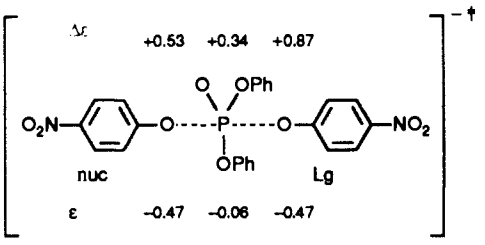

I

increased electron-attracting power of the phenyl compared with the ethyl group; there is little steric requirement at phosphorus in the diphenyl series compared to that in the ethyl series. The reactivity difference, which is relatively small on an energy scale, is unlikely to result from a change in mechanism to a stepwise process in the diethyl case.

The conclusions of this paper refer to symmetrical and unsymmetrical displacements where at least one of the nucleophiles is weakly basic. Kinetically observable pentacoordinate phosphorus species from neutral phosphoacyl anions have always involved strong nucleophiles.[2] Addition intermediates observed in acid-catalyzed phosphoryl group transfer[1a] are neutral and thus possess no driving force to expel a ligand, and they can, thus, exist as observable entities.

General-Base Catalysis. The sterically hindered nucleophiles (2,4,6-trichlorophenolate ion, 2,6-dichlorophenolate ion, and 2,6-dimethylphenolate ion) and the data for acetate ion have reactivities well below those predicted from the regression line (eq 4) and may include some general-base component. The reactivity of the imidazole species, which comes close to that of a phenolate ion of similar pK_a, confirms previous conclusions that this reagent acts as a nucleophile.[12] Otherwise, the reactivity would be at least below that of the above sterically hindered phenolate anions.

Imidazole reacts with the hindered diphenylphosphinyl esters as a general base[12] and with the less hindered dimethylphosphinyl group as a nucleophile.[5b] Our studies indicate that the oxyanion from 2-iodosobenzoic acid[10m] is some 3.9×10^5-fold more reactive against 4-nitrophenyl diphenyl phosphate than a phenoxide ion of similar pK_a; this is consistent with the nucleophile possessing the enhanced reactivity of an "α-nucleophile".

Acknowledgment. We thank the SERC for partial support of this work (Grant GR/E06558), and S.A.B.-S. thanks the government of Saudi Arabia for a studentship.

Appendix

The parameters β_{eq}', β_{eq}'', and β_{eq} refer to the Brønsted-type parameter for the plot of the logarithm of the equilibrium constants for steps k_1 and k_2 and for the overall reaction against the pK_a of the appropriate phenol.

The simple relationship $\beta_{eq} = \beta_{eq}' + \beta_{eq}''$ follows from the relationship between the three equilibrium constants. Thus, $\beta_{eq}'' = \beta_{eq} - \beta_{eq}'$ and β_{eq}'' must, therefore, be greater than 0.9 if $\beta_{eq}' < 0.5$ and $\beta_{eq} = 1.4$.

Supplementary Material Available: Table of reactivity data of 4-nitrophenyl diphenyl phosphate with buffers at different pH's containing phenol (1 page). Ordering information is given on any current masthead page.

(23) Phenoxide ion attack on the 4-nitrophenyl ester of diethyl and diphenyl phosphoric acid has bimolecular rate constants 6.7×10^{-4} M^{-1} s^{-1} at 39 °C[1f] and 4.3×10^{-2} M^{-1} s^{-1} at 25 °C, respectively, with 32% MeOH/water.[16] Hydroxide ion attack on these esters has the rate constants 8.6×10^{-3} M^{-1} s^{-1}[24] and 0.26 M^{-1} s^{-1}[16] at 25 °C in water.

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The β Effect of Silicon in the Synperiplanar Geometry

Joseph B. Lambert*,[1a] and Erik C. Chelius[1b]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113. *Received April 20, 1990*

Abstract: The effect of silicon on the development of β positive charge has been measured for the synperiplanar geometry of the Si-C-C-X fragment in *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl esters (**3**). Solvent effects were used to demonstrate that solvolysis took place by a carbocation mechanism. When the leaving group X was mesylate (**3**-OMs) and the solvent was 97% trifluoroethanol, the β effect was found to be about 10^5 by comparison of the solvolysis rate with the analogous structure lacking the trimethylsilyl group, *endo*-2-norbornyl mesylate (**5**-OMs). Thus, the synperiplanar β effect is much smaller than the antiperiplanar β effect (about 10^{12} under similar conditions). The effect may be smaller because of poorer vertical overlap in the synperiplanar geometry or because the syn leaving group prevents optimal vertical overlap. Alternatively, the antiperiplanar effect may be larger because of contributions from nonvertical participation.

One of the most important electronic properties of silicon is its substantial ability to stabilize positive charge on a β atom, the so-called β effect.[2] Positive charge may be produced solvolytically in solution or by various reactions in the gas phase. The presence of a β silicon atom can produce an acceleration (compared with hydrogen at the same β position) of up to 10^{12} (about 18 kcal mol^{-1}) for secondary systems in solution.[3] Mass spectrometric studies have assessed the β effect for primary systems ($Me_3SiCH_2CH_2^+$) at 39 or 48 kcal mol^{-1},[4,5] the difference resulting from the chosen value of the heat of formation of Me_3Si^+. Li and Stone found the effect to be about 28 kcal mol^{-1} for secondary systems.[5] By ab initio calculation, Jorgensen and co-workers[6] found the β effect to be about 38 kcal mol^{-1} for the primary case, 22 kcal mol^{-1} for the secondary case, and 16 kcal mol^{-1} for the

(1) (a) This work was supported by the National Science Foundation (Grant No. CHE-8910841) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Fellowship recipient from the Division of Organic Chemistry of the American Chemical Society, sponsored by the Rohm & Haas Co. We acknowledge helpful discussions with Professor Xavier Creary of Notre Dame University.

(2) For a comprehensive review, see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677-2689.

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(4) Hajdesz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212-1214.

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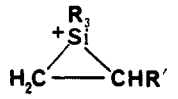
tertiary case (in these theoretical studies the silicon-containing group was SiH_3).

Several mechanisms may contribute to the β effect. (1) Silicon is more electropositive than carbon or hydrogen and may cause an acceleration due to charge induction. In a secondary system,[3] we calculated an inductive contribution of about 10^2 (about 3 kcal mol^{-1}) based on an analogy to β H/D kinetic isotope effects. Jorgensen and co-workers[6] calculated an inductive effect of about 9 kcal mol^{-1} for the primary case but nil for the secondary case. Thus, the exact level of inductive contribution, if any, is unclear. (2) Silicon may serve as a classical nucleophilic neighboring group that displaces the β nucleofuge to form a three-membered ring, **1**. Traylor[7] has termed this process nonvertical because nuclear



motion of silicon takes place. (3) The very high polarizability of the carbon–silicon bond makes it particularly able to stabilize positive charge by hyperconjugation (σ–π overlap or double-bond–no-bond resonance, **2** and **2'**). Traylor called this mode vertical because movement of the silicon nucleus is not necessary.

