References and Notes

(1) J. H. Brewster, *Top. Stereochem.*, **2**, (1967).
(2) A. Claesson, L. Olsson, G. R. Sullivan, and H. S. Mosher, *J. Am. Chem. Soc.*, **97**, 2919 (1975).
(3) W. L. Waters, W. S. Linn, and M. C. Caseiro, *J. Am. Chem. Soc.*, **90**, 6741 (1968).
(4) R. D. Bach, *J. Am. Chem. Soc.*, **91**, 1771 (1969).
(5) If the difference in rotations of Bach's two samples of **7** reflects the difference in stereospecificities of the mercurations and not a partial racemization of the organo mercuric acetate upon demercuration to give **7**, then an adjustment can be made of the maximum rotation for 1,2-cyclononadiene, $[\alpha]^{25}_{max}$ = 223° × 0.81 = 181°. This rotation is in close agreement with Moore's calculated absolute rotation.[6]
(6) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Am. Chem. Soc.*, **91**, 5918 (1969).
(7) W. H. Pirkle, D. L. Sikkenga, and M. S. Pavlin, *J. Org. Chem.*, **42**, 384 (1977).
(8) W. R. Moore, H. W. Anderson, and S. D. Clark, *J. Am. Chem. Soc.*, **95**, 835 (1973).
(9) J. L. Luche, E. Barreiro, J. M. Dollat, and P. Crabbé, *Tetrahedron Lett.*, 4615 (1975).
(10) The percentage of trans isomer in the mixture was determined by NMR comparison with authentic cis material prepared by hydroboration of 3-methoxy-4-heptyne.[11]
(11) H. C. Brown and G. Zwiefel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

Dynamic Stereochemistry of Imines and Derivatives. 12. Bis(*N*-alkylimines) Derived from Tetramethylcyclobutane-1,3-dione[1]

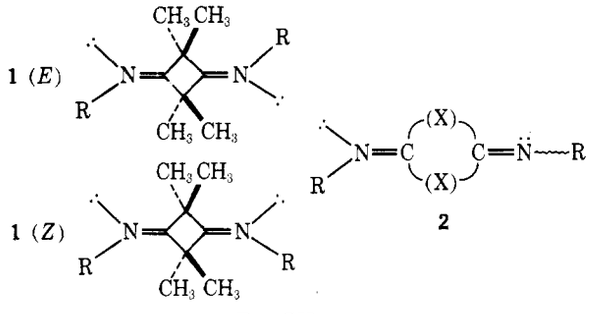
Johannes Bjørgo,[2a] Derek R. Boyd,*[,2a] W. Brian Jennings,*[,2b] Philip M. Muckett,[2b] and Lionel C. Waring[2a]

Department of Chemistry, Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland, and Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

Received April 12, 1977

A series of bisimines **1** where R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, and C_6H_{11} has been prepared in high yield using $TiCl_4$ as catalyst. The *tert*-butyl compound exists exclusively in the *E* configuration, but the other less hindered compounds showed 20–30% *Z* isomer at equilibrium in solution. It is proposed that the *Z* isomer is destabilized by a buttressing interaction between the ring methyl groups and the flanking *N*-alkyl substituents, though dipolar interactions were also evaluated. The rates of *E*–*Z* isomerization were determined, where appropriate, by direct equilibration at 35 °C and by dynamic NMR spectroscopy at higher temperatures. The $\Delta G^{\ddagger}$ values lie in the range 24.8–21.8 kcal mol^{-1} and decrease with increasing bulk of the *N*-alkyl group. The mono(*tert*-butylimine) **4** shows a markedly lower $\Delta G^{\ddagger}$ value of 19.2 kcal mol^{-1}. Some $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data were also determined, and the results are consistent with a lateral shift pathway for isomerization. ^1H and ^{13}C chemical shift data for both isomers are tablulated and discussed.

