an authentic sample. The sensitivity of **12** was calculated by the method described by Sternberg et al.[60] The absolute yield of **11** thus determined was 92 ± 2%. The yield of **12** was about 2% for the above sample, but it increased to 5% after the solution was kept at 100 °C for 21 h. A control experiment in acetic acid at 100 °C for 24 h showed that **11** afforded **12** slowly even in the absence of *p*-bromobenzenesulfonic acid.

Kinetic Procedures. Acetolysis was performed by the usual sealed-ampule method with α-naphtholbenzein as an indicator.[1,61] Trifluoroacetolysis was carried out in a similar manner as reported earlier.[59] Dilution procedures and wavelengths used were different in each case: **3**, 1 mL of 0.02 M solution was diluted to 50 mL with 95% ethanol, measured at 249 nm; **7** (except **7**-γ-d_9), 1 mL of 0.04 M solution was diluted to 50 mL and then 10 mL of this solution was again diluted to 50 mL, measured at 243 nm; **7**-γ-d_9; **9**, 1 mL of 0.03 M solution was diluted to 25 mL and then 10 mL of this solution was again diluted to 50 mL, measured at 247 nm. In the case of **3** at 0 °C and **9** at 25 °C, 1-mL aliquots were pipetted out from a reaction flask placed in a thermostatic bath. In all other cases sealed ampules were used.

Measurement of Carbon-14 Kinetic Isotope Effects. Accurate radioactivity measurement of the purified samples of unreacted esters recovered at various stages of reaction was carried out according to the procedure described earlier.[1] Concentrations of the reaction solutions were the same as those of the respective kinetic runs. The pipetting-out method was employed in the case of trifluoroacetolysis of **9** at 25 °C, and the sealed ampule method was used in all other cases. Radioactivity data for each case appear in supplementary material.

Acknowledgment. We thank Professor Shiner for profitable discussions on the results of closely related reaction systems. We also thank Professors Collins, Hehre, and Morokuma for helpful comments. We are grateful to Idemitsu Kosan Co., Ltd. for a gift of adamantane. The present work was partly supported by a Grant-in-Aid (No. 134044 and 347018) for science research from the Ministry of Education.

Supplementary Material Available: Tables S1-S11 containing radioactivity data of solvolysis of **6**, **7**, and **9** used for calculating carbon-14 kinetic isotope effects (11 pages). Ordering information is given on any current masthead page.

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Deuterium Isotope Effects for Migrating and Nonmigrating Groups in the Solvolysis of Neopentyl-Type Esters[1]

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Abstract: α- and γ-deuterium rate effects on the solvolysis of (1-methylcyclohexyl)methyl, (1-methylcyclopentyl)methyl, and (1-methylcyclobutyl)methyl sulfonate esters have been measured and the solvolysis products examined by ^{2}H NMR spectroscopy. The results indicate that the products of the solvolysis of all these sulfonate esters are predominantly (≥98%) rearranged. In the solvolysis of (1-methylcyclohexyl)methyl triflate, rearranged products with methyl migration slightly dominate over those with ring expansion. Normal isotope effects, 1.057 in 80E and 1.073 in 97T, are observed for the methyl-d_3 compound and an inverse effect, 0.963, is observed in 80E for the methylene-d_4 compound. However, in the solvolysis of both (1-methylcyclopentyl)methyl and (1-methylcyclobutyl)methyl sulfonates, the major products are those of ring expansion. In these examples, inverse effects are observed for the methyl-d_3-labeled species. The observed isotope effects can be separated into respective values of 0.927, 0.913 for the nonmigrating methyl-d_3 group and 1.177, 1.224 for the migrating methyl-d_3 group in the solvolysis of (1-methylcyclohexyl)methyl triflate and (1-methylcyclopentyl)methyl brosylate. This explains the relative intramolecular migratory aptitudes of CH_3/CD_3 of 1.20-1.30 and the low γ-d_9 isotope effect in the solvolysis of neopentyl sulfonates previously reported and makes them consistent with a mechanism which involves neighboring carbon participation during ionization.

Introduction

The solvolysis of neopentyl sulfonate esters yields, nearly completely,[2] products of rearranged carbon skeletal structure. Some controversy still centers around the timing of the rearrangement. Does methyl group migration occur during or after the rate-determining ionization step?[2-4]

Evidence favoring participation in neopentyl derivatives comes from (1) the dominance of rearranged products,[2,3] (2) the failure to trap the neopentyl cation,[5] (3) the observed moderate-sized γ-^{14}C effect (1.05) in the acetolysis of neopentyl *p*-nitrobenzenesulfonate,[6] (4) accelerated rates relative to some model compounds,[2a,7,8] (5) stereochemical results,[9,10] and (6) the lack of ^{18}O scrambling in the solvolytic rearrangement of bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate.[11] However, most of these results provide permissive and suggestive, rather than compelling, evidence for participation.

(1) (a) Taken from the thesis of J. J. Tai, submitted in partial fulfillment of the requirements for the Ph.D. degree at Indiana University, 1979. (b) A preliminary report on part of this work has appeared: Shiner, V. J., Jr.; Tai, J. J. *Tetrahedron Lett.* **1979**, 127.
(2) (a) Diaz, A.; Reich, I. L.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 5635 and references cited in ref 2. (b) Heidke, R. L.; Saunders, W. H., Jr. *Ibid.* **1966**, *88*, 5816. (c) G. M. Fraser and H. M. R. Hoffmann (*Chem. Commun.* **1967**, 561) observed some unrearranged products (≤10%) in the solvolysis of neopentyl *p*-toluenesulfonate at high temperature (129 °C). These products were considered to be formed from the unrearranged neopentyl ion pair. However, at the higher temperature the unrearranged substitution product could possibly be formed by a direct displacement.
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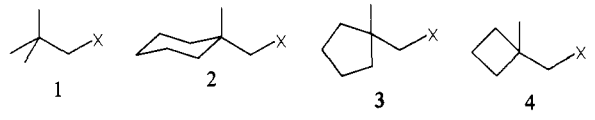
In the early 1970s, Schubert and Henson found a kinetic isotope effect,[4] $k_H/k_{\gamma\text{-}d_9}$, of 1.03 in the trifluoroacetolysis of neopentyl 2,4-dinitrobenzenesulfonate, and also a 20–30% preference for CH_3 group migration relative to CD_3 group migration through ^1H NMR analysis of the products of solvolysis of the reactant labeled with one or two CD_3 groups. Since only a small γ-d_9 *kinetic* isotope effect was observed, they concluded that methyl group rearrangement occurred after ionization of the carbon–oxygen bond. Nevertheless, the small γ-d_9 isotope effects could alternatively be explained by a synchronous rather than a stepwise occurrence of ionization and migration, if the two nonmigrating CD_3 groups caused a large enough inverse isotope effect to nearly cancel the expected normal effect of the migrating group. Inverse γ-d_6 isotope effects have been observed, for example, in the anchimerically assisted solvolyses of isobutyl[12] and neophyl esters.[13] This possibility, later supported by Raber, Harris, and Schleyer,[14] was considered by Schubert and Henson and rejected because they did not expect sufficiently large inverse effects for nonmigrating groups. In order to help resolve this question more firmly, we have studied the solvolysis of the neopentyl-type sulfonate esters **1–4**.



