

The largest isotope effect reported for *tert*-butyl- $d_9$  chloride is 2.624 at 45° (2.79 at 25°) for elimination in acetonitrile-pyridine.<sup>18</sup> The rate is pyridine independent. Ion-pair dissociation is a likely rate-limiting step for this elimination (E1<sup>III</sup>).<sup>19</sup> If so, then the isotope effect represents  $(k_t^H/k_t^D)_{\max}$ . The value  $(2.79)^{1/3} = 1.41$ , an upper limit for the isotope effect per CD<sub>3</sub> for the SN1<sup>III</sup> reaction, is close to that for trifluoroacetolysis of isopropyl brosylate. The evidence is not compelling, however. Shiner's interpretation of the increased isotope effect in trifluoroethanolysis<sup>17</sup> remains a possibility. A direct observation of a  $\beta$ -PIE is not available.

The theoretical finding that transition-state force constants for  $\alpha$ -C-H bonds in TS2 (see ref 1, Figure 1) depends much less strongly on the particular leaving group than do force constants in reactants suggests<sup>20</sup> that  $\alpha$ -PIE's may be approximately proportional to  $(k_t^H/k_t^D)_{\max}$ . This conclusion is supported by PIE estimates for isopropyl derivatives in Table II. The PIE for isopropyl chloride was assumed from other chlorides in Table II.

To summarize, the isotope effect on ionization reflects the ZPE change between the initial state and the transition state for ionization (see ref 1, Figure 1, TS1). The maximum isotope effect reflects the ZPE change between the initial state and the transition for intimate ion-pair separation (see ref 1, Figure 1, TS2). The solvolytic isotope effect for an SN1<sup>III</sup> reaction varies between these limits as intimate ion-pair partitioning varies. An evaluation of the PIE on internal return *vs.* solvent capture of ion pair II is necessary to delineate isotope effects for an SN1<sup>II</sup> reaction.

**Acknowledgment.** Acknowledgment is made to the National Science Foundation for partial support of this work.

(18) D. N. Kevill and J. E. Dorsey, *Chem. Ind. (London)*, 2174 (1967).

(19) Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Amer. Chem. Soc.*, **91**, 4199, 4205 (1969), and references therein.

(20) V. J. Shiner, Jr., M. W. Rapp, M. Wolfsberg, and E. A. Halevi, *ibid.*, **90**, 7171 (1968).

\* Address correspondence to this author.

B. L. Murr,\* M. F. Donnelly

Department of Chemistry, The Johns Hopkins University  
Baltimore, Maryland 21218

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### Origin of Temperature-Dependent Nuclear Magnetic Spectra of *N*-Carbethoxyazonin

Sir:

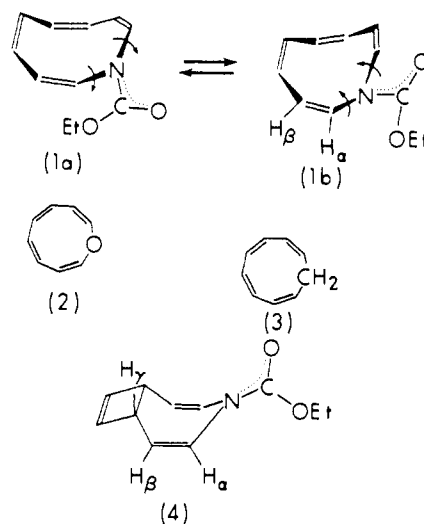
Earlier we reported that *N*-carbethoxyazonin (**1**) exhibited temperature-dependent nmr spectra,<sup>1</sup> whereas those of oxonin (**2**) and *all-cis*-cyclononatetraene (**3**)<sup>2</sup> remained invariant between 0 and -130° (CS<sub>2</sub> + THF- $d_6$ ). An obvious and logical conclusion from the spectral data is that these similar ring systems undergo rapid conformational change (of the rings), and we suggested that "the restricted rotation of N-CO<sub>2</sub>Et is mainly responsible for the temperature-dependent nmr spectra of **1**."<sup>1</sup> Recently, however, Anastassiou, Cellura, and Gebrian,<sup>3</sup> utilizing the same findings,<sup>1,4</sup>

(1) S. Masamune, K. Hojo, and S. Takada, *Chem. Commun.*, 1204 (1969).

(2) S. Masamune and R. T. Seidner, unpublished results.

(3) A. G. Anastassiou, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 375 (1970).

have drawn the conclusion that all the spectral data are accommodated with the presence of a fairly substantial nitrogen inversion barrier in **1**, but are inconsistent with restricted rotation of the carbamate group along the axis of the C-N bond. In view of the current interest in these types of compounds, we wish to point out that their conclusions (measured coalescence temperature -10 to -30°,  $\Delta F_c^\ddagger \approx 13$  kcal/mol) are incompatible with accumulated data and currently accepted interpretations<sup>5</sup> for the inversion of nitrogen and hindered rotation. We demonstrate herein that our original interpretation is entirely acceptable for the system in question.