Tetramethylcyclobutane-1,3-dione should, in principle, condense with primary amines, RNH_2, to form bisimines of structure **1**. These compounds are capable of exhibiting an interesting type of *E*–*Z* isomerism, and are examples of the more general representation depicted in **2**. Other bisimines



a, R = CH_3
b, R = CH_2CH_3
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$
e, R = cyclohexyl

within the scope of this general structure are 1,4-diazabutatriene[3] (**2**, X = –) and the 1,4-benzoquinone bisimines (**2**, X = CH=CH).[4]

The ring methyl groups in **1** provide a useful handle for assigning the stereochemistry by NMR spectroscopy. Tetramethylcyclobutane-1,3-dione has been reported to form bisimines with aromatic amines in the presence of an acid catalyst, but alkylamines were found to give 2,2,4-trimethyl-3-oxopentanamides by ring cleavage.[5] Only in the case where R = cyclohexyl was the bis(*N*-alkylimine) **1** isolated in low yield (ca. 15%). Worman and Schmidt[6] have shown by ^1H NMR spectroscopy that these bisimines were formed as an *E*–*Z* isomeric mixture. The ring methyl signals from both isomers were reported to coalesce on raising the sample temperature above 100 °C, but no kinetic data were reported.

We now report the preparation of a series of *N*-alkyl compounds with structure **1** in good yield, including the very hindered compound where R = *tert*-butyl. The isomer distribution has been investigated and the rates of isomerization have been determined by direct thermal stereomutation and dynamic NMR spectroscopy.

Results and Discussion

Synthesis and Stereochemistry. Titanium(IV) chloride has proven to be a remarkably effective catalyst for the condensation of amines with a wide range of aldehydes and ketones, including relatively unreactive diaryl ketones.[7-9] This method also enabled the new bisimines **1a–d** to be prepared from tetramethylcyclobutane-1,3-dione in high yield. Prolonged reaction in boiling toluene was required, presumably due to steric hindrance around the carbonyl groups. The biscyclohexyl compound **1e**, which had been prepared previously in low yield,[5] was obtained in 65% yield by the above method.

^1H and ^{13}C NMR spectra showed that the bisimines **1a–c** (R = CH_3, CH_2CH_3, and $CH(CH_3)_2$) were present as an *E*/*Z* isomer mixture in solution. Stereochemical assignment was straightforward as the ring carbons C-2 and C-4 and their *gem*-dimethyl groups are nonequivalent in the *Z* form but isochronous in the *E* isomer (as noted previously for other compounds of this type[6]).

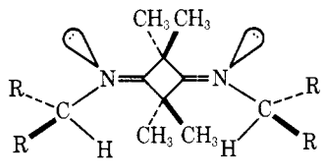
The position of equilibrium markedly favors the *E* configuration (Table I), hence the configuration at one nitrogen

Table I. ^{1}H NMR Data and Equilibrium Isomer Distribution for Bisimines 1[a]

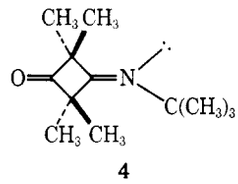
Compd	R	δ (ring CH_3)				δ (*N*-alkyl)		
		E	Registry no.	*Z*	Registry no.	*E*	*Z*	% *Z*[b]
1a	CH_3	1.41	63196-47-4	1.27, 1.60	63297-69-6	3.29[c]	3.30[c]	26
1b	CH_2CH_3	1.40	63268-40-6	1.29, 1.55	63196-48-5	1.23[c]	1.24[c]	24
						3.50[d]	3.51[d]	
1c	$CH(CH_3)_2$	1.40	63196-49-6	1.30, 1.56	63267-70-9	1.17[c]	1.17[c]	21
						3.79[e]	3.79[e]	
1d	$C(CH_3)_3$	1.30	63196-50-9	*f*		1.25[c]	*f*	<0.5
1e	C_6H_{11}[g]	1.39	24627-18-7	1.29, 1.52	24627-17-6	3.41[e]	3.41[e]	~25[h]

[a] Measured in $CDCl_3$ solution (0.5 M) at 35 °C. [b] Precision ±1%. [c] CH_3 group. [d] CH_2 group. [e] CH group. [f] No signals due to the *Z* isomer were detected. [g] Saturated solution <0.5 M. [h] Overlap of the ring methyl and cyclohexyl methylene signals precluded an accurate determination of the isomer ratio.

atom is sensitive to the configuration of the other nitrogen, even though they are fairly remote. A buttress effect between the *gem*-dimethyl moiety and the flanking *N*-alkyl groups may account for the reduced stability of 1 (*Z*) compared with 1 (*E*). Molecular models indicate that these interactions are particulary severe in the *N*-*tert*-butyl compound **1d** which showed no detectable concentration of the *E* isomer. The inability to detect signals from the *Z* isomer of **1d** at 35 °C cannot result from unusually fast *E*–*Z* isomerization (i.e., fast on the NMR time scale), since no additional signals were detected in the NMR spectra even at −50 °C.[10] The *N*-ethyl, *N*-isopropyl, and *N*-cyclohexyl compounds **1b**, **1c**, and **1e** can minimize the interactions with the ring methyl groups by adopting preferred conformations as shown in **3**. Thus, the



3



4

equilibrium concentration of the *Z* isomer in these compounds is much closer to that in the *N*-methyl analogue **1a** than in the *N*-*tert*-butyl compound **1d**.

