Interaction of the Carbon–Germanium or Carbon–Tin Bond with Positive Charge on a β Carbon

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The stereochemical dependence of the interaction of the carbon–germanium or carbon–tin bond with positive charge on a β carbon has been explored. When the geometry between germanium and the leaving group is synclinal (60° Ge–C–C–X dihedral angle), C–Ge provides an acceleration of about 10^5, of which 10^3 may be attributed to hyperconjugation and 10^2 to induction. In an antiperiplanar geometry (180°, in this study corrected for conformational populations), the total acceleration is up to about 10^{13}, of which 10^{11} is hyperconjugative. These factors are about 10 times those for silicon, but the pattern is quite similar. In a synclinal geometry, C–Sn offers an acceleration of at least 10^{11}. The much faster rate of the antiperiplanar system ($>>10^{14}$) suggests that hyperconjugation plays the key role here too. This conclusion is substantiated by solvent studies in trifluoroethanol, but a nucleophilic component may become more important in other solvents.

The interaction of the carbon–silicon bond with β positive charge, as in the fragment Si–C–C$^+$, has been studied extensively over the past 2 decades.[2] Observations are consistent with a strong hyperconjugative interaction (causing a rate acceleration of at least 10^{10} in one case[2]). The interaction depends on the square of the cosine of the dihedral angle between the Si–C bond and the developing empty p orbital, as was shown by measurements on substrates with specific stereochemistries.[2]

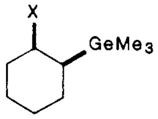
Studies of the interaction of other carbon–metal bonds with β positive charge have not previously reached this level of stereochemical sophistication.[3] Within the group IV (14) series, Eaborn and Pande[4] measured the rates of the protiodemetalation reaction of $ArMR_3$ and found the approximate ratios for Si/Ge/Sn/Pb to be $1/40/4 \times 10^5/2 \times 10^8$. The ratio was explained in terms of the inductive effect of the metal and the strength of the Ar–M bonds. In the σ intermediate, the C–M bond is β to partial positive charge at the two ortho positions. Thus hyperconjugation should be an important factor, although the approximately 30° angle is not quite optimal (in the cosine-squared formula, the maxima are at 0° and 180°). As a further complexity, it was recognized that the weaker C–M bonds of the heavier metals might permit a bimolecular mechanism, in which nucleophilic attack of solvent on the metal becomes kinetically important.[4]

Davis and co-workers studied the acid-catalyzed hydrolysis of systems of the type $R_3MCH_2CHR'OH$ and concluded that the silicon series underwent a unimolecular k_C reaction in which the carbocation was stabilized by Si–C hyperconjugation.[5] Nucleophilic attack by solvent (k_s) on the metal again was found to become increasingly important with the heavier metals. Traylor and co-workers have examined M–C hyperconjugation as a distinct concept through studies of electronic spectroscopy and of the dehydrometalation reaction (M–C–C–H → M–C–C$^+$).[6] For hydride abstraction in the series Et_4M, the approximate relative rates for Si/Ge/Sn/Pb were $1/70/10^5/10^7$. The studies by Traylor were carried out in nonnucleophilic media such as acetonitrile or dichloromethane, so that it would be expected that the nucleophilic component found by Davis in acidic aqueous methanol might have less importance.

In order to understand more fully the relative importance of hyperconjugation and nucleophilic assistance, we have studied the solvolysis of a series of germanium and tin systems of the type M–C–C–X with specific dihedral angles, in solvents of varying nucleophilicities. These results substantiate a dominant role of hyperconjugation for germanium and probably for tin under the conditions studied.[7]

Results

Measurements were made with the esters of *cis*-2-(trimethylgermyl)cyclohexanol (**1**, X = OH), *trans*-2-(trimethylgermyl)cyclohexanol (**2**, X = OH), *cis*-2-(trimethylstannyl)cyclohexanol (**3**, X = OH), and *trans*-2-(trimethylstannyl)cyclohexanol (**4**, X = OH). In addition, *r*-5-*tert*-butyl-*cis*-2-(trimethylstannyl)cyclohexan-*trans*-ol (**5**, X = OH) was prepared. The cis substrates provide a dihedral angle of about 60° between the metal–carbon bond and the bond to the leaving group. The trans substrates provide a dihedral angle of 180° when in the axial–axial conformation. The biased form **5** exists solely in the antiperiplanar arrangement.



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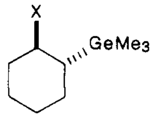

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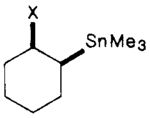

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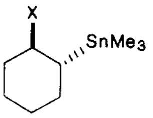

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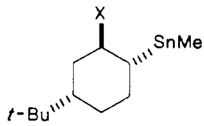

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Preparation of the cis substrates (**1** and **3**) began with 1-chlorocyclohexene, which was treated with sodium and with chlorotrimethylgermanium or -tin to give 1-(trimethylgermanium)- and 1-(trimethylstannyl)cyclohexene. Epoxidation followed by epoxide ring opening with lithium aluminum hydride gave the desired substrates. Unlike in

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[2] For references, see: Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838–7845.

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Table I. Solvolytic Rates of *cis*-2-(Trimethylgermyl)cyclohexyl Trifluoroacetate (1-O(CO)CF_3)

solvent[a]	temp, °C	k, s^{-1}	r
60% TFE	25.0	1.95×10^{-4}	0.9995
80% TFE	25.0	2.30×10^{-4}[b]	
97% TFE	25.0	3.25×10^{-4}[b]	
50% EtOH	50.0	1.18×10^{-3}	0.9995
	40.0	3.41×10^{-4}	0.9993
	25.0[c]	4.53×10^{-5}	
60% EtOH	50.0	8.70×10^{-4}	0.999
	40.0	2.29×10^{-4}	0.996
	25.0[c]	2.61×10^{-5}	
70% EtOH	50.0	6.06×10^{-4}	0.9995
	40.0	1.50×10^{-4}	0.9997
	25.0[c]	1.55×10^{-5}	
80% EtOH	55.0	9.05×10^{-4}	0.9992
	50.0	3.92×10^{-4}	0.9997
	45.0	2.44×10^{-4}	0.9995
	40.0	9.80×10^{-5}	0.9993
	35.0	7.60×10^{-5}	0.9993
	25.0	1.03×10^{-5}	

[a] TFE in weight percentage and EtOH in volume percentage. [b] Average of two runs. [c] Calculated from measurements at higher temperatures.

