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NMR Spectra and Stereochemistry of 5,5-Disubstituted-1,3-Dioxans

Trevor A. Crabb* and Manuchehr Porssa
Department of Chemistry, Portsmouth Polytechnic, Portsmouth, Hampshire PO1 2DT, UK

Norman F. Elmore
ICI Pharmaceuticals, Alderly Park, Cheshire SK10 4TG, UK

The positions of conformational equilibria in a variety of 5,5-disubstituted 1,3-dioxans have been established by low-temperature ^1H and ^{13}C NMR spectroscopy and by reference to the NMR spectra of anancomeric 2,5,5-trisubstituted derivatives.

KEY WORDS ^1H and ^{13}C NMR 1,3-Dioxans Conformational equilibria

INTRODUCTION

The stereochemistry of 1,3-dioxans carrying substituents at the 5-position has been the subject of extensive studies, and the conformational equilibria in these compounds have been shown to be sensitive to dipolar, hydrogen-bonding and steric effects.[1,2] The 5-acetyl-5-methyl system (**1**) has been shown[3] by low-temperature ^{13}C NMR spectroscopy to adopt a conformational equilibrium ($K = 8.1$ in CS_2 at 183 K) favouring the axial acetyl conformer. In addition, equilibration of the 1,3-dioxans **2**, **3**, **5** and **6** under acidic conditions,[4] in which an equilibrium is established by ring opening of the acetal, results in an increased preference for the axial CH(OH)Me in **5** ⇌ **6** than for the COMe in **2** ⇌ **3** as a result of intramolecular hydrogen bonding between the OH and the ring oxygen atom in **6**. In this paper we present the results of a stereochemical and NMR study of related systems possessing a phenyl ring as part of the 5-substituent (**7**–**12**), and on 1,3-dioxans containing an amino function at C-5 (**13**–**17**). In addition, direct low-temperature NMR estimates of the equilibria for **4a** ⇌ **4b**, **10a** ⇌ **10b** and **7a** ⇌ **7b** are described.

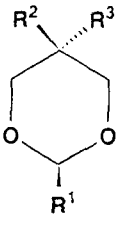
RESULTS AND DISCUSSION

Configurational assignments for the 2,5,5-trisubstituted 1,3-dioxans

The configurations of the 5-(α-hydroxyethyl)-5-methyl-2-phenyl-1,3-dioxans **5** and **6** were established[2] by the presence of intramolecular hydrogen bonding (IR spectra; see Experimental; only weak hydrogen bonding is in fact observed, which has been discussed by Eliel and Banks[5]) in isomer **6**, and by assuming[2,6] an equatorial orientation of the C-2 phenyl substituent. The configurations of the 5-(α-hydroxybenzyl)-5-methyl-2-phenyl-1,3-dioxans **12** (hydrogen bonding) and **11**, the 5-(α-aminoethyl)-5-methyl-2-phenyl-1,3-dioxan **14** (hydrogen bonding) and the 5-(α-aminobenzyl)-5-methyl-2-phenyl-1,3-dioxans **17** (hydrogen bonding) and **16** were assigned on similar grounds. Since **5**, **6**, **11** and **12** were obtained by reduction of the carbonyl group in **2**, **3**, **8** and **9**, this also establishes the configuration of these compounds.

NMR spectra of the 2,5,5-trisubstituted 1,3-dioxans

In the ^1H NMR spectra (Table 1) of the 1,3-dioxans possessing a plane of symmetry, the 4(6)-methylene



