SOLVOLYSIS MECHANISM OF TERTIARY α-SILYL BROMIDES

FRANK K. CARTLEDGE and JOHN P. JONES

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803 (U.S.A.)

(Received July 25th, 1973)

Summary

Preparation and properties of compounds of the formula RMe_2SiCMe_2Br, (I) are reported. Solvolysis of (Ia) (R = Me) in aqueous ethanol results in elimination to produce isopropenyltrimethylsilane in high yield. Effects of solvent, added salts, and variation of R on the rates of solvolysis of (I) are rationalized in terms of a transition state involving substantial electron deficiency on the carbon atom adjacent to Si. When R is a substituted phenyl group, no evidence is apparent that there is phenyl participation in reaching the transition state, as has been proposed for analogous carbon compounds. Relative rates of solvolysis of (I) and carbon analogs are discussed in relation to carbonium ion stabilities.
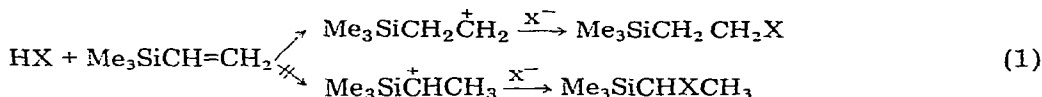
Introduction

Substituent effects associated with the presence of metalloid atoms in organic molecules have been investigated fairly extensively in recent years. Nevertheless, significant questions remain unanswered. Several approaches have been employed to elucidate the nature of electronic effects in organosilanes in which the silicon atom is in a position α or β to an unsaturated organic moiety [1—7]. Three kinds of effects are usually noted: (a) an electron donating inductive effect associated with the presence of the silicon atom either α or β to the site of unsaturation; (b) an electron withdrawing p—$d\pi$ interaction associated with α substitution; and (c) an electron donating hyperconjugation associated with β substitution. Different studies have sometimes given rise to different conclusions, particularly with respect to the relative importance of inductive donation versus p—$d\pi$ withdrawal with α silicon and inductive donation versus hyperconjugative donation with β silicon.

Studies of chemical reactivities have shown the dichotomy just noted. Essentially all early work in the area of organosilicon reactivity was carried out with the assumption that the positive inductive effect of a silyl substituent was significantly greater than that of an alkyl substituent, the assumption presumably be -

ing based on electronegativity differences. However, a number of experimental observations, including several which have been in the literature for some time, do not fit this interpretation.

Organic chemists have established beyond doubt that alkyl substituents stabilize *carbonium ions* and accelerate their formation in ionization processes. In contrast, there seems to be a reluctance for organosilanes to undergo reactions leading to cationic centers α to silicon. Neither the chloride, Me_3SiCH_2Cl, nor the iodide, Me_3SiCH_2I, reacts with refluxing ethanolic silver nitrate under the same conditions which produce copious precipitates of silver halide with similar primary alkyl halides [8]. A second example of this "anomaly" is the non-Markovnikoff addition of hydrogen halides under ionic conditions to vinylsilanes [9]. This observation contrasts reactivity at positions α and β to Si and has been rationalized

$$HX + Me_3SiCH{=}CH_2 \Big\langle \begin{array}{l} \nearrow\ Me_3SiCH_2\overset{+}{C}H_2 \xrightarrow{X^-} Me_3SiCH_2CH_2X \\ \searrow\ Me_3Si\overset{+}{C}HCH_3 \xrightarrow{X^-} Me_3SiCHXCH_3 \end{array} \tag{1}$$

[10] in terms of unusual stability, due to hyperconjugation, of the primary carbon carbonium ion with a β silyl substituent. Support for this view comes from the high reactivity of β-haloorganosilanes, which undergo solvolysis reactions (albeit with fragmentation) at high rates [11]. The importance of hyperconjugative stabilization of β-silylcarbonium ions is swelled to major proportions if one believes at the same time that inductive stabilization of an α-silylcarbonium ion should be a significant effect. If this is the case, then reaction 1 proceeds exclusively through a primary carbonium ion stabilized by C—Si hyperconjugation in preference to a secondary carbonium ion stabilized by induction.

We have been reluctant to adopt the view just stated and have sought alternative means of investigating the stability of α-silylcarbonium ions. We have chosen to take a classic approach to this problem through the solvolysis of tertiary alkyl substrates of the type $R(CH_3)_2SiC(CH_3)_2Br$, (I) which could be expected to undergo rate-determining ionization to an intermediate carbonium ion[*]. The mechanism of solvolysis of (I) is considered in the present paper.

