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Protonation of Trimethylsilyl-Substituted Carbon−Carbon Multiple Bonds in Aliphatic Systems. Conformational Dependence of the β-Silyl Stabilizaton of Carbocations

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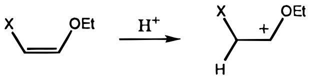
Abstract: Rates of carbon protonation to give carbocation products were measured in concentrated perchloric acid solutions for cyclohexene, propyne, 1-hexyne, and their 1-trimethylsilyl-substituted analogs. The trimethylsilyl substituent accelerated the reaction markedly and provided the following β-silyl carbocation stabilizing effects: $\delta\Delta G^{\ddagger} = 5.7$ kcal/mol^{-1} for the cyclohexyl system and $\delta\Delta G^{\ddagger} = 6.5$ kcal mol^{-1} for both acetylenic systems. These effects are substantially greater than $\delta\Delta G^{\ddagger} = 2.9$ and 3.4 kcal mol^{-1} found previously for the protonation of ethyl vinyl ether and phenylacetylene, which suggests that the silyl effects in these previous systems were attenuated by additional carbocation stabilization provided through their ethoxy and phenyl groups. The present effects, on the other hand, fall far short of $\delta\Delta G^{\ddagger} = 16-17$ kcal mol^{-1} found for conformationally optimum systems. The influence of conformation on the magnitude of β-silyl effects and how this impinges on the presently studied systems is discussed.

It is well known that β-trimethylsilyl substituents can stabilize carbocations strongly:[1] effects of several tens of kcal mol^{-1} have been calculated[2] and observed[3] for systems in the gas phase and stabilizations of 17[4] and 16[5] kcal mol^{-1} have been found for reactions in solution. In contrast to this, effects of only 2.9 and 3.4 kcal mol^{-1} have been observed in the carbon protonation of ethyl vinyl ether[6] and phenylacetylene,[7] eqs 1 and 2, X = H, SiMe$_3$.



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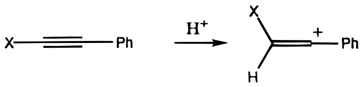

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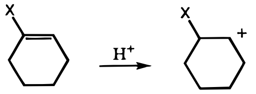
We have attributed this striking difference to the largely hyperconjugative nature of the β-silyl effect[2,4,8] and the fact that the conformational requirements for maximum stabilization, while satisfied in the systems producing the large β-silyl effects,[4,5] were probably not met in the transition states of the vinyl ether and acetylene protonation reactions.[6,7] The developing carbocationic centers in the latter reactions, however, are also stabilized by ethoxy and phenyl groups, and these additional substituents could have served to attenuate the β-silyl effect. In order to determine whether or not this was so, we have now examined the purely aliphatic systems shown in eqs 3−5, X = H, SiMe$_3$. We have found that the β-silyl effects here are substantially greater than those in the additionally stabilized systems of eqs 1 and 2, but that they still fall considerably short of the very large effects found in conformationally optimum systems.[4,5]



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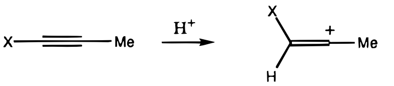

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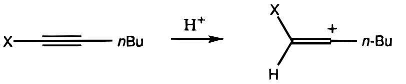

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Experimental Section

Materials. 1-(Trimethylsilyl)cyclohexene was prepared from cyclohexanone via the tosylhydrazone, as described.[4] All other materials were best available commercial grades.

Product Analyses. Large volumes (*ca.* 100 mL) of reaction solutions with substrate and acid concentrations similar to those used in the kinetic measurements were allowed to react for 10 half-lives. These solutions were then extracted with small (2 mL) portions of CDCl$_3$. This was done by shaking the reaction solutions with CDCl$_3$ in flasks to whose bottoms small cones had been fused; the CDCl$_3$ extracts settled into these cones, and could then be easily withdrawn using Pasteur pipets. The extracts were dried over molecular sieves and were then analyzed by NMR. This method produced extracts

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whose product concentrations were substantially greater than the solutions extracted, thus facilitating the NMR analysis.

