The Reaction between *trans*-2-Alkylaminocycloalkanols and Formaldehyde

Peter M. R. Barkworth and Trevor A. Crabb*
Department of Chemistry, Portsmouth Polytechnic, Portsmouth, Hampshire, PO1 2DT, UK

***trans*-2-Alkylaminocyclohexanols and *trans*-2-alkylaminocycloheptanols condense with formaldehyde to give perhydrocycloalkano[*d*][1,3]oxazoles, whereas *trans*-2-alkylaminocyclopentanols give rise to perhydrocyclopentano[*f*][1,3,5]dioxazepines. The two types of ring systems are characterized by differing proton–proton geminal coupling constants and ^{13}C NMR parameters.**

INTRODUCTION

The ^1H NMR spectra of 1,3-oxazolidines in which the nitrogen atom is located at a ring fusion as in perhydro-oxazolo[3,4-*a*]pyridine (**1**) have been well documented,[1–4] whereas systems of the type **2–4** in which R^1 = alkyl have received only scant attention. In particular, the geminal coupling constants [*J*(*gem*)] for the NCH_2O protons in such systems have been recorded only for scattered compounds,[5,6] and vary from −2.5 Hz in **5**[7] and −3.0 Hz in **2**[5] to −4.3 to −5.9 Hz in **3**[6] and −4.2 to −4.5 Hz in **4**.[5]

In order, therefore, to provide additional information on the variation of *J*(*gem*) with structure, the *trans*-2-aminocycloalkanols **6–17** were prepared and condensed with formaldehyde.

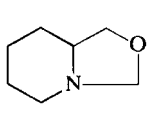
RESULTS AND DISCUSSION

The 2-aminocyclohexanols **11–13** and the 2-aminocycloheptanols **14–17** condense with formaldehyde to yield the perhydrobenzo[*d*][1,3]oxazoles **18–20** and perhydrocycloheptano[*d*][1,3]oxazoles **21–24**, respectively, and the ^1H NMR spectra of these together with that of perhydrocyclo-octano[*d*][1,3]oxazole (**25**) are summarized in Table 1.

The *J*(*gem*) of −2.6 and −2.5 Hz for **19** and **20** is consistent with a pseudoequatorial alkyl group in the half-chair 1,3-oxazolidine ring (I), since this permits efficient overlap of the methylene CH bonds and the adjacent lone pair orbitals resulting in a positive contribution to *J*(*gem*).[8,9] In the NH analogue (**18**)

Table 1. ^1H NMR spectra of perhydrocycloalkano[*d*]-[1,3]oxazoles

Compound	Solvent	Chemical shifts (δ) NCH_2O		CHO	CHN	*J*(gem) (Hz) NCH_2O
18	$CDCl_3$	3.81	3.72	3.40	2.80	−5.7
19	C_6D_6	4.66	3.98	3.40	—	−2.6
20	C_6D_6	4.72	4.35	3.42	—	−2.5
21	$CDCl_3$	4.67	4.45	3.36	2.91	−6.0
22	C_6D_6	4.48	3.96	3.80	2.25	−2.8
23	$CDCl_3$	4.55	4.40	3.65	2.68	−4.7
24	$CDCl_3$	4.63	4.00	3.85	2.20	−3.2
25	$CDCl_3$	4.45	4.25	3.58	3.03	−6.2



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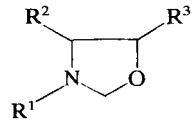
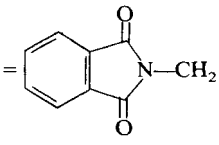
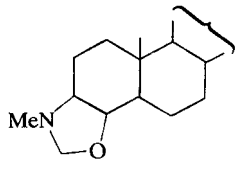


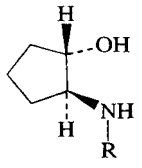
2: R^1 = Cyclohexyl; R^2 = H; R^3 = Me
3: R^1 = Alkyl; R^2 = H; R^3 = Et



