The β-Effect with Vinyl Cations: Kinetic Study of the Protiodemetalation of Silyl-, Germyl-, and Stannylalkynes

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The relative magnitude of the hyperconjugative stabilization of vinyl cations by adjacent C—M bonds (M = Si, Ge, Sn; the β-effect) has been examined by measuring the rate constants for the protonation and subsequent protiodemetalation of group 14 metalated (trimethylsilyl)acetylenes ($R_3MC{\equiv}CSiMe_3$). The relative β-effect arising from the second-order rate constants Sn ≫ Ge > Si (maximum $k_M/k_{Si} = 10^8$, 5×10^2, 1, respectively) follows the same order as that reported for simple carbenium ions. The product ratio from the protonation of $Ph_3GeC{\equiv}CSiMe_3$ was found to be particularly sensitive to acid concentration and strength, leading to loss of Ph_3Ge preferentially with weaker acids. With tin groups, the rate of destannylation decreased with increasing steric bulk, unlike the corresponding situation with silyl groups. The origins of both these observations may be attributed to nucleophilic interaction at the metal center during protonation.

Introduction

It has been known for more than 3 decades that the presence of β-silicon groups facilitates the solvolysis of alkyl halides.[3] In the intervening time, much study has been devoted to understanding and exploiting this effect. It is now well recognized that the silyl group hyperconjugatively stabilizes the intermediate β-carbenium ion (the β-effect).[4] Partially driven by the impact of organosilicon chemistry in organic synthesis,[5] much of its utility related to the β-effect, there has been an increased focus in recent years on the determination of the magnitude of this effect for silicon and the other group 14 elements.

Many synthetically useful reactions, involving vinyl cation intermediates stabilized by β-silyl or β-stannyl groups, have been reported in the literature.[6] However, in contrast to the detailed examination of the β-effect for carbenium ions,[7–14] there are very few studies of the β-effect with group 14 elements for vinyl cations.[15,16]

Jorgensen and co-workers have carried out ab initio calculations on β-SiH_3 vinyl cations and β-SiH_3 allylic cations (Figure 1) at the MP2/6-31G* and HF/6-31G* levels.[17] With all hydrogen substituents, the most stable form of the "vinyl cation" was actually the bridged cation **1** rather than the open form **2**. For "open" propenyl cations, the hyperconjugative stabilization across the shorter double bond **3** was found to be 5 kcal/mol more effective than that across the longer single bond **4**. These calculations are in agreement with the recent experimental data for silyl stabilized vinyl cations in the gas phase[18] which indicate that stabilization of a vinyl cation by a β-$SiMe_3$ group, with respect to hydrogen, is more effective (43.5 kcal/mol) than that for an alkyl cation (39 kcal/mol).[19]

The earliest kinetic study of β-group 14 vinyl cations was reported by Bott, Eaborn, and Walton.[20] They described the effect of substituents X, on the rate of cleavage of some substituted phenyl(triethylgermyl)acetylene compounds **5** by aqueous methanolic perchloric acid (Scheme I). The order of the β-effect, Sn ≫ Ge > Si, that they determined was based upon the assumption that the reaction involves the formation of the intermediate **6** in the rate-determining step.

Cochran and Kuivila[21] reported the kinetics of protiodestannylation of allenyltin compounds by aqueous

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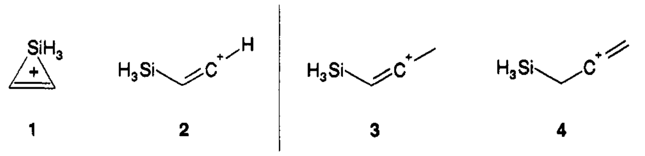
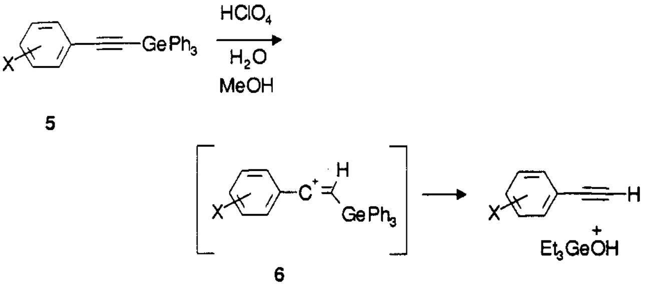
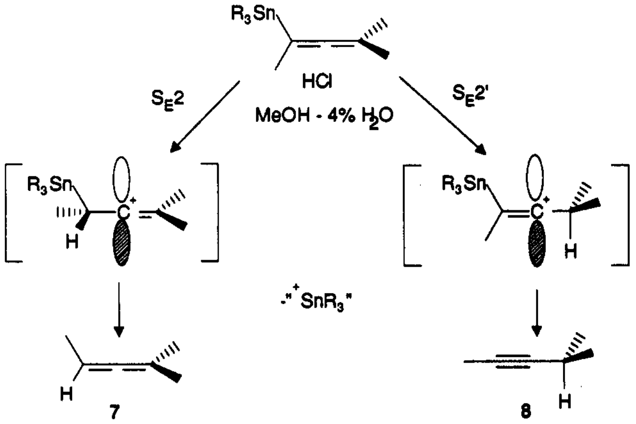


Figure 1.