1 2 3 4

a, X = triflate (CF_3-SO_3-)
b, X = tresylate (CF_3-CH_2-SO_3-)
c, X = brosylate (*p*-BrC_6H_4-SO_3-)

The esters **2–4**, unlike the simple neopentyl esters, **1**, do not have an inherently equal probability of migration of each of the γ carbon atoms. Methyl migration products slightly dominate over those of ring expansion in the acetyolysis of **2** (X = methanesulfonate).[15] This should therefore be reflected in a normal isotope effect for the solvolysis of methyl-d_3-labeled esters of this structure. The strain in the four- and five-membered rings causes ring expansion to be favored over methyl migration in the solvolysis of esters of structures **3** and **4**. Therefore, effects characteristic of deuteration of a nonmigrating γ-carbon should be observed for the methyl-d_3-labeled analogues of **3** and **4**. Even though the migrating vs. nonmigrating roles are not *completely* specific in these reactions, the results can be analyzed quantitatively with the help of observed product yields. In parallel work Ando and co-workers[16] have observed a normal isotope rate effect for acetolysis at 100 °C of (2-methyl-d_3-2-adamantyl)methyl brosylate, a compound that yields only products of methyl migration.

Results and Discussion

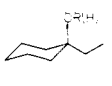
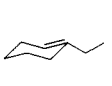
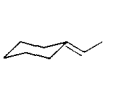
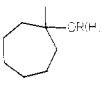
Various aqueous ethanolyses and trifluoroethanolyses of neopentyl trifluoromethanesulfonate (triflate)[12] all yielded α-d_1 isotope effects in the range 1.120–1.125 which are remarkably solvent independent and comparable to those found in the phenyl-assisted solvolysis of neophyl sulfonate esters.[17] These α-deuterium isotope effects are significantly lower than the value 1.15–1.16 associated with unassisted, rate-determining ionization in the solvolysis of 3,3-dimethyl-2-butyl (pinacolyl) sulfonates.[18] The lower α-d effects were attributed to partial transition-state methyl-C_α bonding, which partially compensates for the loss of the H–C_α–O bending force constant on the ionization of the C_α–O bond, and would be expected from the perpendicular effect caused by the greater energy of the unrearranged primary cation relative to that of the unrearranged secondary cation.[19,20]

Table I. Solvolysis Rates[a] and Isotope Effects[b] of (1-Methylcyclohexyl)methyl Trifluoromethanesulfonate at 25 °C

	(1-methylcyclohexyl)methyl trifluoromethanesulfonate	
	97T[f]	80E[f]
k_H, s^{-1}	57.5×10^{-5}	17.67×10^{-5}
$(k_H/k_{\alpha\text{-}d_2})^{1/2}$	1.130	1.120
$k_H/k_{\gamma\text{-}d_3}$[c]	1.073	1.057
$k_H/k_{\gamma\text{-}d_4}$[d]	*e*	0.963

[a] Rates were measured in duplicate by using the conductometric method;[21] reproducibility was 0.1% or better. [b] Corrected to 100% isotopic purity; α-d and γ-d_3 were 99% pure; γ-d_4 was 98%. [c] Deuterium in the methyl group. [d] Deuterium in the methylene groups in the ring. [e] Not determined. [f] Solvent.

Table II. Products of Solvolysis of (1-Methylcyclohexyl)methyl Triflate in 80% Ethanol-Water and 97% 2,2,2-Trifluoroethanol-Water

	% product				
solvent					
80E[a]	47	10	0	33	10
80E[b]	48		2	43	7
97T[b]	55		4	33	8

[a] ^2H NMR analysis of reaction mixture from α-d_2 reactant. [b] ^2H NMR analysis of reaction mixture from γ-d_3 reactant.

As shown in Table I,[1b] in both 97T and 80E the α-d effects for (1-methylcyclohexyl)methyl triflate (**2a**), (1.12–1.13 per D) are the same as those observed for neopentyl sulfonates and indicate participation. The ^2H NMR spectrum of the product reaction mixture from the solvolysis of (1-methylcyclohexyl)-methyl-d_2 triflate in 80E (Table II) indicates that methyl migration occurs to the extent of 57% and ring expansion occurs to the extent of 43%. Very similar product yields are observed in the solvolysis of **2a**-γ-d_3 in 80E and 97T. This dominance of migration of the methyl over the methylene group is also reflected in the normal methyl-d_3 effect on the solvolysis rates, 1.057 in 80E and 1.073 in 97T, which also clearly indicates participation. The inverse methylene-d_4 isotope effect in 80E, 0.963, clearly reflects the dominant nonmigrating role of the methylene group. The product of these two γ-deuterium effects (1.057×0.963) is 1.018, close to the value of 1.03 observed for the γ-d_9 rate effect for neopentyl ester.

If we assume that the characteristic migrating and nonmigrating isotope effects are the same for the CD_3 and CD_2 groups in **2a**, equations can be derived to sort out the intrinsic nonmigrating and migrating group effects which are mixed to produce the experimentally observed rate effects (see Appendix). Thus

$$(k_H/k_{\gamma\text{-}d_3})_{obsd} = R_H^D R_D^H/(aR_D^H + bR_H^D) \quad (1)$$

$$(k_H/k_{\gamma\text{-}d_4})_{obsd} = (R_D^H)^2 R_H^D/(aR_H^D + bR_D^H) \quad (2)$$

where R_H^D is the isotope effect for the part of the reaction in which only the methyl-d_3 group migrates, R_D^H is the isotope effect for the part of the reaction involving ring expansion, and a and b are the respective fractions of methyl migration and ring expansion which were determined from the analysis of product ratios.

Using these two equations and the data in 80E, the nonmigrating isotope effect, R_D^H, is found to be 0.942 and the migrating one, R_H^D, is 1.160. The product $(0.942)^2 \times 1.160$ is 1.029, which

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Table III. Solvolysis Rate Constants[a] and Secondary Deuterium Isotope Effects[b] for (1-Methylcyclopentyl)methyl Sulfonate Esters and (1-Methylcyclobutyl)methyl *p*-Bromobenzenesulfonate at 25 °C

leaving group	solvent[c]	$10^5 k_H$, s^{-1}	$k_H/k_{\alpha\text{-}d_1}$	$k_H/k_{\gamma\text{-}d_3}$	$k_H/k_{\gamma\text{-}d_4}$	$10^5 k_H$, s^{-1}	$k_H/k_{\alpha\text{-}d_1}$	$k_H/k_{\gamma\text{-}d_3}$
brosylate	97T					21.506	1.096	0.973
brosylate	70T	0.6505	1.100	0.927	1.063	27.485[d]	1.097[d]	0.972[d]
tresylate	97T	16.340	1.117	0.980				

[a] With the exception noted under *d* below, rates were measured in duplicate by using the conductometric method; reproducibility was 0.1% or better. [b] Corrected to 100% isotopic purity; α-d_2 and γ-d_3 compounds were 99% pure; γ-d_4 was 92%. [c] 97T refers to 97% trifluoroethanol-3% water etc. [d] Rates were measured in duplicate by using the spectrophotometric method; reproducibility was 0.5% or better.

