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CONFORMATIONAL ANALYSIS OF SUBSTITUTED PERHYDRO-1,2-OXAZOLO[3,2-*c*][1,4]OXAZINES BY NMR SPECTROSCOPY

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The ^{13}C NMR spectra of most of the substituted perhydro-1,2-oxazolo[3,2-*c*][1,4]oxazines (3) at low temperature showed the presence of two isomers of unequal populations. The major isomer is shown to be the *cis* isomer {except in 2-hydroxymethyl-2-methylperhydro-1,2-oxazolo[3,2-*c*][1,4]oxazine (3e)}, which is in equilibrium with the minor isomer (*trans* conformer) by a relatively slow nitrogen inversion. Intramolecular hydrogen bonding in oxazines, having 2-hydroxymethyl substituents, is shown to be an important factor in determining the population ratio of the two isomers. The barrier to nitrogen inversion was determined by detailed band-shape analysis of proton and carbon NMR spectra and were in the range 66·3–72·9 kJ mol^{-1}. The chair inversion had been slowed down, in one case, *trans*-dimethylperhydro-1,2-oxazol[3,2-*c*][1,4]oxazine-2,3-dicarboxylate (3j), to show the presence of the two forms of the *cis* isomers. The barrier to chair inversion is 41·5 kJ mol^{-1} as determined by proton NMR band-shape analysis of 3j.

INTRODUCTION

In our continuing study of *cis–trans* isomerism in 6–5 fused-ring systems, we prepared[1] a series of substituted perhydro-1,2-oxazolo[3,2-*c*][1,4]oxazines (**3**) by 1,3-dipolar cycloaddition reaction of the heterocyclic nitrone 5,6-dihydro-1,4-oxazine 4-oxide (**1**) with alkenes (**2**). The cycloadducts (**3**) can, in principle, exist in three different conformations, the *trans* conformer **3-A** and the *cis*-pair **3-B** and **3-C**. While the *cis* pair is in rapid equilibrium by chair inversion (C_i), one of the *cis* conformers (**3-B**) is converted into the *trans* conformer by a relatively slow nitrogen inversion process. Our study[2] on the cycloaddition products **4**, which lacks an oxygen atom in the ring skeleton of the six-membered ring, indicated an overwhelming preference for the *trans* conformer. The orientation of the lone pair of electrons on nitrogen holds the key for the selection of the regiochemical course in the peracid-induced ring opening of nitrone cycloaddition products **4** to generate new nitrones (**5** and **6**).[3] Conformation analysis of the cycloadducts **3** is thus of both theoretical and practical importance. Hence we undertook a systematic study to determine the *cis* ⇌ *trans* equilibrium constant (K) and nitrogen inversion barrier for several of the

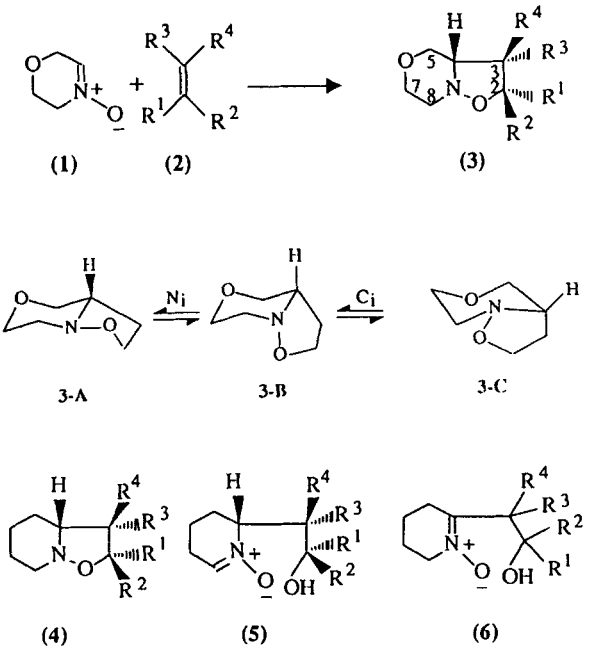

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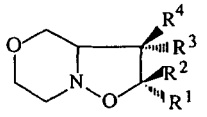
Table 1. Compounds **3** studied



3	R^1	R^2	R^3	R^4
a	H	Ph	H	H
b	CH_2OH	H	H	H
c	H	CH_2OH	H	H
d	H	CH_2OCOCH_3	H	H
e	CH_2OH	CH_3	H	H
f	CH_2OCOCH_3	CH_3	H	H
g	CO_2CH_3	CH_3	H	H
h	H	Ph	CO_2CH_3	H
i	H	CH_3	CO_2CH_3	H
j	H	CO_2CH_3	CO_2CH_3	H
k	H	CO_2CH_3	H	CO_2CH_3

cycloadducts **3** by NMR spectroscopy. The compounds studied are shown in Table 1.

