were unsuccessful in our hands. The conversion was achieved *via* a modified Wittig reaction using the methylsulfinyl carbanion and methyl triphenylphosphonium bromide[14] to give 9-methylenebicyclo[3.3.2]decane (**5**): bp 67–69° (2.5 mm); ir (film) 3040, 1610 cm^{-1}; nmr ($CDCl_3$) δ 4.70 (q, 1, J_{AB} = 2.7 Hz, J_{AX} = 2 Hz), 4.57 (q, 1, J_{BA} 2.7 Hz, quartets collasping to doublets, J = 2.7 Hz, on irradiation with the frequency of the signal for the two H_X protons). Epoxidation of **5** with *m*-chloroperbenzoic acid in chloroform (30 min) or monoperphthalic acid in ether (24 hr) at 0° afforded the epoxide **6**: mp 97–98°; sublimed 60° (5 min); nmr ($CDCl_3$) δ 2.62 (s, 2, OCH_2), 2.0 (m, 3, α-CH, α-CH_2), 1.65 (m, 13), which was cleaved by sodium azide in dimethylformamide containing a catalylic amount of boric acid[15] to the hydroxy azide **7**: ir (film) 3590, 3540, 2100 cm^{-1}. Reduction of **7** in ethanol with hydrogen and Adams' catalyst[16] gave 9-aminomethylbicyclo[3.3.2]decan-9-ol (**8**), characterized as its hydrochloride salt: mp 241–242°; nmr (D_2O–DSS) δ_A 3.04, δ_B 3.22, J_{AB} = 13 Hz ($CH_2NH_3^+$). Demjanov–Tiffeneau expansion in aqueous acetic acid[17] yielded a mixture of the bicyclo[3.3.3]undecan-9- and 10-ones (**9**, **10**): ir 1685 cm^{-1}; nmr ($CDCl_3$) δ 2.9 (m, 0.62, CHCO in **10**), 2.60 (m, 2 × 0.62 + 4 × 0.38, CH_2CO). Wolff–Kishner reduction[18] of the ketone mixture (**9**, **10**) afforded bicyclo[3.3.3]undecane (**1**): mp 155–157°, sublimed 50° (10 mm); nmr ($CDCl_3$) δ 2.3 (m, 2, CH), 1.55 (18, CH_2's).

The implications of structure **1a**, with C_{3h} molecular symmetry, are of interest. All of the methylene bridges point in the same direction. The tertiary hydrogens may be susceptible to direct substitution,[19] and the 1-substituted bicyclo[3.3.3]undecanes would be dissymmetric (chiral), with the possibility of resolution depending upon the activation energy required for the flipping of the three methylene bridges.

1-Azabicyclo[3.3.3]undecane (**2**), with a C_3 axis, is of special interest in that it represents an *un*substituted [3.3.3] ring system capable of existing in enantiomeric forms if the conformational energy barrier is sufficiently large. The favored route to this compound proved to be remarkably simple. 1-Azoniatricyclo[3.3.3.0]undecane bromide (**11**), prepared by the method of Šorm and Beránek,[20] was treated with sodium in liquid ammonia[21] to give 1-azabicyclo[3.3.3]undecane (**2**): mp 150–152°, sublimed 35° (20 mm); nmr ($CDCl_3$) δ 2.85 (m, 6, α-CH_2), 2.57 (m, 1, CH), 1.60 (m, 6, β-CH_2), 1.57 (m, 6, γ-CH_2). The hydrochloride salt **12**, mp 305–307° dec, from ethanol, and the methiodide **13**, mp 273–275°, from ethanol, were prepared, and X-ray single-crystal determinations are in progress.

Further studies of the physical and chemical properties of the bicyclo[3.3.3]undecane compounds are continuing.