Table IV. Products of Solvolysis of (1-Methylcyclopentyl)methyl Sulfonate Esters at 25 °C

leaving group	solvent[a]				
-OBs	70T	6%	2%	38%	54%
-OTr	97T	18%		31%	50%
^{2}H NMR chemical shift		0.99	4.95	1.22	1.78

[a] 97T refers to 97% trifluoroethanol-3% water etc. [b] In ppm relative to Me_4Si-d_{12}.

Table V. ^{2}H NMR Analysis of Solvolysis Products from α-d_2 and γ-d_3 (1-Methylcyclobutyl)methyl *p*-Bromobenzenesulfonate in 70T at 25 °C[a]

	products of the α-d_2 compd			products of the γ-d_3 compd	
product proportions	59%	29%	12%	58%	42%
^{2}H NMR chemical shift[b]	1.71	2.26	5.43	1.27	1.74

[a] 70% trifluoroethanol-30% water. [b] In ppm relative to Me_4Si-d_{12}.

is equal to the experimental value for the isotope effect in solvolysis of the neopentyl γ-d_9 ester. The ratio R_H^D/R_D^H, or 1.23, is the calculated intramolecular isotope effect for CH_3 vs. CD_3 migration; this is well within the range of 1.20–1.30 found by Schubert and Henson.[4] In addition, if it is assumed that the isotope effects per **D**, rather than per group, were constant so that the methylene group isotope effects were equal to the two-thirds power of the methyl effects, the calculated values for $R_{CD_3}^{CH_3}$, 0.927, $R_{CH_3}^{CD_3}$, 1.177, $(R_{CD_3}^{CH_3})^2 R_{CH_3}^{CD_3}$, 1.011, and $R_{CH_3}^{CD_3}/R_{CD_3}^{CH_3}$, 1.270 are still the same, within the range of experimental error.

The normal and inverse γ-deuterium effects experimentally determined for compound **2a** are the result of a weighted combination of migrating and nonmigrating group effects. In an attempt to isolate more cleanly the nonmigrating group effect, (1-methylcyclopentyl)methyl and (1-methylcyclobutyl)methyl sulfonate esters were studied. Owing to the strain energy present in the four- and five-membered rings, the ring expansion reaction is expected to be favored over the reaction involving methyl migration.

The α-d_1 effects in trifluoroethanolysis of both **3c** and **4c**, given in Table III, were all lower than 1.12, the α-d_1 effect for **2a**, and indicate either stronger participation or an earlier transition state. The product mixtures from the solvolyses of deuterium-labeled **3c** and **4c** were examined by ^{2}H NMR. The results, given in Tables IV and V, show that ring expansion occurred almost exclusively (≥98%) for the brosylate ester **4c** in 70T, 94% for the brosylate ester **3c** in 70T, and 82% for the tresylate ester **3b** in 97T. The dominance of ring expansion product was also consistent with the observed acceleration of the solvolysis rates of both compounds relative to the neopentyl esters; **3c** solvolyzes 400 times and **4c** 16 800 times faster than neopentyl brosylate, indicating that some ring-strain relief occurs in the rate-determining step.

The γ-d_3 effects, as shown in Table III, were all inverse for the solvolysis of esters of both compounds **3** and **4**. The smaller observed γ-d_3 inverse effect for compound **3b** in 97T can be attributed to the increasing fraction of methyl migration product which would be accompanied by a normal effect close to the value of 1.177 found in the solvolysis of **2a**. The γ-d_4 effect for solvolysis of the brosylate ester of **3** has also been determined. With the γ-d_3 and γ-d_4 isotope effects, methyl migration and ring expansion fractions, the intrinsic migrating and nonmigrating group isotope effects can be sorted out. $R_{CH_3}^{CD_3}$ and $R_{CD_3}^{CD_3}$ for the solvolysis

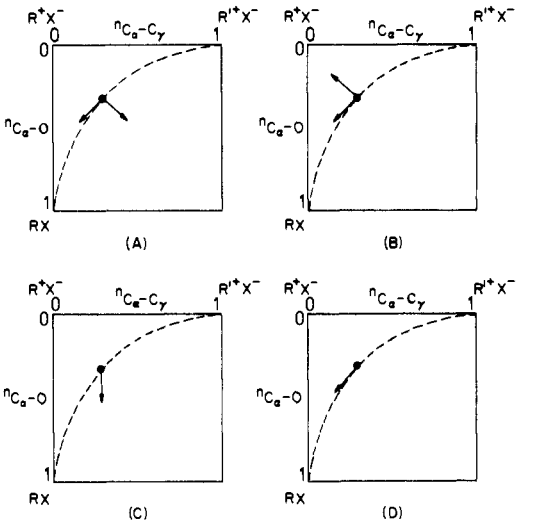

Figure 1. Schematic reaction coordinate diagrams[20] for anchimerically assisted solvolyses. The dashed lines represent the reaction pathway for compound **2a** with the transition state at the point marked by the dot. The arrows in A indicate the predicted direction of parallel and perpendicular effects due to ring strain in compound **3c** and **4c** relative to **2a**, while the arrows in B indicate the predicted direction of parallel and perpendicular effects due to hyperconjugation of the bent σ-C–C bond in compound **4c** relative to **2a**. The arrows in C and D suggest the resultants of the effects for **3c** (A) and **4c** (A and B), respectively.

of the neopentyl analogues (1-methylcyclohexyl)methyl, (1-methylcyclopentyl)methyl, and (1-methylcyclobutyl)methyl are tabulated in Table VI. The variation of migrating group and nonmigrating group effects in the solvolysis of compounds **2a**, **3c**, and **4c** can be explained with the assistance of More O'Ferrall–Jencks' energy diagrams.[19] Both cyclobutyl and cyclopentyl rings have strain energy. There will be a perpendicular effect and a parallel effect (Hammond postulate effect) relative to the transition state for compound **2a** as shown in Figure 1A. In addition, the cyclobutyl group would be expected by bent bond hyperconjugation to stabilize the adjacent cationic center much more than the

Table VI. Comparison of Solvolysis Rates, Isotope Effects, and Product Distributions for Neopentyl, (1-Methylcyclohexyl)methyl, (1-Methylcyclopentyl)methyl and (1-Methylcyclobutyl)methyl Sulfonate Esters

	neopentyl-triflate	(1-methylcyclohexyl)-methyl triflate	(1-methylcyclopentyl)-methyl brosylate	(1-methylcyclobutyl)-methyl brosylate
relative rates	1	4	400	16800
$k_H/k_{\alpha\text{-}d_1}$	1.12	1.12	1.100	1.097
Me migration		58%	6%	0%
ring expansion		42%	94%	100%
$R_{CD_3}{}^{CH_3}$ [a]		0.927	0.913	0.972
$R_{CH_3}{}^{CD_3}$ [b]		1.177	1.224	

[a] Nonmigrating group isotope effect. [b] Migrating group isotope effect.