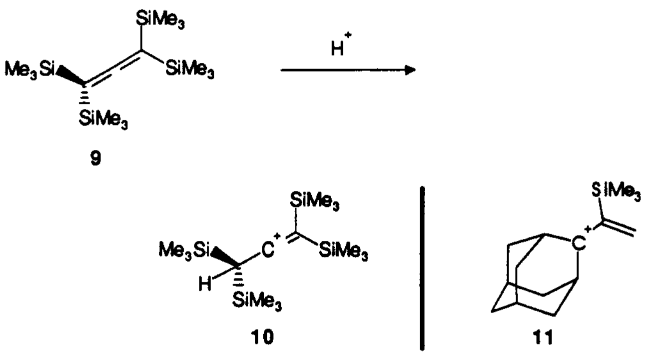
Scheme I



Scheme II



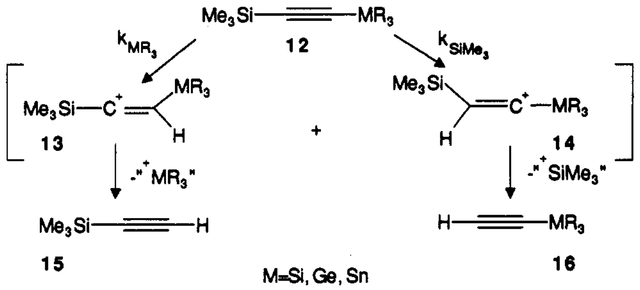
Scheme III



methanolic perchloric acid. The experiment examined the competition between S_E2 and S_E2' mechanisms leading to a mixture of allene 7 and acetylene 8 products via two different vinyl cations (Scheme II). While this qualitatively allows the assignation of the relative stability of different β-stannyl cations and the effect of the nonparticipating ligands on tin, it does not allow a comparison with other group 14 metals.

Using this approach, the very exciting first observance of a persistent β-silylvinyl cation was recently reported.[22] Protonation of allene 9 at low temperature led to the formation of β-silylvinyl cation 10 (Scheme III); the reaction was followed using NMR spectroscopy. A silyl-substituted allylic cation 11 has also been reported.[23]

Scheme IV



In this article, we describe our kinetic investigation of the protiodemetalation reaction of group 14 acetylides and correlate the reaction rates with the β-effect of different group 14 groups for vinyl cations.

Results

The model chosen for our study was the group of dimetalated acetylenes **12a–e**. Electrophilic attack, in our case a proton, should preferentially lead to one of two vinyl cations **13** or **14** via an internal competition. For example, if MR_3 has the larger β-effect, **15** rather than **16** will be the reaction product; subsequent loss of the best stabilizing group will lead to a monometalated acetylene (Scheme IV). This directly provides a relative β-effect between the two groups MR_3 and $SiMe_3$ if the inductive effects (α-effects, vide infra) are the same. In addition, the absolute rate of protonation/demetalation of different dimetalated acetylenes with the same Brønsted acid will reflect the stability of the β-metal vinyl cations in the transition state and allow a further comparison of the β-effect for different group 14 groups.

We used the $SiMe_3$ group as an internal reference in the molecule to minimize changes in the basicity of the triple bond and to facilitate the observation of products.[24] The proton signals of **15** are particularly characteristic in the ^1H NMR spectra. For example, the reaction of $Me_3SnC{\equiv}CSiMe_3$ (δ 0.28, 0.17 ppm) with chloroacetic acid (Table I, entry 1) led to the formation of $Me_3SiC{\equiv}CH$ (δ 0.20, 2.38 ppm) and trimethylstannyl chloroacetate (0.61 ppm). These reactions were performed in $CDCl_3$ rather than protic solvents so that the results would be directly relevant to organic synthesis where nonpolar solvent systems, frequently chlorinated hydrocarbons, are typically used.

The rates of reaction between protic acid(s) and a series of stannyl-, germyl-, and silyl(trimethylsilyl)acetylenes were measured, and second-order rate constants were obtained. The compounds could be readily divided into three classes depending upon whether the internal competition led to loss of $SiMe_3$ (Table II), of MR_3 (Table I), or of a mixture of both (Table III).

Discussion

Reaction Mechanism: Rate-Determining Step. The rate constants observed in these reactions (Scheme IV) involve two steps, protonation and subsequent demetalation. The β-effect is only involved in the first of these. Thus, it is clearly important to establish that protonation is the rate-determining step.

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Table I. Reaction of $Me_3SiC{\equiv}CMR_3$ with Different Acids[a]

entry	MR_3[b] (comp)	acid[c]	pK_a[d]	10^2k (M^{-1} s^{-1})	max k_{MX_3}/k_{SiMe_3}
1	Me_3Sn (**12a**)	$ClCH_2CO_2H$	2.85	1.98 ± 0.15	1.5×10^8
2	Me_3Sn (**12a**)	$ClCH_2CO_2D$	2.85	0.70 ± 0.05	
3	n-Bu_3Sn (**12b**)	$ClCH_2CO_2H$	2.85	0.70 ± 0.05	
4	n-Bu_3Sn (**12b**)	Cl_2CHCO_2H	1.48	65 ± 8	5.1×10^7
5	Ph_3Sn (**12c**)	Cl_2CHCO_2H	1.48	0.38 ± 0.03	
6	Ph_3Sn (**12c**)	Cl_3CCO_2H	0.70	18 ± 2	
7	Ph_3Sn (**12c**)	F_3CCO_2H	0.23	54 ± 6	3×10^5
8	Me_3Ge (**12d**)	F_3CCO_2H	0.23	0.094 ± 0.007	525
9	Me_3Si (**12e**)	F_3CCO_2H	0.23	0.00018 ± 0.00003	1

[a] The reaction was run in $CDCl_3$ with an acid and substrate concentration of 0.05 M and was followed by ^1H NMR. [b] MR_3 was the leaving group; $Me_3SiC{\equiv}CH$, the sole acetylene product in all cases. [c] The acid was added as a solution in $CDCl_3$. [d] pK_a in water.

