

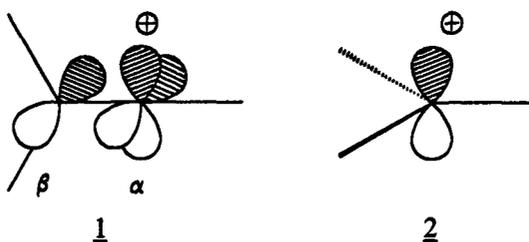
NMR spectroscopic and computational investigations of σ -interactions in carbocations: The β -silyl effect in vinyl cations

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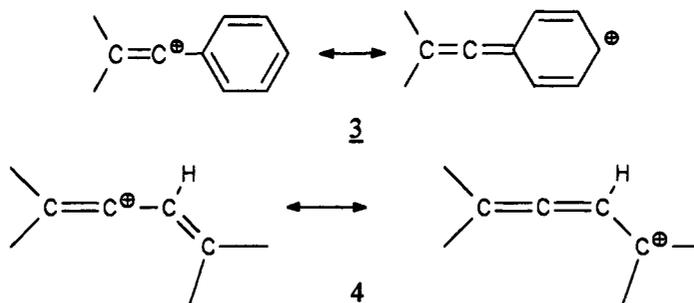
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Abstract: The para carbon chemical shift in 1-mesityl substituted vinyl cations and the torsional barrier for the methoxy group rotation in 1-p-(anisyl)vinyl cations are used to evaluate the magnitude of the silyl effect. The hyperconjugative stabilization by β -silicon groups and the accompanying geometrical distortions are studied experimentally and computationally in dienyl-cations and 1-cyclopropylvinyl cations. A geminal methyl substituent enhances the interaction of a β -silyl group with the vacant p-orbital.

Vinyl cations 1 are disubstituted unsaturated analogs of trisubstituted carbocations 2. The carbon C_α with the formal positive charge is sp hybridized and the “vacant” p-orbital is orthogonal to a $C^+=C_\beta$ double bond.

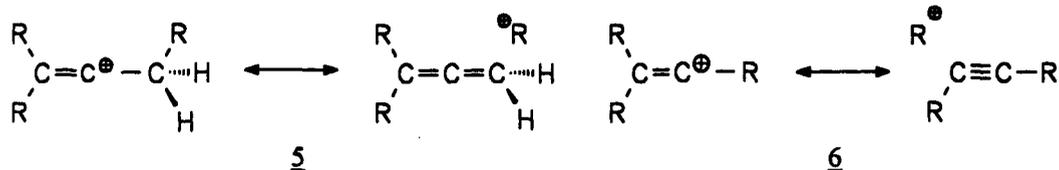


As in saturated carbocations the positive charge in vinyl cations is stabilized by electron donating substituents. Aryl or vinyl groups at the α -carbon delocalize the positive charge by π -conjugation as shown in 3 and 4.



The interaction of the formally vacant p-orbital at C_α with a σ -bond at a β -carbon is called hyperconjugation. In the notation of valence bond theory this is described as no-bond

resonance. For vinyl cations there are two different positions for hyperconjugating substituents. In 5 the β -substituent is attached at the single bonded adjacent carbon as in trigonal carbocations. The β -substituent can also be attached at the doubly bonded β -carbon of the vinyl cation as in 6.



This latter arrangement is particularly effective for hyperconjugative stabilization. The $\text{C}^+=\text{C}_{\beta}$ double bond is shorter than a single bond and the $\text{C}_{\beta}-\text{R}$ σ -bond is fixed in the plane of the "vacant" orbital at the C^+ -carbon, thus allowing maximum overlap of the β - σ and the $2p(\text{C}^+)$ orbitals.

Despite extensive former efforts vinyl cations only recently have been prepared in solution and were characterized by NMR spectroscopy (1 - 11). SbF_5 assisted heterolytic cleavage of the sp^2 $\text{C}-\text{X}$ bond in vinyl halides has been unsuccessful to yield stable vinyl cations. Protonation of alkynes, except ferrocenyl substituted alkynes (2), have generally also failed to yield stable vinyl cations. Using contemporary methodology like matrix co-condensation techniques (3) and carefully controlled experimental conditions we were successful to prepare α -aryl- β -alkyl and α -aryl- β -trialkylsilyl substituted vinyl cations by protonation of the corresponding alkynes (7, 8, 10, 11).