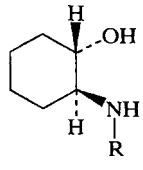
4: R^1 = ; R^2 = Me; R^3 = Aryl



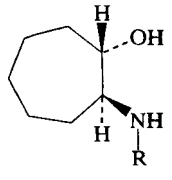
5: (Partial structure from 20α-(dimethylamino)-2′,3β,3′,4β-tetrahydro-3′-methyl-5α-pregn-3-eno[3,4-*d*]oxazole)



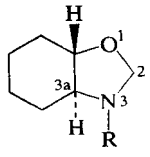
6: R = Me
7: R = Bu
8: R = Isopr
9: R = *t*-Bu
10: R = Hexyl



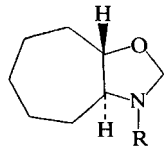
11: R = H
12: R = CH_2Ph
13: R = Cyclohexyl



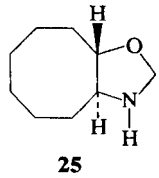
14: R = H
15: R = CH_2Ph
16: R = Cyclohexyl
17: R = Hexyl



18: R = H
19: R = CH_2Ph
20: R = Cyclohexyl



21: R = H
22: R = CH_2Ph
23: R = Cyclohexyl
24: R = Hexyl



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* *Author to whom correspondence should be addressed.*

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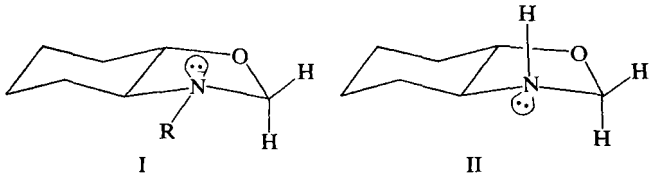
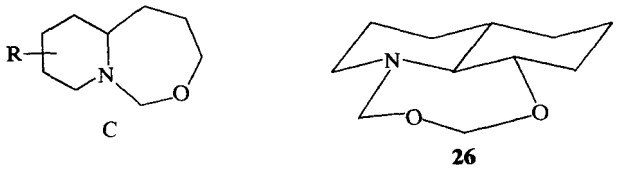
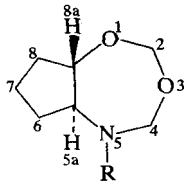


I II

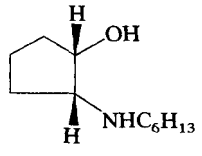
A B



C 26



27: R = Me
28: R = Bu
29: R = Isopr
30: R = *t*-Bu
31: R = Hexyl



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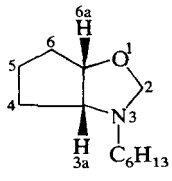

33

J(*gem*) decreases to −5.7 Hz, indicating the pseudo-axial conformation II. These conformational trends are repeated for the cycloheptano series **21–24,** but here the range of *J*(*gem*) values is greater since the *trans*-fusion between the 7- and 5-membered rings permits more partial pseudorotation and, hence, different lone pair-CH geometries. The *J*(*gem*) of −6.2 Hz for the cyclo-octano compound **25** also indicates a predominance of the NH-pseudoaxial conformer.

The ring closure reaction between formaldehyde and the *trans*-2-*N*-alkylaminocyclopentanols **6–10** might have been expected to give the corresponding *N*-alkylperhydrocyclopentano[*d*][1,3]oxazole (A), since although *trans*-bicyclo[3.3.0]octane (B; X = CH_2) is considerably strained,[10] the 3-oxa derivative (B; X = O) seems to be more stable.[11]

