plication by $(k_{-1}/k_2)^{\mathrm{EtOH}} = 1.710$ gives $[k_{-1}{}^{\mathrm{D}}/k_2{}^{\mathrm{D}}]^{\mathrm{EtOH}} = 1.895$, which is indistinguishable from 1.885 found in ethanol-*O-d*. We conclude that there is a nil solvent isotope effect on benzhydryl benzoate ion-pair partitioning in ethanol.

Swain and Pegues found a solvent isotope effect ($k^{\mathrm{MeOH}}/k^{\mathrm{MeOD}} = 1.07$) on the methanolysis of trityl chloride in benzene.[12] They established that the product-forming step is much slower than ion-pair return. A difference between benzene and more polar, hydroxylic solvents is not unreasonable. The absence of a solvent isotope effect in the DDM–HOBz reaction in ethanol suggests either that there is little external ion-pair return or that there is no solvent isotope effect on partitioning of III or both. Both the absence of a solvent isotope effect and the absence of an α-PIE on III are consistent with Ingold's theory of cation capture in hydroxylic solvents.[8] The dependence of isotope effect on ion-pair return suggests that isotope effects on solvolytic processes may prove useful in assessing return.

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

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[12] C. G. Swain and E. E. Pegues, *J. Amer. Chem. Soc.*, **80**, 812 (1958).

* 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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Dissection of α-Isotope Effects on the Solvolysis of Benzhydryl Benzoate

Sir:

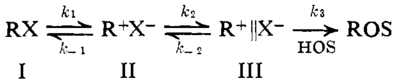
Knowledge of the ion-pair partitioning isotope effect[1] allows dissection of the solvolytic isotope effect into an ionization isotope effect $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}}$ and a fractionation isotope effect $F_{\mathrm{H}}/F_{\mathrm{T}}$, the isotope effect on the fraction of ionizations that results in solvolysis (eq 1).

$$\frac{k_{\mathrm{t}}{}^{\mathrm{H}}}{k_{\mathrm{t}}{}^{\mathrm{T}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{T}}}\frac{F_{\mathrm{H}}}{F_{\mathrm{T}}} \tag{1}$$

We report the separation of the solvolytic isotope effect for benzhydryl benzoate in ethanol and an estimate of the isotope effect on ^{18}O equilibration.

The analysis is based on the minimum elaboration of Winstein's solvolysis scheme[2] consistent with Goering's studies of *p*-chlorobenzhydryl *p*-nitrobenzoate[3] (Scheme I). Steady-state treatment affords eq 2 for $k_{\mathrm{t}}{}^{\mathrm{H}}/k_{\mathrm{t}}{}^{\mathrm{T}}$,

Scheme I



$$\underset{\mathrm{I}}{\mathrm{RX}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{II}}{\mathrm{R^+X^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathrm{III}}{\mathrm{R^+\|X^-}} \xrightarrow[\mathrm{HOS}]{k_3} \mathrm{ROS}$$

where $F_{\mathrm{H}}{}^{\mathrm{III}}$ and $F_{\mathrm{T}}{}^{\mathrm{III}}$ are the fractions of the respective isotopic ion pairs III that solvolyze. The observed solvolysis isotope effect ($k_{\mathrm{t}}{}^{\mathrm{H}}/k_{\mathrm{t}}{}^{\mathrm{T}} = 1.217$, see footnote *b*, Table I) was combined with previously measured quantities[1,4] (eq 2a and 2b) to calculate $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}}$ from eq 2. For benzhydryl benzoate in ethanol $F_{\mathrm{H}}{}^{\mathrm{III}}/$

$$\frac{k_{\mathrm{t}}{}^{\mathrm{H}}}{k_{\mathrm{t}}{}^{\mathrm{T}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{T}}}\,\frac{(k_2{}^{\mathrm{H}}F_{\mathrm{H}}{}^{\mathrm{III}}/k_{-1}{}^{\mathrm{H}}) + [(k_{-1}{}^{\mathrm{T}}/k_{-1}{}^{\mathrm{H}})/(k_2{}^{\mathrm{T}}/k_2{}^{\mathrm{H}})]\dfrac{F_{\mathrm{H}}{}^{\mathrm{III}}}{F_{\mathrm{T}}{}^{\mathrm{III}}}}{(k_2{}^{\mathrm{H}}F_{\mathrm{H}}{}^{\mathrm{III}}/k_{-1}{}^{\mathrm{H}}) + 1} \tag{2}$$