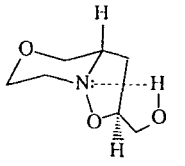
RESULTS AND DISCUSSION

The ^{13}C NMR spectra of all the compounds investigated, except **3c**, showed broad peaks above ambient temperature. On lowering the temperature, the spectral lines sharpened and showed the presence of two distinct isomers. This is the first report of the presence of distinct isomers in these compounds. The ^{13}C NMR chemical shifts of compounds **3** were assigned on the basis of the data[2] on isoxazolidines **4**, general chemical shift arguments and consideration of substituent effects, and are given in Table 2.

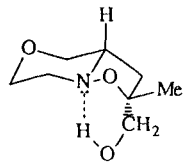
The ^{13}C chemical shifts of the C-2, C-3, C-4 and C-8 of isomers of **3** are similar to those of the isomers of **4** with corresponding substituents. However, the major isomer of **3** showed similar chemical shifts to that of the minor isomer of **4**, and the minor isomer of **3** showed similar chemical shifts to that of the major isomer of **4**. The major isomer of **4** was shown to be the *trans* isomer from x-ray diffraction[4] and chemical shift data. Hence it follows that the major isomer of **3** should have the *cis* conformation **3-B** and **3-C**, whereas the minor isomer should have the *trans* conformation **3-A**. This assignment is further supported by low-temperature ^1H NMR studies (see below). The chemical shifts are given in Table 2.

In any one compound, the carbons of the *cis* isomer are more shielded than the corresponding carbons of the *trans* isomer, except for C-2, which is less shielded in the *cis* isomer. The axial oxygen substituent of the morpholine ring in the *cis* conformer **3-B** will have *γ-gauche* interactions with C-5 and C-7, whereas the axial CH_2 substituent of the *cis* conformer **3-C** will have *γ-gauche* interaction with C-8, leading to shielding. This provides further evidence that the major isomer is indeed the *cis* pair.

Where we observe only one isomer throughout the temperature range -50 to $+50\,^{\circ}C$ as in **3c**, the ring carbon shifts match those of the *cis* (major) isomer. We therefore conclude that **3c** exists almost 100% in the *cis* conformation, since the *cis* is generally preferred over the *trans* conformation in these systems. The additional stability rendered by the intramolecular N:···H—O hydrogen bonding, possible only in the *cis* conformation of **3c**, completely precludes the presence of any *trans* conformer for this compound. The importance of the intramolecular hydrogen bonding is further demonstrated in **3e**, where the major isomer is found to be the *trans* isomer from the chemical shift data. The intramolecular hydrogen bonding in **3e** is possible only in the *trans* conformation and hence this conformer predominates. The corresponding compound of **3e** in the isoxazolidine series **4** exists in solution exclusively as the



(3c)



(3e)

trans conformer, whereas the corresponding compound of **3c** in the series **4** showed the presence of two isomers. Whereas the adduct **3c** remains exclusively in the *cis* form because of the stabilizing N:···H—O bonding, the corresponding acetyl derivative **3d** does not enjoy such stabillzation, as such the *trans* form of **3d** exists to some extent. Changing the adduct **3e** into its acetyl derivative **3f**, the *cis*/*trans* ratio is changed from 18 : 82 to 50 : 50. The N:···H—O bonding which is possible only in the *trans* form of **3e** allows this adduct to be the predominant conformer.