Although a clear-cut distinction has not been made, the general weight of evidence seems to favor vertical stabilization (hyperconjugation) as providing the most important share. Jorgensen's calculations[6] found the bridged form **1** to be about 2.4 kcal mol^{-1} more stable than the open form **2** for the primary case (R, R' = H), and the open form was not a minimum. In the secondary case (R = H, R' = Me), however, the open form was found to be about 4 kcal mol^{-1} more stable than the bridged form, and in this case the bridged form was not an energy minimum. Thus, direct calculation did not provide a clear answer. Moreover, theory addresses only the fully developed carbocation, whereas the actual transition state has only a partial positive charge and an incompletely departed leaving group.

Experiment also has been ambiguous. Traylor and co-workers[7] found that the frequency of the charge-transfer band of Me_3SiCH_2Ph agreed with a vertical mechanism of stabilization, although admittedly this neutral system is not closely related to those carrying positive charge. Eaborn and co-workers[8] concluded that vertical stabilization is insufficient to explain all of the kinetic enhancement by analysis of σ_p^+ values. Davis and Jacocks[9] compared the effect of one β silicon with that of two and found similar levels of acceleration for the first and second silicons. Because only one silyl group can engage in the bridging process to form **1**, this observation strongly favors vertical stabilization. Li and Stone[5] found in the gas phase that the β effect was determined primarily by the substitution pattern at the nucleofuge, as expected for the vertical mechanism but not for the nonvertical mechanism (although fortuitous adding can permit the bridged form in symmetrical cases).

Our own approach has been stereochemical, as each mechanism has a distinct dependence on the dihedral angle of the Si–C–C–X fragment (X is the nucleofuge). The inductive effect should be relatively independent of dihedral angle, as it occurs primarily through bonds. The nonvertical process leading to a bridged species by backside attack on the bond to the nucleofuge should occur uniquely at the antiperiplanar geometry (a dihedral angle of about 180°) with a rapid and monotonic dropoff at smaller angles. Vertical stabilization or hyperconjugation will follow a

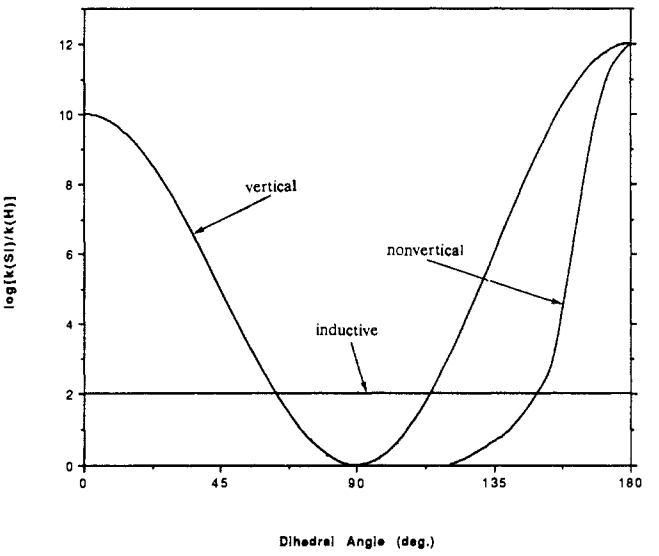
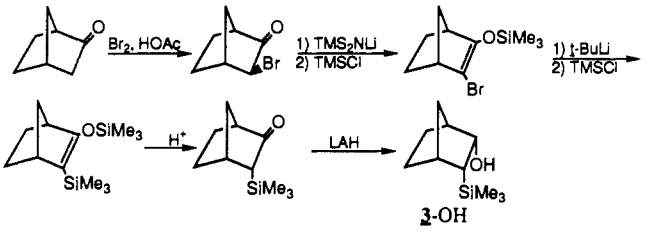


Figure 1. Qualitative dihedral dependences for the inductive, vertical, and nonvertical modes of β stabilization.

Scheme I



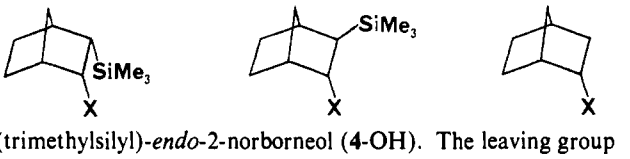
cosine-squared dependence on the dihedral angle, much like the Karplus curve for vicinal coupling constants (H–C–C–H) and the dependence of H/D secondary kinetic isotope effects on the H(D)–C–C–X dihedral angle. By this mechanism, there should be maxima at 0 and 180° and a minimum at 90°. These different dependencies are shown graphically in Figure 1, in which the *y* coordinates are not meant to be quantitative.

In our earlier study[3] we used cyclohexane systems to measure the β effect of silicon (necessarily with secondary leaving groups) at dihedral angles of about 60 and 180°. We found a 10^{12} acceleration at 180° but still a substantial acceleration of 10^4 at 60°. The latter large value at a synclinal (skew or gauche) geometry is consistent with the cosine-squared dependence for vertical stabilization. It is inadmissable for the nonvertical mechanism, unless the entire factor of 10^4 results from induction. Studies in five-membered rings with dihedral angles of about 55 and 150° also were consistent with the vertical model.[10]

Because the large value at 60° can result either from vertical stabilization or from a substantial inductive effect (the large effects at 180° then being due entirely to nonvertical stabilization), we have sought to explore additional geometries. We report herein the synthesis and solvolysis of the first systems with the synperiplanar (~0°) and anticlinal (~120°) geometries.

Results

Synthesis. The successfully prepared molecule with a dihedral angle of about 0° was *endo*-3-(trimethylsilyl)-*endo*-2-norborneol (**3**-OH). That with a dihedral angle of about 120° was *exo*-



3-(trimethylsilyl)-*endo*-2-norborneol (**4**-OH). The leaving group

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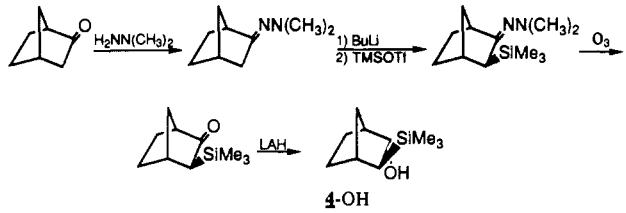
Scheme II



4-OH

X is endo in both **3** and **4**. Considerable effort was expended without success to obtain the exo,exo isomer.