The ^{1}H NMR spectra (Table 2) of the products, however, were not consistent with structure A. In the spectrum of the product derived from **8**, for example, instead of the single AB quartet for the NCH_2O protons expected for A; R = isopropyl, two AB quartets were observed with δ 4.75 and 4.35 [*J*(*gem*) −12 Hz] and δ 5.03 and 4.28 [*J*(*gem*) −6.5 Hz]. These *J*(*gem*) values are not reasonable for NCH_2O protons in a structure such as A (cf. values for **2–5**).[5–7] The higher field AB quartet in the spectrum of the cyclized product is, in fact, typical of NCH_2O methylene protons in a 7-membered ring. For example, *J*(*gem*) was found to lie between −11.1 and −12.8 Hz for the NCH_2O proton in perhydropyrido[1,2-*c*][1,3]oxazepines (C).[12] Similarly, the low field quartet is typical of OCH_2O protons; *J*(*gem*) values for OCH_2O protons in 1,3-dioxanes lie between −5.8 and −6.6 Hz,[13] and in larger 1,3-dioxa-ring systems *J*(*gem*) is approximately −7 Hz.[14] Perhydro-1,3,5-dioxazepino[6,7-*i*; 5,6-*j*]quinoline (**26**), which contains both OCH_2O and NCH_2O moieties within a 7-membered ring, shows in its NMR spectrum the OCH_2O proton signals at δ 4.80 and 4.88 [*J*(*gem*) −4.0 Hz] and the NCH_2O proton signals at δ 4.14 and 4.27 [*J*(*gem*) −9.1 Hz].[15] Thus, the ^{1}H NMR spectral evidence shows that *trans*-2-alkylaminocyclopentanols **6–10** condense with two moles of formaldehyde to yield *N*-alkylperhydrocyclopentano[*f*][1,3,5]dioxazepines **27–31,** and this was in agreement with mass spectral data.

In contrast, *cis*-2-hexylaminocycloalkanol (**32**) condenses with formaldehyde to form *N*-alkylperhydrocyclopentano[*d*][1,3]oxazole (**33**) [^{1}H NMR $CDCl_3$ δ 4.40, 4.03, *J*(*gem*) −4.5 Hz]. To confirm the structure of **31** and **33** the ^{13}C NMR spectra (coupled and decoupled) were recorded (Table 3). The NCH_2O carbon nucleus in the spectrum of **33** absorbed as a triplet at lowest field, δ 86.3, finding its counterpart at δ 86.1 at C-4 in **31**. Both showed similar ^1J(CH) values (153 and 156 Hz). For **31** a triplet at lower field, δ 96.1, corresponded to the OCH_2O carbon nucleus at C-2, the ^1J(CH) value (160 Hz) being larger than for the C-4 carbon in **31**, in agreement with known electronegativity effects on ^1J. The bridgehead carbon nuclei C-3a and C-6a in **33** appeared at δ 68.5 [^1J(CH) 140 Hz] and δ 81.2 [^1J(CH) 152 Hz], respectively, with couplings similar to literature values.[16] The corresponding carbon nuclei C-5a and C-8a in **31** absorbed at δ 70.3 and δ 82.1, with notably smaller

Table 2. ^{1}H NMR Spectra of *N*-alkylperhydrocyclopentano[*f*][1,3,5]dioxazepines and *N*-alkylperhydrocyclopentano[*d*][1,3]oxazoles

		Chemical shifts (δ)						*J*(gem) (Hz)	
Compound	Solvent	NCH_2O		OCH_2O		*CHO*	*CHN*	NCH_2O	OCH_2O
27	C_6D_6	4.73	4.50	5.10	4.75	4.10	2.80	−11.0	−6.0
28	C_6D_6	4.48		5.03	4.40	3.75	2.95	—	−6.2
29	C_6D_6	4.75	4.35	5.03	4.28	3.70	3.00	−12.0	−6.5
30	C_6D_6	4.98	4.36	5.03	4.26	3.65	3.20	−12.8	−6.8
31	$CDCl_3$	4.65		5.03	4.60	4.00	2.85	—	−6.0

Table 3. ^{13}C NMR spectra of *cis*(3a-H,6a-H)-*N*-hexylperhydrocyclopentano[*d*][1,3]oxazole (33) and *trans*-(5a-H,8a-H)-*N*-hexylperhydrocyclopentano[*f*][1,3,5]dioxazepine (31)