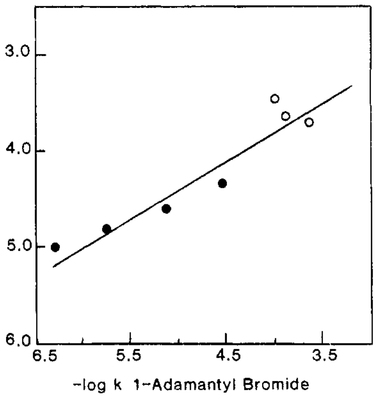

Figure 1. The Raber–Harris plot of *cis*-2-(trimethylgermyl)cyclohexyl trifluoroacetate (1-O(CO)CF_3). The open circles are aqueous trifluoroethanol, and the closed circles are aqueous ethanol.

the case with silicon,[2] cyclohexene oxide reacted smoothly with the trimethylgermyl or trimethylstannyl anion to give the trans alcohols, **2** and **4**, respectively. The biased tin substrate **5** was prepared in a manner analogous to the preparation of the corresponding silicon substrate.[2]

The chemical shift of the CHOH proton is diagnostic of the axial or equatorial disposition of the hydroxyl group, by comparison with the chemical shifts of the *cis*- and *trans*-3-*tert*-butylcyclohexanols.[8] In the germanium series, the CHOH proton resonates at δ 4.2 for **1** (equatorial proton), and at δ 3.5 for **2** (axial proton). Thus **1** exists primarily in the axial-OH, equatorial-Me_3Ge form, and **2** in the diequatorial form. Similar results were obtained with the tin substrates **3** and **4**. The CHOH resonance at δ 4.20 corroborated the diaxial conformation of **5**.

Trifluoroacetate was used as the leaving group in the silicon series because of its convenient rate.[2] Trifluoroethanol was used as the solvent because of its low nucleophilicity. The trifluoroacetate of the cis germanium substrate (1-O(CO)CF_3) was prepared readily and was allowed to react in 60, 80, and 97% trifluoroethanol (TFE). The pseudo-first-order rate constants measured conductometrically are listed in Table I. As a mechanistic test for the molecularity, rates also were measured in the more nucleophilic aqueous ethanol solvent. These data enabled a Raber–Harris molecularity plot to be constructed[9] (Figure 1). As an additional test of molecularity, activation parameters were calculated for 80% ethanol (Table II).

Table II. Activation Parameters of the Germanium and Tin Systems in 80% EtOH at 25.0 °C

system	no. of temp	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
cyclohexyl-$OCOCF_3$	4	17.9	−26.9	25.9
1-$OCOCF_3$	6	25.4	4.5	24.1
2-ODNB[a]	2	20.3	−11.9	23.8
3-OAc	4	17.1	−24.6	24.4

[a] Calculated from measurements in 70% EtOH.

Table III. Rate Measurements of *trans*-2-(Trimethylgermyl)cyclohexyl 3,5-Dinitrobenzoate (2-ODNB)

solvent[a]	temp, °C	k, s^{-1}	r
55% TFE	45.0	3.9×10^{-3}	0.994
	40.0	3.2×10^{-3}	0.9992
	25.0[b]	1.6×10^{-3}	
60% TFE	45.0	3.4×10^{-3}	0.98
	40.0	2.7×10^{-3}	0.996
	25.0[b]	1.4×10^{-3}	
65% TFE	45.0	2.9×10^{-3}	0.994
	40.0	2.3×10^{-3}	0.98
	25.0[b]	1.1×10^{-3}	
70% TFE	45.0	2.4×10^{-3}	0.95
	40.0	1.9×10^{-3}	0.96
	25.0	8.6×10^{-4}	
80% TFE	25.0[c]	5.9×10^{-4}	
97% TFE	25.0[c]	3.0×10^{-4}	
50% EtOH	65.0	2.5×10^{-3}	0.999
	55.0	9.8×10^{-4}	0.997
	25.0[b]	4.2×10^{-4}	
60% EtOH	65.0	1.7×10^{-3}	0.995
	55.0	7.2×10^{-4}	0.999
	25.0[b]	3.4×10^{-5}	
70% EtOH	65.0	1.3×10^{-3}	0.999
	60.0	8.1×10^{-4}	0.992
	25.0[b]	2.2×10^{-5}	

[a] TFE by weight percentage, EtOH by volume percentage. [b] Calculated from measurements at higher temperatures. [c] Extrapolated from other solvents.

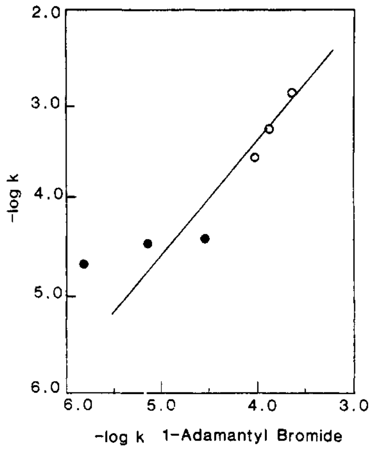

Figure 2. The Raber–Harris plot of *trans*-2-(trimethylgermyl)cyclohexyl 3,5-dinitrobenzoate (2-ODNB).

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Table IV. Rate Measurements of *cis*-2-(Trimethylstannyl)cyclohexyl Acetate (3-O(CO)CH$_3$)

solvent[a]	temp, °C	k, s^{-1}	r
97% TFE	25.0	6.52×10^{-5}	0.9999
80% TFE	25.0	5.92×10^{-5}	0.9997
60% TFE	25.0	4.09×10^{-5}	0.9999
80% EtOH	35.0	2.08×10^{-5}	0.999
	45.0	4.85×10^{-5}	0.998
	55.0	1.09×10^{-4}	0.998
	65.0	2.77×10^{-4}	0.999
	25.0[b]	4.56×10^{-6}	
70% EtOH	45.0	5.92×10^{-5}	0.999
	55.0	1.55×10^{-4}	0.9991
	25.0[b]	7.11×10^{-6}	
60% EtOH	45.0	9.01×10^{-5}	0.9993
	55.0	2.33×10^{-4}	0.9996
	25.0[b]	1.11×10^{-5}	

[a] TFE by weight percentage, EtOH by volume percentage. [b] Calculated from other temperatures.