All this evidence supports the view that the *cis* conformation of the adducts, **3**, with the exception of **3e**, is thermodynamically more stable than the *trans* conformation, whereas in the adducts **4** the preferred isomer is *trans*. Even though the *trans* isomer (e,e) of **4** or its carbocyclic counterpart bicyclo[4.3.0]onane (hydrindane) is more stable than the *cis* isomer (e, a), this preference is considerably less than the corresponding preference for the 1,2-dimethylcyclohexanes.[5] This is attributed to the fact that *trans*-hydrindane, with a torsional angle of 72° of the *trans*-1,2 bond in the five-membered ring being larger than the normal torsional angle of 60° in a six-membered ring, is appreciably strained. The torsional strain results from the increased puckering of the chair against a steep potential barrier. Any change in the ring skeleton that would

Table 2. ^{13}C NMR chemical shifts[a] of adducts **3**

Compound 3	Conformer	C-2	C-3	C-4	C-5	C-7	C-8	Other[b]
a	*cis*	78·36	37·30	59·62	65.00	64·87	49·56	^{i}142·01; ^{o}128·16; ^{p}127·34; ^{m}125·98
	trans	77·32	38·60	64·90	69·67	69·52	55·42	^{i}140·53; ^{o}127·56; ^{p}127·34; ^{m}126·48
b	*cis*	79·95	31·58	58·40	65·33	64·89	57·03	CH_2 65·23
	trans	76·24	32·06	63·90	69·91	65·23	55·53	
c		77·95	30·23	59·84	65·21	64·77	49·67	CH_2 63·78
d	*cis*	74·65	31·45	59·15	65·70	65·09	49·78	CO 170·75 CH_2 64·57
	trans	73·35	33·95	65·10	69·60	69·52	55·68	CH_3 20·70
e	*cis*	84·27	37·16	58·60	68·32	64·07	51·10	Me 24·32 CH_2 69·65
	trans	80·46	38·36	64·99	69·60	65·57	55·48	Me 22·42
f	*cis*	82·00	37·94	64·15	68·76	64·88	51·02	Me 24·79; CO 170·90 CH_2 65·16
	trans	78·41	40·12	64·67	69·86	69·09	55·51	Me 24·84; CH_3 24·65
g	*cis*	80·76	52·64	63·25	64·76	63·79	49·33	^{i}139·64; ^{o}128·53; ^{p}128·11; ^{m}126·41; CO 172·56 OMe 56·38
	trans	79·97	55·78	65·04	68·16	67·06	52·29	^{i}138·48; ^{o}128·38; ^{p}128·11; ^{m}126·41; CO 170·93
h	*cis*	75·28	52·47	62·67	64·90	63·84	49·08	CO 173·16; Me 19·70 MeO 54·23
	trans	74·73	55·66	64·80	68·03	66·62	52·11	CO 171·32; Me 19·12
i	*cis*	76·68	52·42	60·90	62·86	62·86	49·80	CO 170·04, 170·68; Me 52·81
	trans	76·10	56·15	64·62	68·32	65·21	51·75	CO 169·70, 16·51; Me 52·63

[a] In ppm relative to internal TMS at −25 °C.
[b] *i*, *o*, *p* and *m* refer to *ipso*, *ortho*, *para* and *meta* carbons of the phenyl group, respectively.

introduce more attractive (or less repulsive) interactions in the *cis* than in the *trans* conformers may even cause reversal in the order of stability of the isomers.

To pinpoint the origin of the difference between the conformational preference of the compounds **3** and **4**, undoubtedly one has to consider the presence of an additional oxygen in the ring skeleton of **3**. The lone pairs on oxygen in the six-membered ring of **3** have smaller steric demand[6] than the C(6)—H bonds in **4**, and as such the axial substituent in the *cis* conformer **3-C** would experience smaller 1,3-diaxial interactions and should enjoy a smaller repulsive interaction in comparison with the corresponding *cis* conformer of **4**. The six-membered ring in *cis*-hydrindane[5] is considerably flattened towards the flexible form against a soft potential barrier to accommodate the bond angle requirements of the half-chair or envelope form of the five-membered ring. The presence of oxygen would facilitate such ring flattening to a greater extent in **3** than in **4** since bond eclipsing, which accompanies the ring flattening, is less extensive with oxygen in the ring skeleton.[7] The axial substituents in the *cis* conformers of **3** would thus experience (as in any flattened ring) smaller 1,3-diaxial interactions than in the *cis* conformer of **4**. Consideration of all these factors may, presumably, explain the difference in the conformational preference of **3** and **4**.