$$\frac{k_2{}^{\mathrm{H}}F_{\mathrm{H}}{}^{\mathrm{III}}}{k_{-1}{}^{\mathrm{H}}} = \frac{[\mathrm{ROS}]}{[\mathrm{ROBz}]} \approx \frac{k_{\mathrm{t}}}{k_{\mathrm{eq}} + k_{\mathrm{t}}} \tag{2a}$$

$$\frac{(k_{-1}{}^{\mathrm{T}}/k_{-1}{}^{\mathrm{H}})}{(k_2{}^{\mathrm{T}}/k_2{}^{\mathrm{H}})}\frac{F_{\mathrm{H}}{}^{\mathrm{III}}}{F_{\mathrm{T}}{}^{\mathrm{III}}} = \frac{A_{\mathrm{ROBz}}}{A_{\mathrm{ROEt}}} = \mathrm{PIE}^{\mathrm{T/H}} \tag{2b}$$

$F_{\mathrm{T}}{}^{\mathrm{III}} = 1.$[1] The $\mathrm{PIE}^{\mathrm{T/H}}$ and the solvolytic isotope effect were measured at 25 and 100°, respectively. The $\mathrm{PIE}^{\mathrm{T/H}}$ at 100° was calculated from eq 3,[5] which assumes

$$\Delta(\Delta\Delta E_{\mathrm{a}}) = RT\ln(\mathrm{PIE}^{\mathrm{T/H}}) \tag{3}$$

no appreciable isotope effect on the preexponential factor. Product data at 100°[4] and $(\mathrm{PIE}^{\mathrm{T/H}})^{100°}$ gave $(F_{\mathrm{H}}/F_{\mathrm{T}})^{100°}$. Equation 2 gave $(k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}})^{100°}$ and eq 4 gave $(k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}})^{25°}$. The Swain–Schaad relation

$$\Delta\Delta E_{\mathrm{a}} = RT\ln(k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}}) \tag{4}$$

$[(k^{\mathrm{H}}/k^{\mathrm{D}}) = (k^{\mathrm{H}}/k^{\mathrm{T}})^{1/1.44}]$ afforded $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}}$ and $(k_{-1}{}^{\mathrm{D}}/k_{-1}{}^{\mathrm{H}})/(k_2{}^{\mathrm{D}}/k_2{}^{\mathrm{H}})$.[6]

The isotope effect on ^{18}O equilibration is shown in eq 5 where $R_{\mathrm{H}}/R_{\mathrm{T}}$ is the ratio of fractions of ionizations

$$\frac{k_{\mathrm{eq}}{}^{\mathrm{H}}}{k_{\mathrm{eq}}{}^{\mathrm{T}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{T}}}\frac{R_{\mathrm{H}}}{R_{\mathrm{T}}} \tag{5}$$

that give return. Equation 6 gives the isotope effect

$$\frac{k_{\mathrm{eq}}{}^{\mathrm{H}}}{k_{\mathrm{eq}}{}^{\mathrm{T}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{T}}}\,\frac{(k_{-1}{}^{\mathrm{H}}/k_2{}^{\mathrm{H}}F_{\mathrm{H}}{}^{\mathrm{III}}) + [(k_2{}^{\mathrm{T}}/k_2{}^{\mathrm{H}})/(k_{-1}{}^{\mathrm{T}}/k_{-1}{}^{\mathrm{H}})]\dfrac{F_{\mathrm{T}}{}^{\mathrm{III}}}{F_{\mathrm{H}}{}^{\mathrm{III}}}}{(k_{-1}{}^{\mathrm{H}}/k_2{}^{\mathrm{H}}F_{\mathrm{H}}{}^{\mathrm{III}}) + 1} \tag{6}$$

on O^{18} equilibration if k_1 *were* $k_{\mathrm{eq}} + k_{\mathrm{t}}$ (*cf.* eq 2.)[4,7] The discrepancy is apparently not great for benzhydryl benzoate.[7] Expressions for $k_{\mathrm{rac}}{}^{\mathrm{H}}/k_{\mathrm{rac}}{}^{\mathrm{T}}$ (mechanism dependent) have also been derived. Suffice it to say that $k_{\mathrm{rac}}{}^{\mathrm{H}}/k_{\mathrm{rac}}{}^{\mathrm{T}}$ is greater than $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{T}}$ in the absence of tunneling or nucleophilic catalysis in the racemizing process.