The preparation of **3**-OH began with norcamphor in a sequence of procedures similar to those used by Kowalsky et al.[11] (Scheme I). The α bromination, enolization, O-silylation, C-silylation, and hydrolysis proceeded in an overall yield of 62%. Hydride reduction (67%) occurs from the exo side to give the endo alcohol. The synperiplanar geometry of the product was confirmed by the large J_{23} (10.5 Hz). The COSY spectrum of **3**-OH helped verify the structure and stereochemistry.[12]

The preparation of the exo,endo isomer **4**-OH was not possible by the epimerization of the silyl group in the silyl ketone of Scheme I. The successful, albeit low-yield synthesis is shown in Scheme II. The silylated hydrazone was prepared in 60% yield from norcamphor. Removal of the hydrazone group by ozonolysis occurred in very low yield (11%). The major products were devoid of silicon. Because alternative methods were even less successful, the ozonolysis reaction was repeated several times. Hydride reduction occurred in good yield (73%) to give the desired exo,endo isomer, whose stereochemistry was confirmed by the small value of J_{23} (5.8 Hz) and by the COSY spectrum.[12]

Both the trifluoroacetate (**3**-TFA) and the mesylate (**3**-OMs) of the diendo isomer was prepared in high yield. The former was stable at room temperature, but the latter decomposed to norbornene at room temperature and had to be stored at −35 °C. The trifluoroacetate of the exo,endo isomer (**4**-TFA) was prepared in high yield and found to be stable, but the corresponding mesylate was too reactive to be isolated (only norbornene was recovered). The trifluoroacetate of *endo*-2-norborneol (**5**-TFA) was prepared as a kinetic model. It has no silyl group, but the nucleofuge is in the same endo stereochemistry as for **3** and **4**.

2,2,2-Trifluoroethanol (TFE) was chosen as the reaction medium because of its high ionizing power (Y = 1.83 for 97% TFE) and low nucleophilicity (N = −2.79). These properties are optimal for rate-limiting formation of a carbocation (k_c) and minimize competition from nucleophilic attack by solvent (k_s). First-order rate constants were measured for **4**-TFA, **4**-OMs, and **5**-TFA in TFE with varying amounts of water present (Table I). Rate constants for **5**-OMs, which had been measured earlier,[13] are also included in Table I.

Disappointingly and surprisingly, the exo,endo trifluoroacetate (**4**-TFA) was insoluble in TFE and ethanol at all levels of water. Kinetic measurements were carried out in aqueous acetone, which, however, has low ionizing power (Y = 0.66 for 60% acetone) and high nucleophilicity (N = −0.41). Rate constants for **4**-TFA, as well as for **3**-TFA and **5**-TFA, in aqueous acetone are given in Table II.

Acid-catalyzed eliminations were carried out for **3**-OH and **4**-OH in 0.12 M DCl in 91% acetone-d_6. Rate constants were measured by NMR according to the method of Wang[14] and may be found in Table III.

In order to determine whether the reactions of **3**-X, **4**-X, and **5**-X occur by carbocation mechanisms (k_c) or by nucleophilic reactions (k_s), it is necessary to measure rate constants as a function of solvent ionizing power and nucleophilicity.[15] A k_c

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(14) Wang. G.-t. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1988.

Table I. Rate Measurements of Norbornyl Systems and Cyclohexyl Mesylate in Aqueous Trifluoroethanol Solvents

syst	leaving gp	% TFE[a]	temp, °C	r	k, s^{-1}
3 (endo,endo)	TFA	60	60.1[b]	0.9991	4.1×10^{-5}
			50.2[b]	0.99990	1.4×10^{-5}
			25.0[c]		6.6×10^{-7}
		80	69.9[b]	0.991	1.8×10^{-4}
			60.0[b]	0.998	3.8×10^{-5}
			50.2[b]	0.9993	2.45×10^{-5}
			25.0[c]		1.1×10^{-6}
		97	70.0[b]	0.994	1.24×10^{-4}
			65.0[b]	0.98	8.8×10^{-5}
			60.2[b]	0.994	5.2×10^{-5}
			25.0[c]		1.5×10^{-6}
	OMs	80	−4.8[b]	0.997	1.14×10^{-2}
			−12.2[b]	0.9991	5.0×10^{-3}
			25.0[c]		2.06×10^{-1}
		90	−2.9[b]	0.994	1.35×10^{-2}
			−8.5[b]	0.9992	8.1×10^{-3}
			25.0[c]		1.27×10^{-1}
		97	−5.8[b]	0.9995	1.6×10^{-2}
			−12.2[b]	0.995	7.75×10^{-3}
			25.0[c]		3.35×10^{-1}
5 (endo)	TFA	60	79.8	0.99995	4.30×10^{-5}
			70.1	0.99998	2.83×10^{-5}
			25.0[c]		2.85×10^{-6}
		80	82.9	0.9998	2.67×10^{-5}
			75.4	0.99996	1.59×10^{-5}
			25.0[c]		2.37×10^{-7}
		97	25.0[d]		7.6×10^{-10}
endo-norbornyl	OMs	97	25.0[e]		3.56×10^{-6}
		90	25.0[e]		4.90×10^{-6}
		80	25.0[e]		7.62×10^{-6}
		50	25.0[e]		9.46×10^{-6}
cyclohexyl	OMs	97	68.0	0.997	1.53×10^{-4}
			58.6	0.9991	7.21×10^{-5}
			25.0[c]		3.30×10^{-6}

[a] Percent by weight. [b] Average of two or more runs; worst correlation coefficient reported. [c] Extrapolated from other temperatures. [d] Calculated from the OMs/TFA ratio of 4.7×10^3 found for cyclohexyl. [e] Taken from ref 13.

Table II. Rate Measurements of Norbornyl Systems of Aqueous Acetone Solvents

syst	leaving gp	% acetone[a]	temp, °C	r	k, s^{-1}
4 (exo,endo)	TFA	60	65.1	0.996	3.35×10^{-4}
			60.2	0.998	2.24×10^{-4}
			55.2	0.9997	1.43×10^{-4}
			25.0[b]		7.77×10^{-6}
		80	53.2[c]	0.996	4.7×10^{-5}
			45.2[c]	0.995	2.8×10^{-5}
			25.0[b]		6.7×10^{-6}
3 (endo, endo)	TFA	60	75.0	0.99998	5.35×10^{-5}
			70.1	0.99998	3.53×10^{-5}
			65.1	0.99998	1.93×10^{-5}
			25.0[b]		1.59×10^{-7}
5 (endo)	TFA	60	72.0	0.99997	5.12×10^{-5}
			64.1	0.99997	4.06×10^{-5}
			25.0[b]		1.09×10^{-5}

[a] Percent by volume. [b] Extrapolated from other temperatures. [c] Average of two or more runs; worst correlation coefficient reported.

Table III. Rate Measurements of the Acid-Catalyzed Elimination of Norbornyl Systems[a]

syst	temp,[b] °C	r	k, s^{-1}
3-OH	70.9	0.998	2.47×10^{-5}
	66.0	0.9995	1.43×10^{-5}
	25.0[c]		7.24×10^{-8}
4-OH	70.9	0.991	2.96×10^{-5}
	65.8	0.996	1.75×10^{-5}
	25.0[c]		1.26×10^{-7}

[a] Measured in 0.12 M DCl in 91 vol % acetone-d_6 and 9 vol % D_2O. [b] Measured with an anhydrous ethylene glycol standard. [c] Extrapolated from other temperatures.