Experimental

Unless otherwise stated, all preparative reactions were run in three-neck *round bottom flasks* equipped with a mechanical stirrer, reflux condenser, and an addition funnel. Glassware was flame-dried and flushed with argon prior to conducting the experiment under Ar. In general the solvents were dried by refluxing over calcium hydride and distilled, with middle fractions from the distillations being used in the reactions. Where mixed solvents were used, the percent composition quoted is volume percent at $25°$. Melting points were taken on a Drechsel melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained routinely on a Varian A60A, and infrared

---

[*]For a preliminary communication of this work see ref. 12.

(IR) spectra were recorded using a Beckman IR-5. Mass spectral data were collected using a Varian M-66.

2-Bromo-2-trimethylsilylpropane

Lithium sand (4.26 g, 0.66 g-atom) was prepared by rapidly stirring a suspension of melted lithium in mineral oil at ca. 200°. The mixture was allowed to cool to room temperature and washed with dry pentane. The lithium was then placed in a 1000 ml three-neck flask equipped in the usual manner, along with 200 ml of dry pentane which had been stored over sulfuric acid prior to distillation. Freshly distilled 2-chloropropane (24.1 g, 0.33 mole) was placed in the addition funnel and 5 ml was allowed to drain into the lithium—pentane solution to initiate the reaction. Once the reaction had started, 250 ml of the dry olefin-free pentane was added to the addition funnel and this solution was added to the lithium over a period of about 2 h. After the addition was complete, the mixture was stirred for 2 h and was immediately added via an addition funnel to neat trimethylchlorosilane (27 g, 0.25 mole) contained in a 500 ml three-neck flask. The isopropyllithium was added to the silane over a period of about 1 h and stirring was continued overnight. The reaction mixture was then hydrolyzed in a saturated aqueous solution of NH_4Cl, washed with water, and the pentane layer placed over $CaCl_2$ for 12 h. The pentane was then removed with a rotary evaporator and the remaining material was distilled through a six-inch Vigreux column to yield 15 g (55%) of the desired isopropyltrimethylsilane (V): b.p. 87 - 88°/760 mmHg (lit. [13] b.p. 87°/737 mmHg).

In a 100 ml three-neck flask was placed 3.42 g (0.029 mole) of (V) which was then heated to about 60°. Bromine (4.63 g, 0.029 mole) was added at such a rate as to maintain a light red solution. After the addition of bromine was complete, the solid was immediately sublimed under vacuum at room temperature. Pure product was obtained after twice subliming the silane. The yield of 2-bromo-2-trimethylsilylpropane was 3.46 g (64%), m.p. 121 - 123° in a sealed tube (lit. [14] m.p. 124°).

2-Bromo-2-(aryldimethylsilyl)propanes

The aryl derivatives in Table 2 were all prepared by reacting 2-bromo-2-(chlorodimethylsilyl)propane with the appropriate aryllithium reagent. The procedure for the phenyl derivative is representative. To a 500 ml three-neck flask containing neat dimethyldichlorosilane (0.50 mole, 64.5 g) was added isopropyllithium (0.50 mole as determined by acid titration) prepared as described previously. After the addition was complete, the mixture was stirred for 2 h and then filtered under N_2 through a sintered glass funnel. The lithium chloride remaining in the filter was washed several times with dry pentane. The filtrate was then distilled through an 18-inch Vigreux column until the pentane was removed, and the remaining mixture was distilled through a 6 inch Vigreux column to yield 25 g (37%) of chlorodimethylisopropylsilane: b.p. 110 - 112°/760 mmHg (lit. [13] 109.8 - 110°/738 mmHg).

Chlorodimethylisopropylsilane (49 g, 0.36 mole) was brominated and purified in exactly the same manner as described for 2-bromo-2-trimethylsilylpropane. The yield of 2-bromo-2-(chlorodimethyl)silylpropane was 68.5 g, 91%; NMR (CCl_4) δ 0.38 (s, 1, CH_3Si), 1.60 ppm (s, 1, CH_3C).