33			31		
Carbon Nucleus	Chemical Shift (δ)	^1J(CH) (Hz)	Carbon Nucleus	Chemical Shift (δ)	^1J(CH) (Hz)
			C-2	96.1 (t)	160
C-2	86.3 (t)	153	C-4	86.1 (t)	156
C-3a	68.5 (d)	140	C-5a	70.3 (d)	132
C-4 or C-6	33.4 (t)	131	C-6	29.3 (t)	132
C-5	23.5 (t)	131	C-7	19.5 (t)	133
C-6 or C-4	32.4 (t)	130	C-8	29.3 (t)	132
C-6a	81.2 (d)	152	C-8a	82.1 (d)	135
C-7′	54.2 (t)	130	C-9′	53.7 (t)	133
C-8′–11′	31.7 (t)	123	C-10′–13′	31.9 (t)	125
	29.4 (t)	123		28.8 (t)	125
	27.1 (t)	123		27.0 (t)	125
	22.6 (t)	124		22.7 (t)	125
C-12′	14.2 (q)	125	C-14′	14.1 (q)	125

coupling constants [^1J(CH) 132 Hz and 135 Hz, respectively] than for the corresponding nuclei in **33**, which may reflect the differing dihedral angles between the heteroatom lone pairs and the C—H bonds.[17,18]

The differing ring closure reactions of the *trans*-2-alkylaminocycloalkanols **6–10** with formaldehyde may be explained in terms of ring fusion strain in the cyclized products. Thus, the *trans*-fused *N*-alkylperhydrocyclopentano[*d*][1,3]oxazoles (A) are destabilized by ring fusion strain arising from the *trans*-fusion between two 5-membered rings, as in B, X = CH_2, O, S;[10,11] this will be considerably less in a *trans*-fused 7/5 system as in **27–31** as a consequence of the flexibility of the 7-membered ring, and the formation of such compounds will be favoured over A. There is no comparable ring fusion strain in the *cis*-fused **33**. In the *N*-alkylperhydrocyclohexano[*d*]-[1,3]oxazoles **18–20** and the *N*-alkylperhydrocycloheptano[*d*][1,3]oxazoles **21–24**, however, the ring fusion strain present in A is considerably reduced (cf. differences in the stability of *trans*-bicyclo[3.3.0]octane and *trans*-hydrindane[19]) and these 1,3-oxazoles, rather than the 1,3,5-dioxazepines, are formed from the reaction between the amino alcohols **11–17** and formaldehyde.

EXPERIMENTAL

Elemental analyses were carried out by the Analytical Section, Department of Chemistry, Portsmouth Polytechnic, and Butterworth Micro-Analytical Consultancy, Teddington, Middlesex. IR spectra were recorded on Perkin-Elmer 237 and 297 grating instruments as 0.2 M solutions in deuteriochloroform using 0.2 mm matched cells. The ^{1}H NMR spectra were recorded on Varian T60 and Brüker WH 270 spectrometers, as 10% solutions with tetramethylsilane as internal reference. ^{13}C NMR spectra were obtained from the P.C.M.U. at Harwell on a Brüker 90 FT spectrometer operating at 25.2 MHz; spectral width 6024 Hz (decoupled) and 3012 Hz (coupled) with 4096 memory points; pulse width 11 μs; pre-delay time 143 μs; number of scans accumulated 1000–2000 (decoupled) or 20 000–40 000 (coupled). Samples were dissolved in equal volumes of $CDCl_3$ with TMS as internal reference.

trans-2-*N*-Alkylaminocyclopentanols

Two methods of synthesis were used to prepare these compounds.