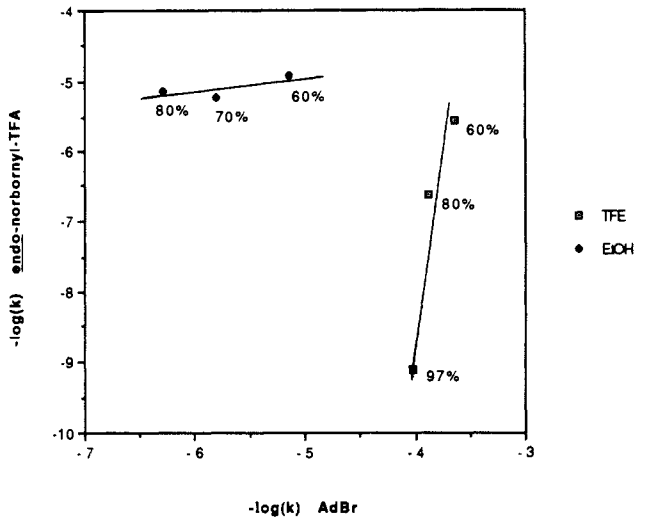

Figure 2. Raber–Harris plot for *endo*-2-norbornyl trifluoroacetate (**5**-TFA).

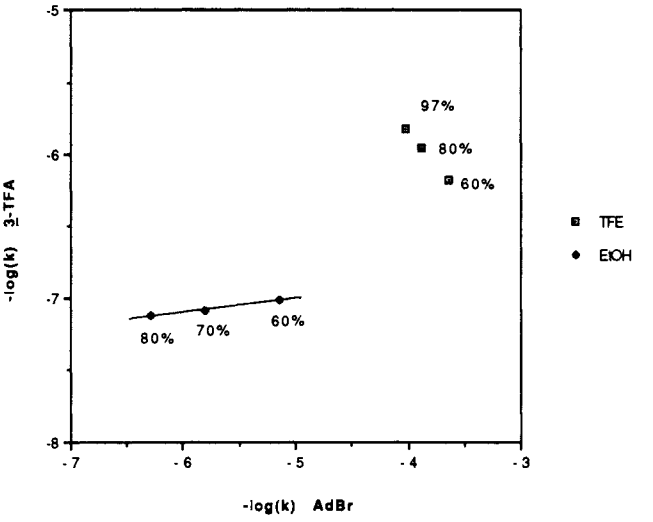

Figure 3. Raber–Harris plot for *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl trifluoroacetate (**3**-TFA).

reaction rate will be insensitive to nucleophilicity, whereas a k_s reaction rate will be insensitive to ionizing power. The ionizing power of aqueous TFE changes little with variation of the water content, and the nucleophilicity of aqueous ethanol is essentially constant with variation of the water content. Therefore, it is useful to compare rates in TFE and ethanol. Rate constants were measured in aqueous ethanol for **3**-TFA, **3**-OMs, **5**-TFA, and **5**-OMs[13] (Table IV). As mentioned earlier **4**-TFA is insoluble in aqueous ethanol.

Product Studies. Products were identified in 97% TFE, 80% TFE, and 60% acetone. Solvolysis of **5**-TFA produced only *endo*-2-norborneol (>98%) in 80% TFE and 60% acetone. Solvolysis of **5**-OMs in 97% TFE gave *exo*-2-norborneol (>95%). Solvolysis of **3**-TFA gave only *exo*-2-norborneol (>98%) in 97% TFE, whereas solvolysis of **3**-OMs in the same solvent gave >75% norbornene, <5% 2-(trimethylsilyl)-2-norbornene, and <20% 3-*endo*-(trimethylsilyl)-*exo*-2-norborneol. In 60% aqueous acetone, **3**-TFA gave 12% norbornene, 22% 2-(trimethylsilyl)-2-norbornene, and 66% 3-(trimethylsilyl)-*exo*-2-norborneol. Solvolysis of **4**-TFA in 60% acetone gave only norbornene (>98%).

Discussion

Molecularity. The β effect could arise from a number of mechanistic sources.[2] Several of these involve nucleophilic attack by solvent on the substrate: at silicon, on the C–X bond to the nucleofuge, or on the carbonyl group when the nucleofuge is trifluoroacetate. For these mechanisms, the reaction rate would increase with nucleophilicity of the solvent and have little dependence on solvent ionizing power. Consequently, the rates of **3**–**5** were measured, when possible, both in aqueous trifluoroethanol (with changing nucleophilicity and constant ionizing power) and in aqueous ethanol (with changing ionizing power and constant nucleophilicity).

Raber, Harris, and co-workers[15] suggested that such measurements could be usefully displayed in a logarithmic plot of the rate of the substrate vs that of 2-adamantyl bromide, which is a prototypical k_c (S_N1) substrate. The Raber–Harris plot for *endo*-2-norbornyl trifluoroacetate (**5**-TFA) is given in Figure 2. The two-line response is typical for a k_s reaction: little sensitivity to ionizing power in ethanol but large sensitivity to nucleophilicity in trifluoroethanol. The reaction appears to be bimolecular in the full range of our solvents.

The Raber–Harris plot for *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl trifluoroacetate (**3**-TFA) is shown in Figure 3. This substrate shows no sensitivity to the water content of ethanol and therefore must be k_s in this solvent. The sensitivity to nucleophilicity in trifluoroethanol, however, has been lost (contrast Figure 2). Moreover, the overall rates in trifluoroethanol are faster than those in ethanol. The mechanism consequently is different in the two solvents and probably has changed to k_c in trifluoroethanol.

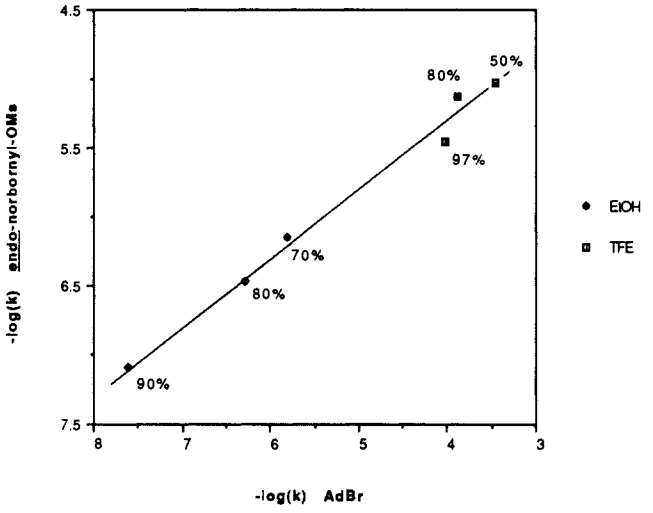

Figure 4. Raber–Harris plot for *endo*-2-norbornyl mesylate (**5**-OMs).