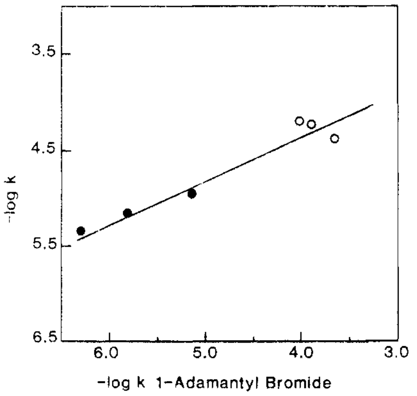

Figure 3. The Raber–Harris plot of *cis*-2-(trimethylstannyl)cyclohexyl acetate (3-O(CO)CH$_3$).

The trifluoroacetate of the trans germanium substrate was too reactive to isolate. Even at −78 °C after 5 min, only cyclohexene and trimethylgermyl trifluoroacetate could be isolated. Consequently, as was done in the case of silicon,[2] the 3,5-dinitrobenzoate was employed, 2-OPNB. The rates are given in Table III, the activation parameters in Table II, and the Raber–Harris plot in Figure 2.

Trifluoroacetates could not be isolated for any of the tin substrates. Moreover, the 3,5-dinitrobenzoates also were not isolable because of high reactivity. Although acetate does not have a reputation as a good leaving group, we were able to isolate this ester of the cis tin substrate, **3**-OAc. This material solvolyzed smoothly, and its rates are given in Table IV. Figure 3 provides the Raber–Harris plot.

Even the acetates of the trans tin substrates, **4** and **5**, were too reactive to isolate, implying a very large trans/cis rate ratio. To substantiate these observations, the acid-catalyzed elimination reaction[5] of the alcohols was examined for 0.12 M DCl in 91% by volume aqueous CD$_3$OD. Rates were measured by ^{1}H NMR spectroscopy. Table V gives rates for the cis and trans silicon and germanium alcohols and for the cis tin alcohol. Even at −50 °C, the trans tin alcohol reacted instantaneously and permitted no quantitative measurements.

Rate ratios are summarized in Table VI, including those for the analogous silicon systems.

Products of solvolysis for the germanium substrates **1**-(O(CO)CF$_3$) and **2**-ODNB were analyzed by GC-MS for 80% ethanol and 97% TFE. The cis isomer gave only cyclohexene in 80% ethanol but also about 7% cyclohexanol in TFE. The trans substrate gave only cyclohexene in both solvents. For the cis tin acetate (**3**-OAc), only cyclohexene was observed for 80% methanol.

Table V. Rates of Acid-Catalyzed Elimination of β-Organometal Alcohols[a]

substrate	[DCl]	temp, °C	k, s^{-1}	trans/cis
cis, Si	0.10	71.0 ± 1.0	8.43×10^{-4}	
	0.10	55.8 ± 0.6	1.12×10^{-4}	
	0.10	25.0[b]	9.97×10^{-7}	
	0.12	55.0 ± 0.2	1.18×10^{-4}	
	0.12	75.0 ± 0.3	9.18×10^{-4}	
	0.12	25.0[b]	3.20×10^{-6}	
trans, Si	0.10	25.0 ± 0.5	1.05×10^{-3}	1.05×10^3
	0.12	25.0 ± 0.2	3.36×10^{-3}	1.05×10^3
cis, Ge	0.12	55.0 ± 0.2	2.82×10^{-4}	
	0.12	70.0 ± 0.3	6.60×10^{-4}	
	0.12	25.0[b]	3.98×10^{-5}	
trans, Ge	0.12	10.0 ± 0.2	1.25×10^{-3}	
	0.12	0.0 ± 0.2	5.12×10^{-4}	
	0.12	25.0[b]	3.67×10^{-2}	9.2×10^2
cis, Sn	0.10	25.0 ± 0.5	1.78×10^{-3}	
	0.12	25.0 ± 0.2	3.62×10^{-3}	
trans, Sn	0.10	−50.0	too fast!	

[a] Measured in 91 vol % CD$_3$OD and 9 vol % D$_2$O mixture. [b] Calculated from other temperatures.

Table VI. Rate Ratios for the Solvolysis of Trifluoroacetates in 97% Trifluoroethanol at 25.0 °C

substrate	k, s^{-1}	k_{rel}	trans/cis[a]	M/Si[b]
cyclohexyl[c]	7.05×10^{-10}	1.0		
Si (cis)[c]	2.36×10^{-5}	3.3×10^4		1.0
Si (trans)[c,d]	4.0×10^0	5.7×10^9	1.7×10^5	1.0
Ge (cis) (**1**)	3.25×10^{-4}	4.6×10^5		13.8
Ge (trans) (**2**)[d]	7.1×10^1	1.0×10^{11}	2.2×10^5	17.8
Sn (cis) (**3**)[e]	$>9.4 \times 10^1$	$> 1.3 \times 10^{11}$		$>4 \times 10^6$
Sn (trans) (**4**)	$\gg 10^5$	$\gg 10^{14}$	$\gg 10^3$	

[a] Ratio for a given metal. [b] Ratio with respect to the silicon substrate with the same stereochemistry. [c] From ref 2. [d] Calculated by multiplication of the rate of the 3,5-dinitrobenzoate by 2.4×10^5 (see ref 2). [e] Calculated by multiplication of the rate of the acetate by 1.5×10^6, given as a minimum.

Discussion

There are several mechanistic possibilities to be considered. (1) A k_C (carbocation) mechanism in which the intermediate (Me$_3$M–C–C$^+$) is stabilized primarily by hyperconjugative (vertical) interactions. (2) A participative mechanism in which the nonvertical interaction leads to a cyclic intermediate. (3) A concerted E2 reaction in which nucleofuge and electrofuge depart simultaneously. (4) Nucleophilic attack by solvent on the metal as the rate-determining step. (5) Nucleophilic attack by solvent at the carbon of the C–X bond as the rate-determining step. Aspects of these mechanisms have been summarized by Davis and Jacocks in terms of a More O'Ferrall–Jencks diagram.[5]

The first three mechanisms take place most easily when the carbon–metal and carbon–nucleofuge bonds are parallel. The stereochemistry between these two bonds should not be important for the last two mechanisms. Nucleophilicity of the solvent should be of paramount importance in the last two mechanisms. The carbon–metal bond energy should be of primary importance in the third and fourth mechanisms.