Kinetics. Reaction rates were determined spectroscopically by monitoring the decrease in alkene or acetylene absorbance at 200−205 nm. Measurements were made with Cary 118 and 2200 spectrometers whose cell compartments were thermostated at 25.0 ± 0.05 °C. Portions (3.0 mL) of aqueous acids contained in cuvettes were first allowed to come to temperature equilibrium with the spectrometer cell compartments, and reactions were then initated by adding 5.0-μL aliquots of stock solutions of substrates dissolved in acetonitrile to these acid solutions; final substrate concentrations in the reaction mixtures were *ca.* 10^{-4} M. Absorbance decreases were followed for several half-lives. The data conformed to the first-order rate law well, and first-order rate constants were obtained by nonlinear least squares fitting of exponential functions. Acid concentrations were determined by titration of weighed samples.

Results

Product analyses were conducted for the reaction of 1-(trimethylsilyl)cyclohexene and 1-(trimethylsilyl)-1-hexyne with aqueous perchloric acid at acid concentrations near the midpoints of the ranges used for kinetic measurements (13.8 and 27.4 wt %, respectively). Proton and carbon-13 NMR spectra of the spent reaction mixtures showed cyclohexene to be the only product formed from the cyclohexene substrate and 1-hexyne to be the only product formed from the hexyne substrate. Elimination of the trimethylsilyl moiety from the carbocations formed in these olefin and acetylene protonation reactions thus occurs more rapidly than capture of the cations by solvent. This is consistent with results obtained in the protonation of (phenyltrimethylsilyl)acetylene[7] and the solvolysis of 2-(trimethylsilyl)cyclohexyl derivatives,[4] as well as with the general propensity of β-trimethylsilyl cations to lose their trimethylsilyl groups.[9]

Rates of protonation of the presently studied alkenes and alkynes were measured in moderately concentrated aqueous perchloric acid solutions. For each substrate, duplicate or triplicate determinations were made at each of 5−6 acid concentrations. The data so obtained are summarized in Table S1.[10]

As is usual for the protonation of carbon−carbon double and triple bonds, rates of reaction of the present substrates increased with increasing acidity of the medium more rapidly than in direct proportion to acid concentration, and an acidity function was therefore used to analyze the data. The Cox−Yates method[11] using the X_0 function[12] appears to be the best procedure currently avialable for this purpose.[13] The data were fitted using the expression shown in eq 6, where k_{H^+} is the bimolecular hydronium ion rate constant that applies in dilute solution and

$$\log (k_{obs}/[H^+]) = \log k_{H^+} + mX_0 \tag{6}$$

m is a slope parameter. The data obtained for all six substrates examined conformed to this relationship well; an example is shown in Figure 1. The values of k_{H^+} obtained in this way are listed in Table 1.

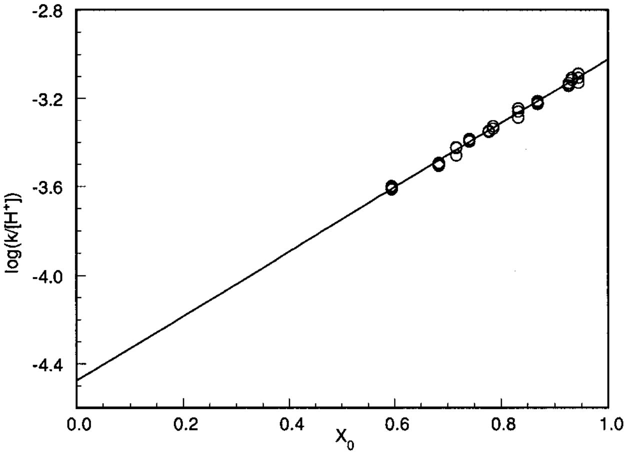

Figure 1. Cox−Yates plot for the protonation of 1-(trimethylsilyl)-1-propyne in aqueous perchloric acid at 25 °C.