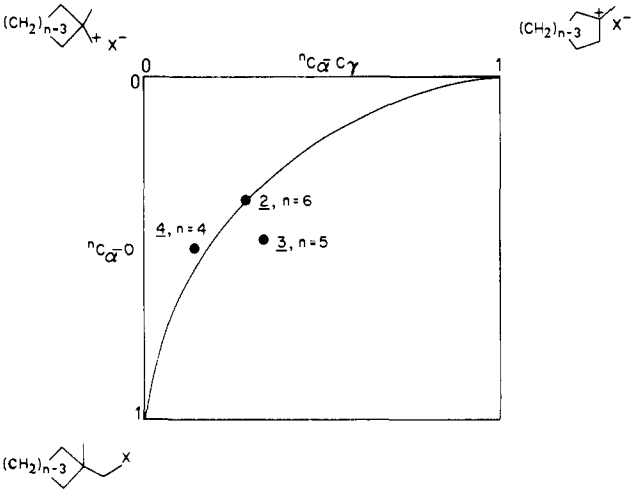

Figure 2. Relative transition-state positions for compounds **2–4** predicted from the resultant effects shown in Figure 1C,D.

cyclohexyl group does. The perpendicular and parallel effect from the ring hyperconjugation stabilization is shown in Figure 1B. Consequently, the resultant effect is for compound **3c** as shown in Figure 1C and for compound **4c** as shown in Figure 1D.

The relative transition-state positions for compounds **2–4** predicted from the resultant effect shown in Figure 1C,D are indicated in Figure 2. Hence, relative to **2a**, compound **4c** has an earlier transition state with less participation, a smaller inverse effect for the nonmigrating group and a lower α-d_1 effect; compound **3c** has also an earlier transition state but with stronger participation, a larger inverse effect for the nonmigrating group and a lower α-d_1 effect. Less ring σ-bond breaking for the transition state of compound **4c** is also reflected in the smaller rate enhancement for compound **4c**, 42, relative to compound **3c** than that for compound **3a**, 100, relative to compound **2a**.[22] This occurs even though the ring strain energy for compound **4c**, 25.6 kcal/mol, is much higher than that for compound **3c**, 6.1 kcal/mol.[23]

In comparing the inverse isotope effects for nonmigrating groups found in reactions showing methyl, phenyl, and hydrogen participation, it is clear that the isotope effect for a nonmigrating group is significantly more inverse for methyl participation than it is for hydrogen participation (0.99 per CD_3 group)[12] or phenyl participation (0.97–0.99 per CD_3 group).[13] This could be attributed to the difference in the amount of positive charge that is carried by each migrating group in the transition state. In the phenyl participation case, some positive charge is delocalized into the phenyl ring and the induction effect on the nonmigrating CD_3 group for phenyl participation will be less than is the case for methyl participation, and therefore a more inverse effect for the nonmigrating group is expected for the reaction going by methyl participation. In the hydrogen participation case, also, the migrating hydrogen is expected to carry more charge than a migrating methyl group does; less charge is dispersed into the β-carbon in the hydrogen participation example, and consequently the nonmigrating group effect will be larger when methyl is the migrating group.

Experimental Section

Boiling points and melting points are uncorrected. NMR spectra were recorded on a Varian Associates T-60 or HR-220 spectrometer. Chemical shifts are recorded in parts per million (ppm) from tetramethylsilane (Me_4Si). Mass spectra were obtained on a Varian MAT CH-7.

Cyclohexanecarboxylic Acid. This compound was purchased from Aldrich Chemical Co.

Methyl Cyclohexanecarboxylate. Cyclohexanecarboxylic acid (95 g, 0.74 mole) was dissolved in 400 mL of methanol. Ten milliliters of 2 N sulfuric acid was added to the mixture. The solution was allowed to reflux for 8 h. Methanol was evaporated, and 200 mL of ether was used to extract the ester. The organic layer was then dried over $BaCO_3$. Eventually, the ester was purified by distillation at 92–95 °C (42mmHg). The yield was 68%. NMR (CCl_4): δ 1.7 (m, 11 H), 3.60 (s, 3 H).

Cyclohexylmethanol. This alcohol was synthesized by following the standard $LiAlH_4$ reduction of methyl cyclohexanecarboxylate. Into a flask equipped with a condenser and an addition funnel was added 0.5 g (0.13 mol) of $LiAlH_4$ and 30 mL of anhydrous diethyl ether. A solution of methyl cyclohexanecarboxylate (2.8 g, 0.20 mol) in 20 mL of ether was added dropwise at 0 °C. After the addition was complete, stirring was continued for 2 h at room temperature, and 2.5 g of H_2O was then added cautiously to the reaction mixture. Subsequently, the white precipitate was removed by filtration and the solution was dried over $MgSO_4$. Eventually, the solvent was removed by rotary evaporation and the yield was 1.7 g (75%). NMR (CCl_4): δ 1.7 (m, 11 H), 3.36 (d, 2 H), 3.71 (b, 1 H).

Cyclohexylmethyl Trifluoromethanesulfonate (Triflate). This compound was synthesized by modification of Seib's procedure.[13] Into a 100-mL flask equipped with an addition funnel and a drying tube were added 1.7 g (0.015 mol) of cyclohexylmethanol and 1.6 g (0.015 mol) of 2,6-lutidine in 50 mL of petroleum ether. Triflic anhydride (4.3 g, 0.015 mol) in 10 mL of petroleum ether was then added dropwise with stirring at −10 °C. The solution was allowed to stir for 1 h at 0 °C. The mixture was filtered through a fine-fritted funnel layered with $MgSO_4$, Norit-A, and sea sand. The solvent was subsequently evaporated and 2.7 g (61% yield) of the clear colorless oil which remained was purified by vacuum transfer. NMR (CCl_4): δ 1.7 (m, 11 H), 4.29 (d, 2 H).

Cyclohexanone-*2,2,6,6,*-d_4. This ketone was prepared from D_2O exchange of cyclohexanone by following the standard procedure.[24] Cyclohexanone (100 g, 1.02 mol), D_2O (25 g, 1.39 mol), and 0.5 g of K_2CO_3 were refluxed together for 12 h. The aqueous layer was extracted with ethyl ether, and the combined organic layer was dried over $MgSO_4$. The solvent was then evaporated, and ketone was isolated. After four such exchanges, the deuterium incorporation was 98% (3.92 (average) deuterium atoms per molecule) determined by mass spectrometry and the overall yield was 72%. NMR (CCl_4): δ 1.81 (b, 6 H).

Triphenylmethylphosphonium Bromide.[25] To a pressure bottle was added 55 g (0.21 mol) of triphenylphosphine dissolved in 45 mL of benzene. The bottle was then cooled in an ice–salt bath, and 28 g (0.29 mol) of previously condensed methyl bromide was added. The bottle was subsequently sealed and allowed to stand at room temperature for 2 days. The white solid was collected by means of suction filtration with the aid of ~500 mL of hot benzene and was dried in a vacuum oven at 100 °C. The yield was 71 g (95%); mp 234–235 °C (lit. 232–233 °C).

