 °C (Found: C, 69.4; H, 6.4; N, 7.1%; *M*⁺ 187. C₁₁H₁₃NO₂ requires C, 69.1; H, 6.8; N, 7.3%; *M*, 191; ν_{\max} 3 380, 3 075, 3 025, 2 950, 2 930, 2 880, 2 815, 1 600, 1 485, 1 355, 1 320, 1 225, 1 190, 1 090, 1 015, 890, 875, and 750 cm⁻¹; δ 2.86 (s, NMe), 3.53 (m, 2 β -H), 4.25 (m, CH₂), 4.53 (s, 4 β -H), 4.67 (s, 3 β -H), and 6.5–7.4 (m, ArH); *m/z* 191 (*M*⁺, 5%), 190 (25), 160 (10), 145 (13), 144 (100), and 77 (10).

3 α -Acetoxy-1-methyl-1,2,3,4-tetrahydro-4 α ,2 α -epoxymethanoquinoline (10).—A solution of the above alcohol (100 mg) in pyridine (1 ml) was treated with acetic anhydride (0.35 ml). After 24 h at 20 °C, water (0.2 ml) was added, and after a further 30 min the mixture was evaporated to dryness. The residual gum was crystallised from hexane–benzene (1:1) to give the acetate (93 mg, 77%) as colourless needles, m.p. 69.5–71 °C (Found: C, 67.0; H, 6.4; N, 5.8. C₁₃H₁₅NO₃ requires C, 67.0; H, 6.4; N, 6.0%; ν_{\max} 1 730, 1 600, 1 490, 1 240, 1 205, 1 090, 1 035, 940, 895, 885, 765, and 755 cm⁻¹; δ 2.14 (s, OAc), 2.92 (s, NMe), 3.67 (m, 2 β -H), 4.23 (m, CH₂), 4.73 (s, 4 β -H), 5.57 (s, 3 β -H), and 6.5–7.4 (m, ArH); *m/z* 233 (*M*⁺, 8%), 232 (37), 145 (14), and 144 (100).

Acid Catalysis Experiments.—Solutions of hydrochloric acid having concentrations in the range 0.5–80mM were obtained by addition of weighed amounts of ethanoyl chloride to ethanol. Equal volumes of each ethanolic hydrochloric acid and a 16.8mM solution of the dimeric diol (6) in ethanol at ambient temperature were combined, and the reaction was monitored by t.l.c. on silica gel [hexane–ethyl acetate (1:1)]. The diol (*R*_F 0.35)

was converted into the bridged alcohol (*R*_F 0.22) and *N*-methylaniline (*R*_F 0.81) almost instantaneously using acid concentrations down to 5mM; at 0.5mM the half-life of the diol was ca. 10 min. In a preparative experiment using 10mM ethanolic HCl, the diol (100 mg) gave the bridged alcohol (38 mg, 61%) and *N*-methylaniline (27 mg, 76%). Considerable bridged alcohol formation was also evident in ethanol alone after 48 h.

Crystal Data.—C₁₈H₂₂N₂O₂, *M* = 298.4. Monoclinic, *a* = 12.141(6), *b* = 6.231(4), *c* = 23.569(13) Å, β = 118.26(4)°, *U* = 1 570.5 Å³, *D*_c = 1.26 g cm⁻³, *Z* = 4, *F*(000) = 640, space group *P*2₁/*c*, μ (Mo-*K*_α) = 0.46 cm⁻¹.

Crystallographic Measurements and Structure Analysis.—*X*-Ray intensities were measured on a Nicolet P3 automated diffractometer using monochromatised Mo-*K*_α radiation. Integrated relative intensities for 2 402 independent reflections with $2\theta < 50^\circ$ were obtained as θ – 2θ scans; 1 580 reflections had *I* > 3 σ (*I*).

The crystal structure was elucidated by direct methods using the 'MITHRIL'¹⁰ program. The H atoms were located on electron density maps calculated at intermediate stages of refinement.¹¹ In the final cycles of full matrix least-squares refinement the positional parameters for all atoms, anisotropic thermal parameters for the C and O atoms and a common isotropic thermal parameter for the H atoms were varied. A unit weighting scheme was adopted and convergence was reached at *R* = 5.7%.

The molecular structure is shown in Figure 1 and the crystal data is recorded in Tables 1–5. Thermal parameters and hydrogen co-ordinates are listed in Supplementary Publication [Sup No. 56537 (4 pp.)].* The calculated and observed structure amplitudes are available on request from the Editorial Office.

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* For details of the Supplementary Publications scheme, see 'Instructions for Authors (1986),' *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

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