Table II. Reaction of $Me_3SiC{\equiv}CMR_3$ with Different Acids[a]

entry	MR_3[b] (comp)	acid[c]	pK_a[d]	10^4k (M^{-1} s^{-1})
1	t-$BuMe_2Si$ (**12f**)	CH_3SO_3H	≈−2	9.6 ± 0.7
2	Me_3Si (**12e**)	CH_3SO_3H	≈−2	7.6 ± 0.9
3	Ph_3Si (**12g**)	CH_3SO_3H	≈−2	0.32 ± 0.07

[a] The reactions were run in $CDCl_3$ with an acid and substrate concentration of 0.05 M and were followed by ^1H NMR (see Experimental Section). [b] $SiMe_3$ was the leaving group; $R_3MC{\equiv}CH$, the sole acetylene product in all cases. [c] The acid was added as a solution in $CDCl_3$. [d] Approximate pK_a in water.

Table III. Products of the Reaction of $Ph_3GeC{\equiv}CSiMe_3$ (12h) with Different Acids

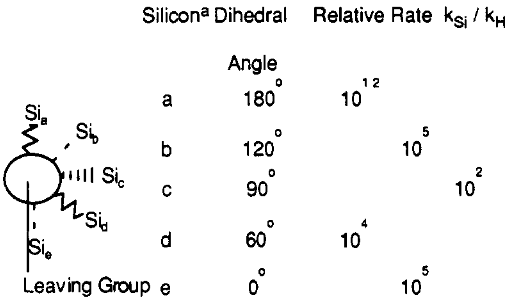
acid	[acid]/ [acetylene]	k (M^{-1} s^{-1})	product ratio $Ph_3GeC{\equiv}CH/HC{\equiv}CSiMe_3$
TfOH	1		1/3[a]
CH_3SO_3H	5[b]	22.5×10^{-3}	1/5
CH_3SO_3H	2.65	8.4×10^{-3}	1/3
CH_3SO_3H	1		1/2
CF_3COOH	10	7.3×10^{-5}	0/1

[a] The ratio varied from 1/3 to 1/9 and was irreproducible. We attribute this to small amounts of water participating in the reaction. [b] Saturated solution.

The kinetics of the reaction were found to be first order in both the acid and the acetylene. Moreover, the rate of reaction for a given compound follows the order of acidity of the acid used[25,26] and not the nucleophilicity of the acid counterions (Table I, entries 5–7). These results and the observed deuterium isotope effect k_{H^+}/k_{D^+} of 2.8, for the reaction of (trimethylstannyl)(trimethylsilyl)acetylene ($Me_3SnC{\equiv}CSiMe_3$) with $ClCH_2CO_2H$ (Table I, entries 1 and 2), confirm that the rate-determining step of the reaction involves the breaking of the acid H–O bond by attack of the triple bond acting as a base, not the subsequent nucleophilic attack of the acid counterion at the metal center. It should be noted, however, that the counterion plays a significant role in the protonation step of the Ge and Sn compounds (vide infra).

β-Effect versus Inductive Effects. Vertical versus Nonvertical Stabilization. The β-effect involves stabilization of a carbocation, normally through the vertical interaction of a C–M σ-bond with an empty p orbital. As has been demonstrated by Lambert and co-workers in the case of carbenium ions, the β-effect follows a type of Karplus relationship in that the observed magnitude is dependent upon the torsional angle between the C–M σ-bond and the empty p orbital, with a minimum at 90° and a maximum at 180° (Figure 2).[8,9]

In a rigid, linear acetylene compound, the C–M bond is orthogonal to the p orbital to be stabilized and is thus in the worst possible geometry to provide stabilization (β-effect) by way of orbital overlap during the protonation process; initially, any hyperconjugative stabilizing interaction between the orbitals is at a minimum.[27] Any rate enhancement due to the β-effect will thus be subject to the extent to which the molecule undergoes the nonvertical rehybridization process[10,28] from sp → sp^2 (e.g., **12** → **13**, Scheme IV). The absolute rates found for reactions of this type, therefore, should be expected to be smaller than those for reactions in which the geometry required for vertical stabilization is already present in the starting material, as in the solvolysis work of Kuivala shown above (Scheme II). Given this constraint, it is necessary to demonstrate that the relative rates for the protonation reactions actually reflect the β-effect rather than inductive or other effects.



[a]Silicon a,d reference 8, b,e reference 9 and c, reference 13.

Figure 2.

Arguments against Inductive Effects. The group 14 metals are electron-releasing with respect to carbon and may be expected to stabilize β-carbenium ions such as **13** through both hyperconjugation and inductive effects. While the protonation reaction of the triple bond of these metalated (trimethylsilyl)acetylene compounds *could* be controlled by inductive effects alone (i.e., basicity of the triple bond[24]), several factors argue against this. On the basis of the similarity of the electronegativity of the silicon, germanium, and tin elements,[29] the inductive effect of the Me_3Si, Me_3Ge, and Me_3Sn groups on the triple bond should be approximately the same and cannot explain the large differences observed in the rate constants between these groups (Table I). The inductive effect of the $SiMe_3$ group, in the case of the formation of β-trimethylsilyl carbenium ions, has been calculated to increase the rate of reaction

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(25) Although the pK_a's of these acids in chloroform-d have not been determined, Rumeau has shown that the general order of pK_a of these acids in chloroform is the same as in water.[26]

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(28) Traylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

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by about 10^2. In contrast, the β-effect of $SiMe_3$ in the same reaction leads to a rate acceleration of 10^{10}.[8,9] Equally large differences in rate constants, for group 14 stabilizing groups with similar inductive effects, have been observed in the studies of stabilization of alkyl β-metalocarbenium ions.[7,30] Thus, we conclude that the β-effect is primarily responsible for the large rate differences shown in Table I.

Measuring Inductive Effects: **α-Effect.** The importance of inductive effects can, furthermore, be readily determined from the rates of reaction given in Table II. In these reactions, the rates shown are for protonation of the triple bond and subsequent loss of the $SiMe_3$ group. Since the β-stabilizing group is the same in all three cases, the differences in rates reflect only differing basicity of the triple bond and α-stabilization of the developing vinyl cation intermediates by the metal; the β-effect does not enter into it.

