measured on facilities supported by RR 00292-03. Additional support from the Andrew Mellon Foundation is gratefully acknowledged.

References and Notes

(1) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179 (1959).

(2) (a) R. W. Kierstead, R. W. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952); (b) P. L. Fuchs, *J. Am. Chem. Soc.*, **96**, 1607 (1974); (c) W. G. Dauben and D. J. Hart, *ibid.*, **97**, 1622 (1975).

(3) J. M. Steward and H. H. Westberg, *J. Org. Chem.*, **30**, 1951 (1965).

(4) J. E. Dolfini, K. Menich, P. Corlias, S. Danishefsky, R. Cavanaugh, and S. Chakrabartty, *Tetrahedron Lett.*, 4421 (1966).

(5) E. J. Corey and P. L. Fuchs, *J. Am. Chem. Soc.*, **94**, 4014 (1972).

(6) The only apparent exception to the requirement of two activating groups involves a thioprenoxide opening. See W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961). It should also be noted that cyclopropanes contained in systems which increase the normal ring strain are also subject to nucleophilic ring opening by one activating group.[8]

(7) J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

(8) A. Cairncross and E. P. Blanchard, *J. Am. Chem. Soc.*, **88**, 496 (1966).

(9) Intramolecular versions of this reaction involving the formation of three-,[10] five-,[11] and six-membered[12] rings can be achieved under relatively mild conditions.

(10) S. Danishefsky, J. Dynak, and M. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 81, (1973).

(11) S. Danishefsky, J. Dynak, W. E. Hatch, and M. Yamamoto, *J. Am. Chem. Soc.*, **96**, 1256 (1974).

(12) S. Danishefsky and J. Dynak, *J. Org. Chem.*, **39**, 1979 (1974).

(13) One exception, wherein a diactivated cyclopropane is opened under relatively mild conditons, is that of cuprate addition to a 1-cyano-1-carbethoxy system.[6] Another is the case[3b] where one of the activating groups is a phosphonium function. Presumably this grouping does not exert strong conformational requirements for activation. Finally, there is some indication[4] that the rather inaccessible 1,1-dicarbonitrile system undergoes facile ring opening, though in very low yield. This finding would be in keeping with the conformational formulations projected above. However, both in terms of availability and flexibility the system shown here is far superior to the dinitrile, even if preliminary results with the dinitrile could be improved upon and generalized.

(14) For the use of a cyclic acylal of malonic acid in a conceptually related way see L. S. Melvin and B. M. Trost, *J. Am. Chem. Soc.*, **94**, 1790 (1972).

(15) P. I. Abell and R. Tien, *J. Org. Chem.*, **30**, 4212 (1965).

(16) Cf. (a) M. Jones, W. Ando, M. E. Hendrick, A. Kulczycki, P. M. Howley, K. F. Hummel, and D. S. Malamant, *J. Am. Chem. Soc.*, **94**, 7469 (1972); (b) P. J. Scheuer and S. G. Cohen, *ibid.*, **80**, 4933 (1958).

(17) This assigned structure is supported by its (a) infrared, NMR, and mass spectra and (b) combustion analysis.

(18) I. Schuster and P. Schuster, *Tetrahedron*, **25**, 199 (1969).

(19) Cf. K. Okhata, T. Sakai, Y. Kubo, and T. Hanafusa, *J. Chem. Soc., Chem. Commun.*, 581 (1974).

(20) K. Pihalaja and M. Seilo, *Acta Chem. Scand.*, **23**, 3003 (1969).

(21) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972, pp 492–494.

(22) For a recent application of the acylal concept to lowering the activation of Diels–Alder reactions see W. G. Dauben, A. P. Kozikowski, and W. T. Zimmerman, *Tetrahedron Lett.*, 515 (1975).