The generation of silyl-substituted carbocations in solution is severely hampered by the reactivity of the silicon center. Due to the high affinity of silicon to oxygen and fluorine, the facile formation of five-coordinated Si-intermediates or transition states, and the polar nature of the carbon silicon bond ($\text{C}^{\delta-}-\text{Si}^{\delta+}$) the $\text{C}-\text{Si}$ bond is prone to facile cleavage (8). $\text{C}_{\beta}-\text{Si}$ bond fragmentation can be slowed down or completely suppressed by larger alkyl substituents at silicon (7).

α -mesityl vinyl cations with different β -trialkylsilyl substituents were obtained by protonation of the corresponding alkynes with $\text{FSO}_3\text{H}/\text{SbF}_5$ in $\text{SO}_2\text{ClF}/\text{SO}_2\text{F}_2$ at -130 °C.



7 ($\text{R} = \text{Si}(\text{Me})_2$ i-pr); 8 ($\text{Si}(\text{Me})_2$ t-but.); 9 ($\text{Si}(\text{Me})_2$ t-hex.); 10 ($\text{Si}(\text{i-pr})_3$)

Fig. 1 shows as a typical example the ^{13}C NMR spectrum of the α -mesityl- β -(triisopropyl)silylvinyl cation 10 measured at -120 °C (7).

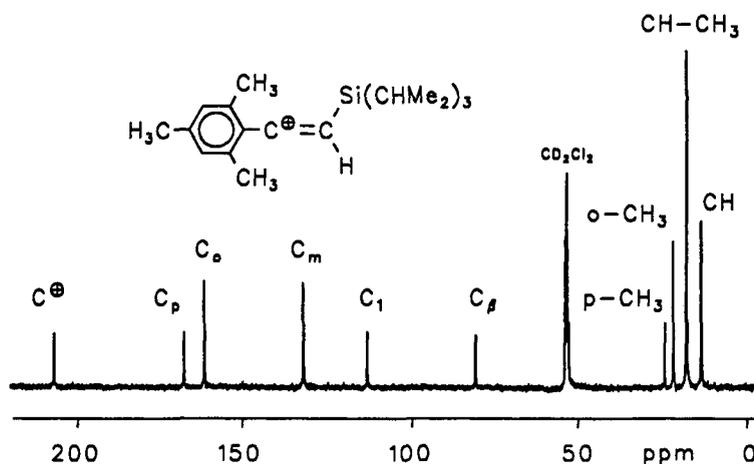
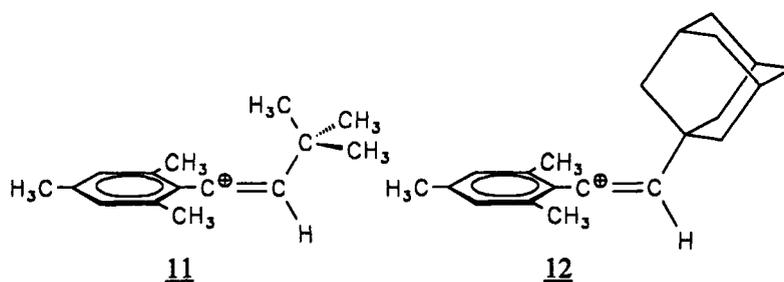


Fig. 1. ^{13}C NMR of α -mesityl- β -(triisopropyl)silylvinyl cation 10 (-120°C)



α -Mesityl- β -alkyl substituted vinyl cations with large β -alkyl groups, like a tert.-butyl group, as in 11, or an adamantyl substituent, as in 12, are accessible under similar conditions by protonation of the corresponding alkynes with $\text{FSO}_3\text{H}/\text{SbF}_5$ in $\text{SO}_2\text{ClF}/\text{SO}_2\text{F}_2$ at low temperatures (7, 10).

The NMR chemical shift data of the vinyl cations 7 - 12 give experimental proof for the superior hyperconjugative charge delocalizing ability of β -silyl groups (Fig. 2) as compared to β -alkyl- and β -H- substituents. The shift of the para carbon is used to monitor the electronic demand of the cation center. Chart 1 shows a comparison of the chemical shift of the para carbon in α -mesityl-substituted vinyl cations with different β -substituents. The para carbon chemical shift of the mesityl-methyl and 1-mesityl-ethyl cations which both have sp^2 hybridized C^+ -carbons are shown for comparison.