The most interesting comparison among these compounds (Table II) is that between entries 1 and 2 (t-$BuMe_2Si$ versus Me_3Si). The *tert*-butyl group has a larger electron-donating effect than a methyl group and, thus, would be expected to form vinyl cation **13** rather than **14** (MR_3 = $SiMe_2$-t-Bu, Scheme IV) due to an enhanced β-effect. Indeed, Mayr has demonstrated, in the addition reaction of electrophiles to allylsilanes, that larger alkyl groups on silicon clearly increase the β-effect of the silyl group.[12] The results here, however, demonstrate that the reaction proceeds via **14**. The stabilization of the vinyl cation provided by the β-effect of a β-$SiMe_3$ group *and* the inductive effect provided by an α-$SiMe_2$-t-Bu group must be better than that provided by a β-$SiMe_2$-t-Bu *and* an α-$SiMe_3$ group.[31,32] That is, since the β-effects are similar, the regiochemistry of protonation is controlled by the α-stabilization of the cation by $SiMe_2$-t-Bu. The small differences in the relative rates provide an evaluation of the inductive effects of the three different silyl groups. Soderquist and Hassner have observed a similar inductive "α-effect" for α-metalated carbenium ions in the hydrolysis of α-metalated methyl vinyl ethers.[33] They found a rate ratio of 30 for k_{SiMe_3}/k_{SiPh_3} which corresponds closely to the rate ratio of entries 2 and 3.

Relative β-Effect. The results in Table I show the rates of reaction when MR_3 was better at stabilizing the intermediate vinyl cation than $SiMe_3$. They have been ordered by decreasing relative rate with which the group is lost with a given acid: the faster the rate, the better the β-effect. The range of reactivity of **12a–e** was very large, and it was impossible to determine the reaction rate with a single acid. Ordering the relative β-effect for these compounds was thus achieved by measuring the rates of reaction with pairs of acids of different strengths.

Our initial assumption was that the difference in rates of reaction for a given compound **12** with different acids depends only on the pK_a of the acid and is independent of the nucleophilic effects of the counterion (for example, Table I, entries 5–7). It is then possible to calculate a relative β-effect for vinyl cations of the different group 14 groups by the pK_a-independent rate ratio k_M/k_{Si} shown in the final column of Table I. Thus, the product of the difference in rates between entries 7 and 8 with CF_3CO_2H (5.7×10^2) and entries 4 and 5 with Cl_2HCCO_2H (1.7×10^2) allows the determination that the relative change upon going from n-Bu_3Sn **12b** (with Cl_2CCO_2H) to Me_3Ge **12d** (with CF_3CCO_2H) is 9.7×10^4. On the basis of these calculations, the $SnMe_3$ group (entry 1) provides a relative rate acceleration in the approach to the transition state of approximately 10^5 and 10^8 greater than the Me_3Ge group (entry 8) and Me_3Si group (entry 9), respectively (Table I). As the nucleophile does play a role by accelerating the reaction, particularly for the Ge and Sn compounds (vide infra), k_M/k_{Si} reflects a maximum value for the relative β-effect.[34]

Our determination that the β-effect is the primary kinetic feature in the reaction examined is consistent with previous reports. The reaction of alkynes with electrophilic reagents, especially protons, has been described by several groups.[20,35–37] Noyce and Schiavelli found a positive secondary isotope effect k_H/k_D of 1.1 in the acid-catalyzed hydration (H_2SO_4/H_2O) of phenylacetylene and phenylacetylene-d ($PhC{\equiv}CD$).[37] This effect was explained by proposing that a hyperconjugative interaction (β-secondary isotope effect) exists in the transition state between the isotopically labeled CH bond and the developing empty p orbital. It was also observed that the secondary isotope effect k_H/k_D for 4-ethynyl-d-anisole was closer to unity (1.07), showing that the hyperconjugative effect is attenuated by the presence of other forms of conjugation. Eaborn and co-workers found the same mechanism in the protiodegermylation reaction of substituted phenyl(triethylgermyl)acetylene compounds in aqueous methanolic solution (Scheme I).[20,38]

Effect of the Substituents on the Metal. Electronic Effects. Groups on the metal that are electron-withdrawing will decrease the electron density in the M—C σ-bond and thus are expected to diminish the β-effect. This has been shown for carbenium ions by the product distribution studies of Brook[11] and kinetic studies of Mayr.[12] The order of the β-effect for metals substituted with ligands of different hybridization is thus expected to be inversely related to the electronegativity of these orbitals ($sp > sp^2 > sp^3$) in agreement with our observations $Me_3Sn > Ph_3Sn > (Me_3SiC{\equiv}C)_3Sn$.[39,40]

Steric Effect of the Substituents on the Metal: Nucleophilic Assistance at the Metal. Large alkyl group substituents on silicon, with better electron-donating ability, increase the magnitude of the β-effect for carbe-

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[30] (a) Hannon, S. J.; Traylor, T. G. *J. Org. Chem.* 1981, *46*, 3645. (b) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* 1981, *46*, 3651 and references cited therein.

[31] An alternative explanation would be the relative ease of nucleophilic attack at the $SiMe_3$ compared with the more sterically hindered t-$BuMe_2Si$ group, as is well-known from their relative utility as protecting groups in organic synthesis.[32] However, compounds bearing silyl groups with much larger nucleophilic susceptibility (e.g., $SiCl_3$, $MeSiCl_2$) also lost the $SiMe_3$ groups.[15]

[32] Hwu, J. R.; Wang, N. *Chem. Rev.* 1989, *89*, 1599.

[33] Soderquist, J. A.; Hassner, A. *Tetrahedron Lett.* 1988, *29*, 1899.