Further evidence for steric congestion in **1d** comes from the observation that tetramethylcyclobutane-1,3-dione gave only the monoimine **4** with *tert*-butylamine under conditions where less bulky amines gave bisimines (see Experimental Section).

Polar effects should also be considered. Thus, the *E* isomer has no net resultant dipole moment, whereas the *Z* isomer will have a dipole moment in the plane of the ring. However, the dipole–dipole repulsive interaction between the two N–R bonds in 1 (*Z*) was estimated[11] to be only ca. 17 cal mol^{-1} using the accepted value[12] of 0.45 D for the N–C bond moment in imines. This interaction is therefore too small to cause any significant perturbation of the *E*:*Z* ratio, and would in any case be mediated by the dielectric of the solvent and the intervening molecular structure.

The isomer ratio in the representative bisimine **1b** was investigated in a number of solvents and the results are given in Table II. It can be seen that the relative proportion of the *Z* isomer, which possesses a dipole moment, increases with increasing solvent dielectric constant. Hydrogen bonding effects may also play a role in methanol solution, as the proportion of the *Z* isomer is larger than would be indicated by the dielectric constant. Previous investigations of other imine systems have shown that alcohols can hydrogen bond to the nitrogen lone-pair electrons.[13,14] Although the bisimines have been depicted with planar rings, the molecule could be oscillating between puckered conformations. X-ray studies[15] on tetramethylcyclobutane-1,3-dione indicate that the ring is

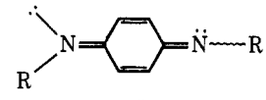
Table II. Equilibrium Isomer Composition of 1b as a Function of Solvent[a]

Solvent	ε[b]	% *Z*[c]
Carbon tetrachloride	2.24	22
Benzene-d_6	2.27	23
Chloroform-*d*	4.80	26
Dichloromethane	9.08	27
Acetone-d_6	20.7	25
Methanol-d_4	32.63	29
Acetonitrile-d_3	38.82	27
Dimethyl-d_6 sulfoxide	48.9	27
Formamide	109	31

[a] Determined at 35 °C on 0.5 M solutions. [b] Solvent dielectric constant as given in "Handbook of Chemistry and Physics", 53rd ed, The Chemical Rubber Co., Cleveland, Ohio, 1972. [c] Considered to be ±1%.

coplanar in the solid state, but other data favor rapid oscillation between puckered forms.[16]

Interestingly, the quinone bisimine **5** (R = 2,6-diethylphenyl), where steric buttressing effects between the N–R groups should be minimal, shows a 50:50 *E*:*Z* ratio.[4]



5

NMR Spectra. ^{1}H and ^{13}C chemical shifts are given in Tables I and III. Assignment of signals to the *E* and *Z* isomers was straightforward due to the large difference in abundance. The ^{13}C spectra were recorded using long pulse intervals, and the nuclear Overhauser effect was suppressed using gated decoupling. The two sets of ring methyl signals in the *Z* isomer were well separated in both the ^{1}H and ^{13}C spectra (by 0.33–0.26 and 1.69–0.33 ppm, respectively). However, assignment to the groups cis or trans to the *N*-alkyl substituents is uncertain, though the former may be at higher field in the ^{13}C spectrum due to a steric compression effect.[17] Assuming that the anisotropic effects of the N–R groups and the imino lone pairs are additive and that the bond lengths and angles are equal in both isomers, the ring methyl groups in the *E* isomer should resonate approximately midway between the two signals for the *Z* form. This was indeed the case in the ^{1}H spectra as the ring methyl signal of the *E* isomer was only 0.02–0.03 ppm from the mean position of the signals from the *Z* isomer (Table I). However, this prediction breaks down for the ^{13}C spectra (Table III).