Germanium Substrates. The Raber–Harris plots explore the solvent dependency of the reaction for ethanol/water and trifluoroethanol/water mixtures.[9] Variation of the water content of ethanol changes its ionizing power without changing its nucleophilicity. On the other hand, variation of the water content of trifluoroethanol changes its nucleophilicity without changing its ionizing power. A log–log plot of the rate of the reaction vs that of 1-adamantyl bromide, which reacts by a k_C mechanism, gives two lines when the reaction under study involves rate-determining reaction with solvent: 1-adamantyl bromide responds along the *x* axis to changes in ionizing power, whereas the substrate responds along the *y* axis to changes in nucleophilicity. A single line is obtained when the substrate reacts by a k_C mechanism[2] since the reactions on both axes are responding to the same stimuli.

Figure 1 gives the Raber–Harris plot for *cis*-2-(trimethylgermyl)cyclohexyl trifluoroacetate (**1**-O(CO)CF_3). The plot is roughly a single line and contrasts markedly with classical k_s Raber–Harris plots,[2] in which the reaction is slower in trifluoroethanol than in ethanol, and the trifluoroethanol points have a large *y* axis variability. Clustering of the trifluoroethanol points (open circles) is characteristic of a reaction that is insensitive to solvent nucleophilicity. Thus both the *x*-axis (1-adamantyl bromide) and the *y*-axis (**1**-O(CO)CF_3) ranges of the rate in trifluoroethanol in Figure 1 are small, indicating little dependence of either substrate's reaction on solvent nucleophilicity.

The solid circles are from ethanol/water reactions. The large *x*-axis dependence is normal for the expected effect of ionizing power on the k_C reaction of 1-adamantyl bromide. The *y*-axis dependence (that of **1**-O(CO)CF_3) on ionizing power in Figure 1 is less than the *x*-axis dependence. We can offer two possible explanations for this behavior. (1) There may be a systematic change in the mechanism as the amount of water in ethanol and hence the ionizing power decreases (right to left in Figure 1). If ionizing power is becoming less important, for example as a k_C mechanism is being replaced by a k_s mechanism, then the dependence of the rate on ionizing power would be diluted. (2) In our ethanol/water mixtures, there was some concern about the measurement of the infinity point. There is the possibility of a systematic error that would lower the left-most point (lowest water content) the most, and each succeeding point from left to right less, resulting in a steeper plot for the solid circles. Despite these reservations, the overall appearance of Figure 1 clearly is typical of a k_C mechanism.

The Raber–Harris plot for *trans*-2-(trimethylgermyl)cyclohexyl 3,5-dinitrobenzoate (**2**-ODNB) (Figure 2) also contrasts considerably with classical k_s plots such as for cyclohexyl[2] but does not given an entirely typical k_C plot. The trifluoroethanol points are faster than the ethanol points, as expected for k_C. The *y*-axis dependence on nucleophilicity (trifluoroethanol, open circles) is somewhat larger than that for **1**-O(CO)CF_3, indicating increased nucleophilicity dependence of the rate. The *y*-axis dependence on ionizing power (ethanol, filled circles) is small, unless again these rates were subjected to a systematic error. The mixed signals of this plot suggest that the mechanism is k_C but that a nucleophilic component may become important as solvent nucleophilicity increases.

Activation parameters, particularly the entropy of activation, also can provide information about molecularity. The k_s reaction of cyclohexyl trifluoroacetate, and of other similar systems,[2] has a large negative activation entropy as the result of considerable ordering required for the bimolecular transition state (Table II). In contrast, the activation entropy for the cis substrate, **1**-O(CO)CF_3, is small and positive. For the trans substrate, **2**-ODNB, the value is negative and slightly larger. These particular measurements were carried out in 70% ethanol. The value of −11.9 eu is not large enough for a nucleophilic reaction. Any nucleophilic component of course would be even less important in trifluoroethanol.

The germanium systems are slightly more reactive than their silicon analogues, the cis form by a factor of about 14, the trans form by about 18 (Table VI). These comparisons are in good agreement with those of Eaborn[4] and Traylor.[6] The overall acceleration for the trans compound is some 11 orders of magnitude compared with cyclohexyl. The most significant aspect of the kinetic measurements is the stereochemical dependence. The trans/cis ratio (**2**/**1**) was calculated for the trifluoroacetate leaving group as described for the silicon systems.[2] For silicon the trans/cis ratio is 1.7×10^5, for germanium 2.2×10^5. Thus the profiles for silicon and germanium are almost identical. The evidence clearly eliminates nucleophilic mechanisms, which should not have an appreciable stereochemical dependence. The concerted E2 mechanism remains a possibility thus far. Neither it nor participation to form a germanonium ion, however, can explain the very rapid reaction of the cis (skew geometry) substrate, **1**-O(CO)CF_3, since both must occur in the antiperiplanar arrangement. Vertical participation (hyperconjugation) can explain acceleration in the cis form, since the effect falls off as a cosine-squared function of the Ge–C–C–X dihedral angle.

We have adapted the theory of secondary deuterium isotope effects to this context.[2,10] The cis form has a dihedral angle of about 60°; in the silicon series conformational biasing by means of a *tert*-butyl group had little effect on the rate. The trans form has a dihedral angle of 180° only in the less stable diaxial form. In the silicon series, we found that use of a *tert*-butyl group to freeze out the diaxial form brought about a 400-fold increase over that of the unbiased trans form analogous to **2**. If the conformational correction is similar for trimethylsilyl and trimethylgermyl, multiplication by this factor of 400 then brings the acceleration caused by trimethylgermyl up to about 4×10^{13} relative to cyclohexyl trifluoroacetate. Analysis following the procedure of ref 2 permits resolution of this acceleration for the 180° case into a term from hyperconjugation (2×10^{11}) and a term from simple induction (2×10^2). Similar resolution for the 60° case reveals a hyperconjugative contribution of about 2×10^3 and an inductive contribution of the same 2×10^2. These ratios are all derived from the data for trifluoroacetates solvolyzing in 97% trifluoroethanol at 25 °C. The data may be interpreted in terms of an extremely dramatic acceleration due to hyperconjugation, along with a small acceleration from the inductive effect. In more nucleophilic solvents there may be some contribution from solvent involvement, as indicated by the Raber–Harris plot and the entropy of activation.