[34] In the rate-determining step, as the H—OZ acid bond is breaking, the C—H bond is forming and, concomitantly, the $Me_3Si{-}C{=}CMR_3H$ angle φ is decreasing from 180°. One of the referees noted that we can strictly compare the magnitude of the vinyl β-effects (ratio k_M/k_{Si}) of these different groups only if all angles φ at the transition states are the same and influences from the counterion and α-effect are absent. The angles φ have not been determined, and the latter effects are present to varying degrees. Thus, the reported ratio k_M/k_{Si} (Table I) will undoubtedly be slightly different from the corresponding ratio that would be found with compounds that can vertically stabilize a β-vinyl cation (for example, the allenyl compounds shown in Schemes II and III) and for which the latter effects are not present.

[35] Eaborn, C.; Pande, K. C. *J. Chem. Soc.* 1960, 1566.

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nium ions compared to $SiMe_3$.[12] However, the results with tin are quite different. Cochran, Kuivila, and co-workers demonstrated, in the protiodestannylation reaction of allyl,[40,41] vinyl,[42] and allenyl[21] tin compounds (Scheme II), that alkyl substitution on tin decreases the reactivity in the order Me > Et > n-Pr $\approx$ n-Bu. The exchange of ethyl for methyl groups decreases the partial reaction rate by a factor of 2.46 and 1.32 for the S_E2 and S_E2' processes, respectively. We have obtained the same general trend for the proton addition to (trialkylstannyl)(trimethylsilyl)acetylene compounds undergoing an S_E2 process; the substitution of methyl groups by n-butyl groups on tin *decreases* the rate of reaction by a factor of 2.8 (Table I, entries 1 and 3).

Two different explanations, both of which involve interaction of a Lewis base with tin in the transition state, have been put forth to explain the different effects of larger alkyl group size on the reaction rate in reactions at silicon and tin. The first of these is solvation. In the electrophilic addition of I_2 to vinyltin compounds, an analogous reaction to the protonation described above, Baekelmans and co-workers have suggested that solvation of the leaving tin atom is required to stabilize the transition state.[43] With larger alkyl substituents on tin, solvation of the metal in the transition state is made more difficult and reaction rates are lower. Similar explanations have been proposed for the electrophilic cleavage of aromatic stannanes in aqueous solution.[35] Davis and Gray observed in an acid-catalyzed deoxymetalation reaction that solvent attack was more important in the heavier elements Sn and Pb.[50] This is in accord with the greater size and ease of expansion of the coordination shell as one goes down the periodic table.

In our experiment, we used a nonpolar aprotic solvent ($CDCl_3$). While the stabilization of the polar transition state by solvation with chloroform-d might be significant, it is unlikely to be substantial.

An alternative explanation[43] for the effect of the steric bulk of the ligands involves a nucleophilic interaction, in the transition state of the protonation, between the electrophile counterion and the tin center (Figure 3). The impact of such an interaction on the β-effect can be predicted from the related case in organosilicon chemistry.

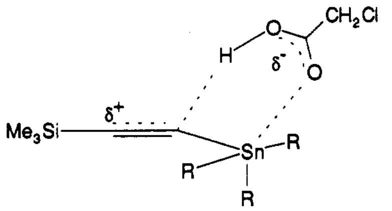

Figure 3.

Upon conversion from a neutral tetracoordinate Si species to a negatively charged pentacoordinate species, it has been shown that the degree of positive charge at the metal center actually increases;[44] simultaneously, the amount of negative charge borne by the outer ligands is also increased and is reflected, among other things, by an enhanced nucleophilicity of the ligands.[45] Assuming similar electronic effects in the case of Ge and Sn, the increased electron density in a pentacoordinate species will act, in our examples, to stabilize the vinyl cation more than in the four-coordinate case; the β-effect in the former case will thus be higher than that in the latter case.[46]

The capacity for extracoordination involves the nature of the metal itself Sn > Ge > Si, the degree of electron withdrawal by the groups on the metal[47] and the size of the groups already present on the metal. The observed protonation rate in all our reactions will thus depend upon the inherent β-effect provided by the tetraccordinate MR_3 group *and* the degree to which the β-effect is enhanced by extracoordination. Since we cannot determine the degree of extracoordination, the ratio k_M/k_{Si} shown in Table I will be a maximum: any additional contribution to the rate from extracoordination will show up as an *apparently* larger β-effect for the group MR_3.

In the case of tin (Table I, entries 1 and 3), larger alkyl groups should increase the β-effect by additional inductive effects.[12] However, any enhancement of the inherent β-effect of SnR_3 will be offset by a reduced ability to undergo extracoordination as a result of the increased difficulty in the approach of the counterion to the tin (i.e., a decrease in the likelihood of forming "R_3Sn–X"). The latter effect in this case is clearly more important than the former, as evidenced from the slower protonation rate.

$Ph_3GeC{\equiv}CSiMe_3$ was the only compound for which a mixture of products was obtained following protonation. To examine in more detail the question of nucleophilic interaction, we examined a series of conditions, acid concentrations, and acid strengths to determine under which circumstances, if any, the product ratio changed. Protonation of the triple bond was found to be the rate-determining step of the reaction; in all cases the rate of the reaction (loss of starting material) decreased with decreasing acid strength. However, as can be seen from the results in Table III, weaker acids, and thus more nucleophilic counterions, led to a preference for loss of Ge at the expense of silicon. The acid counterion is clearly playing a role in the kinetics of the reaction.[48]

A germanium atom has a better ability to expand its coordination sphere than a silicon atom.[49] The different product ratios then reflect the greater propensity of Ge than of silicon to extracoordinate with the acid counterion during the protonation. The stabilizing interaction occurring preferentially at Ge will be enhanced with more

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(48) It might be expected that similar interactions would have been observed in previous β-effect studies involving electrophile additions to allylmetals. We ascribe the absence of such interactions to the geometric differences in the transition state. In this case, the incoming HX and leaving group interact at the same end of the molecule (Figure 3) while in other cases[12] the electrophile is distal to the leaving group **16**.