Carbons C-2 and C-4 are markedly anisochronous in the *Z* isomer (δ = 3.71–5.20 ppm, see Table III). A similar effect has been observed previously in ^{13}C spectra of other imino compounds, and the upfield signal generally arises from the more hindered α carbon which is cis to the substituent on nitrogen.[18,19] Interestingly, in this case, the signal from the *E* iso-

Table III. ^{13}C NMR Data for Bisimines 1[a]

	R	δ (ring CH_3)		δ (C-2, C-4)		δ (C=N)		δ (N-alkyl)	
		E	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*
1a	CH_3	22.55	21.44, 23.13	57.70	56.07, 59.78	180.82	180.30	39.50[b]	38.59[b]
1b	CH_2CH_3	23.15	22.55, 23.13	57.63	55.62, 60.10	179.33	178.74	16.44[b]	16.44[b]
								46.91[c]	45.87[c]
1c	$CH(CH_3)_2$	123.39	23.06, 23.39	57.44	55.03, 60.23	177.25	176.66	24.04[b]	24.04[b]
								52.43[d]	51.26[d]
1d	$C(CH_3)_3$	25.34		54.84		174.00		31.25[b]	
								60.82[e]	

[a] Measured in $CDCl_3$ solution (0.5 M) at 25 °C (digital resolution 0.065 ppm). [b] CH_3 group. [c] CH_2 group. [d] CH group. [e] Quaternary carbon.

Table IV. Kinetic Data and Free Energies of Activation for Imine Isomerization[a]

Compd	Temp, °C	Method	k_{E-Z}, s^{-1}	k_{Z-E}, s^{-1}	$\Delta G^{\ddagger}_{E-Z}$,[b] kcal mol^{-1}	$\Delta G^{\ddagger}_{Z-E}$[b] kcal mol^{-1}
1a	35.0	Equilibration	1.62×10^{-5}	5.35×10^{-5}	24.8	24.1
	176.5	DNMR	11.7	28.9	24.5	23.7
1b	160.5	DNMR	11.2	32.0	23.6	22.7
1c	35.0	Equilibration	0.781×10^{-4}	3.17×10^{-4}	23.9	23.0
	144.8	DNMR	9.44	33.0	22.9	21.8
4	84.5	DNMR	14.3[c]	14.3[c]	19.2[c]	19.2[c]

[a] In 1,2,4-trichlorobenzene solution. [b] Calculated from the Eyring equation: $\Delta G^{\ddagger} = 1.987\ T\ (\ln\ (T/k) + 23.75994)$; error limits ±0.1 kcal mol^{-1}. [c] No *E*–*Z* isomerism is possible for this monoimine; data refer to topomerization.

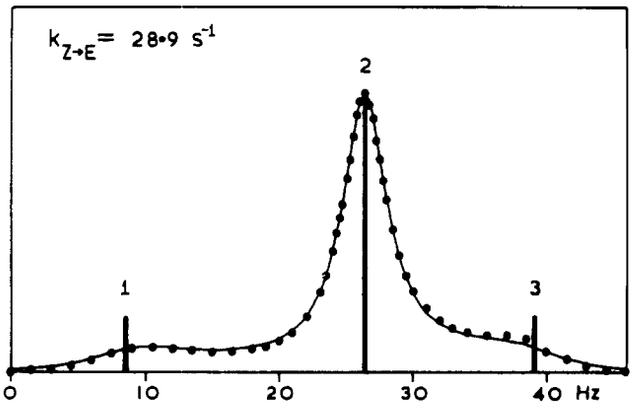


Figure 1. Experimental (●) and "best fit" computed (solid line) dynamic ^1H NMR spectra of the ring methyl groups of **1a** at 176.5 °C in 1,2,4-trichlorobenzene. The preexchange signal positions are also indicated; signals 1 and 3 = *Z* isomer; signal 2 = *E* isomer.

mer is indeed reasonably close to the midpoint of the two signals from the *Z* form.

The imino carbon shifts for both isomers are only slightly different, but the signals move significantly upfield on increasing the bulk of the *N*-alkyl group. Similar effects have been observed in acyclic imines of the type $C_6H_5CH{=}CHCH{=}NR$.[19] The effect of changing the N–R substituent along the series methyl, isopropyl, *tert*-butyl is to shift the imino carbon signal upfield by 4.3 and 7.0 ppm in the latter compounds, compared with shifts of 3.6 and 6.8 ppm in the bisimines 1. The various *N*-alkyl group hydrogens and carbons exhibit very similar shifts in both isomers, though the N–C signals were detectably anisochronous in the *E* and *Z* forms.