(i) The method of Mousseron and Granger[20] was used for the preparation of *trans*-2-*N*-methylaminocyclopentanol, and adapted for the preparation of *trans*-2-*N*-isopropylaminocyclopentanol, *trans*-2-*N*-butylaminocyclopentanol and *trans*-2-*N*-hexylaminocyclopentanol. Cyclopentene oxide[21] (0.2 M, 16.8 g) in ethanol (100 ml) was heated together with the appropriate amine (0.2 M) in a high pressure steel autoclave for 1 to 2 h at 100 °C to 150 °C. When the solution was cold, the solvent was removed by distillation and the residue distilled *in vacuo* to yield *trans*-2-*N*-methylaminocyclopentanol (70%), b.p. 61–62 °C at 0.3 mmHg (lit.,[20] b.p. 104–105 °C at 16 mmHg) (Found: C, 62.4; H, 11.1; N, 12.2. Calc. for $C_6H_{13}NO$: C, 62.6; H, 11.4; N, 12.2%), *trans*-2-*N*-butylaminocyclopentanol (74%), b.p. 70–72 °C at 0.1 mmHg, (Found: C, 68.6; H, 12.0; N, 8.6%. $C_9H_{19}NO$ requires: C, 68.7; H, 12.2; N, 8.9%), *trans*-2-*N*-isopropylaminocyclopentanol (83%), b.p. 72–74 °C at 0.2 mmHg, (Found: C, 67.2; H, 11.8; N, 10.1. $C_8H_{17}NO$ requires: C, 67.1; H, 12.0; N, 9.8%) and *trans*-2-*N*-hexylaminocyclopentanol (10%), b.p. 90–93 °C at 0.1 mmHg, (Found: C, 71.3; H, 12.4; N, 7.3. $C_{11}H_{23}NO$ requires: C, 71.3; H, 12.5; N, 7.6%).

(ii) Cyclopentene oxide (0.2 M, 16.8 g) in ethanol (50 ml) was heated with hexylamine or *t*-butylamine (0.2 M) under reflux for 24 h. The solvent was removed by distillation and the residue distilled *in vacuo* to yield trans-2-N-*hexylaminocyclopentanol* (29.6 g, 80%) b.p. 89–92 °C at 0.1 mmHg or trans-2-N-*t*-*butylaminocyclopentanol* (23.2 g, 74%), b.p. 78–80 °C at 0.1 mmHg. (Found: C, 68.5; H, 12.3; N, 8.8. $C_9H_{19}NO$ requires C, 68.7; H, 12.2; N, 8.9%).

trans-2-*N*-Alkylaminocyclohexanols

Cyclohexene oxide was heated under reflux with equimolar proportions of the appropriate amine to yield *trans*-2-*N*-cyclohexyl- and *trans*-2-*N*-benzylaminocyclohexanol.[22]

trans-2-*N*-Alkylaminocycloheptanols

Cycloheptene oxide (0.2 M, 22.4 g) was heated with the appropriate amine [cyclohexylamine (0.2 M, 19.8 g), benzylamine (0.2 M, 21.4 g) or hexylamine (0.2 M, 20.2 g)] under reflux for 24 h. The resulting solution was distilled *in vacuo* to yield trans-2-N-*cyclohexylaminocycloheptanol* (62%), b.p. 48–50 °C at 2.4 mmHg, (Found: C, 73.9; H, 11.6; N, 6.4. $C_{13}H_{25}NO$ requires: C, 73.9; H, 11.9; N, 6.6%),

trans-2-N-*benzylaminocycloheptanol* (56%), b.p. 54–58 °C at 2.0 mmHg, (Found: C, 76.5; H, 9.3; N, 6.5. $C_{14}H_{21}NO$ requires: C, 76.7; H, 9.6; N, 6.4%) or trans-2-N-*hexylaminocycloheptanol* (75%), b.p. 50–52 °C at 1.8 mmHg, (Found: C, 73.4, H, 13.0; N, 6.5. $C_{13}H_{27}NO$ requires: C, 73.2; H, 12.8; N, 6.6%).