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Detection of a Secondary Isotope Effect on Partitioning of Benzhydryl Benzoate Ion Pairs

Sir:

Shiner's proposal that ion-pair intervention can influence secondary deuterium isotope effects in solvolytic processes[1] suggests that there should be isotope effects on partitioning of ion-pair intermediates. For example, in the solvolysis of *exo*-norbornyl brosylate,[2] which involves partitioning of intimate ion pair II (eq 1) between internal return and irreversible dissociation to III ($k_3 \gg k_{-2}$), the solvolytic rate constant

$$\begin{array}{ccccccc} RX & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & R^+X^- & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & R^+\|X^- & \xrightarrow[HOS]{k_3} & ROS \\ \text{I} & & \text{II} & & \text{III} & & \text{IV} \end{array} \quad (1)$$

k_t is the product of the ionization rate k_1 and the fraction of ion pairs that dissociate, $F^{II} = k_2/(k_1 + k_2)$. The solvolytic isotope effect is given by eq 2 and $F_H{}^{II}/F_D{}^{II}$ by eq 3 (assuming $k_3 \gg k_{-2}$).[3] Any difference in total zero-point energy (ZPE) between the α-C–H bond in TS1 (Figure 1) and TS2 would make

$$(k_t{}^H/k_t{}^D) = (k_1{}^H/k_1{}^D)(F_H{}^{II}/F_D{}^{II}) \quad (2)$$

$$F_H{}^{II}/F_D{}^{II} = \frac{(k_2{}^H/k_{-1}{}^H) + (k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H)}{(k_2{}^H/k_{-1}{}^H) + 1} \quad (3)$$

$(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H) \neq 1$ resulting in a partitioning isotope effect (PIE). If covalent bonding to the leaving group is greater in TS1 than TS2, $(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H) > 1$ and $F_H{}^{II}/F_D{}^{II} > 1$. Since $k_2{}^H/k_{-1}{}^H$ is solvent dependent PIE's could cause solvent effects on *solvolytic* isotope effects, even though $(k_1{}^H/k_1{}^D)$ and $(k_{-1}{}^D/k_2{}^D)/(k_{-1}{}^H/k_2{}^H)$ are solvent independent.

To probe the existence of partitioning isotope effects we have measured the α-tritium isotope effect on partitioning of benzhydryl benzoate ion pair(s) generated from diphenyldiazomethane (DDM) and benzoic acid (HOBz–TOBz) in ethanol-*O-t* and in 90% acetone.[4] This reaction (Chart I) entails rate-determining proton transfer from monomolecular, undissociated HOBz giving diazonium benzoate ion pair that loses nitrogen to form what appears to be the same benzhydryl benzoate "ion pair or spectrum of ion pairs" as in solvolysis.[4,5] Except for the tracer (tritium, introduced as TOBz), the experimental conditions of Diaz and

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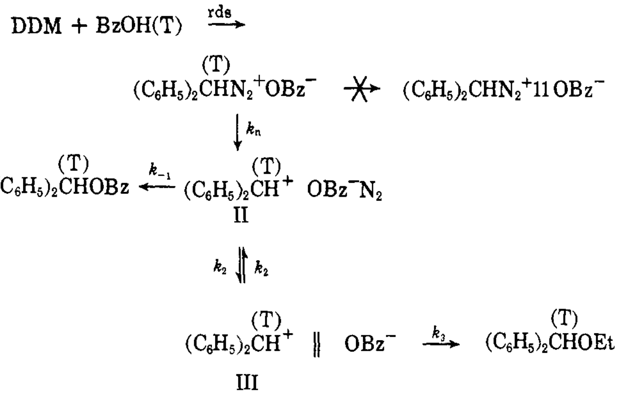
Chart I



$$\mathrm{DDM} + \mathrm{BzOH(T)} \xrightarrow{\mathrm{rds}}$$

$$(C_6H_5)_2\overset{(T)}{C}HN_2^+OBz^- \not\rightarrow (C_6H_5)_2CHN_2^+ \| OBz^-$$

$$\downarrow k_n$$

$$(C_6H_5)_2\overset{(T)}{C}HOBz \xleftarrow{k_{-1}} \underset{\mathrm{II}}{(C_6H_5)_2\overset{(T)}{C}H^+ \ OBz^-N_2}$$

$$k_2 \downarrow\uparrow k_2$$

$$\underset{\mathrm{III}}{(C_6H_5)_2\overset{(T)}{C}H^+ \| OBz^-} \xrightarrow{k_3} (C_6H_5)_2\overset{(T)}{C}HOEt$$

Winstein were used. ROBz and ROEt were assayed by liquid scintillation counting after conversion to benzhydrol by LAH reduction and hydrolysis, respectively. Results are in Table I.