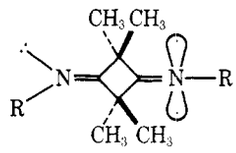
Isomerization Studies. Careful sublimation or recrystallization of **1a** and **1c** afforded crystals of the pure *E* isomer (as shown by ^1H NMR analysis immediately after dissolution of the sample). The stereomutation was monitored at 35 °C in 1,2,4-trichlorobenzene solution by following the appearance of the *gem*-dimethyl signals of the *Z* isomer as a function of time. Imine **1b** was a liquid and not amenable to thermal stereomutation studies.

The degenerate isomerization of **1a**, **1b**, and **1c** was also investigated at high temperature in 1,2,4-trichlorobenzene solution by dynamic ^1H NMR spectroscopy. On raising the probe temperature to between 140 and 180 °C (depending on the compound), both *gem*-dimethyl signals of the *Z* isomer broadened and coalesced with the larger single $C(CH_3)_2$ resonance of the *E* isomer. The site exchange process therefore involves three signals of unequal intensity and two interdependent rate constants (k_{E-Z} and k_{Z-E}). The band shape near the "coalescence temperature" was analyzed using methods described elsewhere.[20] On numbering the ring methyl signals in order of increasing field (i.e., signals 1 and 3 = *Z* isomer; signal 2 = *E* isomer) the elements of the exchange matrix $\mathbf{R}_{ij}$ (see ref 20) were as follows: $\mathbf{R}_{12} = \mathbf{R}_{32} = k_{Z-E}$, $\mathbf{R}_{21} = \mathbf{R}_{23} = k_{Z-E}/2K$, all other $\mathbf{R}_{jk} = 0$ (where $K = k_{Z-E}/k_{E-Z}$). A representative band shape at coalescence in depicted in Figure 1. Rate constants and free energies of activation for **1a–c** determined by dynamic NMR and by direct equilibration are given in Table IV. Kinetic data could not be obtained for the bis(*N*-*tert*-butyl) compound (**1d**), as this imine existed exclusively in the *E* configuration. However, the topomerization of the monoimine **4** was investigated by observing the coalescence of the two sets of ring methyl signals at 84.5 °C. In this case, the exchange is a simple two-site process, though the overlapping *tert*-butyl signal was included in the band shape analysis as an additional nonexchanging site. The results are given in Table IV.

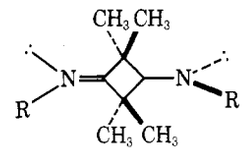
The free-energy barriers to isomerization of **1a–c** decrease with increasing branching of the *N*-alkyl group. The markedly lower barrier in the monoimine **4** is almost certainly due to the large bulk of the *N*-*tert*-butyl group rather than any transannular effect from the carbonyl group. The difference in $\Delta G^{\ddagger}_{E-Z}$ for **1a** and **4** (ca. 5.5 kcal mol^{-1}) closely parallels the situation in imines derived from 4-nitrobenzophenone where the interconversion barrier is lowered by ca. 5.7 kcal mol^{-1} on replacing *N*-methyl with *N*-*tert*-butyl.[9]

In the case of imines **1a** and **1c**, combination of the equilibration and dynamic NMR data for the same solution allowed the activation enthalpy and entropy to be determined. Activation entropies for intramolecular stereodynamic processes are usually very small, since solvation effects are commonly minimal and there are often only small differences in rota-

tional and vibrational contributions between the ground and transition states.[9,21] The $\Delta S^{\ddagger}$ value for **1a** is indeed small (Table V). The transition state **6** for *E–Z* isomerization, assuming a lateral-shift mechanism (see below), lacks the twofold rotational axis present in the ground states **1** (*E*) and **1** (*Z*). Accordingly, there should be a statistical contribution to $\Delta S^{\ddagger}_{E-Z}$ and $\Delta S^{\ddagger}_{Z-E}$ of $\mathbf{R} \ln 2 = 1.4$ cal mol^{-1} K^{-1}. Therefore, the intrinsic contribution to $\Delta S^{\ddagger}$ is indeed close to zero for imine **1a**. The larger (positive) entropy term for **1c** might be due to severe steric hindrance to libration of the isopropyl groups in the ground state. These restrictions are removed for one isopropyl group in the transition state **6**, R = $CH(CH_3)_2$, which should therefore have higher entropy.