1 $R^1 = H$, $R^2 = Me$, $R^3 = COMe$
2 $R^1 = Ph$, $R^2 = Me$, $R^3 = COMe$
3 $R^1 = Ph$, $R^2 = COMe$, $R^3 = Me$
4 $R^1 = H$, $R^2 = Me$, $R^3 = CH(OH)Me$
5 $R^1 = Ph$, $R^2 = Me$, $R^3 = CH(OH)Me$
6 $R^1 = Ph$, $R^2 = CH(OH)Me$, $R^3 = Me$
7 $R^1 = H$, $R^2 = Me$, $R^3 = COPh$
8 $R^1 = Ph$, $R^2 = Me$, $R^3 = COPh$
9 $R^1 = Ph$, $R^2 = COPh$, $R^3 = Me$
10 $R^1 = H$, $R^2 = Me$, $R^3 = CH(OH)Ph$
11 $R^1 = Ph$, $R^2 = Me$, $R^3 = CH(OH)Ph$
12 $R^1 = Ph$, $R^2 = CH(OH)Ph$, $R^3 = Me$
13 $R^1 = H$, $R^2 = Me$, $R^3 = CH(NH_2)Me$
14 $R^1 = Ph$, $R^2 = CH(NH_2)Me$, $R^3 = Me$
15 $R^1 = H$, $R^2 = Me$, $R^3 = CH(NH_2)Ph$
16 $R^1 = Ph$, $R^2 = Me$, $R^3 = CH(NH_2)Ph$
17 $R^1 = Ph$, $R^2 = CH(NH_2)Ph$, $R^3 = Me$

* Author to whom correspondence should be addressed.

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Table 1. ^{1}H NMR spectra of 1,3-dioxans[a]

Compound	Solvent	Temperature (K)	Chemical shifts (δ, ppm) 2eq	2ax	4eq	4ax	6eq	6ax	5-Me	CHOH/CHNH$_2$R	CH(Me)
4	CD_2Cl_2–CS_2	295	4.81	4.73	3.95	3.46	3.73	3.43	0.79	4.00	1.12
4a[b]	CD_2Cl_2–CS_2	183	5.03	4.52	3.86	3.54	3.58	3.46	1.13	3.5	1.01
4b[b]	CD_2Cl_2–CS_2	183	5.05	4.63	4.17	3.42	3.86	3.29	0.59	4.36	1.16
5	$CDCl_3$	295		5.37	4.05	3.83	3.73	3.83	1.28	3.56	1.13
6	$CDCl_3$	295		5.47	4.40	3.67	4.06	3.57	0.70	4.52	1.27
7	$CDCl_3$	295	4.89	4.79	4.42	3.74	4.42	3.74	1.35		
7	CD_2Cl_2–CS_2	295	4.77	4.71	4.32	3.65	4.32	3.65	1.26		
7a	CD_2Cl_2–CS_2	183	4.98	4.48	4.18	3.75	4.18	3.75	1.71		
7b	CD_2Cl_2–CS_2	183	4.92	4.62	4.68	3.47	4.68	3.47	1.15		
8	$CDCl_3$	295		5.42	4.38	4.13	4.38	4.13	1.81		
9	$CDCl_3$	295		5.53	4.88	3.75	4.88	3.75	1.17		
10	$CDCl_3$	295	5.05	4.74	4.30	3.49	3.64	3.26	0.72	5.24	
10	CD_2Cl_2–CS_2	295	4.89	4.63	4.19	3.39	3.54	3.17	0.63	5.11	
10a[b]	CD_2Cl_2–CS_2	183	4.80	4.38	4.20	3.72	3.59	3.12	0.92	5.32	
10b[b]	CD_2Cl_2–CS_2	183	4.88	4.52	4.28	3.29	3.42	3.12	0.48	5.30	
11	$CDCl_3$	295		5.40	3.56	4.02	4.04	4.04	1.23	4.49	
12	$CDCl_3$	295		5.51	4.57	3.66	3.77	3.51	0.67	5.55	
13	$CDCl_3$	295	5.11	4.65	4.14	3.50	4.00	3.45	0.89	3.85	1.46
14	$CDCl_3$	295		5.45	4.34	3.62	4.08	3.53	0.64	3.68	1.15
15	$CDCl_3$	295	5.13	4.64	4.50	3.44	3.55	3.19	0.83	4.97	
16	$CDCl_3$	295		5.36	4.10	3.90	3.52	3.88	1.26	3.76	
17	$CDCl_3$	295		5.51	4.14	3.50	4.00	3.45	0.89	3.85	

[a] The ^{1}H NMR spectra of **2**, **3**, **5** and **6** have been described previously.[2]
[b] **a** and **b** designate axial 5-Me and equatorial 5-Me conformers, respectively.

protons absorb as an AB quartet in the general region δ 3.2–4.6 with low-field signals corresponding to the 4(6)-equatorial protons. The 1,3-dioxans with a chiral centre in the 5-substituent show non-equivalence of the C-4 and the C-6 methylene protons and long-range coupling between the C-4 and C-6 equatorial protons of *ca* 1.3–3.6 Hz.