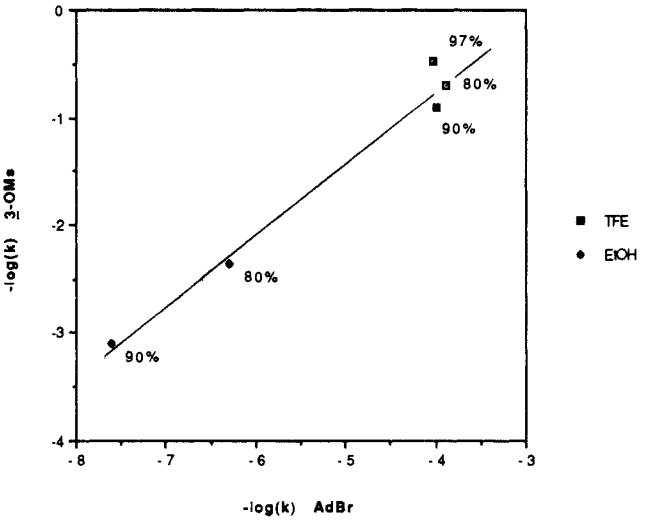

Figure 5. Raber–Harris plot for *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl mesylate (**3**-OMs).

The mesylates of **3** and **5** give classic plots for k_c reactions in all solvents (Figure 4 for **5**-OMs and Figure 5 for **3**-OMs). In

(15) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137–8146. Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *Ibid.* **1978**, *100*, 8147–8156.

Table IV. Rate Measurements of Norbornyl Systems in Aqueous Ethanol Solvents

syst	leaving gp	% EtOH[a]	temp, °C	r	k, s^{-1}
3 (endo,endo)	TFA	60	84.6	0.99997	1.76×10^{-4}
			75.1	0.99994	6.26×10^{-5}
			25.0[b]		9.69×10^{-8}
		70	74.9	0.9997	3.70×10^{-5}
			65.0	0.993	1.27×10^{-5}
			25.0[b]		8.15×10^{-8}
		80	84.6	0.998	7.12×10^{-5}
			74.9	0.9993	2.74×10^{-5}
			25.0[b]		7.67×10^{-8}
	OMs	80	−1.1	0.993	2.41×10^{-4}
			−9.0	0.998	8.91×10^{-5}
			25.0[b]		4.43×10^{-3}
		90	−6.0	0.9996	4.82×10^{-5}
			−14.5	0.99998	1.97×10^{-5}
			25.0[b]		8.19×10^{-4}
5 (endo)	TFA	60	75.0	0.99990	1.50×10^{-4}
			65.0	0.9997	9.59×10^{-5}
			25.0[b]		1.19×10^{-5}
		70	75.0	0.9997	9.12×10^{-5}
			65.0	0.9994	5.64×10^{-5}
			25.0[b]		5.95×10^{-6}
		80	84.7	0.99998	7.89×10^{-5}
			74.9	0.9998	5.63×10^{-5}
			25.0[b]		7.28×10^{-6}
	OMs	70	25.0[c]		7.05×10^{-7}
		80	25.0[c]		3.37×10^{-7}
		90	25.0[c]		8.18×10^{-8}

[a] Percent by volume. [b] Extrapolated from other temperatures. [c] Taken from ref 13.

trifluoroethanol, there is no sensitivity to nucleophilicity and the rates are faster than those in ethanol. Sensitivity to ionizing power now becomes apparent in ethanol. Because 2-adamantyl bromide has the same mechanism and solvent dependence, the plots are linear. Consequently, we may conclude that ionization has taken place in the reaction of these mesylates, and the mechanism may be discussed in terms of cations such as **1** and **2**. Various other mechanisms are inconsistent with these observations. The syn elimination (concerted departure of electrofuge and nucleofuge) and the E_1cb mechanism (rate-determining departure of the electrofuge to form a carbanion) should have shown different solvent effects and may be dropped from consideration.

The insolubility of the *exo*-3-(trimethylsilyl-*endo*-norbornyl substrates (**4**) in trifluoroethanol and ethanol prevented these mechanistic tests from being carried out.

Rate Comparisons. The β effect is calculated by comparing the rate of a silicon-containing substrate with that of the structurally analogous hydrogen-containing substrate, k_{Si}/k_H. These rate ratios are presented in Table V. In order to obtain the value of the β effect for the synperiplanar stereochemistry, we compare the rate of **3** (endo,endo) with that of **5** (endo). The Raber–Harris plot for **5**-TFA (Figure 2), however, clearly shows that the reaction occurs by solvent assistance (k_s). Thus, even though **3**-TFA appears by its Raber–Harris plot (Figure 3) to react by a k_c mechanism in trifluoroethanol, the comparison of rates, k_{Si}/k_H, would give only a minimum for the β effect. In this ratio for the trifluoroacetate leaving group, the comparison is between a k_c reaction in the numerator and a k_s reaction in the denominator. For the H substrate, the k_c reaction must occur by a slower rate than the observed k_s reaction, so therefore the denominator is an overestimation and the ratio (Table V, 2.0×10^3) is too small. The sole product for **5**-TFA is *endo*-2-norborneol. As an S_N2 displacement would have inverted the stereochemistry, the observed retention indicates that the k_s mechanism probably involves acid-catalyzed ester hydrolysis. The sole observed product from **3**-TFA in 97% TFE, *exo*-2-norborneol, is the result of acid-catalyzed addition of water to the presumed primary product, norbornene. Indeed, when norbornene was heated in 97% TFE with a catalytic amount of trifluoroacetate acid, the only product recovered was *exo*-2-norborneol.

Table V. Rates and Rate Ratios at 25 °C

syst	solvent	k, s^{-1}	k_{rel}
5-TFA	97% trifluoroethanol	7.6×10^{-10}	1.0
3-TFA	97% trifluoroethanol	1.5×10^{-6}	2.0×10^3[a]
5-OMs	97% trifluoroethanol	3.56×10^{-6}	1.0
3-OMs	97% trifluoroethanol	3.35×10^{-1}	9.4×10^4[a]
5-TFA	60% acetone	1.09×10^{-5}	1.0
3-TFA	60% acetone	1.59×10^{-7}	0.015[a]
4-TFA	60% acetone	7.77×10^{-6}[b]	0.71[a]
3-OH	0.12 M DCl in 91% acetone	7.24×10^{-8}	
4-OH	0.12 M DCl in 91% acetone	1.26×10^{-7}[c]	

[a] The β effect, k_{Si}/k_H. [b] The **4**/**3** ratio is 49. [c] The **4**/**3** ratio is 1.7.

Because trifluoroacetate gave us an underestimation for the β effect, we sought a better leaving group in mesylate. Indeed, both the endo and endo,endo substrates (**5**-OMs and **3**-OMs) gave Raber–Harris plots clearly diagnostic of carbocation intermediates (Figures 4 and 5). The observed value of the synperiplanar β effect for mesylate (Table V) is approximately 10^5. This ratio should be a valid measure of the β effect, because both components solvolyze by a k_c mechanism.