6



7

The mechanism of imine isomerization is of considerable interest, since at least four possibilities have been considered in the literature, viz: (1) simple rotation around the C=N bond,[21,22] (2) planar nitrogen inversion (lateral shift),[21,22] (3) reversible tautomerization coupled with rapid rotation around the CN single bond in the enamine,[23] and (4) reversible addition of traces of acidic impurity across the double bond, coupled with fast rotation around the CN single bond in the adduct.[24] Isomerization pathways intermediate between pure rotation (1) and planar nitrogen inversion (2) are also possible.[25] Pathway (3) can be excluded for the imines in this investigation, since they have no α-hydrogen atoms. Furthermore, the relatively small positive $\Delta S^{\ddagger}$ values (Table V) are inconsistent with the addition route (4), since this involves a large negative activation entropy.[24] In any case, the samples were carefully purified in order to minimize the possibility of catalysis by trace impurity. Experimental data for other imines generally support the lateral-shift mechanism rather than C=N rotation.[9,22] The close similarity between the barriers in the bisimines **1a–c** and those reported for acyclic *N*-alkylimines, e.g., $(CH_3CH_2)_2C{=}NCH_2C_6H_5$ ($\Delta G^{\ddagger}$ = 24.5 kcal mol^{-1})[23] and 4-$NO_2C_6H_4(C_6H_5)C{=}NCH_3$ ($\Delta G^{\ddagger}_{E-Z}$ = 26.1 kcal mol^{-1})[9], supports a common pathway (nitrogen inversion). The slightly lower $\Delta G^{\ddagger}$ values for **1a–c** may be ascribed to greater steric hindrance in the ground state. Were bond rotation operative, one might have expected that the incorporation of the imino carbon into a four-membered ring would have had a more marked effect on the C=N torsional potential, as this carbon atom is directly involved in the dynamic process. The observed lowering of $\Delta G^{\ddagger}$ with increasing steric bulk of the *N*-alkyl substituents also supports an inversion mechanism. Thus, an inspection of molecular models indicated that the transition state **6** for nitrogen inversion is much less hindered than the ground states, whereas the transition state **7** for C=N rotation still suffers from considerable interactions between the *N*-alkyl substituent and the ring methyl groups. However, it should be emphasized that the present results do not rigorously exclude a rotational or an intermediate pathway for isomerization.

Worman and Schmidt previously invoked a steric effect to account for the higher coalescence temperature (165 °C) of the biscyclohexyl compound **1**, R = C_6H_{11}, compared with the bisphenyl analogue **1**, R = C_6H_5 (T_c ca. 100 °C). This postulate is at variance with our observations that the barrier (and coalescence temperature) *decreases* with increasing bulk of the nitrogen substitutents. The low barrier in the phenyl compound is almost certainly a consequence of conjugation between the aryl group and the nitrogen lone-pair electrons. It is well established in other systems that an *N*-phenyl group stabilizes the transition state for nitrogen inversion.[21,22]

Table V. Enthalpies and Entropies of Activation for Isomerization of Bisimines 1a and 1c

Compd	$\Delta H^{\ddagger}_{E-Z}$,[a] kcal mol^{-1}	$\Delta H^{\ddagger}_{Z-E}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}_{E-Z}$,[b] cal mol^{-1} K^{-1}	$\Delta S^{\ddagger}_{Z-E}$,[b] cal mol^{-1} K^{-1}
1a	25.5	25.0	+2.3	+ 2.8
1c	26.6	26.2	+8.8	+10.5

[a] $\Delta H^{\ddagger}$ values are ±0.5 kcal mol^{-1}. [b] $\Delta S^{\ddagger}$ values are ±1.5 cal mol^{-1} K^{-1}.

Experimental Section

^{1}H NMR spectra were recorded on a Varian XL-100 or Perkin-Elmer R-14 or R-12B spectrometers in CW mode; ^{13}C spectra were obtained on a Jeol FX-60 Fourier instrument.