Previous work[2] has shown that axial 5-Me protons in 1,3-dioxans are deshielded relative to their equatorial counterparts. Examination of the 5-Me ^{1}H NMR shifts in the spectra of the pairs of anancomeric compounds **5** and **6**, **8** and **9**, **11** and **12** and **16** and **17** shows differences consistent with the configurational assignments based on the chemical transformation and IR hydrogen-bonded studies. In addition, those isomers assigned equatorial 5-Me configurations show a greater difference between the C-4 (C-6) methylene shifts than in the axial 5-Me counterpart.

For 5-(α-aminoethyl)-5-methyl-2-phenyl-1,3-dioxan only one isomer (**14**) was obtained, and its NMR spectrum showed a high-field singlet at δ 0.64 for the 5-Me protons. The two AB quartets at δ 4.34, 3.62 and δ 4.08, 3.53 for the 4(6)-methylene protons [J(4ax, 4eq = −11.6 Hz] confirmed structure **14** with an equatorial 5-Me group.

In the ^{13}C NMR spectra (Table 2) of the 5-acetyl- and 5-benzoyl-5-methyl-2-phenyl-1,3-dioxans, isomers **2** and **8** showed lower field absorption for the 5-Me than in the spectra of **3** and **9**. Since it has been shown[7] that in 1,3-dioxans an axial 5-Me ^{13}C nucleus resonates at a lower field than its equatorial counterpart, these shifts confirm the assignments made. The 5-Me shifts in the other pairs of anancomeric 2-phenyl substituted derivatives **5** and **6**, **11** and **12** and **16** and **17** were also in accord with the assignments made on the basis of the ^{1}H NMR spectra.

Conformational equilibria in 1,3-dioxans unsubstituted at C-2

The 1,3-dioxans **1**, **7**, **4**, **10**, **13** and **15** unsubstituted at C-2 may adopt equilibria in solution between the axial methyl conformer **a** and the equatorial methyl conformer **b** as a result of chair–chair interconversion. Low-temperature ^{1}H and ^{13}C NMR spectra of **7**, **4** and **10** in fact froze out the equilibria at 183 K, providing signals for both conformers. These were identified by comparison of signals with the corresponding anancomeric derivatives. Signal assignments were confirmed by spin decoupling. The positions of conformational equilibria (**1**,[3,8] 11% **a**, 89% **b**; **7**, 12% **a**, 88% **b**; **4**, 33% **a**, 67% **b**; and **10**, 5% **a**, 95% **b**) were then obtained by integration of the ^{1}H NMR signals, and similar estimates were obtained from ^{13}C NMR signals (CS_2–CD_2Cl_2 at 183 K). Compound **7**, like **1**,[3,8] shows a marked preference for the axial benzoyl group, presumably as a result of a favourable interaction between the oxygen lone pairs in the 1,3-dioxan ring and the carbonyl function.[4,9]

Conversion of the acetyl group in **1** to the hydroxyethyl function in **4** results in a marked drop in the proportion of the equatorial methyl conformer **4b**. This is not in line with results on acid equilibration of **5** and **6**, which showed a change from 77% **3** to 86% **6**, attributed to relative stabilization of the hydrogen-bonded isomer **6**.