The α-tritium and deuterium effects subject to the errors inherent in eq 3 and 4 are summarized in Table I. The solvolytic isotope effect $k_{\mathrm{t}}{}^{\mathrm{H}}/k_{\mathrm{t}}{}^{\mathrm{D}}$ is substantially greater than the ^{18}O-equilibration isotope effect. The ionization isotope effect is much smaller than $(k_{\mathrm{t}}{}^{\mathrm{H}}/k_{\mathrm{t}}{}^{\mathrm{D}})_{\mathrm{max}}$ (calculated from eq 2 assuming $k_2{}^{\mathrm{H}}/k_{-1}{}^{\mathrm{H}} = 0$), the latter being between Shiner's proposed maximum isotope effect (1.22)[8] and Stewart's experimental equilibrium isotope effect (1.29).[9]

In discussing isotope effects and mechanism it is useful to have a name for each solvolytic pathway. Winstein's ion pair symbols (II, III, and IV) have been used to specify mechanism according to product precursor for the three possible SN1 type mechanisms (Scheme II). The molecularity of the rate-determining

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[1] B. L. Murr and M. F. Donnelly, *J. Amer. Chem. Soc.*, **92**, 6686 (1970).

[2] A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 1904 (1968).

[3] H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

[4] A. F. Diaz and S. Winstein, *ibid.*, **88**, 1318 (1966).

[5] S. Seltzer, *ibid.*, **83**, 2625 (1961); see footnote *a*, Table IV.

[6] C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. Schaad, *ibid.*, **80**, 5885 (1958).

[7] H. L. Goering and R. W. Thies, *ibid.*, **90**, 2968 (1968).

[8] V. J. Shiner, Jr., and W. Dowd, *ibid.*, **91**, 6528 (1969).

[9] M. M. Mocek and R. Stewart, *Can. J. Chem.*, **41**, 1641 (1963).

Table I. Dissection of Solvolysis Isotope Effects for Benzhydryl Benzoate in Ethanol

	100°	25°
Tritium Isotope Effects		
$(k_{-1}^{T}/k_{-1}^{H})/(k_2^{T}/k_2^{H})$	1.12	1.16[a]
F^{H}/F^{T}	1.062	1.093
k_1^{H}/k_1^{T}	1.147	1.180
k_t^{H}/k_t^{T}	1.217 ± 0.010[b]	1.30
$(k_t^{H}/k_t^{T})_{max}$	1.28	1.37
k_{eq}^{H}/k_{eq}^{T}	1.09	1.12
R^{H}/R^{T}	0.952	0.95
Deuterium Isotope Effects		
$(k_{-1}^{D}/k_{-1}^{H})/(k_2^{D}/k_2^{H})$	1.08	1.11
F^{H}/F^{D}	1.04	1.06
k_1^{H}/k_1^{D}	1.10	1.12
k_t^{H}/k_t^{D}	1.145	1.19
$(k_t^{H}/k_t^{D})_{max}$	1.187	1.24
k_{eq}^{H}/k_{eq}^{D}	1.065	1.08
R^{H}/R^{D}	0.97	0.965

[a] Measurement described in ref 1. [b] Measured by Method I, V. Raaen, G. Ropp, and H. Ropp, "Carbon 14," McGraw-Hill, New York, N. Y., 1965, p 53. Average of three independent determinations. Samples were chromatographed and crystallized to constant specific activity.

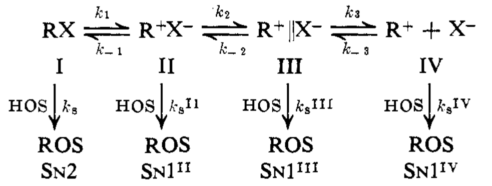
Table II. Estimates of Ionization and Partitioning Isotope Effects for Nonrearranging Systems

Substrate	Solvent	$(k_t^{H}/k_t^{D})_{min}$[a]	(k_t^{H}/k_t^{D})[b]	$PIE^{D/H}$[c]
	α-Isotope Effects per D, 25°			
i-PrOBs	HOAc	1.14[d]	1.22[e]	1.07[f]
	50–80% TFE	1.12[g]	1.22[e]	1.09[f]
	H_2O	1.13[h]	1.22[e]	1.08[f]
i-PrCl	H_2O	1.09[i]	1.15[s]	1.055[f]
i-PrBr	H_2O	1.079	1.12[s]	1.04[f]
i-PrI	H_2O	1.056	1.09[s]	1.03[f]
sec-OcOBs	MeOH	1.11[k]	1.22[e]	1.10[f]
$PhCH_2OBs$	HOAc	1.14[d]	1.22[e]	1.07[f]
$PhCH_2Cl$	50% EtOH	1.086[l]	1.15[f]	1.06[j]
$PhCHCH_3Cl$	50% EtOH	1.098[m]	1.16[f]	1.06[j]
Ph_2CHOBz	EtOH	1.12[n]	1.24[n]	1.11[n]
Ph_2CHCl	80% acetone	1.10[o]	1.15[s]	1.06[j]
Ph_2CHCl	$MeNO_2$	1.05[p]	1.12[f]	1.06[j]
	β-Isotope Effects per CD_3, 25°			
i-PrOBs	H_2O	1.245[q]	1.45[e]	1.165[f]
	H_2O	1.205[r]	1.45[e]	1.205[f]
i-PrCl	H_2O	1.17[q]		
i-PrBr	H_2O	1.153[q]		
i-PrI	H_2O	1.145[q]		