Table 1. Summary of Rate Data for the Protonation of Cyclohexene, Propyne, 1-Hexyne, and Their Trimethylsilyl Derivatives in Aqueous Solution at 25 °C

substrate	k_{H^+}/M^{-1} s^{-1}	m^a	k_{H^+}/k_{D^+}
cyclohexene	1.73×10^{-8}	1.50	
1-(trimethylsilyl)cyclohexene	2.10×10^{-4}	1.54	2.25
propyne	6.11×10^{-10}	1.13	
1-(trimethylsilyl)-1-propyne	3.32×10^{-5}	1.45	1.55
1-hexyne	1.37×10^{-9}	1.02	
1-(trimethylsilyl)-1-hexyne	7.78×10^{-5}	1.26	1.28

[a] Cox−Yates correlation slope.

Some rate constants were also determined for the silyl-substituted substrates in solutions of $DClO_4$ in D_2O. Replicate measurements were made for each substrate at a single acid concentration in the concentration range used for the measurements in H_2O solution; these data are summarized in Table S2.[10] Kinetic isotope effects were evaluated from the results obtained by comparison with H_2O rate constants at the same acid concentration; the latter were obtained by interpolation of the Cox−Yates correlations. The results are listed in Table 1.

Rates of protonation of cyclohexene in aqueous perchloric acid have been measured before,[14] and the dilute-solution hydronium ion rate constant reported, $k_{H^+} = 4.43 \times 10^{-8}$ M^{-1} s^{-1}, though broadly consistent with our result, $k_{H^+} = 1.73 \times 10^{-8}$ M^{-1} s^{-1}, is not in good numerical agreement with it. In the previous study, however, extrapolation to dilute solution was performed using the H_0 acidity function, which is not an appropriate acidity scale for this reaction. Fortunately, the raw data were also published in this earlier report, and reanalysis of that using the Cox−Yates method gives $k_{H^+} = 1.67 \times 10^8$ M^{-1} s^{-1}, in very good agreement with the presently determined value.

Rates of protonation of propyne and 1-hexyne were also determined before,[15] but the previous measurements were made in sulfuric acid rather than the perchloric acid used here. Sulfuric acid solutions at the concentrations employed contain appreciable quantities of undissociated bisulfate ion, which functions as an efficient general acid proton donor and makes rates of protonation in this medium considerably faster than

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(10) Supporting information; see paragraph at the end of this paper regarding availability.

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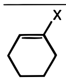
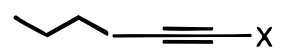
Table 2. Rate Accelerations Provided by β-Trimethylsilyl Substituents in Alkene and Alkyne Protonation Reactions[a]

System (X = H, SiMe$_3$)	k_{SiMe_3}/k_H	$\delta\Delta G^{\ddagger}$/kcal mol^{-1}
	15,200	5.7
—≡—X	54,300	6.5
	56,800	6.5
	129	2.9
Ph—≡—X	312	3.4

[a] In aqueous solution at 25 °C.

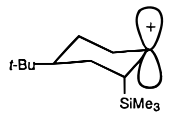
those in a completely dissociated acid such as perchloric; this is so even when comparison is made at the same value of an appropriate acidity function.[16] Numerical agreement of the present and previous results should therefore not be expected, but it is gratifying that Cox−Yates treatment of the previous data gives rate constants that are consistently greater than those determined here.