Methylidenecyclohexane-*2,2,6,6-*d_4. This olefin was prepared from cyclohexanone-*2,2,6,6-*d_4 by following the standard Wittig reaction procedures.[26] Sodium hydride (0.10 mol as a 55% dispersion in mineral oil) in a 500-mL three-neck flask was washed with several portions of petroleum ether under nitrogen atmosphere. Fifty milliliters of dimethyl sulfoxide (Me_2SO) was then introduced, and the mixture was heated at 75–80 °C for 45 min until hydrogen evolution ceased. Triphenylmethylphosphonium bromide (35.7 g, 0.10 mol) dissolved in 100 mL of warm Me_2SO was then added at 0 °C. The resulting dark red solution was stirred at room temperature for 10 min. Freshly distilled cyclo-

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hexanone-2,2,6,6-d_4 (10 g, 0.1 mol) was then added slowly, and the reaction mixture was allowed to stir for 30 min. Methylidenecyclohexane-2,2,6,6-d_4 was immediately distilled from the solution and collected at 42 °C (105mmHg). The yield was 55%. NMR (CCl_4): δ 1.60 (b, 6 H), 4.70 (b, 2 H).

Methyl 1-Methylcyclohexanecarboxylate. *n*-Butyllithium (0.2 mol, 85 mL, 2.45 M in hexane) was added dropwise to a stirred solution of 20.2 g of diisopropylamine in 30 mL of THF at −78 °C. The solution was warmed to room temperature to ensure the evaporation of butane and then cooled again. Methyl cyclohexanecarboxylate (28.4 g, 0.2 mol) was added to the stirred reaction mixture at −78 °C before the solution temperature was raised again to 0 °C to allow the completion of the reaction. Methyl iodide (28.4 g) in 50 mL of THF was subsequently added to the solution at −78 °C and stirred for 8 h at room temperature. All reactions were carried out under nitrogen atmosphere. The reaction mixture was washed with 100 mL of water and extracted twice with 100 mL of diethyl ether. The organic layer was separated and dried over $MgSO_4$. The product was purified by distillation and collected at 89 °C (40mmHg). The yield was 75%. NMR (CCl_4): δ 1.2 (s, 3 H), 1.6 (m, 10 H), 3.6 (s, 3 H).

Methyl 1-Methyl-d_3-cyclohexanecarboxylate. This ester was prepared by the same method described above for the synthesis of methyl 1-methylcyclohexanecarboxylate. Instead of using methyl iodide, methyl-d_3 iodide was introduced (>99 atom % isotopically pure). The yield was 77%. NMR (CCl_4): δ 1.6 (m, 10 H), 3.6 (s, 3 H).

(1-Methylcyclohexyl)methanol and (1-Methyl-d_3-cyclohexyl)methanol. These alcohols were made from $LiAlH_4$ reduction of the corresponding esters. The procedure used was the same as that used for the preparation of cyclohexylmethanol. The yields were around 75%. NMR (CCl_4): H compound, δ 0.95 (s, 3 H), 1.6 (m, 10 H), 2.8 (b, 1 H), 3.2 (s, 2 H); γ-d_3 compound, δ 1.6 (m, 10 H), 2.8 (b, 1 H), 3.2 (s, 2 H).

(1-Methylcyclohexyl)methan-d_2-ol. This compound was prepared from $LiAlD_4$ reduction on methyl 1-methylcyclohexanecarboxylate by following the procedure used for the preparation of cyclohexylmethanol. The yield was 70%. NMR (CCl_4): δ 0.95 (s, 3 H), 1.6 (m, 10 H), 2.8 (b, 1 H).

Trifluoromethanesulfonic Anhydride (Triflic Anhydride).[27] P_2O_5 (48 g, 0.34 mol) and trifluoromethanesulfonic acid (50 g, 0.32 mol) were mixed together in a 100-mL flask which was allowed to stand 24 h at room temperature. The anhydride was then vacuum transferred. To ensure the complete conversion of acid to anhydride, we added another 5 g of P_2O_5 to the transferred anhydride and a second vacuum transfer was carried out. The overall yield was 78%.

(1-Methylcyclohexyl)methyl Triflate, (1-Methylcyclohexyl)methyl-d_2 Triflate, and (1-Methyl-d_3-cyclohexyl)methyl Triflate. These sulfonate esters were prepared from the corresponding alcohols and triflic anhydride by the procedure described earlier for the preparation of cyclohexanemethyl triflate. The yields were around 65%. NMR (CCl_4): H compound, δ 1.02 (s, 3 H), 1.6 (m, 10 H), 4.1 (s, 2 H); α-d_2 compound, δ 1.02 (s, 3 H), 1.6 (m, 10 H); γ-d_3 compound, δ 1.6 (m, 10 H), 4.1 (s, 2 H).

Cyclohexyl-2,2,6,6-d_4-methanol. This compound was synthesized by hydroboration of methylidenecyclohexane-2,2,6,6-d_4. In a three-neck round-bottom flask equipped with a condenser and an addition funnel and maintained under nitrogen atomsphere were placed 3.4 g of boron trifluoride etherate, 4.8 g (0.024 mol) of methylidenecyclohexane, and 100 mL of diethyl ether. A solution of 0.7 g (0.018 mol) of $LiAlH_4$ in 70 mL of anhydrous ethyl ether was added slowly. The mixture was allowed to stir at room temperature for 2 h, and the excess hydride was destroyed by slowly adding 20 mL of acetone. A saturated solution of Na_2SO_4 was added, followed by solid sodium sulfate. The mixture was filtered, and the solvent was evaporated. The residue was subsequently dissolved in 30 mL of 90% ethanol–water solution containing 0.8 g of sodium ethoxide, and 10.2 mL of 20% H_2O_2 was added with stirring. Water and ether were added, and the organic layer was washed with water, dried, and evaporated. Cyclohexyl-2,2,6,6-d_4-methanol was collected (2.9 g), and the yield was 52%. NMR (CCl_4): δ 1.7 (m, 7 H), 3.38 (d, 2 H), 3.76 (b, 1 H).

Cyclohexyl-2,2,6,6-d_4-methyl Triflate. This ester was made from cyclohexyl-2,2,6,6-d_4-methanol and triflic anhydride by following the procedure for the preparation of cyclohexylmethyl triflate. The yield was 68%. NMR (CCl_4): δ 1.7 (m, 7 H), 4.15 (d, 2 H).

Cyclohexane-2,2,6,6-d_4-carboxylic Acid. This acid was made from the oxidation of cyclohexyl-2,2,6,6-d_4-methanol by a modified procedure of Eisenbraum.[28] The chromic acid oxidizing reagent was prepared by dissolving 10.5 g of chromium trioxide in 20 mL of water. To this solution was added 9 mL of concentrated sulfuric acid. This oxidizing reagent was added slowly to a solution of 10 g in 70 mL of acetone at 0 °C. The addition was continued until the orange color of the chromic acid reagent persisted for 20 min. Isopropyl alcohol was then added dropwise until the excess chromic acid was destroyed. The suspension was filtered, and the filtrate was concentrated by evaporating the solvent. The acid was then extracted with diethyl ether twice, and the combined organic layer was dried. Ether was evaporated and the yield was 60%. NMR (CCl_4): δ 1.7 (m, 7 H), 11.2 (b, 1 H).

Methyl Cyclohexane-2,2,6,6-d_4-carboxylate. This compound was prepared from esterification of cyclohexane-2,2,6,6-d_4-carboxylic acid. The procedure used was the same as that used for the esterification of the hydrogen compound. The yield was 67%. Mass spectral analysis gave an average deuterium content of 3.68 atoms/molecule. NMR (CCl_4): δ 1.7 (m, 7 H), 3.6 (s, 3 H).