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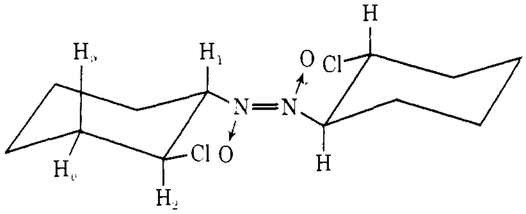
Homospecific and Heterospecific Dimerization of Nitroso Compounds. The Controversy Surrounding the Nature of the 2-Chloronitrosocyclohexane Dimer Obtained by Addition of Nitrosyl Chloride to Cyclohexene

Sir:

Despite existence of voluminous literature concerning the chemistry of nitrosyl chloride,[1-3] surprisingly little is known about the mechanism and the stereochemistry of nitrosyl chloride addition to a carbon–carbon double bond. Pending detailed discussion of both of these aspects in forthcoming papers, we should like to comment here on the controversy[4-7] surrounding the nature of the chloronitroso dimer[8] obtained by nitrosyl chloride addition to cyclohexene.

In previous reports by Ohno[5] and by Zefirov[6] and their coworkers the chloronitroso dimer obtained by nitrosyl chloride addition to cyclohexene in liquid sulfur dioxide or isopentyl nitrite-hydrochloric acid is described as (*E*)-1,1′-dioxidodiazenediylbis(*trans*-2-chlorocyclohexane),[12] mp 153° (ethanol)[5] or 132° dec,[6] respectively. Both groups assigned the configuration about the nitrogen–nitrogen double bond as *E*, and suggested that the addition of nitrosyl chloride occurred anti on the basis of 100-MHz proton NMR spectra. In both spectra the C_1–H and C_2–H appeared as a pair of triplets further split into doublets.[13] Ohno et al.[5] also reported that nitrosyl chloride addition to cyclohexene in methylene chloride, chloroform, or trichloroethylene occurred syn to give the corresponding (*E*)-1,1′-dioxidodiazenediylbis(*cis*-2-chlorocyclohexane), mp 133–135°.

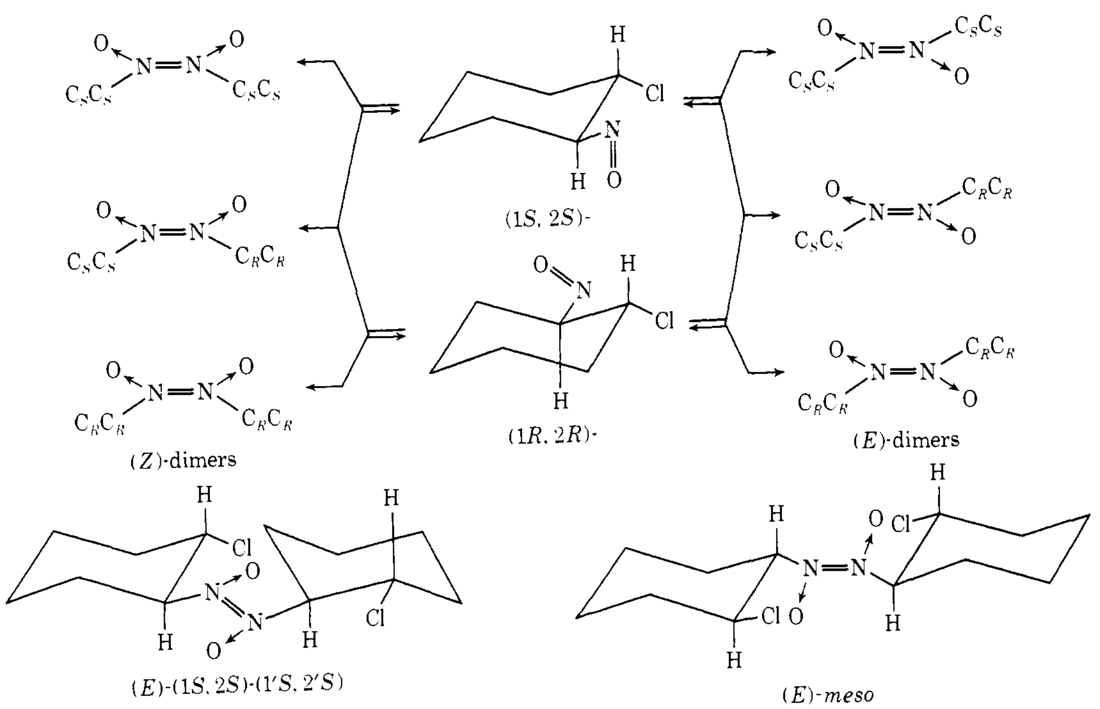
More recently Ponder et al.[7] forcefully challenged Ohno's conclusions. They claimed that, in repeating Ohno's study[5] in the solvents he used as well as in a number of others, they were in no case able to find any evidence for the cis product. They reported that their nitrosyl chloride adduct, like Ohno's trans product, had mp 152–153° after three crystallizations from ethanol. However, contrary to Ohno[5] and Zefirov,[6] they reported that the NMR spectrum at 100 MHz (deuteriochloroform) showed the C_1–H and C_2–H not as a pair of sextets,[13] but as an octet and a multiplet.[14] Ponder argued that the sextet for the C_1–H observed in Ohno's spectrum would result only if $J_{12} = J_{23a} = J_{16a}$, but that "*this is clearly not the case, since we observed eight well resolved lines for this proton.*"[7] And yet Ponder et al. felt that their adduct was the same as Ohno's as "*verified by its ir and uv absorption, melting point and its elemental analysis.*"[7]