Because the exo,endo substrate (**4**) was insoluble in TFE, we were unable to obtain a direct measure of the anticlinal β effect. Rate measurements were possible only in aqueous acetone (Table II), and the high nucleophilicity of this solvent makes a k_s mechanism very likely. The insensitivity of the rate of **4**-TFA to ionizing power is consistent with a nucleophilic mechanism. The values of the β effects for **3** and **4** in this solvent (Table V, 0.015 and 0.71, respectively) therefore are meaningless in the context of carbocation mechanisms. The endo,endo substrate (**3**-TFA) solvolyzed more solwly than the endo substrate (**5**-TFA) in both aqueous ethanol and aqueous acetone. The reverse β effect for **3** (0.015 in 60% acetone) is probably due to steric hindrance by the syn trimethylsilyl group to the nucleophilic reaction. The β effect for the exo,endo substrate (**4**-TFA) (0.71) is essentially unity, indicating very little steric or electronic effect.

Since the rates in aqueous acetone for the exo,endo substrate were not of use, we carried out measurements on the acid-catalyzed elimination of the alcohol (Table III). Under these presumably k_c conditions, the exo,endo substrate (**4**-OH) reacted 1.7 times faster than the endo,endo substrate (**3**-OH). Although the argument is tenuous because the mechanism is not proved to be k_c, it appears that the β effect in the anticlinal stereochemistry is essentially the same as or somewhat larger than that in the synperiplanar stereochemistry, which was 10^5 for the mesylate.

Synperiplanar β Effect. The β effect for the 0° dihedral angle (10^5) has proved to be considerably less than that for the 180° dihedral angle (10^{12}). The two numbers clearly do not fit a simple cosine-squared dependence for hyperconjugation (Figure 1), but the relatively large value at 0° also is inconsistent with bridging, which cannot occur from a 0° dihedral angle. There are several possible explanations for the low value of the synperiplanar β effect.

endo-Norbornyl is different from cyclohexyl. The synperiplanar β effect has been measured in an *endo*-norbornyl system, whereas the antiperiplanar β effect was measured in a cyclohexyl system. We think that this difference is not the source of the low synperiplanar β effect. The β-silyl trifluoroacetates clearly solvolyze by k_c mechanisms in TFE, according to the sensitivity of the rate to water and the Raber–Harris plots. Both carbocation structures are six-membered rings and should not be appreciably different. The reactions of the two nonsilylated systems as mesylates occur at essentially the same rates (Table I, 3.56×10^{-6} for **5**-OMs and 3.30×10^{-6} for cyclohexyl). Thus, we conclude that the skeletal differences should not produce a drastic difference in the β effect.

The dominant model is nonvertical/inductive. According to this model, the β effect of 10^{12} at 180° is largely due to nonvertical participation leading to the bridged ion **1**, and at all other dihedral angles there is an approximately constant β effect of 10^4–10^5 from an inductive effect. This model is not acceptable because there has never been evidence for an inductive effect of such magnitude. In fact, the calculations of Ibrahim and Jorgensen[6] indicated no

significant inductive effect in secondary systems, and our measurements[3] indicated an inductive effect of only 10^2. In the absence of such evidence, the large values of the β effect at 0° (10^5) and 60° (10^4) appear to require vertical participation (hyperconjugation) at least in this dihedral region.

The dominant model is vertical. If the dominant model is vertical, then there must be a very substantial difference between overlap within the syn- and antiperiplanar geometries. Calculations on the free ion cannot demonstrate such differences, as the geometries become equivalent in the complete absence of the leaving group. Calculations of the β effect have not taken effects of the leaving group into consideration. It has long been known that antiperiplanar overlap is superior to synperiplanar overlap. Thus, the Karplus curve for vicinal coupling constants, which is also based on a cosine-squared relationship, is not symmetrical, $J(180°)$ being larger than $J(0°)$ (in $CH_2{=}CH_2$, the two couplings are 19.0 and 11.7 Hz, respectively).[16] The preferred antiperiplanar stereochemistry of the elimination reaction may stem from similar causes. Theory has supported the superiority of the antiperiplanar overlap. One explanation is that orbital phases are continuous in the antiperiplanar stereochemistry but discontinuous in the synperiplanar stereochemistry.[17]

There also may be a steric deficiency of the synperiplanar stereochemistry. Calculations by Jorgensen and co-workers[6] and by us[10] have shown that the so-called vertical transition state actually involves considerable movement of the silicon atom. In the simple models for bridged (**1**) and unbridged (**2**) transition states, the Si–C–C$^+$ valence angles appear to be about 60 and 109°, respectively. The calculated optimum for the unbridged (vertical) transition state, however, has a Si–C–C$^+$ angle of about 100°. Hyperconjugation is apparently improved by moving the Si–C bond closer to the empty π orbital by diminishing the Si–C–C$^+$ angle. The presence of the nucleofugal leaving group in the transition state may inhibit the optimization of the angle when the silicon atom and the leaving group are syn to each other. For this reason, full σ–π overlap is not achieved in the transition state, and the β effect is reduced. In the antiperiplanar stereochemistry, silicon and the leaving group are far away, so full optimization can occur. A combination of this steric effect and the previously described electronic effect may suffice to explain the lower β effect in the synperiplanar stereochemistry.

Both vertical and nonvertical mechanisms are present. Although we can provide an explanation for the reduced synperiplanar β effect entirely in terms of vertical participation, we cannot exclude the possibility that nonvertical participation contributes substantially to the acceleration at the 180° stereochemistry (vertical participation still providing a cosine-squared acceleration throughout the dihedral range). For example, if vertical stabilization provides 10^5 acceleration on the syn side (0°) and 10^7 on the anti side (180°), nonvertical stabilization, which can occur only on the anti side, would provide the additional factor of 10^5. Without being able to assess the effect of the leaving group quantitatively, we cannot distinguish between these last two explanations.

Conclusions

The effect of silicon on the development of β positive charge has been assessed quantitatively for the synperiplanar stereochemistry between the electrofuge and the nucleofuge. The factor of 10^5, evaluated from the endo,endo stereochemistry within the norbornyl framework, is considerably smaller than 10^{12} evaluated for the antiperiplanar stereochemistry within the cyclohexyl framework. It is unlikely that this large difference comes from the use of two different skeletal frameworks, nor is it likely that the acceleration at the synperiplanar (10^5) or synclinal (10^4) geometries is entirely due to the inductive effect of silicon. Steric and electronic factors may serve to reduce vertical overlap in the synperiplanar stereochemistry, compared with the antiperiplanar stereochemistry. Alternatively, nonvertical participation to form the bridged intermediate **1**, which can occur only in the antiperiplanar stereochemistry, may provide a significant proportion of the 10^{12} acceleration. The remainder of the antiperiplanar effect plus all of the synperiplanar and synclinal effects then would be due to vertical participation with its cosine-squared dependence.