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nucleophilic counterions, leading increasingly to Ge-C cleavage; that is, the β-effect of Ph_3Ge is less than $SiMe_3$ but that of extracoordinated "Ph_3Ge–X" is greater than $SiMe_3$. These effects will be magnified with group 14 elements further down the periodic table that more readily undergo coordination expansion, as has been described above for tin.[35,50]

Since the rate of the reaction for a given compound follows the order of acidity of the acid used and not the nucleophilicity of the acid counterions (Table I, entries 5–7), we infer that the magnitude of the nucleophilic interaction in the rate-determining step is small compared to the magnitude of the β-effect stabilization provided by C–Sn or C–Ge, sufficiently small that it is only apparent when the β-effects of the groups being compared are similar.

Conclusion

A scale of the relative magnitude of the β-effect provided by some stannyl, germyl, and silyl groups toward vinyl cations has been determined; the order obtained is the same as that for β-metalocarbenium ions Sn ≫ Ge > Si (k_M/k_{Si} $10^8 > 5 \times 10^2 > 1$). The relative reaction rates for protonation and demetalation of germanium and tin (trimethylsilyl)acetylides, with respect to $SiMe_3$, demonstrated the susceptibility of the stabilizing Ge and Sn groups to nucleophilic interaction during the protonation step. The magnitude of change in reaction rates arising from the interaction of the counterion with the stabilizing group, however, was smaller than that of the β-effect itself toward vinyl cations.

Experimental Section

The boiling points (bp) obtained by distillation under vacuum are not corrected.

^1H and ^{13}C NMR spectra were obtained on Bruker AC-200 (200-MHz) and WM-500 (500-MHz) spectrometers. For preliminary quality checks a Varian EM-390 (90-MHz) was used for ^1H NMR. Spectra were internally referenced by the signal from $SiMe_4$, by the residual solvent signal of $CHCl_3$ in $CDCl_3$, or by an internal CH_2Cl_2 signal at 5.3 ppm. ^{29}Si and ^{119}Sn NMR spectra were performed on a Bruker WR-250 (250-MHz) spectrometer using the signals of Me_4Si and Me_4Sn, respectively, as external references (0 ppm).

Infrared spectra were run on a Perkin-Elmer 283 spectrometer in $CHCl_3$ or CCl_4 solution, as a film on an NaCl disk or as a KBr pellet.

Electron impact (EI) and chemical ionization (CI) mass spectra were recorded at 70 eV with a source temperature of ca. 200 °C on either a VG Micromass 7070-F mass spectrometer equipped with a data system composed of a PDP8A with VG 2000 software or a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectral (HRMS) data were obtained with the VG ZAB-E instrument by the EI method.

Tetrahydrofuran (THF) and benzene were freshly distilled under a nitrogen atmosphere from benzophenone/potassium.

Chloroform-*d* ($CDCl_3$, 99.8 atom % D) and water-d_2 (D_2O, 99.9 atom % D) were obtained from Merck Sharp and Dohme Canada (MSD Isotopes) and were used without purification from a fresh bottle. (Trimethylsilyl)acetylene ($Me_3SiC{\equiv}CH$) was obtained from Aldrich or prepared according to experimental procedure.[51] All other materials were obtained from Aldrich and were purified by distillation with the exception of methanesulfonic acid (CH_3SO_3H) and triflic acid (CF_3SO_3H) which were used from a fresh bottle without purification.

Due to the instability of the reagents toward hydrolysis, all syntheses were performed with dry glassware, under a nitrogen atmosphere, using syringe techniques or in a glovebag which was dried with anhydrous phosphorus pentoxide (P_2O_5) and continuously purged with dry nitrogen.

Chloroacetic Acid-*d*: $ClCH_2COOD$. The hydrolysis of chloroacetic anhydride was carried out with deuterium oxide (D_2O) in THF under nitrogen atmosphere. The solvent was removed by simple distillation, and excess D_2O was removed by azeotropic distillation with benzene to give a white solid (NMR analysis showed 94+ atom % D incorporation).

(*tert*-Butyldimethylsilyl)acetylene:[52] $HC{\equiv}CSiMe_2$-*t*-Bu. In a 500-mL three-neck flask under an acetylene atmosphere was placed THF (170 mL). After cooling to 0 °C, a solution of *n*-BuLi (2.5 M in hexanes, 30 mL, 75 mmol) was added. A white solid, the lithium acetylide, immediately formed, and the mixture was stirred for 1 h at 0 °C. A solution of *t*-$BuMe_2SiCl$ (10.92 g, 72.45 mmol) in THF (40 mL) was added, and the mixture was stirred at 0 °C for 1.5 h, warmed to room temperature, and allowed to stir a further 12 h. The clear yellowish solution was quenched at 0 °C with 10% HCl (300 mL) and extracted with ether (6 × 200 mL). The combined organic layers were washed successively with 5% $NaHCO_3$ and brine and dried over $MgSO_4$, and the ether was removed under reduced pressure. Distillation led to 9.16 g (90%) of the product. Bp: 117–119 °C; lit. 110 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.11 (s, 6H), 0.92 (s, 9H), 2.32 (s, 1H). ^{13}C NMR ($CDCl_3$), 62.9 MHz): δ (ppm) −4.77, 16.28, 25.68, 88.22, 93.71.