To our knowledge these conclusions[7] were questioned neither by Ohno nor by Zefirov. In a forthcoming paper we shall discuss in detail solvent dependence of the stereochemical course of the nitrosyl chloride addition to a carbon–carbon double bond. Here we present a reconciliation of the apparent discrepancies among Ponder's, Zefirov's, and Ohno's proton NMR spectra of the (*E*)-chloronitroso dimer.

Upon addition of nitrosyl chloride to cyclohexene in liquid sulfur dioxide at −20° we obtained, in over 90% yield, a slightly colored solid which precipitated partially during the reaction. Purification of this solid via preparative TLC (silica gel, benzene) revealed three components with R_f values of 0.45, 0.35, and 0.05. Compound **1** (R_f = 0.45) melted at 153° (ethanol). Elemental analysis and mass spectrum confirmed the molecular formula of a nitroso dimer $C_{12}H_{20}N_2O_2Cl_2$ and the uv and ir spectra[15] established that the configuration of the nitrogen–nitrogen double bond was *E*. A 100-MHz proton NMR spectrum in deuteriochloroform showed two single proton signals at δ 4.32 and 5.49 as a pair of sextets. Thus it appears that **1** was identical with Ohno's (*E*)-1,1′-dioxidodiazenediylbis(*trans*-2-chlorocyclohexane). Compound **2** (R_f = 0.35) melted at 142–144° (chloroform–hexane), and elemental analysis, mass spectrum, and the uv and ir spectra[16] clearly established that this compound too was a nitroso dimer $C_{12}H_{20}N_2O_2Cl_2$ with the *E* configuration about the nitrogen–nitrogen dou-

Scheme I



ble bond, as in **1**. A 100-MHz proton NMR spectrum of **2** in deuteriochloroform showed two single proton signals at δ 4.36 and 5.46 as a pair of sextets as expected for a trans-1,2-disubstituted cyclohexane.[17] The compound **3** (R_f = 0.05) was present in small quantities and was proved to be 2-chlorocyclohexanone oxime by comparison with an authentic sample. A 100-MHz proton NMR spectrum of equal parts of **1** and **2** in deuteriochloroform showed two single proton signals at δ 4.33 and 5.51, the former as a multiplet and the latter as an octet consistent with the two overlapping sextets from **1** and **2**. Furthermore, a solution of either **1** or **2** in deuteriochloroform on standing at room temperature, or, faster, on warming to 60°, produced the NMR spectrum identical in every respect with that of the mixture of **1** and **2**. Thus, it is clear that in solution both **1** and **2** undergo facile equilibration to the same mixture.[18]

Addition of nitrosyl chloride to the double bond of cyclohexene provides a pair of enantiomeric *trans*-(1*S*,2*S*)- and *trans*-(1*R*,2*R*)-2-chloronitrosocyclohexanes. Dimerization of the two like or two different enantiomers, hereafter described as *homospecific or heterospecific dimerization*, respectively, would then give either (*Z*)-*SS-SS*, (*Z*)-*SS-RR*, and (*Z*)-*RR-RR*, or (*E*)-*SS,SS*, (E)-*SS-RR*, and (E)-*RR-RR* nitroso dimers (Scheme I).