Experimental Section

***endo*-3-(Trimethylsilyl)-2-norcamphor.** The compound was prepared after the procedure of Kowalski and co-workers for the preparation of 3-(trimethylsilyl)camphor.[11] The product was distilled (bp 52–53 °C, 0.2 mmHg) to yield a colorless oil (62% from norcamphor): ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.40 (m, 1 H), 1.5–1.6 (m, 2 H), 1.6–1.7 (m, 2 H), 1.7–1.8 (m, 2 H), 2.52 (d, 1 H), 2.64 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.3, 23.5, 25.9, 38.7, 41.2, 47.7, 51.1, 219.8.

***endo*-3-(Trimethylsilyl)-*endo*-2-norborneol (3-OH).** Into a flame-dried, 500-mL, three-necked, round-bottomed flask was weighed 1.35 (35.6 mmol) of lithium aluminum hydride. This material was covered with 200 mL of anhydrous ether, and 5.0 g (27.5 mmol) of *endo*-3-(trimethylsilyl)-2-norcamphor in 50 mL of anhydrous ether was added dropwise. Once addition was complete, the reaction was stirred for 2.5 h and then quenched with water. The layers were separated, and the aqueous layer was extracted with 2 × 100 mL of ether. The combined organics were dried ($MgSO_4$), and the solvents were removed on a rotary evaporator. The crude product was flash chromatographed (silica gel, 80/20 hexane/ether) and then distilled (bp 52 °C, 0.5 mmHg) to yield 3.4 g (18.5 mmol, 67%) of a colorless oil. GC and NMR indicated that only one isomer was present: ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 1.18 (m, J_{23} = 10.5 Hz, 1 H), 1.2–1.45 (m, 5 H), 1.55 (m, 1 H), 1.82 (m, 1 H), 2.2–2.3 (m, 2 H), 4.47 (m, J_{23} = 10.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.4, 19.6, 26.9, 37.7, 40.60, 40.65, 44.0, 75.5; IR (KBr) 3300–3650 cm^{-1} (OH). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94; Si, 15.24. Found: C, 65.10; H, 10.89; Si, 14.68.

***endo*-3-(Trimethylsilyl)-*endo*-2-norbornyl Trifluoroacetate (3-TFA).** Into a 125-mL Erlenmeyer flask were weighed 1.00 g (5.4 mmol) of the alcohol (3-OH) and 0.43 g (5.4 mmol) of pyridine. This solution was diluted with 15 mL of anhydrous ether, and the flask was cooled in an ice bath. A solution of 1.13 g (5.4 mmol) of trifluoroacetic anhydride in 10 mL of anhydrous ether was added dropwise. Once addition was complete, the reaction was stirred for 10 min. The solids were removed by filtration, and the organics were washed with 2 × 15 mL of saturated $CuSO_4$ and 2 × 15 mL of saturated $NaHCO_3$. The organics were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to yield 1.25 g (4.5 mmol, 83%) of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.3–1.65 (m, 7 H), 2.37 (br s, 1 H), 2.71 (m, 1 H), 5.48 (dd, 1 H); IR (KBr) 1785 cm^{-1} (C=O).

***endo*-3-(Trimethylsilyl)-*endo*-norbornyl Mesylate (3-OMs).** Into a 10-mL round-bottomed flask were placed 0.50 g (2.7 mmol) of the alcohol (3-OH) and 2 mL of pyridine. Methanesulfonyl chloride (0.60 g, 5.2 mmol) in 2 mL of pyridine was added dropwise. Once addition was complete, the flask was stoppered and placed in a freezer (−35 °C) for 24 h. The flask was opened, and the contents were decanted away from the solids and then diluted with ether. The organics were washed twice with saturated $CuSO_4$ and once with saturated $NaHCO_3$ and then were dried ($MgSO_4$). The solvent was removed on a rotary evaporator to yield a white solid (very unstable, must be stored at −35 °C): ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.35–1.6 (m, 6 H), 1.82 (m, 1 H), 2.31 (br s, 1 H), 2.66 (br s, 1 H), 2.98 (s, 3 H), 5.31 (dd, 1 H).

Norcamphor *N*,*N*-Dimethylhydrazone. Into a 1-L round-bottomed flask was weighed 50.0 g (0.455 mol) of norcamphor. After this material was covered with 500 mL of absolute ethanol and 60.0 g (1.00 mol) of dimethylhydrazine, 2.5 mL of glacial acetic acid was added. This reaction mixture was heated at reflux for 60 h. The solvent was removed on a rotary evaporator, and the yellow residue was distilled (bp 45–50 °C, 0.4 mmHg) to yield 66.5 g (0.44 mol, 97%) of the hydrazone: ^{1}H NMR ($CDCl_3$) δ 1.25–1.53 (m, 5 H), 1.6–1.8 (m, 2 H), 2.28 (m, 1 H), 2.47 (s, 6 H), 2.51 (br s, 1 H), 2.80 (br d, 1 H).

***exo*-3-(Trimethylsilyl)-2-norcamphor *N*,*N*-Dimethylhydrazone.** Into an oven-dried 1-L, three-necked, round-bottomed flask was weighed 30.0 g (0.197 mol) of the hydrazone. This material was covered with 500 mL of anhydrous ether, and the resulting solution was cooled to −78 °C. Butyllithium (140 ml, 1.6 M in hexane) was added dropwise. Once addition was complete, the reaction was allowed to warm to 0 °C and then was recooled to −78 °C. The reaction was quenched with an excess of trimethylsilyl triflate. The organics were washed twice with water and then were dried ($MgSO_4$). The solvents were removed on a rotary evaporator, and the residue was distilled (bp 63–67 °C, 0.2 mmHg) to yield 27.5 g (0.123 mol, 62%) of the silylated hydrazone: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 1.15–1.35 (m, 4 H), 1.6–1.7 (m, 3 H), 2.30 (s, 6 H), 2.46 (br s, 1 H), 2.74 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.0, 27.7,

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(17) Inagaki, S.; Iwase, K.; Mori, Y. *Chem. Lett.* **1986**, 417–420 and references therein.

30.4, 36.9, 39.5, 41.5, 44.7, 46.0, 180.7.

***exo*-3-(Trimethylsilyl)-2-norcamphor.** Into a 200-mL, three-necked, round-bottomed flask was weighed 3.37 g (15 mmol) of the silylated hydrazone. This material was covered with 120 mL of anhydrous CH_2Cl_2, and the resulting solution was cooled to -78% °C. Ozone was bubbled through the solution until the blue of excess ozone persisted. Nitrogen was bubbled through the solution as it warmed to room temperature. The organics were washed once with a dilute solution of acetic acid and twice with water and then were dried ($MgSO_4$). The solvent was removed on a rotary evaporator to yield a light yellow residue. The residue was purified by flash column chromatography (10/90 ether/hexane on silica gel) to yield 0.30 g (1.6 mmol, 11%) of the product: ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.35-1.41 (m, 2 H), 1.49 (m, 1 H), 1.55 (d, 1 H), 1.68 (m, 1 H), 1.73-1.80 (m, 2 H), 2.52 (br d, 1 H), 2.61 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.1, 24.8, 30.2, 36.8, 38.2, 50.1, 50.4, 219.2.