A solution of 0.1 mole of phenyllithium in ether was prepared in the usual manner and added immediately to 2-bromo-2-(chlorodimethylsilyl)propane (21.5 g, 0.10 mole) dissolved in ether and contained in a 500 ml three-neck flask. The addition of the lithium reagent was complete in 30 min and the mixture was stirred for 2 h. The reaction mixture was then added to an ice-cold solution of saturated aqueous ammonium chloride, washed with ice water, and the ether layer placed over $CaCl_2$ for 12 h. The ether was then removed with a rotary evaporator and the residue distilled through an annular Teflon spinning band column. Pure compound (15 g, 60%) was collected at 110 - 111° /5 mmHg.

Product studies

2-Bromo-2-trimethylsilylpropane (3.86 g, 0.0198 mole) was placed in a 100 ml single-neck flask equipped with a reflux condenser which was connected to a CCl_4 —Br_2 trap. To the flask was added 60 ml of 80% aqueous ethanol and this mixture was refluxed for 4 days. Daily monitoring of the CCl_4 —Br_2 trap by NMR gave no indication that alkene was being evolved during the time of refluxing. To the reaction mixture was then added 20 ml of distilled water causing two layers to form in the reaction flask. The NMR spectrum of the bottom layer indicated that only ethanol, water, and starting material were present. The whole mixture was added to a separatory funnel and the two layers separated. The aqueous ethanol layer was discarded after being washed 5 times with 10 ml portions of pentane. The pentane was placed over $CaCl_2$ overnight to dry. Distillation yielded approximately 0.60 g of starting material and a minute amount of isopropenyltrimethylsilane (identified by NMR but not isolated). It was apparent from the odor of the pentane that it still contained some of the starting material even after distillation. The top layer in the separatory funnel was placed over molecular sieves to dry. The NMR spectrum of this layer indicated it to be pure isopropenyltrimethylsilane [15]* (1.10 g, 60%); NMR (CCl_4) δ 0.07 (s, 9, CH_3Si), 1.80 (t, 3, CH_3C), 5.21 (m, 1, HC=C), 5.50 ppm (m, 1, HC=C).

Kinetic measurements

A weighed quantity of the silyl halide (sufficient to yield a solution approximately 0.014M in substrate) was dissolved in 125 ml of aqueous ethanol. Portions of 5 ml were then pipetted into 5 ml ampoules which were sealed and placed in a constant temperature oil bath at 80.0 ± 0.1° maintained by a Sargent thermonitor. At definite time intervals an ampoule was removed from the bath and placed immediately in an ice bath to stop the reaction. The contents of the ampoule were then poured into 25 ml of absolute ethanol at 0°. The reactions were usually followed to at least 80% completion with generally 10 points determined per run. The HBr formed was titrated with standard (ca. 0.01 M) sodium hydroxide using cresol red as the indicator. The original concentration of the halide was determined by allowing the reaction to proceed at 80° through about 10 half-lives and determining in the usual manner the amount of HBr pro-
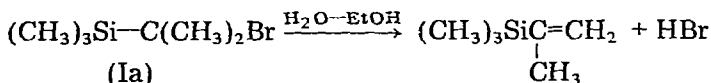
---

*The NMR data cited contain a typographical error. The data given here have been confirmed in a private communication from Professor Seyferth (1972).

duced. Agreement between calculated and found amount of HBr in the infinity titration was in each case within ± 0.2 ml or 2 to 3%.

All reactions showed good first order kinetics throughout the runs. Correlation coefficients from least-squares treatment of the kinetic data were 0.995 or better. The rate constants reported are averages of two or more runs. Reproducibility among runs was in general better than ± 4%, the worst single example showing a deviation of 7.7% from the mean.

Results and discussion

Mechanistic criteria which allow the conclusion that ionization is the rate-determining step in the solvolysis of alkyl halides are probably the most extensively investigated in organic chemistry. A number of these criteria has been applied to the present system. An important experiment in any kinetic work is the determination of reaction products, but it is particularly relevant with (I), since it is not uncommon in reactions of nucleophiles with organosilanes that nucleophilic attack occurs at the silicon atom. This behaviour has been observed with α-halosilanes [16]. When (Ia) (R = CH₃) was refluxed in 80% ethanol for 4 days, the only detectable* reaction product was isopropenyltrimethylsilane. In contrast, the methanolysis of the compounds, $(CH_3)_3CC(CD_3)_2X$ (X = Cl and

$$(CH_3)_3Si-C(CH_3)_2Br \xrightarrow{H_2O-EtOH} (CH_3)_3SiC=CH_2 + HBr$$
$$\text{(Ia)} \qquad\qquad\qquad\qquad \underset{CH_3}{|}$$

3,5-dinitrobenzoate), is reported [17] to produce substitution product as well as elimination product. If a limiting carbonium ion mechanism were involved in solvolysis of both silicon and carbon analogues, it is perhaps surprising that (Ia) should give no substitution product, since the cation produced from (Ia) should be more sterically open to nucleophilic attack at carbon than the tert-butyl-dimethyl cation.