Since the *SS-SS* and *RR-RR* dimers (e.g., with *E* configuration of the nitrogen–nitrogen double bond) have only a single twofold axis of symmetry, and belong to point group C_2, they are disymmetric nonsuperimposable mirror images of each other. Consequently, in solution they exist as a racemic modification or a *dl-pair*. The *SS-RR* dimer has a center of symmetry, belongs to point group C_i, and is therefore an optically inactive meso compound.

We have established that many other nitroso compounds also undergo homospecific and heterospecific dimerization, a concept which had not been previously recognized.[19]

The spectroscopic and chemical evidence presented clearly demonstrate that the two isolated (*E*)-1,1′-dioxidodiazenediylbis(*trans*-2-chlorocyclohexanes)[20] **1** and **2** are indeed the expected two (out of four possible) diastereoisomers, the thermodynamically more stable (*E*)-*dl*-pair and (*E*)-meso-compound.[18,21] The discrepancies among Ohno's,[5] Zefirov's,[6] and Ponder's[7] interpretations were obviously a consequence of fortuitous circumstances and reflect the lack of a general understanding of the basic principles involved not only in the dimerization of nitroso compounds but also in many other related transformations.[19] Apparently, both Ohno and Ponder separated **1** from a mixture of the diastereomers **1** and **2** without recognizing the separation. While Ohno's spectroscopic measurements were made with homogeneous **1**, Ponder's NMR spectrum was evidently taken after isomerization of the pure **1** (isolated) to an equilibrium mixture of **1** and **2** had occurred.

References and Notes

(1) L. J. Beckham, W. A. Tessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951).

(2) M. Plungunian and F. E. DeVry, "Nitrosyl Chloride", An Annotated Bibliography, Hercules Technical Informational Center, 1970.

(3) P. P. Kadzyauskas and N. S. Zefirov, *Usp. Khim.*, **37,** 7 (1968).

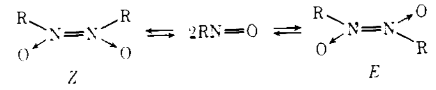
(4) Z. Yoshida and K. Nakagava, *Tetrahedron Lett.*, 2763 (1965).

(5) M. Ohno, M. Okamoto, and K. Nukada, *Tetrahedron Lett.*, 4047 (1965).

(6) N. S. Zefirov, P. P. Kadzyauskas, Yu. A. Ustynyuk, and Yu. K. Yur'ev, *Zh. Obshch. Khim.*, **36,** 764 (1966).

(7) B. D. Ponder, T. E. Walton, and N. Y. Pollock, *J. Org. Chem.*, **33,** 3957 (1968).

(8) Gowenlock[9] and also Smith[10] showed that the dimerization of nitroso compounds produces the corresponding disubstituted diazene 1,2-dioxides which often exist as a pair of interconvertible geometrical *Z* and *E* isomers. It is now well documented that the dimerization initially pro-



duces the *Z* isomer which under thermodynamic conditions isomerizes to the more stable *E* form.[11]

(9) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

(10) J. W. Smith, *J. Chem. Soc.*, 1124 (1957).

(11) B. G. Gowenlock and W. Lüttke, *Q. Rev., Chem. Soc.*, **12,** 321 (1958).

(12) The nomenclature used in this communication is based on J. H. Fletcher, O. C. Dermer, and R. B. Fox, *Adv. Chem. Ser.*, **No. 126** (1974).

(13) In Ohno's[5] spectrum ($CDCl_3$) C_1–H and C_2–H appeared at δ 5.49 and 4.32 as two triplets with *J* = 11 Hz further split into doublets with *J* = 3.5 Hz; in Zefirov's[6] spectrum ($CDCl_3$) the corresponding protons appeared as a pair of sextets at δ 5.53 and 4.34 with *J* = 10.7 and 4.5 Hz, respectively.

(14) In Ponder's spectrum the C_1–H and C_2–H appeared at δ 5.53 and 4.27 as an octet and a multiplet.

(15) Uv_{max} (EtOH), 294.5 nm (ϵ 8000); ir (KBr) 1227, 1216, 1193 cm^{-1}.