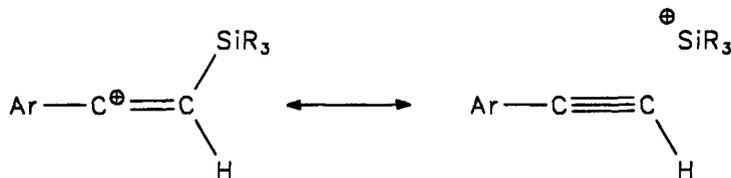


Fig. 2. β -C-Si hyperconjugative stabilization in α -aryl- β -silylvinyl cations

The more the positive charge in the vinyl cations is stabilized by σ - or π -electron donation of the β -substituent, the lower is the demand for charge delocalization into the aromatic ring and thus the para carbon is less deshielded. The similar range of the para-carbon chemical shifts in

the β -silyl substituted vinyl cations **7** - **10** (168 - 170 ppm) to that in the α -mesityl- γ -dimethylallyl cation (166 ppm), which in addition to α -aryl conjugative is stabilized by β -allyl resonance, shows that the hyperconjugative interaction of a β -Si σ -bond with the "vacant" 2p orbital on the C⁺-carbon (Fig. 2) is about as efficient in dispersing the positive charge as β - π conjugation.

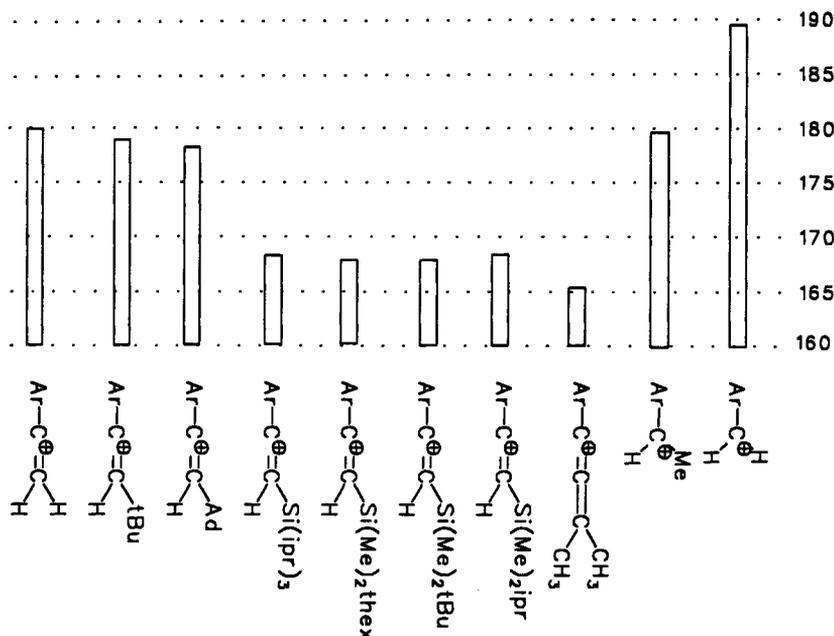
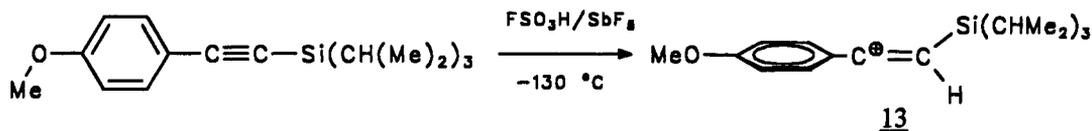
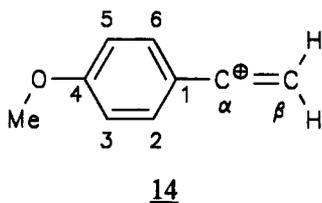


Chart 1: Comparison of the para carbon NMR chemical shift (ppm) in α -mesitylvinyl cations and sp^2 -hybridized model cations (Ar = mesityl).

The torsional barrier for the rotation of the methoxy group in 1-(*p*-anisyl)vinyl cations is another measure of the electron demand of the cationic center. The 1-(*p*-anisyl)-2-(triisopropyl)silylvinyl cation (**13**) is obtained by protonation of 1-(*p*-anisyl)-2-(triisopropyl)silylethyne with FSO₃H/SbF₅ at -130 °C.⁸



The β -silyl-group in **13** is readily cleaved at -115 °C and the 1-(*p*-anisyl)vinyl cation (**14**) is obtained.