Discussion

Simple alkenes and alkynes such as the cyclohexene, propyne, and 1-hexyne used in the present study undergo hydration to the corresponding alcohols in concentrated aqueous mineral acids; in the case of alkynes, the alcohols formed are enols, which then tautomerize to their keto isomers. It is now well established that the first and rate-determining step in these processes is carbon protonation to give carbocation reaction intermediates, as shown in eqs 3−5.[14,15] The trimethylsilyl derivatives of these substrates examined here also undergo carbon protonation, but now the carbocations formed lose their labile trimethylsilyl groups rather than become hydrated. Nevertheless, the carbon protonation step is still rate-determining, as indicated by the normal isotope effects ($k_H/k_D > 1$) that these reactions give and also by the fact that their Cox−Yates slope parameters are in the range expected for a rate-determining proton transfer reaction.[11b,17]

The protonation of each of these trimethylsilyl substituted substrates is considerably faster than that of its unsilylated counterpart. The rate ratios, listed in Table 2, range from 15 000 to 57 000 and correspond to β-silyl effects, expressed as differences in free energy of activation, of $\delta\Delta G^{\ddagger} = 5.7$ to 6.5 kcal mol^{-1}. These effects are considerably greater than those found before for the protonation of ethyl vinyl ether, $\delta\Delta G^{\ddagger} =$ 2.9 kcal mol^{-1},[6] and phenylacetylene, $\delta\Delta G^{\ddagger} = 3.4$ kcal mol^{-1}.[7] This difference indicates that the β-silyl effects in the vinyl ether and phenylacetylene systems were in fact attenuated by the cation-stabilizing ability of their ethoxy and phenyl groups.

The presently determined β-silyl effects, however, are still much less than the 16−17 kcal mol^{-1} stabilizations found for generation of the 2-(trimethylsilyl)cyclohexyl cation **1**[4] and the 9-((trimethylsilyl)methyl)fluorenyl cation **2**[5] in solution. We believe this difference to be due to the now quite well established hyperconjugative nature of the β-silyl effect[2,4,8] and the fact that the conformational requirements for maximum hyperconjugative interaction were met in the systems for which these large effects were observed, but were not met in the presently studied cases.



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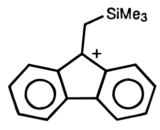

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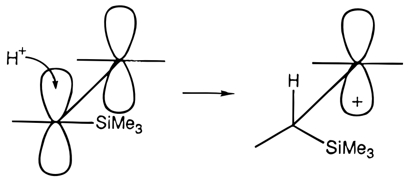
Hyperconjugative stabilization of a carbocation involves interaction between the filled orbital of the stabilizing bond and the vacant orbital of the cationic center. This interaction will be maximum when these orbitals are coplanar, *i.e.*, when the dihedral angle between them is zero. This angle was constrained to be zero in **1** by the conformationally biasing 4-*tert*-butyl group and the *trans* arrangement of the trimethylsilyl substituent and the leaving group in the cation precursor,[4] and it was probably zero in **2** as well, for that would put its trimethylsilyl substituent in a plane perpendicular to the aromatic framework, free of steric interaction with peri hydrogens in the 1 and 8 positions; the β-silyl effect in the case of **2**, moreover, was on an equilibrium constant rather than a rate constant, and it should consequently refer to **2** in its most stable equilibrium position.[5]

In the presently studied cyclohexyl system, on the other hand, this dihedral angle was not zero. In the carbon protonation of an olefin such as cyclohexene, the proton attacks the olefinic π-system in a direction perpendicular to its σ-bond framework, forming a bond with one of the π-system's constituent p-orbitals and converting the other into the vacant p-orbital of the cationic center. In the case of (trimethylsilyl)cyclohexene, attack occurs at the carbon atom bearing the silyl substituent, as shown in eq 7, and the state of hybridization of this carbon atom changes from sp^2 to sp^3. At the beginning of this process, the dihedral angle between the carbon−silicon bond and the forming vacant p-orbital is $\theta = 90°$, as shown in the Newman projection **3**, and at the end of the process it reaches the nominal value $\theta =$ 60°, as shown in **4**. In the transition state of this reaction the dihedral angle will have some value between these limits, but it is unlikely to be less than 60°. If, as is commonly believed, the interaction varies as the cosine of the dihedral angle squared, then the hyperconjugative stabilization in the protonation of 1-(trimethylsilyl)cyclohexene will not be greater than $(\cos 60°)^2$ $= 0.25$ of the maximum value expressed in a conformationally optimum system.