(16) Uv_{max} ($CHCl_3$), 296 nm (ϵ 9923); ir (KBr) 1222, 1212, 1188 cm^{-1}.

(17) In both **1** and **2** each sextet consisted of a triplet with *J* = 11 Hz further split into doublet with *J* = 3.5 Hz.

(18) When the crude reaction product after filtration from the sulfur dioxide

solution was treated with chloroform, a partial fractionation occurred. Elemental analysis and mass spectrum of the solid that was not readily soluble in chloroform confirmed molecular formula for a nitroso dimer $C_{12}H_{20}N_2O_2Cl_2$, and the uv and ir spectra (uv_{max} (EtOH) 278.0 nm (ϵ 7640); ir (KBr) 1420, 1300, 1110, 1045 cm^{-1}) indicated that this was a *Z* dimer. In ethanol, on standing, the intensity of the absorption at 278.0 nm gradually decreased and finally disappeared while at the same time a new absorption at 294.5 nm appeared, showing that the isomerization of the *Z* dimer to the thermodynamically more stable *E* isomer was taking place. On further standing the intensity of the absorption at 294.5 nm gradually decreased, and, when it had completely disappeared, the solution contained 2-chlorocyclohexanone oxime. Furthermore, a 100-MHz proton NMR spectrum of the crude reaction product in sulfur dioxide at 0° clearly showed that the crude reaction product was a mixture of both the (*Z*)- and (*E*)-1,1'-dioxidodiazenediylbis(*trans*-2-chlorocyclohexanes), which on standing underwent relatively fast isomerization to both *E* isomers, **1** and **2**, and a small amount of **3**.

(19) Numerous reports dealing with nitroso dimers have disregarded the possibility that the dimers investigated may exist as mixtures of the corresponding *dl* and meso compounds; e.g., (a) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961); (b) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964); (c) K. H. Bell, *Aust. J. Chem.*, **24**, 1089 (1971); (d) B. W. Ponder and P. W. Wheat, *J. Org. Chem.*, **37**, 543 (1972); (e) Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Can. J. Chem.*, **48**, 157 (1970); (f) C. Shive and L. B. Clapp, *J. Org. Chem.*, **36**, 1169 (1971); (g) K. A. Ogloblin and V. P. Semenov, *Dokl. Akad. Nauk SSSR*, **155**, 145 (1964); (h) H. C. Hamann and D. Swern, *J. Am. Chem. Soc.*, **90**, 6481 (1968); also references 1–7, 11, and many others. That the lack of understanding of the basic principles involved is not restricted only to the dimerization of nitroso compounds is illustrated by a recent paper by D. D. Tanner, N. Nychka, and T. Ochiai, *Can. J. Chem.*, **52**, 2573 (1974).

(20) However, from the available information it is not possible to decide which one of the two isolated diastereoisomers is the *dl* pair and which one is the meso compound. ^{13}C NMR spectra of (*E*)-1,1'-dioxidodiazenediylbis(*trans*-2-chlorocyclohexanes) and several other diastereoisomeric nitroso dimers will be presented elsewhere.

(21) Due to the great ease with which the *Z* isomers isomerize in solution to the *E* isomers,[11] it was not possible to achieve a similar separation of the diastereoisomeric (*Z*)-*dl*-pair and (*Z*)-meso compound.

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Conformational Equilibrium Trapping by High-Vacuum Cryogenic Deposition

Sir:

High-energy conformations are difficult to study directly because of their low equilibrium concentrations at room or low temperatures. This problem is especially serious when the barrier separating two conformations is relatively low, e.g., <15 kcal/mol, and the minor form lies more than 1 kcal/mol or so above the major one. Low temperatures are required under these conditions to avoid averaging effects in NMR spectroscopy, but this results in a very small population of the minor form. We now report a method for observing the NMR spectra of high-energy conformations for systems which have barriers of about 8 kcal/mol or higher.

