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STABILIZATION IN THE ORDER I>Br>Cl AMONG TRIMETHYLSILYLMETHYL HALIDES, COMPARED TO CARBON ANALOGS. POSSIBLE ROLE OF ELECTRONEGATIVITY IN ORGANOSILICON CHEMISTRY

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ABSTRACT: Electronegativities may be used to rationalize the observation that the equilibrium, $CH_3(CH_2)_3I + (CH_3)_3SiCH_2Cl \rightleftharpoons CH_3(CH_2)_3Cl + (CH_3)_3SiCH_2I$, lies to the right.

I wish to report that halomethyltrimethylsilanes exhibit the <u>stabilization order I>Br>Cl</u> relative to alkyl halides, represented by butyl or pentyl halides. The stability order was revealed with the equilibrium or equation 1, established in the absence of solvent and in the presence of approximately 5 mole percent of C-8 to C-10 alkyltrimethylammonium chloride (Adogen[1]), was found to lie to the right. Quantitative results for this reaction and other related reactions which we investigated are given in Table I.

$$CH_3(CH_2)_3I + (CH_3)_3SiCH_2Cl \rightleftharpoons CH_3(CH_2)_3Cl + (CH_3)_3SiCH_2I \qquad (1)$$

We were prompted to carry out the above mentioned reactions by qualitative molecular orbital considerations which suggested that (as was subsequently observed) trimethylsilylmethyl halides, in equilibrium with carbon analogs, might show an inverse order of stability and reactivity relative to trimethylsilylhalides where the stability[2] and reactivity range[3] appears to be particularly large. Colin G. Pitt in a study of the role of hyperconjugation in group IV chemistry,[4] used CNDO-2 calculations, sometimes with inclusion of d orbitals, to estimate the energies and to obtain key atomic orbital coefficients of the groups CH_3, SiH_3, CH_2CH_3, CH_2SiH_3, and SiH_2CH_3. Pitt concluded that interactions involving hyperconjugation to unfilled orbitals of predominant s and p character were probably important. It was noted[4] that for compounds $R_3M{\cdot}MR_3'$, conjugation between vacant orbitals in R_3M and filled orbitals in MR_3' (σ^{-1}-σconjugation) is favored by alternating polarity, $R^{\delta-}$-$M^{\delta+}$-$M^{\delta-}$-$R^{\delta+}$.

For $(CH_3)_3SiCH_2I$ the effects described by Pitt may be pictured in terms of a four orbital model involving the anti or syn approach of $C^{\delta-}$-$Si^{\delta+}$ and $C^{\delta-}$-$I^{\delta+}$ fragments to form $C^{\delta-}$- $Si^{\delta+}$ $C^{\delta-}$- $I^{\delta+}$. Note that iodine is slightly electropositive relative to carbon on some commonly

Table I. Equilibrium Constants[a] for Halogen Interchanges of Alkyl Halides and Trimethylsilylmethyl Halides, 75.0°

Reactants			K or K-1
R in RX	X in RX	X in $(CH_3)_3SiCH_2X$	
$CH_3(CH_2)_3$	I	Cl	43[b]
$CH_3(CH_2)_3$	Cl	I	48[c]
$CH_3(CH_2)_3$	I	Br	12.7[b]
$CH_3(CH_2)_3$	Br	I	11.3[c]
$CH_3(CH_2)_3$	Br	Cl	4.9[b,d]
$CH_3(CH_2)_3$	Cl	Br	5.1[c,d]
$CH_3(CH_2)_4$	I	Cl	70
$CH_3(CH_2)_4$	I	Br	13.6

[a] Equilibrium constants were determined by integration of ^1H nmr spectra (90 MHz). Reactants were approximately equimolar.

[b] K for the forward reactions, eq. 1.

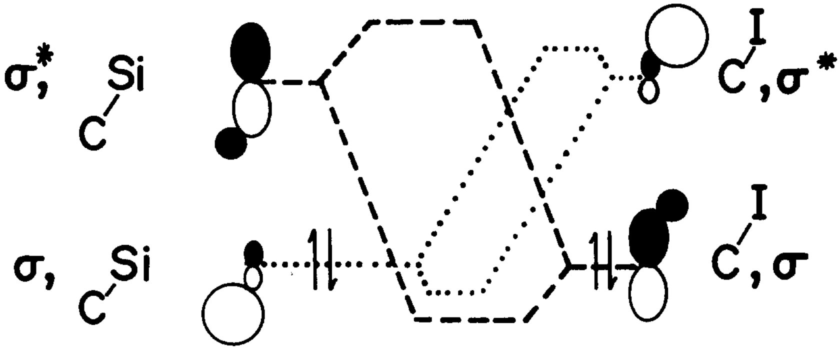
[c] K_{-1} for the reverse reaction. This is equal in principle to the preceding K value, except for minor solvent effects arising from small variations in concentrations.

[d] In the absence of solvent effects this would be equal to the quotient of the preceding values (i.e. 43/12.7 or 48/11.3).

used scales.[5] In the figure, the anti approach is shown using spherical terminal orbitals to represent group (alkyl) or atomic (hydrogen) orbitals of appropriate symmetry to interact with the p_z orbitals of the internal Si or C atoms. As a consequence of the electronegativities, the coefficients of hyperconjugating p_z orbitals are large in the filled C-I orbital and the vacant C-Si orbital, leading to a bias in favor of hyperconjugative stabilization by electron transfer from right to left as the figure is drawn. In the figure the sizes of the orbitals indicate the magnitudes of the coefficients.

A comparable diagram indicates a bias in favor of a dominant hyperconjugative stabilization from left to right in $CH_3(CH_2)_3Cl$, compared to that in $(CH_3)_3SiCH_2Cl$. The interactions in $(CH_3)_3SiCH_2I$ are pictured as similar to those in $(CH_3)_3Si\ddot{C}H_2^-$ (stabilization by Si) whereas those in $(CH_3)_3SiCH_2Cl$ are similar to those in $(CH_3)_3SiCH_2^+$ (destabilization by Si,[6a] although counterbalancing effects have been noted in $H_3SiCH_2^+$ [6b,c]).

Figure



Although the four orbital models are a convenient device to aid in remembering relative stabilities, it is recognized that the effects of coefficient sizes and the related overlap integrals often are overshadowed by other terms in quantum calculations. In addition, the role of n-π* (non-bonding to π*) interactions in halides[7a] and n-σ* interactions in sulfur stabilized carbanions (still controversial despite ab initio calculations[7b,7c]) are relevant to our study, as is a study of n-σ* interactions in silylketones.[8] For what it is worth, however, we note that coefficients in a three orbital model indicate a bias in favor of larger n-σ* interactions in $(CH_3)_3SiX$ than in $(CH_3)_3CX$, but in favor of larger interactions in $CH_3(CH_2)_3X$ than in $(CH_3)_3SiCH_2X$, in accord with the observed effects (reference 2 and this study).

Regardless of their origin, the stability relationships which we have observed indicate that ground state stability effects should be considered, along with transition state effects, in comparing reactivities of alkyl and silylmethyl halides, particularly when different halogens are involved. A case in point is the radical forming halogen abstraction reactions of $(CH_3)_3SiCH_2Cl$.[9] That the ground state effects may have some solvent dependence may be indicated by the relatively larger K value (70) for reaction of iodopentane with $(CH_3)_3SiCH_2Cl$. The longer chain constitutes a less polar solvent, since the neat halides serve as the solvent.

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