Although some hydrogen bonding is noted in **4b**, this

Table 2. ^{13}C NMR spectra of 1,3-Dioxans

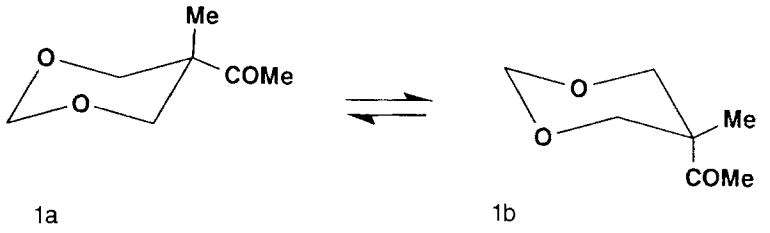
Compound	Solvent	Temperature (K)	Chemical shifts (δ, ppm) C-2	C-4/C-6	C-5	C=O	C–Me	Aryl	
7[a]	$CDCl_3$	295	94.2	73.5	47.6	205.0	19.1	138.25, 127.8 128.5, 131.5	
7	CD_2Cl_2–CS_2	295	94.1	73.1	47.6	204.8	19.0	138.2, 127.8 128.5, 131.5	
7a[b]	CD_2Cl_2–CS_2	183	93.0	71.9	45.2	202.3	19.1	132.5, 126.95 127.9, 131.2	
7b[b]	CD_2Cl_2–CS_2	183	93.3	72.4	47.2	204.7	17.7	136.6, 127.2 128.3, 131.0	
						CH(OH)			CH(OH)*Me*
4	$CDCl_3$	295	94.3	74.35, 73.7	38.9	68.4	14.4		17.6
4	CD_2Cl_2–CS_2	295	94.2	74.25, 73.7	37.9	68.3	14.4		17.7
4a[b]	CD_2Cl_2–CS_2	183	93.0	73.6, 72.9	37.0	69.3	13.6		16.4
4b[b]	CD_2Cl_2–CS_2	183	93.3	73.2, 72.3	37.4	64.2	12.1		16.3
5	$CDCl_3$	295	101.6	74.4, 74.0	37.0	70.7	15.4	138.4, 126.1 128.2, 128.8	17.65
6	$CDCl_3$	295	101.9	74.8, 73.6	36.95	67.6	13.55	138.3, 126.0 128.2, 128.8	17.7
						C=O			
8	$CDCl_3$	295	101.6	73.0	46.3	204.8	19.9	138.1, 137.3, 132.0, 128.9 128.45, 128.2, 127.75, 126.1	
9	$CDCl_3$	295	102.2	73.2	77.4	206.2	18.2	139.1, 138.1, 138.6 128.9, 128.2, 127.15, 126.3	
						CH(OH)			
10	$CDCl_3$	295	94.45	74.2, 73.65	38.8	73.9	13.7	141.4, 127.7 127.8, 128.8	
10	CD_2Cl_2–CS_2	295	94.4	74.0, 73.8	38.7	73.6	13.8	141.4, 127.7 127.8, 128.1	
10a[b]	CD_2Cl_2–CS_2	183	92.9	72.8, 72.6	37.0	76.1	14.25	139.25, 126.5 126.8, 127.6	
10b[b]	CD_2Cl_2–CS_2	183	93.0	72.5, 72.2	37.6	70.5	11.9	140.5, 126.9 127.3, 127.7	
11	$CDCl_3$	295	101.5	74.0	37.5	77.7	16.2	140.2, 138.7, 128.7, 128.2 128.1, 128.0, 126.9, 126.1	
12	$CDCl_3$	295	102.2	74.4, 73.9	37.9	72.9	12.8	141.0, 138.3, 128.9, 128.25 127.8, 127.6, 127.4, 126.1	
						$CH(NH_2)$			$CH(NH_2)Me$
13	$CDCl_3$	295	95.2	75.7, 72.7	36.4	52.85	14.4		15.8
14	$CDCl_3$	295	101.9	74.8, 74.2	36.5	46.2	13.3	138.4, 126.1 128.1, 128.7	18.5
15	$CDCl_3$	295	95.4	75.1, 73.1	37.5	60.0	15.85	135.3, 129.4 129.8, 130.15	
16	$CDCl_3$	295	101.6	75.3, 74.9	36.8	60.7	16.0	141.8, 138.6, 128.6, 128.0 127.5, 127.4, 126.1	
17	$CDCl_3$	295	102.3	74.7, 74.4	37.5	54.7	13.2	142.8, 138.7, 129.3, 128.8 128.2, 127.85, 127.6, 126.9	

[a] NMR spectrum previously recorded in the literature.[8]
[b] **a**, **b** designate axial 5-Me and equatorial 5-Me conformers, respectively.