[a] Estimate of k_1^{H}/k_1^{D}. [b] Estimate of $(k_1^{H}/k_1^{D})(k_{-1}^{D}/k_{-1}^{H})/k_2^{D}/k_2^{H})$, eq 7. [c] Estimate of $(k_{-1}^{D}/k_{-1}^{H})/(k_2^{D}/k_2^{H})$. [d] K. Mislow, S. Borčić, and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957). [e] References 8 and 11. [f] Calculated, see text. [g] Reference 17. [h] Reference 14. [i] Estimated from Br and I[14] as suggested in ref 20. [j] Assumed, see text. [k] Reference 16. [l] Reference 10. [m] V. J. Shiner, *et al.*, *J. Amer. Chem. Soc.*, **90**, 418 (1968). [n] This work. [o] Calculated from eq 2 and $k_\alpha/k_t = 2.5$ (S. Winstein, *et al.*, *Tetrahedron Lett.*, **No. 22**, 12 (1960)) assuming $k_\alpha = k_1$. [p] A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 5010 (1964). [q] Reference 15. [r] Pinnacolyl brosylate; V. J. Shiner, *et al.*, *J. Amer. Chem. Soc.*, **91**, 7748 (1969). [s] Maximum value from ref 20 and private communication from Professor V. J. Shiner, Jr.

step is not used in classifying mechanism. Intramolecular ion-pair ^{18}O equilibration is designated S_Ni^{II} or S_Ni^{III}.[7]

Scheme II



Benzhydryl benzoates, which solvolyze by an S_N1^{III} process,[3] would exhibit a minimum isotope effect $(k_t^{H}/k_t^{D})_{min} = k_1^{H}/k_1^{D}$ when $k_2 \gg k_{-1}$ and $k_s^{III} \gg k_{-2}$ (Scheme II). The same isotope effect is possible for an S_N1^{II} reaction if $k_s^{II} \gg k_{-1}$ and $k_s^{II} \gg k_2$. Thus, the mechanism is not uniquely defined by the isotope effect as noted by Shiner.[10]

The maximum solvolytic isotope effect $(k_t^{H}/k_t^{D})_{max}$ (eq 7) for the S_N1^{III} process would be observed if

$$(k_t^{H}/k_t^{D})_{max} = \frac{k_1^{H}}{k_1^{D}}\frac{(k_{-1}^{D}/k_{-1}^{H})}{(k_2^{D}/k_2^{H})} \qquad (7)$$

$k_{-1} \gg k_2$. The ratio $(k_t^{H}/k_t^{D})_{max}:(k_t^{H}/k_t^{D})_{min}$ provides the PIE if k_1^{H}/k_1^{D} is solvent insensitive. The solvolytic isotope effect can vary smoothly between $(k_t^{H}/k_t^{D})_{min}$ and $(k_t^{H}/k_t^{D})_{max}$ as k_2^{H}/k_{-1}^{H} varies from 0 to 10.

In Table II are summarized estimates of the magnitudes of α- and β-PIE's for several nonrearranging systems. Some of these estimates are necessarily inexact and they are presented only to show that PIE's can be substantial. Values of $(k_t^{H}/k_t^{D})_{min}$ are for the most part experimentally observed isotope effects. In most of the cases, experimentally observed $(k_t^{H}/k_t^{D})_{max}$ values were combined with $(k_t^{H}/k_t^{D})_{min}$ values to calculate $PIE^{D/H}$. In the other cases, $PIE^{D/H}$ was estimated and $(k_t^{H}/k_t^{D})_{max}$ or $(k_t^{H}/k_t^{D})_{min}$ was calculated.