The apparatus used is very similar to that employed in flash vacuum pyrolysis.[1] The compound, as a low pressure gas (ca. 0.2 Torr), is heated by passing it through a glass or quartz tube (2 × 30 mm) that is surrounded by an electrically heated resistance wire. The gas, which contains a relatively high proportion of the minor form because of its high temperature, is allowed to impinge in a high vacuum on a copper surface cooled to liquid nitrogen or other temperature. The deposited compound cools so rapdily that the conformational equilibrium set up at the high temperature is trapped.[2] The nonequilibrium population of the minor form remains unchanged for a time that depends on the temperature and the barrier separating the minor from the major form. At −170°, a free energy barrier of 8 kcal/mol gives a half-life of 8 hr, which is ample for NMR observation or other physical measurements. The NMR spectrum of a deposited sample is obtained by slowly condensing a suitable solvent onto the cold sample and allowing the solution to drip into a cold NMR tube, which is then transferred to a precooled NMR probe.

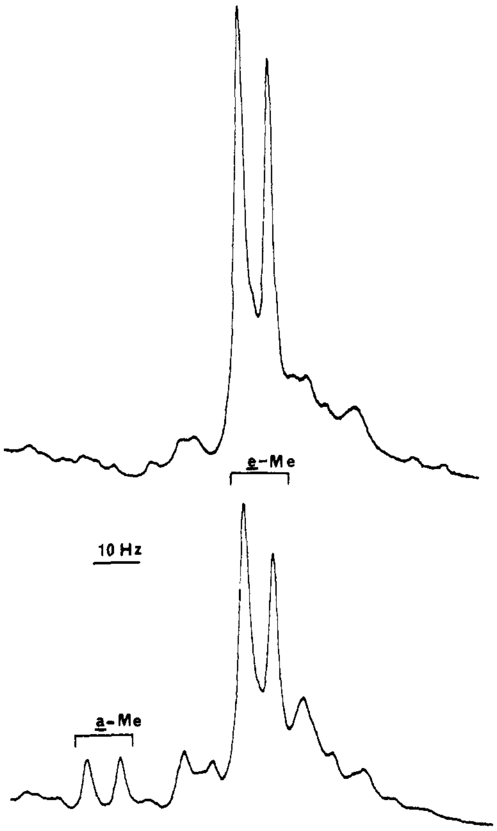
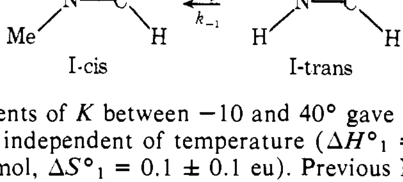


Figure 1. Bottom: 251-MHz ^{1}H NMR spectrum at −160° of methylcyclohexane obtained by high-vacuum deposition from a temperature of 500° onto a surface cooled to −175° (only the high-field region is shown). Top: same sample as at bottom after warming to −128° and recooling to −160°.

The instrumentation described above has been used to study the cis-trans isomerism in *N*-methylformamide (I) and the axial-equatorial equilibrium in methylcyclohexane, two systems that were chosen to test the practicality of the method. Compound I was deposited at −65° from a temperature of 540° and the ^{1}H NMR spectrum was measured in 1,2-dichloroethane. Integration of the signals showed 25% of the minor (cis) form[3] and this corresponds to a $\Delta G°$ (see below) in the gas phase at 540° of −2.2 kcal/mol, provided that the equilibrium is perfectly trapped. The equilibrium constant and the rate for return to equilibrium at −10.4° were measured and gave $K_{equil} = 16$, $\Delta G° = -1.44$ kcal/mol, $k_1 = 3.5 \times 10^{-4}$ sec^{-1}, $k_{-1} = 2.2 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger}_1 = 19.48$ kcal/mol, $\Delta G^{\ddagger}_{-1} = 20.92$ kcal/mol for the following reaction.



I-cis I-trans

Measurements of K between −10 and 40° gave $\Delta G°$'s that are almost independent of temperature ($\Delta H°_1 = -1.46 \pm 0.04$ kcal/mol, $\Delta S°_1 = 0.1 \pm 0.1$ eu). Previous NMR line-shape measurements[4] on I at 60° in the same solvent gave $\Delta G^{\ddagger}_1 = 19.0$ and $\Delta G^{\ddagger}_{-1} = 20.6$ kcal/mol, from which $\Delta G°$ can be calculated to be −1.6 kcal/mol, in satisfactory