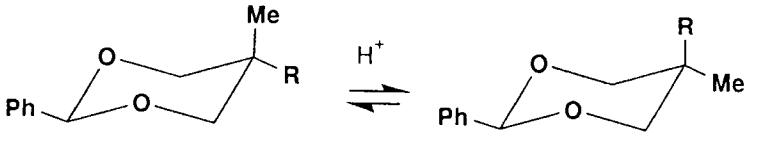
is only weak, indicating only a small proportion of the hydrogen-bonded conformer. Thus hydrogen bonding is not expected to contribute to stabilization of conformer **4b**. The CH(OH)Me group is bulky, however, and also lacks the opportunity for stabilization between the carbonyl and ring oxygen atoms as in **1b**.

The shift in equilibrium for **10** is strongly in favour of the axially substituted conformer **10b**, reflecting the delicate balance between, among others, the interactions involving the substituent (Me or Ph) in the 5-hydroxymethyl group and the 5-methyl substituent in both **a** and **b** conformers and with the C-4 and C-6 methylene groups in the **a** conformer.

The equilibria for the 5-amino derivatives **13** and **15** were not frozen out at 183 K, but comparison of the NMR spectral data with those of the anancomeric derivatives show a marked preference for conformation **b** carrying the bulky substituent in the axial position.

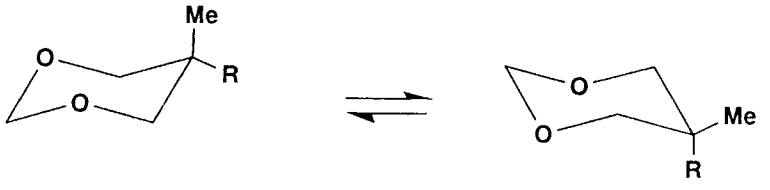


1a 1b



2 R=COMe
5 R=CH(OH)Me

3 R=COMe
6 R=CH(OH)Me



4a R=CH(OH)Me
7a R=COPh
10a R=CH(OH)Ph

4b R=CH(OH)Me
7b R=COPh
10b R=CH(OH)Ph

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ solution in 5-mm tubes, on a JEOL GSX-270 (^1H, ^{13}C) Fourier transform spectrometer at 270.16 (^1H) and 67.97 (^{13}C) MHz, using the deuterium signal of the solvent as the lock and TMS as internal standard. The most important measurement parameters were as follows: sweep width 3 kHz (^1H) and 18 kHz (^{13}C), pulse width 3 μs (^1H) and 4.2 μs (^{13}C) (*ca.* 40° and 45° flip angle, respectively), acquisition time 5.459 or 0.901 s, number of scans 16–320 K (^1H) and 1–20K (^{13}C) and computer memory 32K.

IR spectra were obtained on a Perkin-Elmer Model 683 dual-beam instrument as 0.0005 M solutions in carbon tetrachloride using 1-cm silica cells and 0.2-mm NaCl cells. Elemental analyses were carried out by ICI Pharmaceutical Division. Melting points are uncorrected. 5-Acetyl-5-methyl-1,3-dioxan, 2-acetyl-2-methylpropane-1,3-diol, the 5-acetyl-5-methyl-2-phenyl-1,3-dioxans and 5-(α-hydroxyethyl)-5-methyl-1,3-dioxan were prepared by published routes.[2]

5-Benzoyl-5-methyl-1,3-dioxan

A mixture of propiophenone (134 g, 1 M), paraformaldehyde (120 g, 4 M) and *p*-toluenesulphonic acid (40 g) in 1,4-dioxan (120 ml) was boiled under reflux for 18 h, cooled and poured into water (200 ml). The crude white solid produced was filtered off, washed with saturated sodium carbonate solution followed by water, and recrystallized from light petroleum (b.p. 40–60 °C)–diethyl ether (2:1) to yield 5-benzoyl-5-methyl-1,3-dioxan (155 g, 75%) as long, colourless needles, m.p. 90–91 °C (found: C, 70.1; H, 7.1; $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.9%).

2-Benzoyl-2-methylpropane-1,3-diol

A solution of propiophenone (80 ml, 0.6 M), 37% aqueous formaldehyde (100 ml) and methanol (22 ml) containing 30% aqueous sodium hydroxide solution (4 ml) was stirred and warmed gently for 15 min. After stirring overnight, the reaction was extracted with chloroform (3 × 100 ml), the extracts were washed with

water (100 ml) and dried (Na_2SO_4) and the solvent was removed *in vacuo*. The residue was distilled under reduced pressure, giving 2-benzoyl-2-methylpropane-1, 3-diol (34 g, 29%), b.p. 140–144 °C at 0.6 mmHg, which crystallized on standing. Recrystallisation from light petroleum (b.p. 40–60 °C)–diethyl ether (2:1) gave the product as colourless needles, m.p. 80 °C (lit.[10] m.p., 79–80 °C).