Methyl 1-Methylcyclohexane-2,2,6,6-d_4-carboxylate. This ester was made from methylation of methyl cyclohexane-2,2,6,6-d_4-carboxylate by following the same procedure described earlier for preparation of the hydrogen compound. The yield was 69%. NMR (CCl_4): δ 1.2 (s, 3 H), 1.7 (m, 6 H), 3.6 (s, 3 H).

(1-Methylcyclohexyl-2,2,6,6-d_4)methanol. This alcohol was synthesized from $LiAlH_4$ reduction of methyl 1-methylcyclohexane-2,2,6,6-d_4-carboxylate by following the standard $LiAlH_4$ reduction procedure. The yield was 72%. NMR (CCl_4): δ 0.95 (s, 3 H), 1.6 (m, 6 H), 2.8 (b, 1 H), 3.2 (s, 2 H).

Methyl Cyclopentanecarboxylate. Eighty-four grams of cyclopentanecarboxylic acid was esterified in 400 mL of methanol by the acid-catalyzed procedure used for the preparation of methyl cyclohexanecarboxylate. The yield of the desired ester was 80%. NMR (CCl_4): δ 1.75 (m, 8 H), 2.60 (m, 1 H), 3.62 (s, 3 H).

Methyl 1-Methylcyclopentanecarboxylate. This compound was prepared in 78% yield by the method described earlier for the preparation of methyl 1-methylcyclohexanecarboxylate. NMR (CCl_4): δ 1.21 (s, 3 H), 1.73 (m, 8 H), 3.60 (s, 3 H).

Methyl 1-Methyl-d_3-cyclopentanecarboxylate. This ester was prepared by the same procedure as that used for the preparation of methyl 1-methylcyclopentanecarboxylate, using CD_3I instead of CH_3I. The yield was 70%. NMR (CCl_4): δ 1.75 (m, 8 H), 3.60 (s, 3 H).

(1-Methylcyclopentyl)methanol. This alcohol was prepared by $LiAlH_4$ reduction of methyl 1-methylcyclopentanecarboxylate by using the standard method. The yield was 80%. NMR (CCl_4): δ 0.98 (s, 3 H), 1.74 (m, 8 H), 2.9 (b, 1 H), 3.3 (s, 2 H).

(1-Methylcyclopentyl)methan-d_2-ol. This compound was prepared by $LiAlD_4$ reduction of methyl 1-methylcyclopentanecarboxylate. The procedure used was the same as that used for the preparation of (1-methylcyclohexyl)methan-d_2-ol. The yield was 75%. NMR (CCl_4): δ 0.98 (s, 3 H), 1.74 (m, 8 H), 2.9 (b, 1 H).

(1-Methyl-d_3-cyclopentyl)methanol. This alcohol was synthesized by $LiAlH_4$ reduction of methyl 1-methyl-d_3-cyclopentanecarboxylate by using the standard method. The yield was 82%. NMR (CCl_4): δ 1.74 (m, 8 H), 2.9 (b, 1 H), 3.32 (s, 2 H).

(1-Methylcyclopentyl)methyl 2,2,2-Trifluoroethanesulfonate (Tresylate). This ester was prepared by a modification of the method described earlier.[29] To a solution of 1 g (0.0088 mol) of (1-methylcyclopentyl)-methanol and 0.98 g (0.009 mol) of triethylamine in 20 mL of petroleum ether at −10 °C was added 1.76 g (0.0097 mol) of 2,2,2-trifluoroethanesulfonyl chloride in 10 mL of petroleum ether and 5 mL of methylene chloride mixture over a 10-min period. The reaction mixture was allowed to stir for 1 h at 0 °C. The mixture was filtered through a fine-fritted funnel layered with $MgSO_4$, charcoal, and sea sand. The solvent was subsequently evaporated and the product purified by vacuum transfer; the yield was 58%. NMR (CCl_4): δ 1.01 (s, 3 H), 1.65 (m, 8 H), 3.80 (quartet, 2 H), 4.05 (s, 3 H).

(1-Methylcyclopentyl)methyl *p*-Bromobenzenesulfonate (Brosylate). This brosylate was synthesized by using a modified Tipson procedure.[30] To a flask was added 4.9 g (0.019 mol) of *p*-bromobenzenesulfonyl chloride dissolved in a minimum amount of pyridine. The mixture was cooled in an ice-water bath, and 2 g (0.017 mol) of (1-methylcyclopentyl)methanol was added. The solution was then stirred for half an hour and placed in the refrigerator for 8 h. Ten milliliters of ice-water was added slowly to the reaction mixture, and the brosylate was extracted with ethyl ether. The combined organic layer was washed subsequently with 2 N H_2SO_4 and saturated $NaHCO_3$ and then dried over magnesium sulfate. The solvent was removed, and the sulfonate ester was recrystallized twice from petroleum ether. The yield was 65%; mp 54–55 °C. NMR (CCl_4): δ 0.98 (s, 3 H), 1.74 (m, 8 H), 3.75 (s, 2 H), 7.70 (s, 4 H).

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Cyclopentanone-2,2,5,5-d_4. This ketone was synthesized from D_2O exchange with cyclopentanone. The procedure used was the same as that used for the preparation of cyclohexanone-2,2,6,6-d_4. After three exchanges, the deuterium incorporation was more than 98% as determined by mass spectra and ^1H NMR. The overall yield was 59%. NMR (CCl_4): δ 2.0 (b).

1-Bromocyclopentane-2,2,5,5-d_4. This bromide was prepared from bromination of cyclopentanol-2,2,5,5-d_4 with PBr_3. To a flask equipped with an addition funnel and a drying tube was added 20 g of cyclopentanol-2,2,5,5-d_4, and the solution was then cooled to −10 °C. PBr_3 was added slowly, and the mixture was allowed to stir for 3 h after the addition was completed. 1-Bromocyclopentane-2,2,5,5-d_4 was then distilled from the solution under reduced pressure and collected at 42 °C (20mmHg). The crude bromide was dissolved in methylene chloride, and saturated $NaHCO_3$ solution was added to wash out the hydrogen bromide. The organic layer was dried over $MgSO_4$ and 1-bromocyclopentane-2,2,5,5-d_4 was purifed again by reduced pressure distillation. The overall yield was 53%. Less than 4% deuterium scrambling was found by ^2H NMR. NMR (CCl_4): δ 1.81 (m, 4 H), 4.40 (b, 1 H).

(Cyclopentane-2,2,5,5-d_4)carboxylic Acid. This acid was prepared by a Grignard synthesis. To a 500-mL flask equipped with a reflux condenser and an addition funnel and maintained under nitrogen pressure was added 3 g (0.12 mol) of magnesium turnings in 100 mL of anhydrous diethyl ether. Ethylene bromide was used to initiate the reaction, and 15 g (0.1 mol) of 1-bromocyclopentane-2,2,5,5-d_4 dissolved in 100 mL of ether was then added at a rate sufficient to maintain a gentle reflux. After the addition was complete, the solution was refluxed for 1 h and then cooled to 0 °C. Excess powdered dry ice was added to the mixture. Saturated aqueous NH_4Cl was added slowly. The aqueous layer was acidified with 5 N H_2SO_4 and extracted with ether twice. The organic layer was then combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The yield was 64%. NMR (CCl_4): δ 1.62 (m, 4 H), 2.61 (b, 1 H), 11.0 (b, 1 H).