A recent report [18] describes the generation in non-nucleophilic medium of what is believed to be the carbonium ion which correspond to that produced in the solvolysis of (Ia). The products observed are totally different from those produced by (Ia) in aqueous ethanol. The reaction pathways for a carbonium ion in nitromethane are not necessarily those expected for the same carbonium
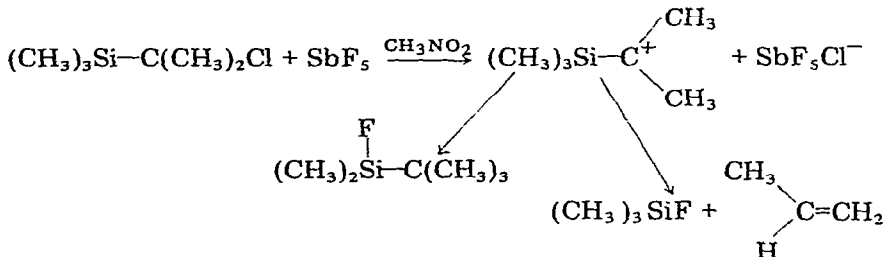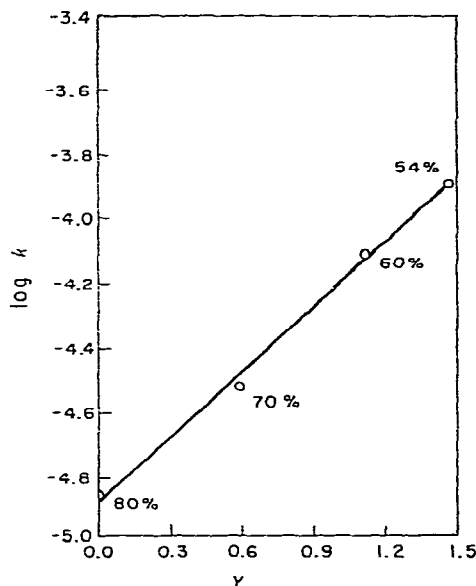

Fig. 1. Log of solvolysis rate of (Ia) vs. Winstein-Grunwald Y values for various ethanol-water mixtures. Percentages are by volume.

ion in aqueous ethanol. Nevertheless, the observation of a completely different pathway is suggestive that a limiting carbonium ion mechanism is not operating in aqueous ethanol.

Solvent effects

Effects on the rate of solvolysis of (Ia) produced by changes in solvent composition and temperature are given in Table 1. Treatment of the data in aqueous ethanol by means of the Grunwald-Winstein mY relationship [19] gives the plot shown in Fig. 1. Least-squares determination of the slope gives a value of $m = 0.66$. This value, although larger than that usually observed [20] for solvolysis

TABLE 1

RATE CONSTANTS FOR SOLVOLYSIS OF Me_3SiCMe_2Br

Solvent[a]	Temp. (°C)	Added salt	$k \times 10^5 (sec^{-1})$[b]
54% EtOH/H$_2$O	50		0.34 ± 0.02
54% EtOH/H$_2$O	70		4.1 ± 0.1
54% EtOH/H$_2$O	80		10.2 ± 0.1
54% EtOH/H$_2$O	85		24.2 ± 0.4[c]
54% EtOH/H$_2$O	80	0.03 M NaOH[d]	15.6 ± 0.4
60% EtOH/H$_2$O	80		6.4 ± 0.2
70% EtOH/H$_2$O	80		2.5 ± 0.1
80% EtOH/H$_2$O	80		1.15 ± 0.05
65% MeOH/H$_2$O	80		13.2 ± 0.2
65% MeOH/H$_2$O	80	0.10 M LiBr[e]	15.5 ± 0.3

[a]Percentage by volume at 25°. [b]Data is reported with the standard deviation among runs. [c]Temperature dependence of the rate in 54% EtOH/H$_2$O led to the activation parameters: $\Delta H^{\ddagger} = 27$ kcal/mole; $\Delta S^{\ddagger} = -1.2$ cal/(mole·K). [d]Initial concentration of silane, 0.012 M. [e]Initial concentration of silane, 0.019 M.