Metalated (Trimethylsilyl)acetylides: General Procedure. The syntheses of the metalated (trimethylsilyl)acetylides were performed with some modifications to the literature preparations:[52]

To a solution of *n*-BuLi (2.32 M in hexane, 0.78 mL, 1.80 mmol) was added a solution of (trimethylsilyl)acetylene (0.26 mL, 1.81 mmol) in THF (10 mL) at −78 °C. The solution was allowed to warm to 0 °C over 30 min. To the mixture was slowly added a solution of the metal chloride (e.g. Me_3GeCl, 0.22 mL, 1.75 mmol) in THF (5 mL). After stirring at −78 °C for 30 min, the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water and extracted 3 times with ether, the combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to give a light yellow oil. Distillation gave 0.26 g (70%) of a colorless oil.

(Trimethylstannyl)(trimethylsilyl)acetylene:[53] $Me_3SnC{\equiv}CSiMe_3$ (12a). Yield: 71%; lit. 68%. Bp: 25 °C/1 mmHg; lit. 25 °C/1 mmHg. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.16 (s, 9H), 0.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) −7.4, 0.5, 113.2, 117.6. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −20.9. ^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ (ppm) −73.6. IR (neat) ν (cm^{-1}) 2965 (st), 2920 (st), 2905 (st), 2370 (w), 2075 (w), 1450 (m), 1405 (m), 1305 (w), 1245 (st), 1190 (w), 830 (st), 750 (st), 690 (st). MS (EI, *m/z*, reported for ^{119}Sn isotope): 247 ($M^+ - CH_3$, 100), 217 (12), 185 (6). HRMS (M^+ reported for ^{119}Sn isotope): mass observed for $M^+ - CH_3$, 246.9984; mass calculated for $M^+ - CH_3$, 246.9965.

(Tri-*n*-butylstannyl)(trimethylsilyl)acetylene:[54] $Bu_3SnC{\equiv}CSiMe_3$ (12b). Yield: 90%; lit. 91%. Bp: 134–137 °C/8 mmHg; lit. 89 °C/0.27 mmHg. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.16 (s, 9H), 0.9 (t, 9H), 0.9–1.0 (m, 6H), 1.20–1.45 (m, 6H), 1.45–1.67 (m, 6H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ (ppm) 0.4, 11.3, 13.7, 27.0, 29.0, 113.1, 118.9. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −21.2. ^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ (ppm) −71.0. IR (neat) ν (cm^{-1}) 2950 (st), 2920 (st), 2865 (st), 2845 (st), 2065 (w), 1945 (w), 1845 (w), 1450 (st), 1410 (m), 1370 (m), 1335 (w), 1285 (w), 1240 (st), 1170 (w), 1130 (w), 1065 (m), 950 (w), 845

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(st), 830 (st), 750 (st), 685 (st), 590 (m). MS (CI + CH_4, *m/z*, reported for ^{119}Sn isotope): 373 ($M^+ - CH_3$, 24), 331 (100), 291 (89), 269 (14), 235 (17), 177 (6), 97 (5), 83 (24), 73 (32).

(Triphenylstannyl)(trimethylsilyl)acetylene:[55] **$Ph_3SnC{\equiv}CSiMe_3$ (12c).** Yield: 92%; lit. 61%. Mp: 73–74 °C; lit. 74–76 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.3 (s, 9H), 7.5–7.4 (m, 9H), 7.75–7.65 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 0.17, 108.7, 121.4, 129.2, 129.5, 136.7, 139.9. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −19.5. ^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ (ppm) −175.4. MS (EI, *m/z*, reported for ^{119}Sn isotope): 448 (M^+, 3), 433 (5), 371 (39), 341 (4), 294 (3), 274 (35), 221 (27), 197 (37), 159 (50), 135 (32), 120 (100), 97 (18). HRMS (M^+ reported for ^{119}Sn isotope): mass observed, 448.0677; mass calculated, 448.0669.

(Trimethylgermyl)(trimethylsilyl)acetylene:[56] **$Me_3GeC{\equiv}CSiMe_3$ (12d).** Yield: 70%; lit. 68%. Bp: 65 °C/55 mmHg; lit. 150–151 °C/750 mmHg. Mp: 32–33 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.16 (s, 9H), 0.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) −0.1, 0.1, 112.1, 114.1. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −20.2. MS (EI, *m/z*, reported for ^{74}Ge isotope): 216 (M^+, 2), 201 (100), 120 (56), 118 (59), 97 (19).

(*tert*-Butyldimethylsilyl)(trimethylsilyl)acetylene:[57] **$t\text{-}BuMe_2SiC{\equiv}CSiMe_3$ (12f).** Yield: 74%. Bp: 45–55 °C/8–9 mmHg. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.09 (s, 9H), 0.16 (s, 9H), 0.93 (6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) −4.4, 0.2, 16.7, 26.3, 112.2, 114.4. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −9.6, −19.6. IR (neat): ν (cm^{-1}) 2960 (st), 2940 (st), 2900 (st), 2860 (st), 1460 (m), 1405 (m), 1385 (w), 1360 (m), 1250 (st), 1000 (m), 850 (st), 840 (st), 820 (st), 770 (st), 755 (st), 690 (m), 670 (m). MS (EI, *m/z*): 212 (M^+, 2), 197 (7), 155 (100), 125 (4), 97 (4), 83 (5), 73 (14). HRMS: mass observed 121.1415; mass calculated; 212.1417.

(Triphenylsilyl)(trimethylsilyl)acetylene:[55] **$Ph_3SiC{\equiv}CSiMe_3$ (12g).** Yield: 55%; lit. 73%. Mp: 70–71 °C; lit. 42–44 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.27 (s, 9H), 7.3–7.5 (m, 9H), 7.6–7.7 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) −0.13, 108.1, 119.5, 127.9, 129.9, 133.4, 135.5. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −30.9, −18.4. IR (CCl_4) ν (cm^{-1}) 3050 (w), 3030 (m), 3000 (m), 2955 (m), 2870 (w), 1955 (w), 1880 (w), 1820 (w), 1770 (w), 1530 (w), 1475 (w), 1420 (w), 1245 (m), 1100 (m), 830 (st), 760 (st), 690 (st).