Methyl Cyclopentane-2,2,5,5-d_4-carboxylate. This compound was prepared by the esterification of (cyclopentane-2,2,5,5-d_4)carboxylic acid in methanol as outlined for the preparation of methyl cyclohexanecarboxylate. Distillation of the crude product yielded 66% of the desired ester. NMR (CCl_4): δ 1.6 (m, 4 H), 2.61 (b, 1 H), 3.60 (s, 3 H).

Methyl 1-Methylcyclopentane-2,2,5,5-d_4-carboxylate. Five grams (0.034 mol) of this ester was prepared from 6.45 g (0.049 mol) of methyl cyclopentane-2,2,5,5-d_4-carboxylate and 7 g (0.049 mol) of CH_3I by the procedure used for the preparation of methyl 1-methylcyclohexanecarboxylate. The yield was 69%. NMR (CCl_4): δ 1.21 (s, 3 H), 1.61 (m, 4 H), 3.59 (s, 3 H).

(1-Methylcyclopentyl-2,2,5,5-d_4)methanol. Two grams (0.014 mol) of methyl 1-methylcyclopentane-2,2,5,5-d_4-carboxylate was reduced with 0.35 g (0.009 mol) of $LiAlH_4$ by the procedure used to prepare (1-methylcyclohexyl)methanol. The yield was 76%. NMR (CCl_4): δ 1.00 (s, 3 H), 1.62 (b, 4 H), 3.30 (s, 2 H).

(1-Methylcyclopentyl)methyl-d_2 Brosylate and (1-Methyl-d_3-cyclopentyl)methyl Brosylate. These esters were prepared from the corresponding alcohols and *p*-bromobenzenesulfonyl chloride in about 60% yield by the Tipson procedure.[30] NMR (CCl_4): δ α-d_2 ester, same as for the protio compound except δ 3.75 (s, 2 H), was absent; γ-d_3 ester, same as for the protio compound except δ 0.98 (s, 3 H) was absent.

(1-Methylcyclopentyl-2,2,5,5-d_4)methyl Brosylate. This sulfonate ester was prepared from (1-methylcyclopentyl-2,2,5,5-d_4)methanol and *p*-bromobenzenesulfonyl chloride by the modified Tipson procedure.[30] The yield was 68%; mp 54.5–55 °C. NMR (CCl_4): δ 1.00 (s, 3 H), 1.63 (b, 4 H), 3.81 (s, 2 H), 7.7 (s, 4 H).

(1-Methylcyclopentyl)methyl-d_2 Tresylate and (1-Methyl-d_3-cyclopentyl)methyl Tresylate. These esters were prepared from the corresponding alcohols and 2,2,2-trifluoroethanesulfonyl chloride in ~60% yield by using the procedure referred to above for the preparation of the protio compound. NMR (CCl_4): α-d_2 ester, same as for the protio compound except δ 4.05 is absent; γ-d_3 ester, same as for the protio compound except δ 1.01 is absent.

Methyl Cyclobutanecarboxylate. This compound was prepared by esterification of cyclobutanecarboxylic acid with methanol. The procedure used was the same as that described previously for the preparation of methyl cyclohexanecarboxylate, and the yield was 75%. NMR (CCl_4): δ 2.11 (m, 6 H), 2.95 (m, 1 H), 3.60 (s, 3 H).

Methyl 1-Methylcyclobutanecarboxylate. This compound was prepared in 60% yield by the method described for the preparation of methyl 1-methylcyclohexanecarboxylate. NMR (CCl_4): δ 1.40 (s, 3 H), 1.95 (m, 6 H), 3.60 (s, 3 H).

Methyl 1-Methyl-d_3-cyclobutanecarboxylate. Four grams (0.03 mol) of this ester was obtained from 5 g (0.044 mol) of methyl cyclobutanecarboxylate and 6.5 g (0.044 mol) of CD_3I by the procedure used for the preparation of methyl 1-methyl-d_3-cyclohexanecarboxylate. NMR (CCl_4): δ 1.95 (m, 6 H), 3.60 (s, 3 H).

(1-Methylcyclobutyl)methanol and (1-Methyl-d_3-cyclobutyl)methanol. These alcohols were obtained from $LiAlH_4$ reduction of the corresponding esters. The yields were around 70%. NMR (CCl_4): protio ester, δ 1.16 (s, 3 H), 1.90 (m, 6 H), 3.01 (b, 1 H), 3.35 (s, 2 H); γ-d_3 ester, same as for the protio compound except δ 1.16 (s, 3 H) was absent.

(1-Methylcyclobutyl)methan-d_3-ol. Two grams (0.015 mol) of methyl 1-methylcyclobutanecarboxylate was reduced with 0.39 g (0.0092 mol) of $LiAlD_4$ by the procedure used to obtain (1-methylcyclopentyl)-methan-d_2-ol. The yield was 75%. NMR (CCl_4): δ 1.16 (s, 3 H), 1.90 (m, 6 H).

(1-Methylcyclobutyl)methyl Brosylate, (1-Methylcyclobutyl)methyl-d_2 Brosylate, and (1-Methyl-d_3-cyclobutyl)methyl Brosylate. These sulfonate esters were prepared from their corresponding alcohols and *p*-bromobenzenesulfonyl chloride in ~70% yield by the Tipson procedure;[30] mp 40–41 °C. NMR (CCl_4): protio compound, δ 1.00 (s, 3 H), 1.75 (m, 6 H), 3.80 (s, 2 H), 7.70 (s, 4 H); α-d_2 compound, same as for the protio compound except δ 3.80 (s, 2 H) was absent; γ-d_3 compound, same as for the protio compound except δ 1.00 (s, 3 H) was absent.

Kinetic Study. Rates were measured by using the precise conductometric method which has been described earlier.[21,31]

Product Analysis. The reaction mixture containing 0.1 M reactant and 0.15 M sodium hydroxide was sealed in NMR tubes and allowed to react at 25 °C for 10 half lives. The ^2H NMR spectra were recorded at 33.77 MHz, and the product ratio was determined by comparison of peak areas. Chemical shifts are in parts per million relative to external tetramethylsilane-d_{12}.