Bisimines (1) from Tetramethylcyclobutane-1,3-dione. The titanium(IV) chloride procedure described previously[7,8] proved to be satisfactory, though more vigorous conditions were necessary (particularly for the highly hindered *tert*-butyl compound **1d**). Typically, titanium(IV) chloride (0.05 M) in dry toluene (50 cm^3) was added slowly to tetramethylcyclobutane-1,3-dione (0.05 M) and excess amine (0.50 M) in dry toluene (100 cm^3) at ca. −10 °C under nitrogen. The mixture was then allowed to assume ambient temperature and refluxed for ca. 20 h. The cooled solution was then filtered and the residual solid washed thoroughly with dry benzene. Concentration of the filtrate and sublimation in vacuo (or distillation in the case of **1b**) gave the bisimine in ca. 50% yield. Further purification was achieved by recrystallization from hexane. In the case of *tert*-butylamine, the above procedure afforded the *mono*(*tert*-butylimine) **4**. However, the bisimine **1d** was obtained by employing an excess of titanium(IV) chloride (0.10 M) and continuing reflux for 4 days until infrared spectra indicated that the monoimine has been completely converted to the bisimine. Physical properties and microanalytical data for the bisimines are given below:

Bis(methylimine) (1a): mp 72 °C. Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.2; H, 10.9; N, 16.85. Found: C, 72.1; H, 10.9; N, 16.85.

Bis(ethylimine) (1b): bp 54–56 °C/2.0 mm. Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.2; H, 11.4; N, 14.4. Found C, 74.0; H, 11.1; N, 14.4.

Bis(isopropylimine) (1c): mp 113–115 °C. Anal. Calcd for $C_{14}H_{26}N_2$: C, 75.6; H, 11.8; N, 12.6. Found: C, 75.6; H, 11.7; N, 12.4.

Bis(*tert*-butylimine) (1d): mp 83–84 °C. Anal Calcd for $C_{16}H_{30}N_2$: C, 76.7; H, 12.1; N, 11.15. Found: C, 76.7; H, 12.1; N, 11.2.

Bis(cyclohexylimine) (1e): mp 149–151 °C (lit.[5] mp 152 °C).

Mono(*tert*-butylimine) (4): mp 60–62 °C. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.8; H, 10.8; N, 7.2. Found: C, 73.6; H, 10.6; N, 7.0.

Kinetic Studies. Thermal equilibrations were performed in the probe of the Perkin-Elmer (permanent magnet) spectrometer which is constantly maintained at 35.0 °C. The 1,2,4-trichlorobenzene used as solvent was washed with base and stored over anhydrous potassium carbonate to remove traces of acidic material. The solvent was preheated to 35 °C and the isomerization was followed on a freshly dissolved sample of the pure *E* isomer by integration and peak-height measurements. Rate constants were determined from the usual plot of ln $(x_e/x_e - x)$ vs. time for a reversible first-order approach to equilibrium.

Dynamic NMR studies were performed on the XL-100 using the same sample that had been previously studied by direct equilibration. Probe temperature was measured using a digital readout temperature indicator attached to a copper–constantan thermocouple which was inserted into the sample at the level of the receiver coil. Exchange rates for the three-site collapse were determined by computer analysis of the digitized experimental band shape.[20] Signal positions and the isomer distribution were measured at a series of temperatures in the slow-exchange region and extrapolated to the coalescence temperature.

Registry No., 63196-51-0; tetramethylcyclobutane-1,3-dione, 933-52-8.

References and Notes

(1) Part 11: J. Bjørgo, D. R. Boyd, D. C. Neill, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 1*, 254 (1977).
(2) (a) Queen's University of Belfast. (b) University of Birmingham.