Tin Substrates. The Raber–Harris plot for *cis*-(trimethylstannyl)cyclohexyl acetate (**3**-OAc) (Figure 3) is in agreement with a carbocation mechanism. The trifluoroethanol points are faster than those for ethanol. Moreover, the trifluoroethanol points cluster together in a typical fashion for a reaction that is not sensitive to solvent nucleophilicity. There does not appear to be an important bimolecular component in trifluoroethanol. The entropy of activation, however, is large and negative (Table II). Thus there may be a nucleophilic component in aqueous ethanol, the solvent in which the activation parameters were measured. Indeed, the *y*-axis dependence for the filled circles in Figure 3 is small. The importance of nucleophilicity in trifluoroethanol, in which we make our kinetic comparisons, however, is small.

The present results, particularly the relative rates summarized in Table VI, provide further evidence for an as-

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[10] For a discussion, see ref 2. Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* 1977, *99*, 5000–5005. Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 174–180.

tonishing reactivity of β-stannyl-substituted organic leaving groups, as already noted by Eaborn[4] and Traylor.[6] As a neighboring group to trifluoroacetate, synclinal (skew) trimethylstannyl provides an acceleration of at least 11 orders of magnitude compared with cyclohexyl trifluoroacetate. The only uncertainty in fixing this number is deciding how much less reactive acetate is than trifluoroacetate. We have taken the factor of 1.5×10^6 of Royce and Virgillo in 1-phenylethyl,[11] but this factor may be too small. The rates of Table IV were multiplied by 1.5×10^6 to get the relative rates of Table VI, but these have been denoted as lower limits to recognize the limitation of the $O(CO)CF_3/OAc$ factor.

The factor of 10^{11} is some 6 or 7 orders of magnitude more than for the analogous synclinal silicon and germanium systems. Moreover, there is good evidence from the solvent effects that the synclinal **3**-OAc reacts with little nucleophilic involvement in trifluoroethanol, since the rate is insensitive to changes in the water content of the solvent (Figure 3). Thus bond breaking of the tin–carbon bond cannot be contributing significantly to the transition state, unless it occurs unimolecularly. Such a process, however, should be independent of the relative stereochemistry of the trimethylstannyl group and the nucleofuge. The fact that the trans system is much faster than the skew system is strong evidence against unimolecular C–Sn bond scission. The remaining possible explanation is that most of the acceleration in trifluoroethanol is caused by hyperconjugation between the C–Sn bond and the developing positive charge. Small contributions from induction may also be present, but neither the E2 elimination nor participation to a cyclic stannonium ion is possible in the cis (skew) geometry.

We have not been able to quantify the extent to which the trans system **4** exceeds **3** in reactivity. No trans substrate with a suitable leaving group could ever be isolated; even the alcohol under acidic conditions at −50 °C reacted instantaneously. To ensure that these conditions were sensitive to trans/cis differences, we carried out kinetic measurements directly on the silicon and germanium alcohols (Table V). The trans/cis ratio was somewhat diluted for this leaving group in aqueous methanol, compared with trifluoroacetate in 97% trifluoroethanol, but the factor still was about 10^3 for both silicon and germanium. A factor of at least a thousand also is required for tin, simply by rough consideration of the 75 °C difference in temperature between the cis and trans observations. We have used 10^3 to set lower limits for the trans tin system in Table VI, but of course the ratios ought to be much larger. Such a large stereochemical difference for β-tin-activated leaving groups has not previously been recorded. For these conditions of trifluoroethanol and methanol, we can conclude that the stereochemical arrangement of the Sn–C–C–X portion is important in the transition state. Such a conclusion is not possible in a mechanism based entirely on differences in the energy of the carbon–metal bond or one requiring rate-determining attack of solvent on the metal. Thus hyperconjugation must play a significant, though not necessarily exclusive, role in these reactions.

A useful but perhaps not entirely valid exercise is to calculate the rate acceleration expected for the 180° angle system (**4**), provided that the acceleration observed for the 60° system (**3**) follows the Sunko–Hehre equation for secondary deuterium isotope effects.[2,10] If the factor of 10^{11} in Table VI for **3** is composed of 10^3 from induction (an upper limit) and 10^8 from hyperconjugation, and if the inductive factor is angle independent, then the cosine-squared dependence requires that the maximum acceleration, found at 0° or 180°, would be 10^{32} from hyperconjugation and the same 10^3 from induction, or a total acceleration of 10^{35}. Even if induction should provide an unlikely acceleration as high as 10^6, the hyperconjugative effect would still be 10^{20}, for a total β-tin effect of 10^{26}. Given these numbers, our failure to measure kinetics from the trans system **4** and **5** is not surprising.

Conclusions

A β germyl group activates nucleofuges to a very similar extent to a β silicon group. We estimate the maximum acceleration (for a system frozen into the antiperiplanar geometry) to be about 10^{13}, which is composed approximately of a hyperconjugative factor of 10^{11} and an inductive factor of 10^2. The analogous maximum figure for silicon is about 10^{12}, composed of 10^{10} from hyperconjugation and 10^2 from induction.[2] In the gauche or skew Ge–C–C–X geometry, an overall acceleration of 10^5 is observed. These conclusions assume that the major mechanism is unimolecular formation of a carbocation at the β position to germanium. The solvent effects and the activation entropies are reasonably definitive in ruling out nucleophilic involvement when the solvent is trifluoroethanol. The high reactivity of the synclinal **1**-$O(CO)CF_3$ does not support an E2 elimination mechanism or direct participation by germanium to form a germanonium ion, although these mechanisms are not eliminated as contributors to the antiperiplanar **2**-ODNB.