Firstly, crystalline structures of amides and carbamates have shown<sup>6</sup> that these molecules possess planar trigonal nitrogen atoms and the C-N bond (of the amide N) and four atoms attached to these C and N atoms are coplanar or nearly so (in general coplanar to within 0.01 Å). In solution, these conformations are assumed to be at potential minima of rotation along the C-N axis. Thus the nitrogen pyramid of basic amines is flattened in amides and carbamates and the inversion rate of nitrogen, if not completely coplanar, increases enormously by conjugation with the carbonyl group.<sup>7</sup>

Secondly, they argued that the chemical shift of the  $\alpha$  hydrogen of **1** should be more affected than that of the  $\beta$  by the restricted rotation. Inspection of a Dreiding model, using a *trigonal (planar) nitrogen atom*, shows that the carbonyl group (or ethoxyl group) of **1** is nearly as close to the  $\beta$  hydrogen of the ring as to the  $\alpha$  in one of the two likely (ring) conformers (**1a** and **1b**) which are readily interconvertible by pseudorotation (see arrows in **1a** and **1b**) of the two C-N bonds of the

(4) S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

(5) For a recent review, see H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

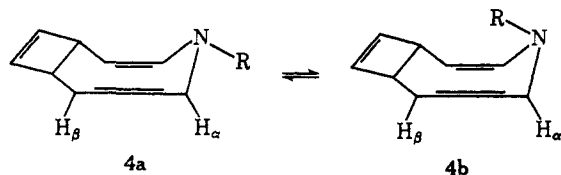
(6) For instance, see I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Amer. Chem. Soc.*, **90**, 5023 (1968); J. L. Katz and B. Post, *Acta Crystallogr.*, **13**, 324 (1960).

(7) An extreme example in which the double-bond character of the C-N bond effected by conjugation with C=O is suppressed is methoxy-carbonylaziridine, and yet the inversion rate of this compound is exceedingly high [ $T_c = -138^\circ$ ;  $\Delta F_c^\ddagger = 7.6$  kcal/mol; F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 324 (1967)], in spite of the fact that *N*-ethylaziridine inverts very slowly, compared with ordinary amines. On the other hand, acylpyrroles where the double-bond character of the C-N bond is assumed to be small for another reason exhibited a significant rotational barrier [e.g., acetylpyrrole,  $\Delta F_c^\ddagger = 13$  kcal/mol; T. Matuo and H. Shosenji, *Chem. Commun.*, 501 (1969)].

ring. Roughly estimating the shielding effect of the carbethoxyl group based on distance and angle, we find it very difficult to state clearly which one,  $\alpha$  or  $\beta$ , is more affected. We have examined the spectral behavior of compound **4**.<sup>8a</sup> If the  $H_\alpha$  and  $H_\beta$  signals of **4** are temperature variable and the resulting two conformers are found to be equally populated, then this nmr temperature dependence is caused by restricted rotation of the carbethoxyl group (because of the presence of symmetry ( $\sigma$ ) in the ring), but not likely by nitrogen inversion.<sup>8b</sup> Compound **4** showed two doublets,  $H_\alpha$  at  $\tau$  3.30 (d,  $J = 10.5$ ) and  $H_\beta$  at  $\tau$  5.10 (d,  $J = 10.5$ ) (proton  $H_\gamma$  is irradiated), at room temperature, but two overlapping doublets,  $\tau$  3.25, 3.35 (dd,  $J = 10.5$ ) and  $\tau$  5.05, 5.15 (dd,  $J = 10.5$ ), at  $-50^\circ$ ,  $T_c -25^\circ$  ( $CS_2 + THF-d_6$ , 100 MHz),  $\Delta F_c^\ddagger \approx 13$  kcal, each doublet being equally intense. The ethyl signal begins to broaden around  $-100^\circ$ , very likely due to slow inversion of the ring system of **4** below this temperature. The chemical shifts of the  $\alpha$  and  $\beta$  protons of **4** are almost equally affected. The situation is entirely different in the case of pyrrole,<sup>7</sup> where the ring geometry is fixed and the chemical shift of  $H_\alpha$  is expected to be affected much more than that of  $H_\beta$ , as observed. Anastassiou, *et al.*, discussed the temperature independence of the ethyl signal of **1** but the chemical environments of the two rotamers (not invertomers) are equivalent, providing pseudorotation is rapid.<sup>9</sup> Below  $-125^\circ$  the ethyl group of **1** exhibited broadening which may be partly due to freezing of this pseudorotation.