5-Benzoyl-5-methyl-2-phenyl-1,3-dioxan

A solution of 2-benzoyl-2-methylpropane-1,3-diol (19.4 g, 0.1 M) and benzaldehyde (10.6 g, 0.1 M) in dry benzene (200 ml) was boiled under reflux in the presence of a trace of *p*-toluenesulphonic acid using a Dean and Stark water separator. When the calculated amount of water (0.1 M) had been collected, the residual benzene was removed *in vacuo* giving a mixture of isomers of 5-benzoyl-5-methyl-2-phenyl-1,3-dioxan as a white solid (28 g, 99%). This was recrystallized from light petroleum (b.p. 40–60 °C)–diethyl ether (2:1) to give *c*-5-benzoyl-5-methyl-*r*-2-phenyl-1,3-dioxan (16 g) as white needles, m.p. 126 °C (found: C, 76.4; H, 6.6; $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%). The mother liquor was evaporated to dryness leaving a white solid (9 g) in which the second isomer was concentrated. Isomer separation (5 g of sample) was achieved by column chromatography over Grade IV Wöelm alumina (500 g) using light petroleum (b.p. 40–60 °C)–diethyl ether (3.2) as the eluent. Evaporation of the first 80 fractions (15 ml) gave t-5-benzoyl-5-methyl-*r*-2-phenyl-1,3-dioxan (3 g) as white needles, m.p. 52–53 °C (found: C, 76.1; H, 6.3; $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%).

Preparation of 5-(α-hydroxyethyl)- and 5-(α-hydroxybenzyl)-substituted 1,3-dioxans

The appropriate ketone was reduced by lithium aluminium hydride in diethyl ether or tetrahydrofuran to give, after the usual work-up, the following: 5-(α-hydroxybenzyl)-5-methyl-1,3-dioxan as white needles from light petroleum (b.p. 40–60 °C), m.p. 80 °C (found: C, 69.5; H, 7.8, $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.8%), ν_{max} 3627, 3539 cm^{-1}; *c*-5-(α-hydroxyethyl-5-methyl-*r*-2-phenyl-1,3-dioxan as white needles, m.p. 68 °C (lit.[2] m.p., 67–68 °C), ν_{max} 3637, 3558 cm^{-1}; *t*-5-(α-hydroxyethyl)-5-methyl-*r*-2-phenyl-1,3-dioxan, m.p. 52 °C (lit.[2] m.p., 52–53 °C) (found: C, 70.4; H, 8.2; $C_{13}H_{18}O_3$ requires C, 70.3; H, 8.2%), ν_{max} 3635 cm^{-1}; *c*-(α-hydroxybenzyl)-5-methyl-*r*-2-phenyl-1,3-dioxan as colourless needles, m.p. 104 °C (found: C, 76.1; H, 7.2. $C_{18}H_{20}O_3$ requires C, 76.0; H, 7.1%), ν_{max} 3629 and 3550 cm^{-1}; and *t*-5-(α-hydroxybenzyl)-5-methyl-*r*-2-phenyl-1,3-dioxan as needles, m.p. 97–98 °C (found: C, 75.9; H, 7.2. $C_{18}H_{20}O_3$ requires C, 76.0; H, 7.1%), ν_{max} 3620 cm^{-1}.