Nitrogen inversion

^{13}C NMR spectra show well separated signals for the two isomers; the *trans* conformer and the *cis* pair down to $-50\,^{\circ}C$. Integration of relevant peaks gives the population trends in these systems. In the ^{1}H NMR spectrum, the C-2 proton shows distinct peaks for the two isomers at low temperatures. Equilibrium constants for the *cis* $\rightleftharpoons$ *trans* isomerization were calculated from the integration of ^{1}H NMR and ^{13}C NMR peaks and the values are reported along with the corresponding ΔG^{0} values at 298 K in Table 3.

To measure the barrier to nitrogen inversion, the coalescence temperature method could not be used as the populations for the two exchanging sites are widely different. Hence, a complete band-shape analysis, corresponding to a non-coupled two-site exchange with unequal populations was employed (see Experimental). The C(2)-H protons offered convenient signals to study the band shapes with variable temperatures, as these signals are away from any overlapping signals and show only first-order couplings. The adduct **3g** does not have C-2 protons, but the methyl protons at C-2 were singlets and the band shapes of these were used in the analysis. Compound **3e** also does not have protons at C-2 and these were no well separated methyl proton signals for the two isomers. In order to overcome this difficulty, the band shape of the ring carbon resonances of **3e** were utilized. For this purpose, three ring carbon signals were used at each temperature and the rate constants obtained are an average of three calculated values.

Table 3. Free energies of activation for nitrogen inversion, equilibrium constants and standard free energy changes for *cis* $\rightleftharpoons$ *trans* Isomerization of **3** at 298 K in $CDCl_3$

Compound **3**	$\Delta G^{\neq}$ (kJ mol^{-1})	K	ΔG^{0} (kJ mol^{-1})
a	68·6	0·25	+3·4
c	—	0·0	—
d	ND[a]	0·11	+5·4
e	66·3	4·5	−3·8
f	ND[a]	1·0	0·0
g	69·5	0·11	+5·4
h	66·6	0·53	+1·5
i	66·4	0·53	+1·5
j	70·2	0·20	+3·9
k	72·9	0·11	+5·4

[a] Not determined.

Obtaining accurate exchange rate constants by fitting NMR band shapes is well known to be fraught with difficulties, and considerable errors in thermodynamic parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ if Eyring plots are used.[8] In fact, many of the errors are systematic in nature, and those resulting for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are often mutually compensatory so that $\Delta G^{\neq}$ is better defined near the coalescence temperature. Although $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained, we ascribe little significance to them for the reasons stated above, and they are not reported here. The $\Delta G^{\neq}$ values calculated for $+25\,^{\circ}C$ (near the coalescence temperature) are reported in Table 3. (In making use of Eyring plots it was assumed that the transmission coefficient was unity.) To the best of our knowledge, this is the first report on a nitrogen inversion barrier in any morpholine system.

The nitrogen inversion barrier is expected to be high when an oxygen atom is directly attached to the nitrogen as in isoxazolidines.[9] A high inversion barrier of 65·3 kJ mol^{-1} has been reported[10] for

$$\overline{CH_2CH_2CH_2ON}(Me)$$

in deuterochloroform. For the compounds in series **4**, the nitrogen inversion barriers are in the range 65·2–69·0 kJ mol^{-1}. The nitrogen inversion barriers determined in this study are in the range 66·3–72·9 kJ mol^{-1}. The data indicate a slight increase in barrier in going from **4** to **3**. The structural change of introducing an oxygen atom in the six-membered ring may lead to an increase in the barrier. The similarity in the range of values further confirms that we are indeed measuring the nitrogen inversion barrier rather than the chair inversion barrier, as the morpholine ring inversion barrier is much lower than that of piperidine.[11]

Chair inversion

The efforts to slow down the chair inversion in the series **4** had been unsuccessful even at temperatures down to $-110\,^{\circ}C$. This is also true for all compounds studied here except **3j**. The major isomer signals of **3j** started to broaden as the temperature was taken below $-60\,^{\circ}C$. Further lowering of the temperature resulted in further broadening of the signal and then it reappeared as two sets of peaks of unequal intensity corresponding to the two *cis* isomers. The signals of the *trans* isomer remained sharp throughout the low temperature range (Figure 1). This is the first case where all three isomers have been observed in a 6–5 fused system with nitrogen at the fused position. The two *cis* isomers were in a ratio 1·6:1 at $-95\,^{\circ}C$ in CD_2Cl_2 whereas in toluene-d_8 at $-95\,^{\circ}C$ the ratio was 4·2:1.