Cation **14** has a higher demand for α -aryl π -stabilization (Fig. 3) compared to the β -silyl substituted vinyl cation **13**, which in addition to α -aryl stabilization is further stabilized by β -C-Si hyperconjugation (Fig. 2).

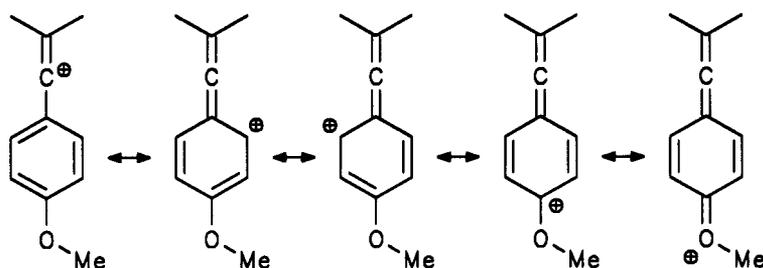


Fig. 3 α -Aryl π -resonance delocalization in 1-(*p*-anisyl)vinylium cations

In the α -anisylvinylium cation **14** more positive charge is delocalized to the methoxy group. This enhances the partial double bond character of the C₄-O-bond and consequently a higher torsional barrier for the rotation of the methoxy group is observed. The two ortho and two meta positions are nonequivalent and four distinct signals are observed in the ¹H and ¹³C NMR spectra of the β -unsubstituted cation **14** whereas for the β -silyl substituted vinyl cation **13** these positions remain equivalent even at the lowest accessible temperatures.

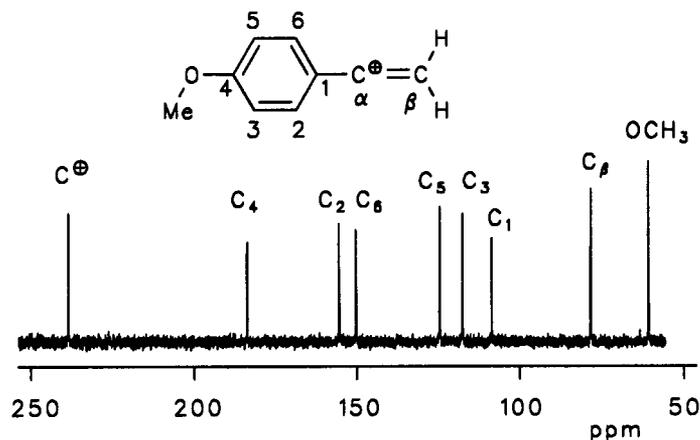


Fig. 4 100.6 MHz ¹³C NMR spectrum of α -(*p*-anisyl)vinylium cation **14** at -102 °C.

The experimentally determined torsion barrier for **13** (< 8 kcal mol⁻¹, 33 kJ mol⁻¹) and **14** (9.0 ± 1 kcal mol⁻¹, 37 ± 4 kJ mol⁻¹) are in reasonable agreement with ab initio molecular orbital calculations (6-31G) (8). Figure 5 shows the calculated geometry for the minimum structure of cation **14** and the transition state structure **14-TS** for the rotation of the methoxy group.

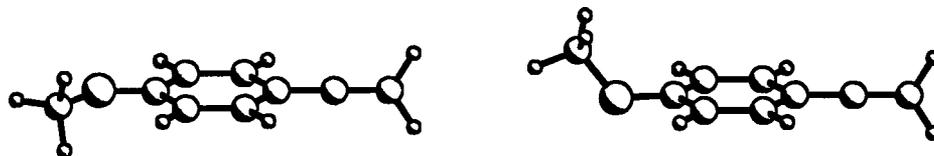
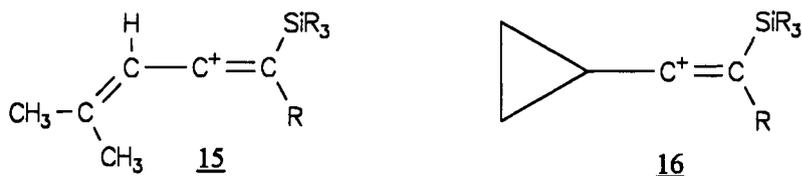


Fig. 5. Calculated geometry for cation structures, **14** and **14-TS**

The calculated geometrical data and the charge distribution for cation **14** and model structures β -SiH₃-**14** and β -CH₃-**14** show the effects of π resonance stabilization by the α -aryl substituent and hyperconjugative stabilization by the β -substituent. Even in highly π -stabilized α -anisyl carbocations, σ bond hyperconjugation contributes to the dispersal of positive

charge. The hyperconjugative stabilization effect of β -substituents follows the order silyl > alkyl > H. Comparing β -silyl substituted vinyl cations with different α -aryl substituents, like ferrocenyl-, anisyl-, mesityl-, and tolyl-groups, shows that the stabilizing effect of a β -silyl group is not constant but is dependent on the electron demand of the carbocation (10).