***exo*-3-(Trimethylsilyl)-*endo*-2-norborneol (4-OH).** Into a 50-mL, flame-dried, three-necked, round-bottomed flask was weighed 0.20 g (5.3 mmol) of lithium aluminum hydride. This material was covered with 25 mL of anhydrous ether and cooled to 0 °C in an ice bath. The ketone (1.5 g, 8.2 mmol) in 15 mL of anhydrous ether was added dropwise. Once addition was complete, the ice bath was removed and the reaction was stirred for 2 h. The reaction was cooled again and quenched with water. The aqueous layer was separated and extracted once with ether. The combined organics were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to give 1.1 g (6.0 mmol, 73%) of the alcohol. The alcohol was purified by sublimation before use: mp 40-42 °C; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.10 (dd, J_{23} = 5.8 Hz, 1 H), 1.1-1.4 (m, 5 H), 1.58 (m, 1 H), 1.86 (m, 1 H), 2.08 (br s, 1 H), 2.20 (t, 1 H), 4.07 (m, J_{23} = 5.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.6, 19.5, 33.9, 36.8, 38.9, 39.7, 43.1, 75.7; IR (KBr) 2700-3100 cm^{-1} (OH); HRMS for $C_{10}H_{20}OSi$, calcd m/z 184.1283, found m/z 184.1279. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 65.20; H, 10.94.

***exo*-3-(Trimethylsilyl)-*endo*-2-norbornyl Trifluoroacetate (4-TFA).** Into a 125-mL Erlenmeyer flask was placed 0.30 g (1.6 mmol) of the alcohol (4-OH). This material was covered with 15 mL of anhydrous ether, and 0.30 g (3.8 mmol) of pyridine was added. The mixture was cooled to 0 °C in an ice bath, and 0.40 g (1.9 mmol) of trifluoroacetic anhydride in 10 mL of ether was added dropwise. The reaction was allowed to stand for 20 min, and the white crystals were removed by filtration. The organics were washed twice with saturated $CuSO_4$ and once with saturated $NaHCO_3$ and were dried ($MgSO_4$). The solvent was removed on a rotary evaporator to yield a colorless oil: ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.58 (dd, 1 H), 1.2-1.45 (m, 4 H), 1.6-1.75 (m, 2 H), 2.21 (br s, 1 H), 2.61 (br s, 1 H), 5.13 (m, 1 H).

***endo*-2-norbornyl Trifluoroacetate (5-TFA).** Into a 125-mL Erlenmeyer flask were weighed 0.70 g (6.3 mmol) of *endo*-2-norborneol (Aldrich) and 0.50 g (6.3 mmol) of pyridine. Ether (15 mL) was added, and the flask was cooled to 0 °C in an ice bath. A solution of 1.32 g (6.3 mmol) of trifluoroacetic anhydride in 10 mL of ether was added dropwise. Once addition was complete, the reaction was allowed to stir for an additional 10 min. The solids were removed by vacuum filtration, and the organics were washed with 2 × 15 mL of saturated $CuSO_4$ and 2 × 15 mL of saturated $NaHCO_3$. The organics were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to yield a colorless oil: ^1H NMR ($CDCl_3$) δ 1.13 (dt, 1 H), 1.3-1.5 (m, 4 H), 1.61 (m, 1 H), 1.76 (m, 1 H), 2.09 (m, 1 H), 2.30 (br s, 1 H), 2.60 (br s, 1 H), 5.16 (m, 1 H).

Kinetics by Conductivity. The conductivity measurements were performed on solutions with substrate concentrations of approximately 10^{-3} M. The conductance cell had a 35-mL capacity and Pt electrodes. The solutions were either cooled in a Techne RB-5 refrigerated bath or warmed in a Precision H8 heating bath. The temperature was measured to 0.1 °C with factory-certified (NBS standard) thermometers. The conductivity of the solutions was followed for 1-3 half-lives with a YSI Model 32 conductance meter. Linear first-order rate plots were obtained for up to 3 half-lives.

Kinetics by NMR. The probe of the Varian XLA-400 spectrometer was heated to the desired temperature and allowed to equilibrate for at least 15 min. The exact temperature was measured with an ethylene glycol standard. The sample to be studied was prepared, inserted into the probe, and allowed to equilibrate for 15 min. The time between acquisitions was set up as an array, which allowed the spectra to be acquired automatically overnight. Both the decrease of the peaks at δ 4.07 (4-OH) or δ 4.47 (3-OH) and the increase of the alkene peak at δ 6.0 could be used to calculate the rate constants.

Product Studies. A 0.3-0.5 M solution of the substrate in the solvent of choice (1-3 mL) was prepared in either an NMR tube or a Pyrex test tube. The tubes were sealed and heated in a water bath. After the reaction was complete, the products were identified by GC, GCMS, and NMR. Norbornene, *exo*-2-norborneol, and *endo*-2-norborneol were identified by comparison of the GC and NMR data with the authentic compounds. 2-(Trimethylsilyl)-2-norbornene was identified by MS peaks at 166, 138, and 73. 3-(Trimethylsilyl)-*exo*-2-norborneol was identified by MS peaks at 184, 94, 73, and 66. In order to obtain NMR spectra, the products were first extracted out of the aqueous solvents with ether and then dissolved in chloroform-*d*.

Investigation of the Mechanisms of Ene Reactions of Carbonyl Enophiles by Intermolecular and Intramolecular Hydrogen-Deuterium Isotope Effects: Partitioning of Reaction Intermediates

Zhiguo Song and Peter Beak*

Contribution from the Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801. *Received April 13, 1990*

Abstract: The mechanisms of ene reactions of selected carbonyl enophiles with methylenecyclohexane (**1**) and 1-methylenetetralin (**2**) have been investigated by determinations of intermolecular and intramolecular hydrogen-deuterium isotope effects. In the thermal ene reactions of **1** with dimethyl dioxosuccinate (**7**) and of **1** with diethyl oxomalonate (**8**), both of the isotope effects are primary and substantial, consistent with a concerted mechanism for each reaction. In the ene reactions of **1** with **8** catalyzed by tin tetrachloride and of **1** with acetylium hexachloroantimonate, both the intermolecular and intramolecular isotope effects are small, results that are inconsistent with either a stepwise reaction via an equilibrating intermediate or a concerted mechanism. The ene reaction of **2** with acetic anhydride catalyzed by zinc chloride has a small intermolecular and a large intramolecular isotope effect, consistent with rate-determining formation of an equilibrated intermediate. A general quantitative kinetic model is proposed to account for the observed isotope effects for these reactions in which the reactants form an intermediate that can partition between dissociation, equilibration between different isomers, and product formation.

The ene reaction, defined as the addition of an olefin bearing an allylic hydrogen, the ene component, to a double bond, the enophile, with migration of the olefinic double bond and transfer of the allylic hydrogen from the olefin to the enophile, is illustrated

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