Table I. Specific Activity Ratios of Products of Diphenyldiazomethane–Benzoic Acid Reaction at 25°

Solvent	Isotope	$A_{\mathrm{ROBz}}/A_{\mathrm{ROEt}}$	
Ethanol	T	1.155	1.15 ± 0.02[a]
Ethanol	T	1.165	1.17 ± 0.02
90% acetone	T	1.147	1.15 ± 0.02
Ethanol	^{14}C	1.710	1.71 ± 0.01
Ethanol-*O-d*	^{14}C	1.885	1.89 ± 0.01

[a] Errors are composite statistical counting errors in both ROBz and ROS.

The rapidity of proton transfer between solvent and benzoic acid ensures that an ion pair of constant specific activity is produced in ethanol as long as the solvent H:T ratio is sensibly constant. This is not true in 90% acetone where a slow exchange removes tritium. The exchange does not vitiate the acetone experiment because the product ratio is not altered by the tracer.

If $k_{-1}^T/k_{-1}^H = k_2^T/k_2^H$ (no PIE) the specific activities of ROBz and ROEt would be identical. Assuming for the moment that $k_3 \gg k_{-2}$, the specific activity of ROBz (A_{ROBz}) is determined by $k_{-1}[R_T^+OBz^-]/k_{-1}\cdot[R_H^+OBz^-]$ and that of ROEt (A_{ROEt}) by $k_2^T[R_T^+OBz^-]/k_2^H[R_H^+OBz^-]$. The $[R_T^+OBz^-]$ and $[R_H^+OBz^-]$ are concentrations of the respective isotopic ion pairs. The specific activity ratio (eq 4) gives the PIE for ion pair II. We find $A_{\mathrm{ROBz}}/A_{\mathrm{ROEt}} = 1.16$.

$$\frac{A_{\mathrm{ROBz}}}{A_{\mathrm{ROEt}}} = \frac{(k_{-1}^T/k_{-1}^H)}{(k_2^T/k_2^H)} = \frac{(k_{-1}^T/k_2^T)}{(k_{-1}^H/k_2^H)} = \mathrm{PIE} \qquad (4)$$

That $A_{\mathrm{ROBz}}/A_{\mathrm{ROEt}}$ provides a minimum isotope effect for partitioning of II even if there is return from III ($k_3 \approx k_{-2}$) is apparent from eq 5 and 6 ($F^{\mathrm{III}} = k_3/k_{-2} + k_3$) which allow for return from III.

$$\frac{A_{\mathrm{ROBz}}}{A_{\mathrm{ROEt}}} = \frac{(k_{-1}^T/k_{-1}^H)}{(k_2^T/k_2^H)}\frac{F_{\mathrm{H}}^{\mathrm{III}}}{F_{\mathrm{T}}^{\mathrm{III}}} \qquad (5)$$

$$\frac{F_{\mathrm{H}}^{\mathrm{III}}}{F_{\mathrm{T}}^{\mathrm{III}}} = \frac{(k_3^H/k_{-2}^H) + [(k_{-2}^T/k_{-2}^H)/(k_3^T/k_3^H)]}{(k_3^H/k_{-2}^H) + 1} \qquad (6)$$