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Appendix. Derivation of Equations 1 and 2

The first-order rate constant for solvolysis of the hydrogen compound, k_H, can be expressed as eq a, where k_H^m is the

$$k_H = k_H^m + k_H^r \quad \text{(a)}$$

first-order rate constant for that part of the reaction which involves migration of the methyl group and k_H^r is the first-order rate constant for that part of the reaction which involves ring expansion. If the fraction of methyl migration product is "a" and the fraction of ring expansion product is "b", then

$$k_H^m/k_H^r = a/b \quad \text{(b)}$$

$$k_H = (1/b)k_H^r \quad \text{(c)}$$

$$k_H = (1/a)k_H^m \quad \text{(d)}$$

Similarly, where $k_{\gamma\text{-}d_3}$ is the first-order rate constant for the solvolysis of the γ-d_3 compound

$$k_{\gamma\text{-}d_3} = k_{\gamma\text{-}d_3}^m + k_{\gamma\text{-}d_3}^r \quad \text{(e)}$$

then

$$(k_H/k_{\gamma\text{-}d_3}) = k_H/(k_{\gamma\text{-}d_3}^m + k_{\gamma\text{-}d_3}^r) = 1/[(k_{\gamma\text{-}d_3}^m/k_H) + (k_{\gamma\text{-}d_3}^r/k_H)] \quad \text{(f)}$$

and, substituting for k_H from eq c and d

$$k_H/k_{\gamma\text{-}d_3} = 1/[a(k_{\gamma\text{-}d_3}^m/k_H^m) + b(k_{\gamma\text{-}d_3}^r/k_H^r)] = 1/[(a/R_H^D) + (b/R_D^H)] = R_H^D R_D^H/(aR_D^H + bR_H^D) \quad \text{(g)}$$

where R_H^D is $k_{\gamma\text{-}d_3}^m/k_H^m$, the isotope effect in that part of the reaction with methyl or methyl-d_3 migrating, and R_D^H is $k_H^r/k_{\gamma\text{-}d_3}^r$, the isotope effect for that part of the reaction in which the ring expands and methyl (or methyl-d_3) is nonmigrating. For the γ-d_4 compound one similarly derives

$$k_H/k_{\gamma\text{-}d_4} = 1/a(k_{\gamma\text{-}d_4}^m/k_H^m) + b(k_{\gamma\text{-}d_4}^r/k_H^r) \quad \text{(h)}$$

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Then, with the assumption that the isotope effects for methyl and methylene groups are the same

$$k_H^m/k_{\gamma\text{-}d_4}^m = (R_D^H)^2 \quad \text{(i)}$$

because there are two deuterated methylene groups not migrating in this part of the reaction of the γ-d_4 compound and

$$k_H^r/k_{\gamma\text{-}d_4}^r = (R_D^H)(R_H^D) \quad \text{(j)}$$

because for ring expansion in the γ-d_4 compound one CD_2 group migrates and one does not migrate. Thus,

$$k_H/k_{\gamma\text{-}d_4} = 1/[(a/(R_D^H)^2) + (b/(R_D^H)(R_H^D))] = (R_D^H)^2R_H^D/(aR_H^D + bR_D^H) \quad \text{(k)}$$

In one assumes that the isotope effects are the same *per D* in methyl and methylene groups, the last equation becomes

$$k_H/k_{\gamma\text{-}d_4} = (R_D^H)^{4/3}(R_H^D)^{2/3}/[a(R_H^D)^{2/3} + b(R_D^H)^{2/3}] \quad \text{(l)}$$

Acid-Catalyzed Decomposition of Trialkyltriazenes: Protected Alkyldiazonium Ions

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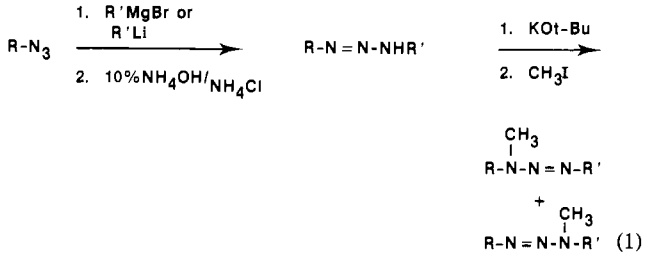
Abstract: The acid-catalyzed decomposition of 1,3-di-*n*-butyl-3-methyltriazene and the synthesis and decomposition of 1,3-bis(cyclopropylcarbinyl)-3-methyltriazene are reported. A kinetic study of the acid-catalyzed decomposition of 1,3-di-*n*-butyl-3-methyltriazene indicates that the reaction is subject to general acid catalysis. The rates of reaction have been studied by monitoring the disappearance of a triazene UV absorption band (263 nm). A plot of the buffer concentration vs. k_{obsd} was a straight line, whose slope gave $k_{cat} = 1.84 \times 10^{-2}$ min^{-1} M^{-1}. A linear dependence of the log (k_{obsd}) on pH (6.9-8.4) was observed, along with a solvent isotope effect (k_D/k_H) of 2.05. The products of the decomposition of the butyltriazene (*n*-butyl and *sec*-butyl alcohols and 1- and 2-butene) were accounted for by the intermediacy of a diazonium ion. The mechanism was corroborated by the product analysis of the decomposition of the (cyclopropylcarbinyl)triazene. The alcoholic products isolated were cyclopropylcarbinyl alcohol (48%), cyclobutyl alcohol (48%) and 3-buten-1-ol (4%). This distribution is conclusive evidence that these trialkyltriazenes decompose in aqueous media to produce alkyldiazonium ions or directly to produce carbonium ions in cases where the alkyl group is capable of stabilizing a positive charge.

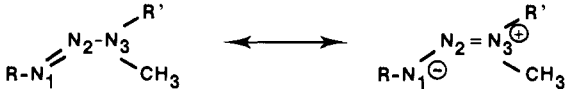
Introduction

The chemistry of trialkyltriazenes is relatively unknown since only a few isolated instances of preparation of these substances exist in the literature.[1-5] We recently reported[6] a general, high-yield synthesis of this class of compounds starting from alkyl azides (eq 1). Some properties of trialkyltriazenes are similar



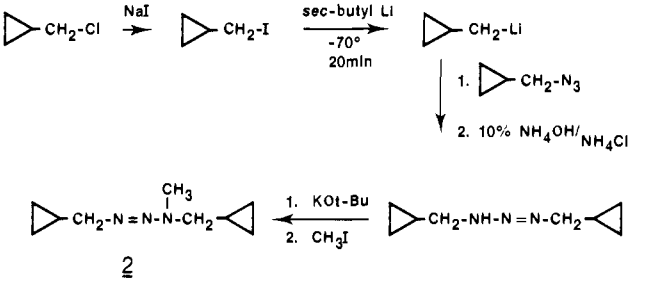
(1)

to their better known analogues, the aryldialkyltriazenes, including a barrier to rotation about the N(2)-N(3) bond,[6]



the magnitude of which was calculated to be around 10.5-11.5 kcal/mol, about 3 kcal/mol lower than that of the aryl analogues. Trialkyltriazenes were also found to be extremely acid sensitive, decomposing rapidly with the evolution of nitrogen. Their lack of reactivity toward alkylating agents such as methyl iodide, dimethyl sulfate, and methyl fluorosulfonate mirror the behavior of 1-phenyl-3,3-dimethyltriazene.

Scheme 1



The intermediacy of the alkyldiazonium ion in the acid-catalyzed decomposition of alkylaryltriazenes and in the nitrous acid deamination of primary amines has been the subject of extensive research.[7-10] The decomposition of RNNNHPh in aqueous acids is known to give ROH, N_2, and $PhNH_2$ as products,[8-10] and it is known that the decomposition of alkylphenyltriazenes in HX-H_2O proceeds by an ionic mechanism.[8-10] In the absence of HX, decomposition in media such as H_2O-CH_3OH or H_2O-C_6H_6 was

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