Thirdly, their "most compelling evidence in favor of suppressed nitrogen inversion derives from the effect of solvent polarity on the temperature of coalescence ( $T_c$ ),"<sup>3</sup> comparing their data with those reported by Griffith and Roberts.<sup>10</sup> We must point out that the latter authors investigated only pyramidal nitrogen compounds, *N*-benzyl-*O,N*-dimethylhydroxylamine and its related compounds, and that it is not appropriate to compare these decisively different systems. Moreover, the solvent dependence of  $T_c$  for **4** was found to be parallel with that for **1**<sup>3</sup> ( $T_c$  for **4**,  $-23^\circ$  in  $CDCl_3$ ,  $-41^\circ$  in  $CD_3CN$ ;  $T_c$  for **1**,  $-10^\circ$  in  $CDCl_3$ ,  $-28^\circ$  in  $CD_3CN$ ), both **1** and **4** showing an  $18^\circ$  difference in  $T_c$  on changing the solvent from chloroform ( $\epsilon$  4.8) to acetonitrile ( $\epsilon$  38.8). *N*-Acylpyrroles behaved similarly: *N*-acetylpyrrole;  $T_c$  ( $CDCl_3$ )  $-18^\circ$ ;<sup>11</sup> ( $CD_3CN$ )  $-33^\circ$ ;<sup>11</sup>

(8) (a) S. Masamune and N. T. Castellucci, *Angew. Chem., Int. Ed. Engl.*, **3**, 582 (1964). (b) A referee suggested the addition of the following explanation to clarify this statement. If slow nitrogen inversion occurs between **4a** and **4b**, it could cause a temperature dependence of the nmr spectra of **4**. In this case, it is highly unlikely that **4a** and **4b**



will be exactly equally populated, as Dreiding models indicate a large difference in stability between the two conformers.

(9) *N*-Carbethoxyazepineiron tricarbonyl, which is quoted in ref 3 as an example to exhibit the splitting of the ethyl group, is obviously not an appropriate model, because at cold temperatures  $Fe(CO)_5$  is fixed on one side, destroying the symmetry of the whole ring system. The ethyl group of the two rotamers resulting from hindered rotation of the carbethoxyl group experiences different chemical environments.

(10) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4089 (1965).

(11) These temperatures are corrected and somewhat different from those reported (*cf.* ref 7).

*N*-carbethoxypyrrole;  $T_c$  ( $CDCl_3$ )  $-41^\circ$ ; ( $CD_3CN$ ) below  $-45^\circ$  (solvent frozen). Their argument that "rotation is restricted more effectively in polar (acetonitrile) than in nonpolar solvent (chloroform)" is not applicable to these cases. On the contrary, the reverse trend is observed, as shown above, and these phenomena of solvent dependence may possibly be general for the type of compounds in question.<sup>12</sup> Although in the absence of extensive studies, it is difficult to evaluate the data accurately, a simple and tentative explanation can be offered. Both **1**, **4**, and the *N*-acylpyrroles possess a substantial polar character in the transition state of hindered rotation due to the conjugation of the lone pair of nitrogen with ring double bonds. Thus  $T_c$  is lowered with increasing solvent polarity.

There is no reason to believe that the nitrogen atom is a typical pyramid, and if it deviates slightly from trigonal coplanarity, the inversion barrier should be low and cannot be as high as the measured value, approximately 13 kcal/mole. In contrast, the rotational barrier for *N,N*-dimethylcarbamate is 16.5 kcal/mol.<sup>13</sup> Considering the well-known fact that the introduction of a double bond in conjugation with the lone pair of nitrogen lowers the barrier,<sup>7,14</sup> 13 kcal/mol is just as expected for the energy required for the hindered rotation of **1**. Finally, we wish to point out that  $C_2$  symmetry for ring systems **1**, **2**, and **3** is justified when the pseudorotation of the C-X-C ( $X = O, NR, CH_2$ ) bond mentioned above proceeds very rapidly, compared with the nmr time scale, or **1** possesses an energy minimum at the middle point of this pseudorotation.

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(12) For the cases of simple disubstituted amides, see J. C. Woodbrey and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 13 (1962).

(13) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

(14) D. G. Gehring and W. A. Mosher, *J. Org. Chem.*, **31**, 3436 (1966); *cf.* the behavior of **4**.

\* Address correspondence to this author.

K. Hojo, S. Masamune\*

Department of Chemistry, University of Alberta  
Edmonton, Alberta, Canada

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## Energy Barriers for Rotation about Carbon-Carbon Bonds in Allyl Cations

Sir:

For  $I \rightarrow II$  and  $II \rightarrow III$ , isomerization rates gave  $E_a$  of 17.5 and 24.0 kcal/mol and  $\log A$  of 11.8 and 14.0, respectively.<sup>1</sup> Three paths were considered: (a) rotation about  $C = C$ ; (b) recombination to a neutral allyl derivative, rotation, and dissociation; and (c) disrotatory closure and opening. Path c was eliminated because it requires  $I \rightarrow III$  whereas paths a and b require eq 1 as observed. A fourth path (d) must be added. This is loss of proton to the diene, rotation, and reprotonation. Path d requires the sequence in eq 1. No evidence was available for distinguishing paths a, b, and d.

(1) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).