of secondary alkyl bromides in aqueous ethanol, is nevertheless significantly less than 1.0 and suggestive of solvent assistance. Solvolysis of (Ia) in the presence of added 0.10 M LiBr shows no common ion rate depression (k/k^0 = 1.1). This is, of course, the expected result unless a "free" carbonium ion is being generated. Solvolysis in the presence of added strong nucleophile (0.03 M NaOH in 0.012 M silane) also led to only minor rate acceleration (k/k^0 = 1.5). Clearly hydroxide ion is not participating to any major extent under these conditions. The magnitudes of both rate changes in the presence of added salts seem understandable in terms of ionic strength effects. Temperature dependence of the rate of solvolysis of (Ia) led to activation parameters given in Table 1. The values are not remarkable, being in a reasonable range for solvolytic processes.

Arylsilanes

A series of compounds (I) (R = substituted phenyl) was prepared for the purpose of determining the effects of substituents on silicon on the solvolysis rate. The properties of these compounds are noted in Table 2. NMR spectra of the derivatives are as expected. Except for one case, the mass spectra show highly specific cleavage resulting in loss of $C(CH_3)_2Br$, leaving $R(CH_3)_2Si^+$ as the base peak. That a silyl cation should be the base peak is not surprising but in all except one case, the single mode of cleavage predominates to the extent that there

TABLE 2

PROPERTIES OF COMPOUNDS WITH THE FORMULA $R(CH_3)_2SiC(CH_3)_2Br$

R	B.p. ($^{\circ}$C/mmHg)	Analysis found (calcd.)(%)		^{1}H NMR^a		Mass spectrum^b
		C	H			
CH_3	121-123^c	36.78 (36.92)	7.70 (7.75)	CH_3Si,	0.12	73(100)
				CH_3C,	1.70	196(<1)
C_6H_5	110-111/5	51.65 (51.36)	6.89 (6.66)	CH_3Si,	0.48	135(100)
				CH_3C,	1.68	199(5)
				Arom,	7.2-7.7	201(5)
						258(<1)
p-$CH_3OC_6H_4$	85/0.1	49.79 (50.17)	6.65 (6.66)	CH_3Si,	0.42	108(100)
				CH_3C,	1.63	165(65)
				CH_3O,	3.72	137(22)
				Arom,	7.12	288(<1)
p-$CH_3C_6H_4$	94/10	53.30 (53.13)	7.21 (7.07)	CH_3Si,	0.45	149(100)
				CH_3C,	1.59	272(<1)
				CH_3Ar,	2.23	
				Arom,	7.25	
m-$CH_3C_6H_4$	60-61/0.1	53.39 (53.13)	7.24 (7.07)	CH_3Si,	0.45	149(100)
				CH_3C,	1.68	272(<1)
				CH_3Ar,	2.35	
				Arom,	7.2-7.6	
p-FC_6H_4	57-58/0.1	47.94 (48.00)	5.94 (5.86)	CH_3Si	0.45	153(100)
				CH_3C,	1.68	276(<1)
				Arom,	7.30	
p-ClC_6H_4	70-71/0.05	45.25 (45.29)	5.54 (5.53)	CH_3Si,	0.45	169(100)
				CH_3C,	1.65	292(<1)
				Arom,	7.39	
p-BrC_6H_4	96-97/0.2	39.20 (39.30)	4.79 (4.79)	CH_3Si,	0.52	215(100)
				CH_3C,	1.68	337(<1)
				Arom,	7.40	
m-ClC_6H_4	79-80/0.15	45.19 (45.29)	5.57 (5.53)	CH_3Si,	0.45	169(100)
				CH_3C,	1.68	292(<1)
				Arom,	7.2-7.6	

^{a}Assignment, δ (ppm) relative to TMS. All peaks other than those in the aromatic region are singlets. Relative areas are those expected. ^{b}m/e value followed by relative abundance at 70 eV. ^{c}M.p. in a sealed tube.