Activation of the nucleofuge by a β tin group is much larger than for either germanium or silicon. The enormous acceleration (10^{11}) observed for the 60° dihedral angle system (**3**-OAc) could be interpreted in terms of enhanced hyperconjugation or by a new nucleophilic mechanism, whereby solvent attack at tin initiates the reaction. For **3**-OAc, the insensitivity of the rate to the water content in trifluoroethanol argues strongly against the nucleophilic contribution. Truly nucleophilic (k_s) reactions such as the solvolysis of cyclohexyl[2] or cyclopentyl[12] tosylate or trifluoroacetate show very large dependencies on the water content of trifluoroethanol. The activation entropy of **3**-OAc and the appearance of the Raber–Harris plot suggest that nucleophilicity may become important in solvents of higher nucleophilicity and lower ionizing power than trifluoroethanol, as suggested by Davis.[5]

Further definition of the mechanism of these β-tin systems was provided by the observation that the antiperiplanar geometry available to **4** or **5** was far more reactive than the synclinal geometry of **3**. The trans form was observably at least 1000 times more reactive than the cis form. This geometrical dependence of the rate again argues against a solely nucleophilic mechanism, since attack of the nucleophile at tin should be independent of the dihedral angle between the C–Sn bond and the bond to the nucleofuge. The geometrical dependence also argues against unimolecular cleavage of the C–Sn bond in the transition state for the same reason. Again, the extremely high reactivity of the synclinal system (at least 11 orders of magnitude faster than cyclohexyl) argues against the E2 and participative (leading to a cyclic stannonium ion) mechanisms. The data are best interpreted in terms of a hyperconjugative mechanism, with some contributions from the solvent in solvents of greater nucleophilicity. The assumption that all the acceleration in the synclinal tin

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system, except perhaps 10^3 from induction, is due to hyperconjugation leads to the expectation of a total acceleration of 10^{35} in an antiperiplanar or synperiplanar system, because of the cosine-squared dependence of hyperconjugation on the dihedral angle. Such enormous reactivity might be able to be exploited in ways now under study in our group.

Experimental Section

1-(Trimethylgermyl)cyclohexene. In a flame-dried three-necked flask were mixed 300 mL of dry diethyl ether, 10 g of chlorotrimethylgermane (64 mmol), and 3.92 g of Na (170 mmol). After the mixture was stirred under N_2 flow for 4 h, a solution of 1-chlorocyclohexene (9 g, 20% excess) was added dropwise via a syringe. The mixture was allowed to stir at room temperature for 10 days, and H_2O (30 mL) was added carefully. The resulting brown mixture was worked up by separating phases, drying ($MgSO_4$), and solvent evaporation. Distillation of the residue gave the desired product as a clear liquid: 7.77 g, 67%; bp 60–63 °C (2.5 mmHg); ^1H NMR ($CDCl_3$) δ 0.1 (s, 9, $GeMe_3$), 1.4–1.6 (m, 4, β-CH_2), 1.8–2.1 (m, 4, α-CH_2), 5.75 (br m, 1, vinyl proton).

1-(Trimethylgermyl)cyclohexene Oxide. *m*-Chloroperbenzoic acid (3.9 g, 18 mmol) was dissolved in 100 mL of CH_2Cl_2. Under N_2 atmosphere, a solution of 1-(trimethylgermyl)cyclohexene (2.36 g, 11.9 mmol) in 10 mL of CH_2Cl_2 was added dropwise to the flask, which had been cooled to 0 °C. After 8 h, the solid (*m*-chlorobenzoic acid) was removed by filtration. The filtrate was washed with 10% aqueous NaOH solution and H_2O. Evaporation of solvent from the dried mixture produced an oil. Distillation at reduced pressure provided the desired product: 1.8 g, 71%; bp 74–76 °C (0.5 mmHg); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9, $GeMe_3$), 1.0–2.1 (br m, 8, CH_2), 2.95 (m, 1, CH).

***cis*-2-(Trimethylgermyl)cyclohexanol (1-OH).** Under N_2 atmosphere, 1-(trimethylgermyl)cyclohexene oxide (1.8 g, 8.4 mmol) in 10 mL of dry diethyl ether was added dropwise to a slurry of $LiAlH_4$ (1.6 g, 42 mmol) in 30 mL of ether, cooled with an ice bath. Water (10 mL) was added very carefully after the mixture had stirred overnight at room temperature. The solid was then removed by filtration. The aqueous phase was extracted with ether, and the combined organic phase was dried ($MgSO_4$) and evaporated. The resulting crude solid product was recrystallized in pentane: 1.1 g, 61%; mp 50–51 °C; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9, $GeMe_3$), 1.0–1.8 (br m, 10, CH_2, OH, and CHGe), 4.15 (br s, 1, CHO); MS, *m/z* 216 ($M^{\cdot +}$); IR (mull) 3350 (O–H), 1231 cm^{-1}. Anal. Calcd for $C_9H_{20}OGe$: C, 49.87; H, 9.23; Ge, 33.50. Found: C, 50.13; H, 9.22; Ge, 33.41.

***trans*-2-(Trimethylgermyl)cyclohexanol (2-OH). Method A.** All the glassware was flame-dried, and the reaction was carried out under N_2 atmosphere. To a deep blue solution of potassium (4.29 g, 110 mmol) in hexamethylphosphoramide (HMPA, 30 mL) was added dropwise a mixture of chlorotrimethylgermane (7.5 g, 48.9 mmol) and 5 mL of HMPA. After 1 h of stirring, cyclohexene oxide (2.5 g, 25 mmol) was added slowly via a syringe, turning the mixture yellow. The mixture was stirred overnight, and H_2O (5 mL) was added. The mixture was extracted with pentane (5 × 100 mL). The combined pentane solution was washed with aqueous NaCl solution and dried. After rotary evaporation of the solvent, distillation of the residue gave an oil as the crude product, which contained a significant amount of HMPA according to the ^1H NMR spectrum. The crude product was further washed with H_2O and redistilled with a 5-in. Vigreux column: 3.17 g, 30%; bp 90 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9, $GeMe_3$), 0.8–2.0 (br m, 10, CH_2, OH, and CHGe), 3.5 (m, 1, CHO).