(3) M. S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, **90**, 2471 (1968).
(4) R. W. Layer and C. J. Carman, *Tetrahedron Lett.*, 1285 (1968).
(5) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).
(6) J. J. Worman and E. A. Schmidt, *J. Org. Chem.*, **35**, 2463 (1970).
(7) H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, **32**, 3246 (1967); I. Moretti and G. Torre, *Synthesis*, 141 (1970).
(8) J. Bjørgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2*, 757 (1974).
(9) W. B. Jennings, S. Al-Showiman, D. R. Boyd, and R. M. Campbell, *J. Chem. Soc., Perkin Trans. 2*, 1501 (1976).
(10) The coalescence temperature in **1d** would be expected to be reasonably close to that determined for the monoimine **4** (84.5 °C).
(11) The dipole–dipole repulsion was calculated using the equations cited by J. M. Lehn and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1113 (1963). Coplanar geometry and standard bond lengths and angles were used. The resulting value of 17 cal mol^{-1} would correspond to <1% change in the isomer distribution at 35 °C. The lone-pair moment is not *directly* included in this estimation. However, even if this moment is assumed to be ca. 1.0 D, the dipole repulsion would still only exert a minimal effect on the *E*:*Z* ratio.
(12) O. Exner, "Dipole Moments in Organic Chemistry", Thieme, Stuttgart, 1975, p 33.
(13) J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J. Chem. Soc., Perkin Trans. 2*, 1081 (1974).
(14) W. B. Jennings, S. Al-Showiman, and M. S. Tolley, *Org. Magn. Reson.*, **9**, in press (1977).
(15) P. H. Friedlander and J. M. Robertson, *J. Chem. Soc.*, 3083 (1956); C. D. Shirrell and D. E. Williams, *Acta Crystallogr., Sect. B*, **30**, 245 (1974).
(16) C. Y. Chen and R. J. W. Le Fèvre, *Aust. J. Chem.*, **18**, 1293 (1965), and references therein.
(17) A referee has suggested that ^{13}C assignments for the ring methyls may be the reverse due to a deshielding δ effect, cf., H. Pearson, *Chem. Commun.*, 912 (1975).
(18) G. E. Hawkes, K. Herwig, and J. D. Roberts, *J. Org. Chem.*, **39**, 1017 (1974).
(19) N. Naulet, M. L. Filleux, G. J. Martin, and J. Pornet, *Org. Magn. Reson.*, **7**, 326 (1975).
(20) J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2*, 1052 (1976).
(21) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).
(22) H. O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973).
(23) W. B. Jennings and D. R. Boyd, *J. Am. Chem. Soc.*, **94**, 7187 (1972).
(24) W. B. Jennings, S. Al-Showiman, M. S. Tolley, and D. R. Boyd, *J. Chem. Soc., Perkin Trans. 2*, 1535 (1975).
(25) M. Raban, *Chem. Commun.*, 1415 (1970); M. Raban and E. Carlson, *J. Am. Chem. Soc.*, **93**, 685 (1971).

Rearrangement of α-Chloroaldimines: Synthesis of 2-Imidazolidinethiones[1]

Norbert De Kimpe,*[2] Roland Verhe, Laurent De Buyck, and Niceas Schamp

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure 533, B-9000 Gent, Belgium

J. P. Declercq,[2] G. Germain, and M. Van Meersche

Laboratory of Physical Chemistry and Crystallography, University of Louvain, B-1348 Louvain-La-Neuve, Belgium

Received April 4, 1977

1-Substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones have been prepared by reaction of *N*-1-(2-chloro-2-methylpropylidene)amines with potassium thiocyanate in methanol under reflux. The 1-substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones were conveniently converted into the corresponding 1-substituted 5,5-dimethyl-2-imidazolidinethiones by lithium aluminum hydride treatment in ethereal medium. The structure elucidation was based on NMR, IR, and mass spectrometry next to x-ray crystallographic analysis. The formation of the heterocyclic five-membered rings was explained by a mechanism involving an aziridine intermediate, which underwent competitive opening.

N-1-(2-Chloro-2-methylpropylidene)amines (1), easily obtained from isobutyraldimines and *N*-chlorosuccinimide, are a new class of simple bifunctional compounds which have been used recently as synthetic blocks in organic synthesis.[3,4] An entry into the heterocyclic chemistry is presented here.

Results and Discussion

In continuation of work on the reactivity of α-halogenated imino compounds, the reaction of α-chloroaldimines **1** with KSCN in methanol has been found to provide a convenient preparation of 1-substituted 4-methoxy-5,5-dimethyl-2-imidazolidinethiones (**2**) (Table I).

Treatment of compounds **2** with methyl iodide in dry acetone afforded imidazoline hydriodides **4**, which were converted into the 2-methylthioimidazolines **6** by alkali treatment (Scheme I). The structure of these products, which involved rearrangement of the imino nitrogen, was established by x-ray crystallographic analysis of 1-cyclohexyl-4-methoxy-5,5-dimethyl-2-methylthioimidazoline hydriodide (**4b**).

The molecular structure of compound **4b** as determined by the x-ray analysis is shown in Figure 1 together with the atom labeling system used. The final coordinates, standard deviations, and bond distances are listed in Tables II and III, included in the microfilm edition of this journal. The experimental conditions for the x-ray crystallographic analysis are further given in the Experimental Section.

A further support of the presence of a CH_3OCHN moiety in the heterocycles described here was provided by the conversion of **2** into the nonmethoxylated compounds **3**, i.e., 1-substituted 5,5-dimethyl-2-imidazolidinethiones, by reaction

Scheme I