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SOLVOLYSIS OF 2-BROMO-2-TRIMETHYLSILYLPROPANE AND RELATED COMPOUNDS

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There are numerous instances in the literature where a series of carbon compounds has been studied and compared directly with an analogous system containing a silicon atom[1]. In most instances the differences between the two series of compounds can be explained by (1) the low electronegativity of silicon, (2) the large size of the silicon atom relative to carbon, and (3) the availability of low lying, empty d-orbitals on the silicon atom. We have also prepared such a series of compounds in an effort to compare the transmission of electrical effects by alkyl and silyl moieties which are adjacent to an incipient carbonium ion. We wish to report the synthesis of such a system along with data which lead to significant conclusions about the mode of stabilization of carbonium ions by both kinds of substituent groups.

We have prepared 2-bromo-2-trimethylsilylpropane (I)[2] by bromination of trimethylisopropylsilane, and also 2-bromo-2,3,3-trimethylbutane (II) by the addition of t-butylmagnesium chloride to acetone followed by hydrolysis to the alcohol and bromination with concentrated HBr. Both compounds were purified by successive sublimation and each was solvolyzed in 60% ethanol-water. The solvolysis of II has been investigated previously[3]. It leads to mainly elimination product, but with some substitution, and ionization to a carbonium ion is certainly the rate-determining step. Solvolysis of I in the presence of LiBr(0.1 M in 0.019 M silane) or NaOH(0.03 M in 0.012 M silane) leads to only a very slight increase in rate(k/k^{o}=1.1 and 1.4 respectively). Solvent dependence studies show a Winstein-Grunwald 'm' value[4] of 0.70 for the silane substrate in ethanol-water (60% to 85%

by volume). Analysis of the reaction mixture indicates that only the elimination product, isopropenyltrimethylsilane, is obtained. It is interesting to note that we do not obtain the same products as reported by O'Brien[5] for generation of the carbonium ion derivable from I in non-nucleophilic medium, namely, t-butyldimethylfluorosilane and trimethylfluorosilane. We believe that we are dealing with an E2 elimination, but one with considerable carbonium ion character. This belief arises largely from the fact that we observe no substitution product from solvolysis of I, whereas substitution does compete with elimination in solvolysis of II.[3]

The rate data along with the activation parameters for both compounds are given in Table I. The ratio of rate constants(k^{II}/k^{I}) at 25° is 38,000. Even if I is proceeding through a fully developed carbonium ion (E1), the rate difference is large, and we believe the factor of 38,000 to be only a minimum rate difference for carbonium ion formation in the two systems. It is also interesting that the ratio of k^{III}/k^{I} is only 1.

Table I Summary of Solvolysis Data[a]

Compound	$10^5k, sec^{-1}$					$\Delta H^{\ddagger}$,kcal/mole[c]	$\Delta S^{\ddagger}$,esu.[c]
	$25^{\circ\,b}$	50°	70°	80°	85°		
I	0.016	0.342	4.15	10.5	24.2	26.9	-1.2
	-9°	2°	15°	25°			
II	4.07	31.7	167	610		21.7	+2.6
				80°			
III(isopropylbromide)				10.8			

[a] Compounds run in 60% ethanol-water by volume(density=0.90412). Rates were determined titrimetrically. [b] Extrapolated value from the four rates at higher temperature. [c] Calculated for 25°.

A number of factors must certainly be involved in determining the relative rates, and probably the most obvious one is the expected steric acceleration in going from I to II due to shorter bond lengths in II. The observed difference in rates is much too large to be explained in terms of steric interactions alone. Although it is not possible to predict the magnitude of steric acceleration quantitatively, Brown[3] has made the significant observation that II undergoes solvolysis at a rate faster than t-butylbromide by a factor of only 2. t-Butylbromide may not be a good model for I, but even so it seems inconceivable that the rate difference of 38,000 could in any large measure be due to steric factors.

There is also the possibility of a 1,3-interaction[1,6] between the lone pairs of electrons on bromine and the empty d-orbitals of silicon which could materially affect the rate of solvolysis of I. Although this idea has not been completely ruled out, infrared data involving the carbon-bromine bond stretch($584cm^{-1}$ in I and $550cm^{-1}$ in II) seem to indicate that there is no particular ground state stabilization in the silyl system relative to the all carbon compound. We also feel that if a 1,3-interaction were involved, the entropy of activation would be more positive since the restriction of rotation in the ground state due to this interaction would be relieved in going to the transition state.

We believe that the major portion of the observed rate differences between I and II can be explained in terms of the absence of any stabilizing hyperconjugative effects from the trimethylsilyl group on the developing carbonium ion center. Hyperconjugation is generally accepted to be a highly stabilizing factor when an alkyl group is adjacent to a cationic center[7]. However, in the case of the trimethylsilyl group the large carbon-silicon bond lengths and probably other factors as well, such as displacement of electron density more toward carbon in the C-Si bonds, make significant interaction of the empty 'p' orbital on the carbonium ion center and the sigma electrons of the methyl-silicon bond unfavorable.

Based upon electronegativity values of carbon (ca. 2.5) and silicon (ca. 1.8)[8], it must be predicted that a positive inductive effect would be greater for the Me_3Si group than for the Me_3C group. This factor would act to accelerate the ionization of I relative to II. Recent data published by Traylor, however, seem to indicate that the inductive effect of the trimethylsilyl entity is minor[9]. We feel that we cannot asses the inductive effect quantitatively (because of factors to be mentioned shortly) but can say that the inductive effect appears to be minor here also, and in a system which should be crying for inductive stabilization.

From the work of Schleyer[10] we realize that there are complications in interpreting the rate data, since the rate for isopropylbromide is certainly solvent-assisted and the rate for I may be also, even though the 'm' value for I is significantly closer to unity than one observes for isopropyl systems. We cannot therefore conclude on the basis of the rate data alone that the Me_3Si group is not better at stabilizing a carbonium ion than is H. It does not appear, however, to be very significantly better, and if indeed the inductive effect of a Me_3Si group is small, it is only reasonable to conclude that it is even smaller for the more electronegative Me_3C group. It therefore appears that since I does not approach II in rate the major effect afforded to the incipient carbonium ion by the t-butyl group is a hyperconjugative effect and the inductive effect is minor indeed. The rate data presented here is to our knowledge the first data available which allows a comparison of the ability of an alkyl group to stabilize an adjacent cation with the ability of a much more electropositive substituent. The system has the potential for giving a means of separating the hyperconjugative and inductive effects of alkyl substituents.

We are extending our studies with systems of this type to help us gain a better understanding of the effect of the silicon atom adjacent to a carbonium ion center.

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