***trans*-2-(Trimethylgermyl)cyclohexanol (2-OH). Method B.** All glassware was oven-dried, assembled while hot, and flame-dried after assembly. The reaction was carried out under N_2 atmosphere. 1-(Trimethylgermyl)cyclohexene (2.4 g, 12 mmol) was mixed with 5 mL of dry tetrahydrofuran (THF) in a three-necked flask, equipped with a gas inlet, a refluxing column, and an addition funnel. To the flask was added dropwise a 0.5 M solution of 9-BBN in THF (30 mL, 15 mmol) via the addition funnel. The mixture was refluxed for 4 days and then allowed to cool to room temperature. Aqueous NaOH solution (3 M, 6 mL) was then added, followed by addition of 6 mL of 30% H_2O_2. The mixture was stirred at room temperature for 3 h and extracted with ether. The combined ethereal solutions were dried ($MgSO_4$). Distillation of the residue after solvent evaporation gave the product: 0.75 g, 28%; bp 89–91 °C (5 mmHg); ^1H NMR ($CDCl_3$), same as above (method A).

***cis*-2-(Trimethylgermyl)cyclohexyl Trifluoroacetate (1-O(CO)CF_3).** *cis*-2-(Trimethylgermyl)cyclohexanol (0.217 g, 1 mmol) and pyridine (0.088 g, 1.1 mmol) were dissolved in 2 mL of dry diethyl ether, cooled to 0 °C. With stirring, a solution of trifluoroacetic anhydride (0.23 g, 1.1 mmol) in 1 mL of ether was added slowly. After 40 min, the mixture was filtered through a glass wool plug, and the filtrate was washed with saturated aqueous $CuSO_4$ solution and 10% aqueous $NaHCO_3$ solution and dried. Removal of solvent by rotary evaporation gave an oil: ^1H NMR ($CDCl_3$) δ 0.05 (s, 9, $GeMe_3$), 0.5–2.1 (br m, 9, CH_2 and CHGe), 5.3 (br m, 1, CHO); IR (mull) 1772 cm^{-1} (C=O).

***trans*-2-(Trimethylgermyl)cyclohexyl 3,5-Dinitrobenzoate (2-ODNB).** 3,5-Dinitrobenzoyl chloride (0.28 g, 1.2 mmol) was dissolved in 5 mL of pyridine, cooled with an ice bath. A solution of *trans*-2-(trimethylgermyl)cyclohexanol (0.217 g, 1 mmol) in 1 mL of pyridine was then added. The mixture was stirred for 3 h and then poured into 5 mL of ice water. This mixture was extracted with $CHCl_3$. The combined organics were dried and filtered. Evaporation of the solvent gave a solid, which was recrystallized from hexane to give a colorless crystalline material: 0.26 g, 63%; mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9, $GeMe_3$), 1.2–2.4 (br m, 9, CH_2 and CHGe), 5.1 (br m, 1, CHO), 9.2 (br m, 3, aromatic); IR (KBr) 1714 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{22}GeN_2O_6$: C, 46.76; H, 5.40; N, 6.82. Found: C, 45.77; H, 5.59; N, 6.56.

1-(Trimethylstannyl)cyclohexene. Chlorotrimethyltin (23.7 g, 119 mmol) and 1-chlorocyclohexene (15 g, 128 mmol) were mixed in 300 mL of dry ether in a round-bottomed flask. The mixture was stirred for 7 days at room temperature under N_2 atmosphere, and H_2O (100 mL) was added. The two phases were separated, and the aqueous layer was extracted with ether. The combined ethereal solution was dried and filtered. Distillation of the residue after solvent evaporation gave the product: 13.7 g, 47%; bp 88 °C (12 mmHg); ^1H NMR ($CDCl_3$) δ –0.1 (s, 9, $SnMe_3$), 1.1–2.2 (br m, 8, CH_2), 5.8 (m, 1, vinyl proton).

1-(Trimethylstannyl)cyclohexene Oxide. A solution of 1-(trimethylstannyl)cyclohexene (13.7 g, 56 mmol) in 60 mL of CH_2Cl_2 was added dropwise to a solution of *m*-chloroperbenzoic acid (11.8 g, 56 mmol) in CH_2Cl_2 (400 mL) cooled in an ice bath. The mixture was stirred for 6 h, and the solid was filtered. The filtrate was washed with 10% aqueous NaOH solution, dried, and concentrated by rotary evaporation. Distillation of the residue gave the product: 7.7 g, 54%; bp 83–85 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ –0.1 (s, 9, $SnMe_3$), 1.1–2.2 (br m, 8, CH_2), 3.1 (br m, 1, CHO).

***cis*-2-(Trimethylstannyl)cyclohexanol (3-OH).** Under N_2 atmosphere, a solution of 1-(trimethylstannyl)cyclohexene oxide (7.7 g, 29.5 mmol) in 10 mL of anhydrous diethyl ether was added slowly to a slurry of $LiAlH_4$ in 50 mL of ether, which had been cooled with an ice bath. The mixture was then allowed to warm to room temperature and was stirred for 4 days. After that, the reaction was quenched by addition of H_2O (5 mL). The solid was removed by filtration, the filtrate was separated, and the organic portion was dried ($MgSO_4$). After removal of the solvent, distillation of the residue gave the desired product: 1.88 g, 24.7%; bp 96–98 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ –0.2 (s, 9, $SnMe_3$), 1.1–2.1 (br m, 10, CH_2, CHSn, and OH), 4.1 (br s, 1, CHO). Anal. Calcd for $C_9H_{20}OSn$: C, 41.11; H, 7.67; Sn, 45.15. Found: C, 41.44; H, 7.64; Sn, 45.98.

***trans*-2-(Trimethylstannyl)cyclohexanol (4-OH).** Glassware was flame-dried and the reaction was carried out under N_2 atmosphere. Through an addition funnel, a solution of chlorotrimethyltin (4.0 g, 20 mmol) in 20 mL of THF was added slowly to a mixture of Li (1.4 g, 200 mmol) and 50 mL of THF, which had been cooled to 0 °C. After 2 days of stirring at room temperature, the mixture was cooled with an isopropanol–dry ice bath, and a solution of cyclohexene oxide (2.0 g, 20 mmol) was added dropwise. The mixture was again stirred overnight. The excess Li was removed by filtration, and H_2O (50 mL) was added to the filtrate. The solution was then extracted with ether. The combined ethereal solution was dried, filtered, and evaporated.