Shiner[8] has shown that trifluoroacetolysis of isopropyl brosylate is an S_N1^{III} reaction with $k_{-1} \gg k_2$ (Scheme II).[11] Hence, the trifluoroacetolysis α- and β-isotope effects[12] provide estimates of $(k_t^{H}/k_t^{D})_{max}$. Kinetics and stereochemistry (complete inversion) of hydrolysis,[13a] alcoholysis,[13a,b] and acetolysis[13b] of *sec*-octyl sulfonates place these solvolyses in the S_N1^{II} category.[2] The corresponding isotope effects provide estimates of k_1^{H}/k_1^{D}. The isotope effects on hydrolysis[14,15] and alcoholysis[16,17] are lower limits to k_1^{H}/k_1^{D} because of a possible S_N2 component. The acetolysis isotope effects provide upper limits to k_1^{H}/k_1^{D} because of a PIE on II of unknown magnitude. Actually, the latter PIE cannot be very large judging by the isotope effects on solvolyses of isopropyl brosylate. Lower limits to internal return have been established for secondary brosylate,[2] but Shiner's experiment showed that ^{18}O equilibration grossly underestimates return.[8] The ratio k_s^{II}/k_{-1} probably varies greatly for hydrolysis, methanolysis, and acetolysis but the isotope effect shows only minor variation. Consequently, the hydrolysis isotope effect for all isopropyl derivatives appears to provide a good estimate of k_1^{H}/k_1^{D}.

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(10) V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, Jr., *J. Amer. Chem. Soc.*, **92**, 232 (1970).

(11) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(12) A. Streitwieser and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

(13) (a) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, **87**, 287, 292 (1965); (b) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682, 3686 (1965).

(14) K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *Can. J. Chem.*, **38**, 1505 (1960).

(15) K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *ibid.*, **38**, 2171 (1960).

(16) E. S. Lewis and R. R. Johnson, *Proc. Chem. Soc.*, 52 (1958).

(17) V. J. Shiner, Jr., N. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969).

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.[18] The rate is pyridine independent. Ion-pair dissociation is a likely rate-limiting step for this elimination ($E1^{III}$).[19] 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_3 for the S_N1^{III} reaction, is close to that for trifloroacetolysis of isopropyl brosylate. The evidence is not compelling, however. Shiner's interpretation of the increased isotope effect in trifluorethanolysis[17] remains a possibility. A direct observation of a β-PIE is not available.

The theoretical finding that transition-state force constants for α-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[20] that α-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 S_N1^{III} 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 S_N1^{II} reaction.

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

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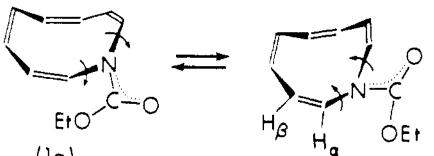
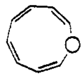
Origin of Temperature-Dependent Nuclear Magnetic Spectra of *N*-Carbethoxyazonin

Sir:

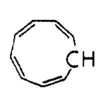
Earlier we reported that *N*-carbethoxyazonin (**1**) exhibited temperature-dependent nmr spectra,[1] whereas those of oxonin (**2**) and *all-cis*-cyclononatetraene (**3**)[2] remained invariant between 0 and −130° (CS_2 + THF-d_8). An obvious and logical conclusion from the spectral data is that these similar ring systems undergo rapid conformational change (of the rings), and we suggested that "the restricted rotation of $N-CO_2Et$ is mainly responsible for the temperature-dependent nmr spectra of **1**."[1] Recently, however, Anastassiou, Cellura, and Gebrian,[3] utilizing the same findings,[1,4] 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°, $\Delta F_C^{\ddagger} \simeq 13$ kcal/mol) are incompatible with accumulated data and currently accepted interpretations[5] for the inversion of nitrogen and hindered rotation. We demonstrate herein that our original interpretation is entirely acceptable for the system in question.



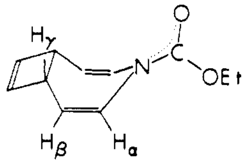
(1a) (1b)



(2)



(3)



(4)

Firstly, crystalline structures of amides and carbamates have shown[6] 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.[7]

Secondly, they argued that the chemical shift of the α hydrogen of **1** should be more affected than that of the β 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 β hydrogen of the ring as to the α 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

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[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).

[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, 624 (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 methoxycarbonylaziridine, and yet the inversion rate of this compound is exceedingly high [$T_c = -138°$; $\Delta F_c^{\ddagger} = 7.6$ kcal/mol: F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, 89, 352 (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.*, acetypyrrole, $\Delta F_c^{\ddagger} = 13$ kcal/mol: T. Matuo and H. Shosenji, *Chem. Commun.*, 501 (1969).