Detailed band-shape analysis of C-2 proton signals of the two *cis* isomers was carried out over the temperature range -80 to $-30\,^{\circ}C$. Using the Eyring plot, the free energy of activation for the ring inversion from the major *cis* isomer to the minor *cis* isomer was calculated to be 42·7 kJ mol^{-1} at $-60\,^{\circ}C$. If we assume that the chair inversion passes through an intermediate twist-boat form, then a transmission coefficient of 0·5 should be used in the Eyring equation. If we use a coefficient of 0·5, then $\Delta G^{\neq}$ has a value of 41·5 kJ mol^{-1} at $-60\,^{\circ}C$. The chair inversion barrier for morpholine has been determined[11] from the coalescence temperature ($-70\,^{\circ}C$) to be 41·2 kJ mol^{-1}. This further proves that the lower barrier is for the chair inversion and the higher barrier is for the nitrogen inversion.

In most systems studied here and in the isoxazolidine series **4**, chair inversion could not be slowed at the temperatures accessible in the NMR probe with common solvents. This may be due to the chemical shifts of the two *cis* isomers being not sufficiently far apart and/or the amount of one of the *cis* isomers being exceedingly small. Since the rate of nitrogen inversion is relatively slow at $-100\,^{\circ}C$, we carried out a study at this temperature using crystals of **3a**, to investigate the nature of the conformation in the solid state. A few crystals of **3a** were added to a pre-cooled sample ($-150\,^{\circ}C$) of CD_2Cl_2 in an NMR tube. The NMR tube was then quickly transferred to the probe maintained at $-95\,^{\circ}C$ and the spectra were recorded at intervals of 2 min. Up to about 10 min, the spectra showed the presence of only one isomer, a broad quartet at δ 5·46 corresponding to the major (*cis*) isomer, with no peaks at δ 5·04 for the minor isomer. After 10 min, the sample was warmed to room temperature and then returned to $-95\,^{\circ}C$ in the probe. The spectrum recorded showed clearly the presence of the minor isomer (*ca* 20%). This experiment shows clearly that **3a** crystallizes solely in the *cis* conformation and at $-95\,^{\circ}C$ the rate of interconversion to *trans* is extremely slow owing to the high nitrogen inversion barrier. Since only one quartet was evident around δ 5.46 for 2-H, it is possible that only one form of the *cis* isomers is present for **3a** or the other form is found only in trace amounts. This may also explain the inability to slow the chair inversion with many of the compounds studied here. We feel that the major of the *cis* isomer has the conformation **3-B** as an oxygen substituent is better tolerated in the axial position than an alkyl substituent. An x-ray diffraction study of **3a** crystals is in progress to confirm the geometry in the solid state.