If k_3 involves solvent attack at carbon, the ZPE at TS3 (Figure 1) should be greater than or equal to that at TS2 for external ion-pair return. Thus, $(k_{-2}^T/k_{-2}^H)/(k_3^T/k_3^H) \leq 1$ so $F_{\mathrm{H}}^{\mathrm{III}}/F_{\mathrm{T}}^{\mathrm{III}} \leq 1$. Roberts' salt and solvent effects[6] suggest an upper limit of 20% return from III. While results in 90% acetone show no isotope effect on partitioning of III, if there were 20% return and $(k_{-2}^T/k_{-2}^H)/(k_s^T/k_s^H) = 0.90$, we calculate $F_{\mathrm{H}}^{\mathrm{III}}/F_{\mathrm{T}}^{\mathrm{III}} = 0.982$ (eq 6) and $(k_{-1}^T/k_{-1}^H)(k_2^T/k_2^H) = 1.18$ (eq 5).

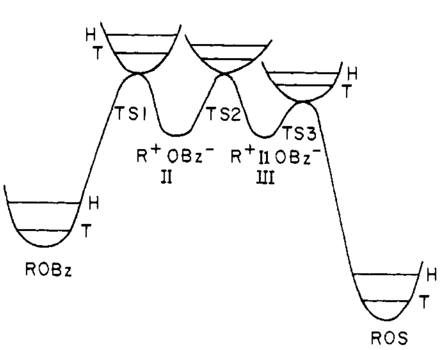


Figure 1. Free-energy and ion-pair partitioning. TS1, TS2, and TS3 are transition states for ionization, intimate ion-pair dissociation, and solvent capture, respectively.

To assess the isotope effect on partitioning of III we have measured $A_{\mathrm{ROBz}}/A_{\mathrm{ROH}}$ from DDM and TOBz in 90% acetone. Goering found >50% return from III (R = *p*-chlorobenzhydryl) in 90% acetone.[7] The result (1.147) is indistinguishable from that in ethanol. In our simplest working hypothesis we have assumed solvent independence of PIE. If this hypothesis is correct, our 90% acetone experiment establishes that there is no isotope effect on partitioning of III. If there is an isotope effect on partitioning III, the isotope effect on partitioning of II in ethanol must change to compensate in 90% acetone. This appears unlikely between solvents of such similar *Y* values. The results suggest that there is little covalent attachment of water in the rate-determining transition state for product formation. This result is reasonable if Ingold's theory of solvent capture of cations is correct,[8a] or if product arises principally from dissociated cation.[8b]

The product ratio ROBz/ROEt has been determined in ethanol and ethanol-*O-d* by isotopic dilution using a random ^{14}C label in one phenyl group of DDM. The ethanol ratio $(k_{-1}/k_2)^{\mathrm{EtOH}} = 1.710$ is in accord with reported values.[4,9,10] This agreement establishes the validity of our experimental technique because it demonstrates the absence of a ^{14}C-isotope effect on ion-pair partitioning. The observed ethanol-*O-d* product ratio gives $(k_{-1}^D/k_2^D)^{\mathrm{EtOD}} = 1.885$. From our measured $[(k_{-1}^T/k_{-1}^H)/(k_2^T/k_2^H)^{\mathrm{EtOH}} = 1.16$, the corresponding value of $[(k_{-1}^D/k_2^D)/(k_{-1}^H/k_2^H)^{\mathrm{EtOH}}$ is 1.109 reckoned from the Swain–Schaad relation.[11] Multi-

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(9) E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **89**, 165 (1967).

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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.

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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).

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

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 $k_t^{\mathrm{H}}/k_t^{\mathrm{T}}$,

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 ($k_t^{\mathrm{H}}/k_t^{\mathrm{T}} = 1.217$, 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 $F_{\mathrm{H}}^{\mathrm{III}}/F_{\mathrm{T}}^{\mathrm{III}} = 1.$[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

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

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

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

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

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* $k_{\mathrm{eq}} + k_t$ (*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 $k_t^{\mathrm{H}}/k_t^{\mathrm{D}}$ is substantially greater than the ^{18}O-equilibration isotope effect. The ionization isotope effect is much smaller than $(k_t^{\mathrm{H}}/k_t^{\mathrm{D}})_{\max}$ (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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