Distillation of the residue at reduced pressure gave the product: 3.45 g, 66%; bp 126–128 °C (20 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.1 (sh t, 9, SnMe$_3$), 1.1–2.1 (br m, 10, CH$_2$, CHSn, and OH), 3.5 (br s, 1, CHO). Anal. Calcd for $C_9H_{20}OSn$: C, 41.11; H, 7.67; Sn, 45.15. Found: C, 41.64; H, 7.80; Sn, 46.02.

***cis*-2-(Trimethylstannyl)cyclohexyl Acetate (3-OAc).** *cis*-2-(Trimethylstannyl)cyclohexanol (0.26 g, 1.0 mmol) and pyridine (0.08 g, 1.1 mmol) were dissolved in 1 mL of dry ether cooled to 0 °C. With stirring, acetyl chloride (0.08 g, 1.1 mmol) was added dropwise. The mixture was then allowed to warm to room temperature and was stirred overnight. The solution was filtered through a glass wool plug to remove solid product. The filtrate was washed with a cooled saturated aqueous CuSO$_4$ solution and with a 10% NaHCO$_3$ solution and was dried (MgSO$_4$). Rotary evaporation of the solvent gave an oil: ^{1}H NMR (CDCl$_3$) δ −0.3, 0.1, 0.4 (sh t, 9, SnMe$_3$), 0.7–2.1 (m, 9, CH$_2$ and CHSn), 2.0 (s, 3, COCH$_3$), 5.1 (m, 1, CHO); IR (mull) 1736 cm^{-1} (C═O).

***r*-5-*tert*-Butyl-*cis*-2-(trimethylstannyl)cyclohexan-*trans*-ol (5-OH).** Under N$_2$ atmosphere, a solution of chlorotrimethyltin (4.0 g, 20 mmol) in 20 mL of anhydrous THF was added dropwise to a mixture of Li wire (1.4 g, 0.2 mol) and 50 mL of dry THF cooled with an ice bath. After 24 h, a solution of *trans*-4-*tert*-butylcyclohexene oxide[2] (3.1 g, 20 mmol) in 10 mL of THF was added dropwise to the mixture, which was then cooled with an 2-propanol–dry ice bath. The solution was stirred at room temperature overnight, and the excess Li was removed by filtration. The filtrate was washed with H$_2$O (3 × 50 mL). The mixture was dried over MgSO$_4$, and the solvent was evaporated to provide a solid that was recrystallized in pentane: 3.45 g, 53%; mp 54–56 °C; ^{1}H NMR (CDCl$_3$) δ −0.1, 0.1, 0.3 (sh t, 9, SnMe$_3$), 0.8 (s, 9, CH$_3$), 1.0–2.0 (br m, 8, CH$_2$ and CH), 4.3 (br s, 1, CHO).

Solvents and Conductometric Measurements. See ref 2.

Kinetics (^{1}H NMR Measurements of the Acid-Catalyzed Elimination of the Alcohols). A JEOL FX-270 NMR spectrometer was used in the variable temperature mode. The probe was adjusted to the desired temperature before insertion of the sample tube. At least 5 min was allowed for thermal equilibration for runs above room temperature. In case of low-temperature runs, the solvent was cooled to −78 °C in a NMR tube before the sample was added. About 10–20 spectra were recorded at a desired time interval. Spectra were saved on floppy disks and processed later. For the calculations, either the increase of the peak at δ 5.8 (vinyl proton of product cyclohexene) or the decrease of the peak at δ 4.2 (for cis alcohols) or δ 3.5 (for trans alcohols) could be used. For the germyl-substituted substrates, increase of the sharp singlet at δ 0.8 or decrease of the sharp singlet at δ 0.1 could be conveniently monitored. The solvent peak was used as reference to assure that integrations were all on the same scale.

Electron-Transfer Reactions in Pulping Systems. 5. Application of an Intramolecular Cyclization Reaction as a Detector of the Formation of Quinonemethide Radical Anions

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Compound **6**, which incorporates a hex-5-enyl group on a quinonemethide precursor, has been synthesized and reacted in 1 M NaOH at 135 °C in the presence of various pulping additives. Reduction of **6** either prior to or after cyclization to a five-membered ring provides evidence that a quinonemethide radical anion intermediate had formed. Some additives such as anthrahydroquinone and glucose were effective electron-transfer agents for the probe quinonemethide, while others such as sodium sulfide and sulfite were ineffective. The probe, therefore, provides information on the nature of chemical reactions that may be occurring during the pulping of wood. Anthrahydroquinone and glucose provided significantly different amounts of cyclized products. Glucose gave high yields of cyclized products, including three unique tricyclo[7.3.0.0^{2,7}]dodecatrienes. Apparently glucose reduces the radical intermediates relatively slowly, providing time for cyclization to occur. With no additives, other than 1 M NaOH, and long reaction times, the probe compound **6** provided some cyclized products; the electron-transfer agent in this case presumably is a phenolate ion.

Introduction

The rapid rates observed during anthraquinone (AQ) pulping have generally been attributed to the ability of anthrahydroquinone (AHQ), a reduced form of AQ, to promote lignin fragmentation reactions.[1-5] One proposed mechanism for the fragmentation process is that AHQ^{2-} adds to a quinonemethide (QM), forming a QM–AHQ^{2-} adduct, which subsequently undergoes an elimination reaction, producing fragmented products and AQ. Simple adducts of model compounds have been prepared and shown to exhibit this kind of chemistry.[2-5] However, since adduct formation reactions are reversible,[6] it is not clear whether adducts are key intermediates to fragmentation or just part of side reactions.

An alternative mechanism for an AHQ-induced lignin fragmentation process is one involving reduction of quinonemethides by AHQ ions via electron-transfer processes (Scheme I).[1] For simplicity, the electron-transfer steps are shown here, and in other drawings, as single steps. This may or may not be the case, as will be discussed later.

Quinonemethides are generated when phenolic lignin polymer end units, which have leaving groups at the para α-carbon, are heated, i.e., **1** → **2**. The QM **2** shown in

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