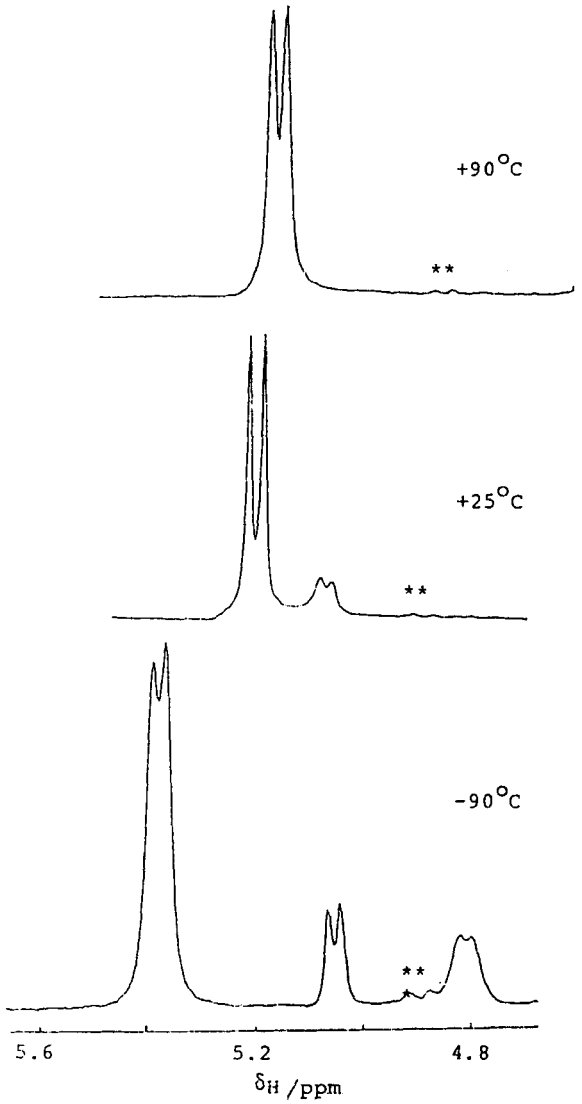


Figure 1. C(2)H signals of dimethyl fumarate adduct **3j** in toluene-d_8 at three temperatures. At $-90\,^{\circ}C$, all three isomers show distinct peaks; at $+25\,^{\circ}C$, averaged *cis* isomers and the *trans* isomer; at $+90\,^{\circ}C$, all three isomers are averaged out. *Peaks due to impurities

EXPERIMENTAL

The variable-temperature ^{13}C NMR spectra were recorded on Varian XL-200 NMR spectrometer, operating in the Fourier transform mode, with a digital resolution of 0·31 Hz at 50·3 MHz. The oxazines **3** were studied as 50 mg ml^{-1} solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The spectra were obtained in the usual way with wide-band proton decoupling and off-resonance decoupling to determine multiplicities of signals. Temperature control was achieved using the XL-200 temperature controller and calibrated using standard chemical shifts of methanol and glycol for low and high temperatures selectively. The temperatures were accurate to ±0·5 °C. ^1H NMR spectra were recorded at 200·05 MHz on the same instrument.

Simulations of exchange-affected ^{13}C NMR spectra were carried out using a computer program, AXEX,[12] corresponding to a two non-coupled sites exchange with unequal populations. At least three ring carbon resonances were utilized at each temperature, and matching of simulated and experimental spectra was carried out by eye (by superposing calculated spectra over the experimental spectra). The rate constant obtained at each temperature was an average of three