β -Silyl substituted dienyl cations 15 and α -cyclopropyl- β -silylvinyl cations 16 were also investigated both experimentally and computationally (11).



Cations of type 15 are stabilized by allyl resonance. The ^{13}C NMR chemical shift of the allyl position can be used to determine the hyperconjugational effect of a β -silyl group. For 15 with $\text{R} = \text{H}$ the allyl carbon is ~ 25 ppm less deshielded compared to the cation with CH_3 instead of SiR_3 . If the second substituent R at the β -carbon is a methyl group the hyperconjugative effect of the β -silyl group is enhanced, because more partial charge can be accommodated at C_β if $\text{R} = \text{CH}_3$ as compared to $\text{R} = \text{H}$. This leads to lower demand for allyl resonance stabilization. The chemical shift of the allyl carbon of 15 with $\text{R} = \text{CH}_3$ is ~ 36 ppm shielded compared to the β -dimethyl substituted vinylcation.

The barrier for rotation of the α -cyclopropyl ring in vinyl cations 16 is dependent on the hyperconjugative effect of the β -substituent. Similar to 15 in 16 an additional methyl group at the β -vinyl carbon enhances the stabilizing effect of the silyl group. The torsional barrier decreases from about 8.4 kcal (35 kJ mol^{-1}) in 16 ($\text{R} = \text{H}$) to 6.8 kcal mol^{-1} (28 kJ mol^{-1}) in 16 ($\text{R} = \text{CH}_3$).

Computational studies (MP2/6-31G*) for β - SiH_3 substituted model cations for 15 and 16 and for other vinyl cations with different α -substituents show the geometrical distortions accompanying β -silyl hyperconjugation (12). The $\text{C}_\beta\text{-Si}$ bond distance is elongated and the $\text{C}_\alpha\text{C}_\beta\text{Si}$ bond angle is reduced when the electron demand of the cation is increasing. An additional methyl group at the β -carbon has a pronounced effect of on the geometry as shown in Fig. 5. Comparing 16 ($\text{R} = \text{H}$) and 16 ($\text{R} = \text{CH}_3$), the $\text{C}_\beta\text{-Si}$ bond length is increased from 195.4 to 197.2 pm and the $\text{C}_\alpha\text{C}_\beta\text{Si}$ bond angle is reduced from 116° to 104° .



Fig. 5 Calculated Geometry for vinyl cation structures 16 ($\text{SiR}_3 = \text{SiH}_3$, $\text{C}_\beta\text{R} = \text{H}$ and CH_3)

Conclusions

For the first time β -silyl substituted carbocations were generated in solution. The NMR data confirm the stabilization of positive charge by a β -silyl substituent. The order of hyperconjugative stabilization of a positive charge by β -substituents is H < alkyl < silyl. The β silyl effect is not constant but dependent on the electron demand of the carbocation. The combined application of experimental and theoretical methods show that the chemical shifts the rotational barriers, determined experimentally and computationally, as well as the computed geometrical parameters and charges are useful tools to investigate the varying degree of π -conjugation and σ -hyperconjugative in these type of carbocations. In particular the results of quantum chemical calculations at levels of theory which include electron correlation (i.e. MP2/6-31G*) show that any stabilization of positive charge in carbocations by delocalization, may it be π -conjugative or σ -hyperconjugative, has more or less always geometrical consequences for the structure. The geometrical changes accompanying β -silicon hyperconjugation in carbocations are much more pronounced than for β -C-H or β b-C-C hyperconjugation. The term vertical stabilization, which implies no geometrical reorganization of the atoms, should no longer be used to describe β -silyl hyperconjugation in carbocations.

Acknowledgment

I gratefully acknowledge the contributions of my skillful coworkers and cooperation with colleagues. Their names are cited in the references. The work was supported by the Deutsche Forschungsgemeinschaft (DFG). Thanks go to the Japanese Society for the Promotion of Science (JSPS) for support of a visiting professorship at the Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University, Fukuoka, Japan.

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