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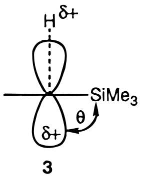

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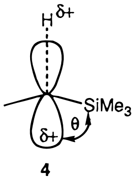

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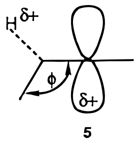

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The situation is somewhat different in the case of the acetylenic systems studied here, because now the substrate has two π-systems formed from p-orbitals at right angles to one another. Proton attack will occur on one of these π-systems, leaving the other intact. This will create a vinyl cation in which, as shown in eq 8, the carbon−silicon bond and the vacant

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[16] Kresge, A. J.; Hakka, L. E.; Mylonakis, S.; Sato, Y. *Discuss. Faraday Soc.* **1965**, *39*, 75−83. Kresge, A. J.; Mylonakis, S.; Hakka, L. E. *J. Am. Chem. Soc.* **1972**, *94*, 4917−4199.

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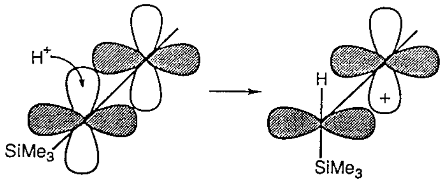

(8)

p-orbital lie in the same plane and the dihedral angle consequently has its optimum value of zero. This dihedral angle, moreover, will be zero throughout the entire protonation process. There is another angle, however, designated ϕ in side view **5**, that must be considered in acetylenic systems. At the beginning of the proton addition process, the carbon−silicon bond is colinear with the acetylenic carbon−carbon triple bond and $\phi = 180°$. In this configuration, the carbon−silicon bond and the developing p-orbital are perpendicular to one another and no hyperconjugative interaction is possible. Hyperconjugation will of course develop as the protonation process progresses, for ϕ will change toward its nominal sp^2 value of 120° and approach the optimum value of 90° for exactly parallel orbitals. In the transition state of the reaction, however, the change will not be complete and hyperconjugative stabilization will be less than it would be in a conformationally optimum system. If the cosine squared relationship holds here as well, then the magnitude of the interaction will vary in proportion to $(\cos(\phi - 90°))^2$, and for a transition state in which the geometrical change is half complete and $\phi = 150°$, $(\cos(150° - 90°))^2 = 0.25$, and the stabilization will be only a quarter of its maximum value.

The value of an angle corresponding to ϕ will also influence the magnitude of hyperconjugative interactions in nonacetylenic systems, but in those cases this angle will be much less unfavorable. In the systems showing the very large β-silyl effects,[4,5] for example, the silyl substituent was connected to the cationic center by a saturated carbon atom for which the nominal value of ϕ is 109.5° and $(\cos(109.5° - 90°))^2 = 0.89$, not far from its maximum value of 1.00 for exactly parallel orbitals with $\phi = 90°$. In the cyclohexyl case studied here, this aspect of the conformational problem was also quite good. The carbon atom connecting the silyl substituent to the cationic center there changed from olefinic to saturated as the reaction progressed, and ϕ therefore varied from 120° to 109.5°. The corresponding values of $(\cos(\phi - 90°))^2$ are 0.75 and 0.89, again not far away from the optimum 90° value of 1.00.

These considerations show that, whereas the angle ϕ plays a dominant role in controlling the magnitude of the β-silyl effect in the protonation of acetylenes, it has much less influence on this effect in the protonation of alkenes. In the latter reaction, on the other hand, the magnitude of the β-silyl effect is strongly reduced by unfavorable values of the dihedral angle θ.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supporting Information Available: Tables S1 and S2 of rate data (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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