trans-2-Aminocycloalkanols

trans-2-Aminocyclohexanol was prepared by the published method,[23] which was adopted for the preparation of *trans*-2-aminocyclopentanol, *trans*-2-aminocycloheptanol and *trans*-2-aminocyclo-octanol. The cycloalkene oxide (0.3 M) was heated with 0.88 ammonium hydroxide solution (7.7 M, 500 ml) and ethanol (200 ml) in a high pressure stainless steel autoclave at 120–140 °C for 5 h. Solvents were removed by distillation and the product purified by distillation *in vacuo* to yield *trans*-2-aminocyclopentanol (21.5 g, 71%), b.p. 73–77 °C at 0.25 mmHg (lit.,[20] 114–116 °C at 16 mmHg) (Found: C, 59.1; H, 11.1; N, 13.8. Calc. for $C_5H_{11}NO$: C, 59.4; H, 11.0; N, 13.8%), *trans*-2-aminocycloheptanol (20.9 g, 54%), b.p. 58–64 °C at 25 mmHg (lit.,[20] 129–130 °C at 16 mmHg) (Found: C, 64.7; H, 11.5; N, 10.5. Calc. for $C_7H_{15}NO$: C, 65.0; H, 11.6; N, 10.8%) and *trans*-2-aminocyclo-octanol (27.9 g, 65%) b.p. 84–86 °C at 0.8 mmHg (lit.,[20] 132–133 °C at 16 mmHg) (Found: C, 67.6; H, 12.3; N, 9.8. Calc. for $C_8H_{17}NO$: C, 67.1; H, 12.0; N, 9.8%).

N-Alkylperhydrocyclopentano[*f*][1,3,5]dioxazepines

(i) The *trans*-2-*N*-alkylaminocyclopentanol (0.1 M) (**7**, **8**, **9**, **10**) was dissolved in benzene (100 ml) and heated with paraformaldehyde (0.1 M, 3.0 g) under reflux using a Dean and Stark water separator until no further water separated out. Solvent was removed by distillation and the residue distilled *in vacuo* to yield the N-*butylperhydrocyclopentano*[f][1,3,5]*dioxazepine* (45%) b.p. 71–73 °C at 0.08 mmHg, (Found: C, 66.5; H, 10.9; N, 7.1. $C_{11}H_{21}NO_2$ requires: C, 66.3; H, 10.6; N, 7.0%), N-*isopropylperhydrocyclopentano*[f]-[1,3,5]*dioxazepine* (39%) b.p. 60–62 °C at 0.1 mmHg, (Found: C, 64.7; H, 10.5; N, 7.9. $C_{10}H_{19}NO_2$ requires: C, 64.8; H, 10.3; N, 7.6%), N-t-*butylperhydrocyclopentano*[f][1,3,5]*dioxazepine* 62%) b.p. 66–68 °C at 0.05 mmHg, (Found: C, 66.1; H, 10.6; N, 6.9. $C_{11}H_{21}NO_2$ requires: C, 66.3; H, 10.6; N, 7.0%) and N-*hexylperhydrocyclopentano*[f][1,3,5]*dioxazepine* (26%) b.p. 93–95 °C at 0.07 mmHg, (Found: C, 68.6; H, 11.0; N, 6.4. $C_{13}H_{25}NO_2$ requires: C, 68.7; H, 11.1; N, 6.2%).

(ii) *trans*-2-*N*-Methylamino- and *trans*-2-*N*-hexylaminocyclopentanol (0.05 M, 5.75 g) and (0.03 M, 6.25 g), respectively, were shaken with excess aqueous 40% formaldehyde solution (0.13 M, 10 ml) and (0.066 M, 5 ml), respectively, for 0.5 h. The mixture was basified with 30% aqueous sodium hydroxide solution and extracted with ether. The combined ether extracts were dried (Na_2SO_4) and evaporated to leave an oil which was distilled *in vacuo* to yield N-*methylperhydrocyclopentano*[f][1,3,5]*dioxazepine* (2.74 g, 35%) b.p. 61–64 °C at 0.07 mmHg, (Found: C, 61.3; H, 9.3; N, 9.1. $C_8H_{15}NO_2$ requires C, 61.1; H, 9.6; N, 8.9%) or N-*hexylperhydrocyclopentano*[f][1,3,5]*dioxazepine* (1.8 g, 26%) b.p. 93–95 °C at 0.07 mmHg, (Found: C, 68.7; H, 11.2; N, 6.1. $C_{13}H_{25}NO_2$ requires C, 68.7; H, 11.1; N, 6.2%). N-*Hexylperhydrocyclopentano*[*d*][1,3]*oxazole* was also obtained together with the latter compound (0.1 g, 0.02%) b.p. 80–86 °C at 0.25 mmHg, (Found: C, 72.9; H, 12.1; N, 7.0. $C_{12}H_{23}NO$ requires C, 73.0; H, 11.7; N, 7.1%).