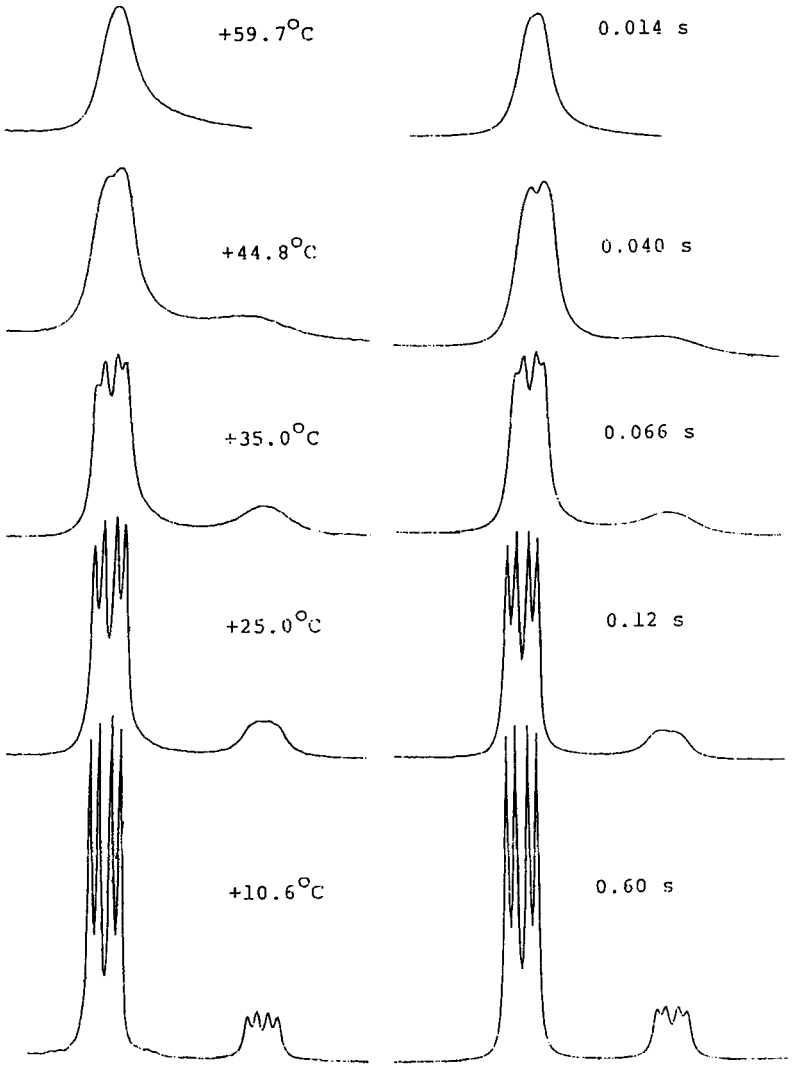


Figure 2. Experimental and calculated band shapes of the C(2)H signals of **3a** at different temperatures. The temperatures and the corresponding lifetimes of the major species are indicated on the experimental and the calculated spectra, respectively

calculated values. Simulation of exchange-affected ^1H NMR spectra was carried out by modifying the library two-site exchange program used above. The first-order coupling of the protons was simply assumed as giving overlapping two-site exchanges with same population ratio and equal rates of exchange. The intensity at each point was calculated applying the Hahn–Maxwell[13] and McConnell (HMM) equations[14] for two-site exchange, for each of the overlapping cases, which were displaced from one another by certain frequencies corresponding to the coupling constant, and then the intensities were summed to give the band shape at that point. For cases of coupling to two and three equivalent protons, appropriate intensity ratios were also taken into account. Experimental and calculated spectra for **3a** are shown in Figure 2.

All the cycloadducts except **3d** and **3f** were prepared as described.[1] The acetates **3d** and **3f** were prepared by heating a sample (1 mmol) of **3c** and **3e**, respectively, in acetic anhydride (2 ml) at 60 °C for 12 h. After removal of excess of acetic anhydride the residue was purified by silica gel chromatography using ethyl acetate–hexane (1 : 1) as the eluant to give the acetates (90%).

For most of the compounds, the ratio of the conformers was determined by integration of ^1H NMR signals of the C-2 protons or methyl protons attached to C-2. Integration of ^{13}C NMR signals was used to determine the ratio of conformers in **3d**, **3e** and **3f** since they do not have well separated proton signals for the two isomers in each case. The intensities of completely proton-decoupled ^{13}C signals may not be correlated rigorously with the abundances of the isomers because they are perturbed by the irradiation. However, the ^{13}C integration will not differ much between isomers, since we are measuring ratios under identical irradiation conditions. Strictly, the geometric differences could cause a difference in the nuclear Overhauser effect, which in our case should be very small. Indeed, for most of the compounds the ratio determined by ^1H integration[1] matches that of ^{13}C within experimental error.

2-Acetoxymethylperhydro-1,2-oxazolo[3,2-c][1,4]oxazine (*3d*). Colourless liquid (found, C 53·54, H 7·40, N 6·85; $C_9H_{15}NO_4$ requires C 53·72, H 7·51, N 6·96%); IR, $\nu_{max.}$ (neat) 2975, 2920, 2864, 1741, 1453, 1371, 1237, 1124, 1045, 974, and 849 cm^{-1}; NMR, δ_H ($CDCl_3$ at 35 °C) 1·85 (2H, m), 2·11 (3H, s), 2·80–4·00 (7H, m), 4·15 (2H, m) and 4·60 (1H, m).

2-Acetoxymethyl-2-methylperhydro-1,2-oxazolo[3,2-c][1,4]oxazine (*3f*). Colourless liquid (found, C, 55·65, H 7·83, N 6·37; $C_{10}H_{17}NO_4$ requires C 55·80, H 7·96, N 6.51%); IR, $\nu_{max.}$ (neat) 2995, 2883, 1743, 1456, 1374, 1238, 1089, 1043, 902, and 851 cm^{-1}; NMR, δ_H ($CDCl_3$ at 35 °C) 1·32 (3H, s), 1·88 (2H, m), 2.10 (3H, s) and 3·05–4·25 (9H, m).

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