TABLE 3

RATE CONSTANTS FOR SOLVOLYSIS OF $XC_6H_4(CH_3)_2SiC(CH_3)_2Br$[a]

X	$k \times 10^5 (sec^{-1})$[b]
p-CH_3O	9.57 ± 0.41
p-CH_3	7.60 ± 0.41
m-CH_3	6.06 ± 0.37
H	5.17 ± 0.13
p-F	3.87 ± 0.08
p-Cl	3.04 ± 0.03
p-Br	2.86 ± 0.01
m-Cl	1.83 ± 0.15

[a]First order rate constants measured in 54% $EtOH/H_2O$ at 80°. [b]Data is reported with the standard deviation among runs.

is not another fragment with a relative abundance greater than 5% of the base peak.

Rates of solvolysis of the aryl derivatives (Table 3) correlated well with Hammet σ constants [21] (Fig. 2) with a ρ value of -1.1. ρ is small, as one would expect considering the spatial separation between reaction site and substituent, but nevertheless clearly negative in keeping with the expectation of significant charge development in the transition state for solvolysis. Brown and Kim have published rate data for the solvolysis in 80% aqueous ethanol of four compounds of the formula, $XC_6H_4(CH_3)_2CC(CH_3)_2Cl$ (III) [17]. A Hammett plot showed decided curvature, particularly with the p-MeO substituent. Substituents seem to have a slightly greater effect on rates of solvolysis of the chlorides (III) when compared with the silanes in the present work. The comparison
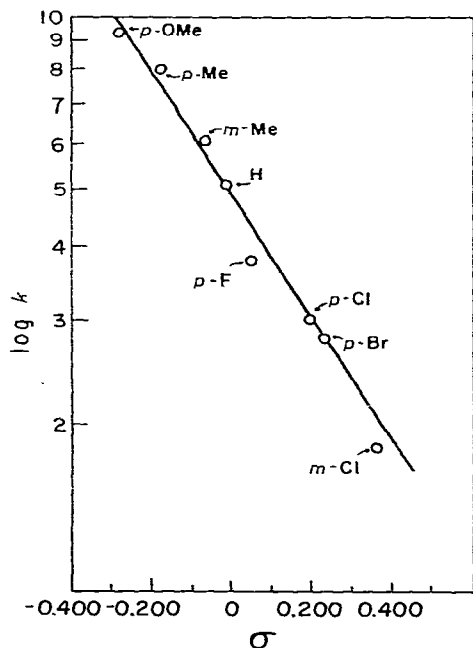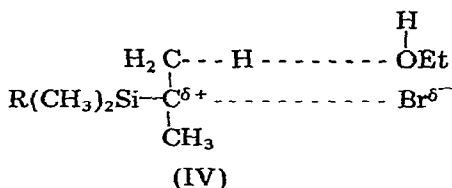

Fig. 2. Log of solvolysis rate of $XC_6H_4Me_2SiCMe_2Br$ vs. σ.

cannot be a direct one, because we do not know the extent of mechanistic differences between the two series. Brown and Kim postulate for (III) that solvolysis is assisted by nucleophilic participation of the aryl group, particularly with the *p*-MeO substituent, and that the varying extent of participation with various substituents gives rise to the curved Hammett plot observed. With a wider range of substituents than was used in that study, and including *p*-MeO, we observe no curvature in the Hammett plot for the silanes. Clearly there is no reason to postulate aryl participation in the solvolysis. It is not surprising that aryl participation is smaller with the silanes, since the aryl group is substantially further removed in space from the reaction site.

Conclusions

The elimination with (I) in aqueous ethanol proceeds through a transition state which we believe can be represented by (IV). There is clearly a substantial

$$
\begin{array}{c}
\overset{\displaystyle H}{|} \\
H_2 C\text{- - -}H\text{- - - - - - - -}OEt \\
R(CH_3)_2Si\text{---}\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}^{\delta+}\text{- - - - - - - - - -}Br^{\delta-} \\
\end{array}
$$

(IV)

amount of positive character at the carbon adjacent to silicon in the transition state, although the extent of nucleophilic participation by solvent is not completely clear.

We have reported previously [12] that solvolysis of $(CH_3)_3CC(CH_3)_2Br$ proceeds 38000 times faster than the reaction of its silicon analog, (Ia). We believe that the most reasonable interpretation of this data is that the trimethylsilyl group is substantially poorer at stabilizing an adjacent carbonium ion than is a tert-butyl group. Such an argument based on rate comparisons is only valid when it can be shown that two reactions are substantially identical in mechanism, i.e., transition states are very similar, and that there is not a ground state effect of major proportions in one of the compounds. The mechanistic results presented here make clear that the first of the two criteria is met for a comparison of (Ia) and its carbon analog. The uncertainty concerning the extent of solvent assistance is important in a quantitative comparison but not a qualitative one. The second criterion is the more troublesome one in the present work. With presently available data we are not able to eliminate the possibility that there is a significant interaction between non-bonding electron pairs on bromine (a 1,3-interaction [22]) and the empty $3d$ orbitals on Si, or that there is an interaction involving the C—Br σ electrons. Further work aimed at elucidating ground state interaction in α-halosilanes is in progress.