(Triphenylgermyl)(trimethylsilyl)acetylene: $Ph_3GeC{\equiv}CSiMe_3$ (12h). Yield: 81%. Mp (recrystallized from 2-propanol): 68–69 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.30 (s, 9H), 7.35–7.5 (m, 9H), 7.6–7.75 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm) 0.05, 107.3, 117.2, 128.4, 129.5, 134.5, 135.1. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ (ppm) −18.9. IR ($CHCl_3$): ν (cm^{-1}) 3060 (m), 3010 (m), 2970 (m), 1960 (w), 1890 (w), 1820 (w), 1770 (w), 1480 (w), 1435 (w), 1300 (w), 1200 (m), 1085 (m), 840 (st), 730 (st), 720 (st), 710 (st), 690 (st), 660 (st). MS (EI, *m/z*, reported for ^{74}Ge isotope): 402 (M^+, 20), 387 (62), 325 (46), 228 (100), 159 (12), 135 (11). HRMS (reported for ^{74}Ge isotope): mass calculated, 402.0859; mass found, 402.0842. Anal. Calcd for $C_{23}H_{24}GeSi$: C, 68.87; H, 6.03; Si, 7.00. Found: C, 68.74; H, 6.30; Si, 7.25.

Kinetic Experimental Procedure. Generally, reactions were carried out using 0.5 mL of a 0.05 M solution of the acetylene compound (0.025 mmol) in chloroform-*d* ($CDCl_3$) in an NMR tube (5 mm). The reactions were followed by NMR spectroscopy on Bruker AC-200 (200-MHz) and WM-500 (500-MHz) spectrometers. The reaction rates were measured on a Bruker AC-200 (200-MHz) at room temperature (the temperature was maintained at 23 °C), and the time was recorded at the end of each spectrum of four scans. A kinetic program provided by Bruker AC-200 software was used for the fast reactions.

In the case of the stannyl(trimethylsilyl)acetylene compounds (Table I, entries 1–7), the reactions were initiated by the addition of the carboxylic acid solution in $CDCl_3$ (10 μL, 2.5 M in $CDCl_3$, 0.025 mmol) to a solution of the compound in an NMR tube (0.5 mL, 0.05 M in $CDCl_3$, 0.025 mmol). The adjustment of the NMR spectrometer required an average of 90 s, after which the spectra were recorded. In a special case, for the fast reaction between the (tri-*n*-butylstannyl)(trimethylsilyl)acetylene with $Cl_2CHCOOH$, the spectra were recorded after 50 s with a rapid adjustment of the "shim" of the spectrometer and by taking only one scan for each spectrum.

The reactions of (trimethylgermyl)(trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene were initiated by the addition of CF_3COOH solution (0.1 mL, 0.25 M in $CDCl_3$, 0.025 mmol) to a solution of the compound (0.4 mL, 0.0625 M in $CDCl_3$, 0.025 mmol) in an NMR tube.

The degree of completion of the reaction was measured by the change of the relative intensity of the proton signal of the methyl substituent (singlet) for each silyl, germyl and stannyl groups. The relative intensity was best evaluated by the manual measurement of the peak height. The order of the reaction was shown by the linearity of second-order plots (correlation coefficient >0.95); the data were treated with a least-squares fit to a straight line using a computer program (Quattro, Borland).

The reactions of $n\text{-}Bu_3SnC{\equiv}CSiMe_3$ (**12b**) with 1 equiv dichloroacetic acid (Table III, entry 4) and $Ph_3SnC{\equiv}CSiMe_3$ (**12c**) with 1 equiv trifluoroacetic acid (Table III, entry 7) were very fast for the NMR method. As no data points could be taken before the half-life, second-order data for these reactions were inferred from the other experiments.

The reactions between (trimethylgermyl)(trimethylsilyl)acetylene (**12d**) and particularly bis(trimethylsilyl)acetylene (**12e**) with F_3CCO_2H were very slow. To be sure that the rates were accurate, the compounds were also reacted with several different, higher stoichiometric ratios of F_3CCO_2H. The observed rate constant was found to be linearly dependent on the acid concentration, indicating that the reaction is also affected by the ionic strength of the solution.[58] Extrapolation of the k_{obs} versus [acid]/[acetylene] line confirmed the rate constant at the 1:1 acid/acetylene stoichiometry.

For the results shown in Table III the following techniques were used (final acid molarity shown in parentheses):

Entry 1: F_3CSO_3H (2.2 μL, 0.025 mmol, 0.05 M) was added to 0.5 mL of a 0.05 M solution of $Ph_3GeC{\equiv}CSiMe_3$ in $CDCl_3$.

Entry 2: CH_3SO_3H (1.6 μL, 0.025 mmol, 0.05 M) was added to 0.5 mL of a 0.05 M solution of $Ph_3GeC{\equiv}CSiMe_3$ in $CDCl_3$.

Entry 3: CH_3SO_3H (4.2 μL, 0.066 mmol, 0.13 M) was added to 0.5 mL of a 0.05 M solution of $Ph_3GeC{\equiv}CSiMe_3$ in $CDCl_3$.

Entry 4: CH_3SO_3H (10.4 μL, 0.16 mmol, 0.33 M, gives a saturated solution of acid) was added to 0.5 mL of a 0.05 M solution of $Ph_3GeC{\equiv}CSiMe_3$ in $CDCl_3$.

Entry 5: CF_3CO_2H (0.10 mL, of 2.5 M in $CDCl_3$, 0.5 M) was added to 0.4 mL of a 0.0625 M solution of $Ph_3GeC{\equiv}CSiMe_3$ in $CDCl_3$.

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