N-Alkylperhydrobenzo[*d*][1,3]oxazoles. These compounds were prepared from *trans*-2-*N*-cyclohexylamino- and *trans*-2-*N*-benzylaminocyclohexanols as described previously.[22]

N-Alkylperhydrocycloheptano[*d*][1,3]oxazoles

trans-2-*N*-Hexylaminocycloheptanol (0.1 M, 21.3 g), *trans* - 2 - *N* - cyclohexylaminocycloheptanol (0.1 M, 21.1 g) or *trans* - 2 - *N* - benzylaminocycloheptanol (0.1 M, 22.1 g) were shaken with excess 40% aqueous formaldehyde solution (0.13 M, 10 ml) for 0.5 h. The mixture was basified with 50% aqueous sodium hydroxide solution and ether extracted. The combined ether extracts were dried (Na_2SO_4) and evaporated to leave a colourless oil which was distilled *in vacuo* to yield N-*hexylperhydrocycloheptano*[d][1,3]*oxazole* (78%) b.p. 94–96 °C at 0.18 mmHg, (Found: C, 74.5; H, 12.3; N, 6.0. $C_{14}H_{27}NO$ requires: C, 74.6; H, 12.1; N, 6.2%), N - *cyclohexylperhydrocycloheptano*[d] - [1,3]*oxazole* (61%) b.p. 106–108 °C at 0.3 mmHg, (Found: C. 75.0; H, 11.4; N, 6.3. $C_{14}H_{25}NO$ requires: C, 75.3; H, 11.3; N, 6.3%) or N-*benzylperhydrocycloheptano*[d][1,3]*oxazole* (80%) b.p. 126–128 °C at 0.1 mmHg, (Found: C, 77.9; H, 9.2; N, 6.4. $C_{15}H_{21}NO$ requires: C, 77.9; H, 9.1; N, 6.1%).

Perhydrocycloalkano[*d*][1,3]oxazoles

Perhydrobenzo-, perhydrocycloheptano and perhydrocyclo-octano[*d*][1,3]oxazoles were prepared by dissolving the appropriate *trans*-2-aminocycloalkanol (0.1 M) in benzene (100 ml) and boiling the solution under reflux with paraformaldehyde (0.1 M, 3.0 g) using a Dean and Stark water separator. Boiling was continued until the required volume of water (1.8 ml) had separated out. Solvent was removed by distillation and the residue distilled *in vacuo* to yield *perhydrobenzo*[d][1,3]*oxazole* (18%) b.p. 62–63 °C at 1.0 mmHg, (Found: C, 66.4; H, 10.4; N, 10.8. $C_7H_{13}NO$ requires: C, 66.1; H, 10.2; N, 11.0%), *perhydrocycloheptano*[d][1,3]*oxazole* (21%) b.p. 57–58 °C at 0.9 mmHg, (Found: C, 67.9; H, 10.5; N, 9.8. $C_8H_{15}NO$ requires: C, 68.0; H, 10.7; N, 9.9%) or *perhydrocyclo-octano*[d][1,3]*oxazole* (12%) b.p. 62–65 °C at 0.35 mmHg (Found: C, 69.4; H, 10.8; N, 8.6. $C_9H_{17}NO$ requires: C, 69.6; H, 11.0; N, 9.0%).

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