References

1 E.A.V. Ebsworth, in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. I, Part I, Marcel Dekker, New York, N.Y., 1968, Ch. 1;
C.J. Attridge, Organometal. Chem. Rev. Sect. A, 5 (1970) 323.
2 A.J. Smith, W. Adcock and W. Kitching, J. Amer. Chem. Soc., 92 (1970) 140;
W. Adcock, S.Q.A. Rizvi, W. Kitching and A.J. Smith, ibid, 94 (1972) 369;
J. Lipowitz, ibid., 94 (1972) 1582;
W. Adcock, S.Q.A. Rizvi and W. Kitching, ibid., 94 (1972) 3657.
3 O.W. Steward, J.E. Dziedzic, J.S. Johnson and J.O. Frohliger, J. Org. Chem., 36 (1971) 3480.
4 A.R. Bassingdale, C. Eaborn, D.R.M. Walton and D.J. Young, J. Organometal. Chem., 20 (1969) 49;
H.J. Berwin, Chem. Commun., (1972) 237.
5 B.E. Cooper and W.J. Owen, J. Organometal. Chem., 29 (1971) 33.
6 W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 7476;
H. Bock and H. Alt, ibid., 92 (1970) 1569;
C.G. Pitt, J. Organometal. Chem., 23 (1970) C35;
C.G. Pitt and H. Bock, Chem. Commun., (1972) 28.
7 Y. Vignollet, J.C. Maire, A.D. Baker and D.W. Turner, J. Organometal. Chem., 18 (1969) 349;
U. Weidner and A. Schweig, ibid., 39 (1972) 261;
U. Weidner and A. Schweig, Angew. Chem. Int. Ed. Engl., 11 (1972) 146;
P. Mollere, H. Bock, G. Becker and G. Fritz, J. Organometal. Chem., 46 (1972) 89;
P.E. Rakita, M.K. Hoffman, M.N. Andrews and M.M. Bursey, ibid., 49 (1973) 213.
8 F.C. Whitmore and L.H. Sommer, J. Amer. Chem. Soc., 68 (1946) 481.
9 C. Eaborn and S. Parker, J. Chem. Soc., (1956) 126.
10 C. Eaborn and R.W. Bott, in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. I, Part I, Marcel Dekker, New York, N.Y., 1968, p. 446.
11 L.H. Sommer and G.A. Baughman, J. Amer. Chem. Soc., 83 (1961) 3346;
A.W.P. Jarvie, A. Holt and J. Thompson, J. Chem. Soc. B, (1970) 746;
M.A. Cook, C. Eaborn and D.R.M. Walton, J Organometal. Chem., 24 (1970) 301.
12 F.K. Cartledge and J.P. Jones, Tetrahedron Lett., (1971) 2193.
13 L.H. Sommer, D. Bailey, J. Gould and F. Whitmore, J. Amer. Chem. Soc., 76 (1954) 801.
14 A.D. Petrov and G.I. Nikishin, Zh. Obsch. Khim., 26 (1956) 1233.
15 D. Seyferth and L.G. Vaughan, J. Organometal. Chem., 1 (1963) 138.
16 C. Eaborn and J. Jeffrey, J. Chem. Soc., (1957) 137.
17 H.C. Brown and C.J. Kim, J. Amer. Chem. Soc., 90 (1968) 2082.
18 T.J. Hairston and D.H. O'Brien, J. Organometal. Chem., 29 (1971) 79.
19 E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 70 (1948) 846.
20 J.L. Fry, C. Lancelot, L.K.M. Lam, J.M. Harris, R.C. Bingham, D.J. Raber, R.E. Hall and P.V.R. Schleyer, J. Amer. Chem. Soc., 92 (1970) 2538.
21 L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, N.Y., 1940, p. 144ff.
22 O.W. Steward and O.R. Pierce, J. Amer. Chem. Soc., 83 (1961) 4932;
J.M. Bellama and A.G. MacDiarmid, J. Organometal. Chem., 24 (1970) 91.