Preparation of 5-(α-aminoethyl)-5-methyl-1,3-dioxan and 5-(α-aminobenzyl)-5-methyl-1,3-dioxan

The appropriate oxime (**1** oxime or **7** oxime, Table 3) was dissolved in absolute ethanol (100 ml) containing concentrated hydrochloric acid (4 ml) and reduced with hydrogen in a Parr hydrogenator in the presence of Adams platinum oxide catalyst (1 g). The usual work-up gave 5-(α-aminoethyl)-5-methyl-1,3-dioxan as white flattened needles from toluene, m.p. 150–151 °C (found: C, 57.8; H, 10.4; N, 95; $C_7H_{15}O_2N$ requires C, 57.9; H, 10.4; N, 9.7%), ν_{max} 3610, 3500 cm^{-1}, or 5-(α-aminobenzyl)-5-methyl-1,3-dioxan as white flattened needles from toluene, m.p. 230–232 °C (found: C, 69.3; H, 8.2; N, 6.5; $C_{12}H_{17}O_2N$ requires C, 69.5; H, 8.3; N, 6.8%), ν_{max} 3627, 3539 cm^{-1}.

Preparation of *c*-5-(α-aminoethyl)-5-methyl-*r*-2-phenyl-1,3--dioxan and the 5-(α-aminobenzyl)-5-methyl-*r*-2-phenyl-1,3-dioxans

The appropriate oxime (**3** oxime, **9** oxime, **8** oxime, Table 3) in a mixture of absolute ethanol (30 ml) and ammonia solution (150 ml) was hydrogenated over 20% palladium on carbon (1.5 g). The usual work-up gave the following: *c*-5-(α-aminoethyl)-5-methyl-*r*-2-phenyl-1, 3-dioxan as white needles from light petroleum, m.p. 57 °C (found: C, 70.5; H, 8.8; N, 6.0; $C_{13}H_{19}O_2N$ requires C, 70.6; H, 8.7; N, 6.3%), ν_{max} 3616, 3530 cm^{-1}; *c*-5-(α-aminobenzyl)-5-methyl-*r*-2-phenyl-1,3-dioxan as a colourless oil, b.p. 110–112 °C at 0.05 mmHg (found: C, 76.1; H, 7.3; N, 4.8; $C_{18}H_{21}O_2N$ requires C, 76.3; H, 7.5; N, 4.9%), ν_{max} 3610, 3525 cm^{-1}; and *t*-5-(α-aminobenzyl)-5-methyl-*r*-2-phenyl-1,3-dioxan as colourless needles, m.p. 99 °C (found: C, 76.3; H, 7.5; N, 4.9; $C_{18}H_{21}O_2N$ requires C, 76.3; H, 7.5; N, 4.9%), ν_{max} 3620 cm^{-1}.

Table 3. Physical data on oximes of 1, 7, 3, 9 and 8

Compound	Yield%	M.p. (°C)	Elemental analysis (observed/calculated) C (%)	H (%)	N (%)
1 oxime	80	90–91	52.9/52.8	8.3/8.2	8.8/8.8
7 oxime	92	154	65.1/65.1	6.8/6.8	6.2/6.3
3 oxime	81	155–156	66.4/66.4	7.3/7.3	5.9/5.9
9 oxime	92	164	72.7/72.7	6.5/6.4	4.7/4.7
8 oxime	88	185	72.7/72.7	6.5/6.4	4.7/4.7

REFERENCES

1. E. L. Eliel and H. D. Banks, *J. Am. Chem. Soc.* **92**, 4730 (1970).
2. T. A. Crabb and R. F. Newton, *Tetrahedron* **26**, 693 (1970).
3. G. W. Buchanan, S. H. Preusser and V. L. Webb, *Can. J. Chem.* **62**, 1308 (1984).
4. S. E. Drewes, M. W. Drewes, I. J. McNaught and A. Tuinman,

S. Afr. J. Chem. **38**, 101 (1985); *Chem. Abstr.* **105**, 23777j (1985).
5. E. L. Eliel and H. D. Banks, *J. Am. Chem. Soc.* **92**, 4730 (1970); **94**, 171 (1972).
6. E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.* **88**, 5347 (1966).
7. E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.* **90**, 682 (1968); A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber and W. F. Bailey, *J. Am. Chem. Soc.* **93**, 4772 (1971).
8. A. Denis, M. Delmas, A. Gaset and J. P. Gorrichon, *Can. J. Chem.* **60**, 1962 (1982).
9. S. Mager and E. L. Eliel, *Rev. Roum. Chim.* **18**, 1387 (1973; *Chem. Abstr.* **80**, 70759e (1973).
10. B. Wesslen, *Acta Chem. Scand.* **21**, 713 (1967).