

ORGANOSILICON COMPOUNDS. XCV.*

STRUCTURE AND SOLVENT EFFECTS IN SOLVOLYSIS OF (2-CHLOROETHYL)ARYLDIMETHYLSILANES

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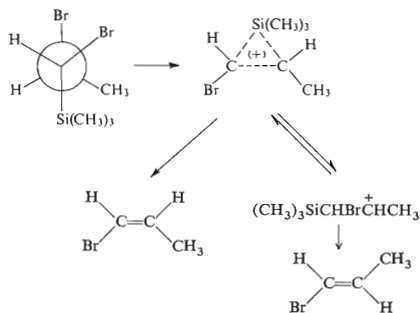
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A kinetic study was made of the solvolysis of (2-chloroethyl)aryldimethylsilanes of the type $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ ($\text{X} = p\text{-CH}_3, \text{H}, p\text{-F}, p\text{-Cl}, m\text{-Cl}, m\text{-CF}_3$) in aqueous ethanolic (95–50%) and methanolic (96.8–60%) media at 50°C. It was found that with the exception of 95% ethanol and 96.8% methanol the rate data can be well correlated with σ substituent constants. The rate constants for individual members of the series were also linearly dependent on Grunwald-Winstein Y values. The deviations from the Hammett correlation observed with the derivatives substituted by electron-donating substituents in 95% ethanol and 96.8% methanol were discussed in terms of a mechanism involving two independent solvolytic paths, the formation of a non-classical carbonium ion and a solvent-assisted process.

Within the framework of a systematic study of structure-reactivity relationships in the chemistry of organofunctional silicon derivatives in the previous work¹ we dealt with acid catalysed solvolysis of (2-hydroxyethyl)aryldimethylsilanes. As a continuation of this study we now report the results of a kinetic study of solvolysis of structurally related substances, (2-chloroethyl)aryldimethylsilanes. The aim of this study was to contribute to the knowledge of the mechanism of this reaction. Some general features of the reaction had already been established by Sommer and Baughman²: the solvolysis proceeds with evolution of ethylene, is electrophilic and is not base-catalysed. From the kinetic point of view, it is first-order in the substrate. As found in a study of solvent effects on solvolysis rate, its transition state is as ionic as the transition state of the solvolysis of tert-butyl chloride. This led the authors to conclude that the reaction proceeds via formation of a siliconium ion in the rate determining step. Later, the transition state was proposed to be a silyl-substituted carbonium ion³, a four-centre state⁴, and the state in which the solvent is coordinated to the silicon atom of the substrate⁵. Finally, from the stereochemistry of the solvolysis of erythro-1,2-dibromopropyltrimethylsilane, which was found to be highly *trans*-stereospecific, Jarvie and coworkers⁶ concluded that, at least in this case, the solvolysis proceeds as an E_1 -like elimination (Scheme 1). The participation of the silicon during the cleavage of the carbon-halogen bond, *i.e.* the formation of a non-classical, silacyclopropenium ion, was proved also in the solvolytic elimination reaction of (2-bromoethyl-2,2 d_2)trimethylsilane⁷. In contrast to previous mechanisms, the last one is thus well experimentally documented. However, it is not yet clear whether it is a general mechanism for solvolyses of 2-halogenoethylsilanes in protic media.

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We hoped that some information concerning this problem could also be provided by a study of structure effects by means of extrathermodynamic relations such as *e.g.* the Hammett equation. This approach, although not so safe as the stereochemical study, has already been used with success by Schleyer and coworkers in the chemistry



SCHEME I

of carbonium ions^{8,9}. In this work we have chosen a series of (2-chloroethyl)aryldimethylsilanes of the type $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ ($\text{X} = p\text{-CH}_3, \text{H}, p\text{-F}, p\text{-Cl}, m\text{-Cl}, m\text{-CF}_3$) as model compounds and followed kinetically their solvolysis at 50°C in several aqueous methanolic and aqueous ethanolic media of varying ionizing power. Grunwald-Winstein Y value¹⁰ of the media varied in the former case from -0.722 to $+1.492$ and in the latter from -1.287 to $+1.65$.

EXPERIMENTAL

(2-Chloroethyl)aryldimethylsilanes were prepared by the reaction of corresponding 2-hydroxyethyl derivatives¹ with thionyl chloride, using the procedure reported by Baughman³. Their purity was checked by g.l.c. (Pye Argon Chromatograph, 20% Silicone E 301 or 20% Apiezon APL on Celite 545, $160\text{--}190^\circ\text{C}$ oven temperature, 15 ml/min nitrogen flow rate). Their structure was confirmed by IR and NMR spectroscopy. The yields, physical properties and elemental analyses of the compounds are presented in Table I.

Kinetic measurements were carried out at $50 \pm 0.05^\circ\text{C}$, using the same procedure as in the previous work¹. The measurements were made with $3\text{--}7$ mg of $0.5\text{--}2M$ solution of the 2-chloroethyl derivative in anhydrous methanol or ethanol and 3 ml of the solvent saturated with ethylene. The volume of the ethylene evolved during the reaction was followed to the complete conversion of the starting derivative to the products, and the so obtained value was used to calculate the rate constant¹ k_1 . The exception were very slow solvolyses in the media of very low ionizing power (Table II). In this case the measurements were carried out with $0.01\text{--}0.03$ mol of the substrate and the reaction was followed only to $20\text{--}30\%$ conversion. The rate constants were determined by differential method with the use of theoretical volume of the evolved ethylene, which was

calculated from the weighted amount of the 2-chloroethylsilane. Rate constants k_1 , obtained with the average relative error of $\pm 4\%$, are presented in Table II.

RESULTS AND DISCUSSION

In agreement with Sommer and Baughman², the solvolysis of the series studied proceeds as a first-order reaction, and that with all compounds and in all the solvents

TABLE I
Yields and Physical Properties of (2-Chloroethyl)aryldimethylsilanes $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$

X	Yield, %	B.p., °C n_D^{25}	Formula m.w.	Calculated/Found	
				% C	% H
H	21.5	79—81/1 ^a	$\text{Si}_1\text{C}_{10}\text{H}_{15}\text{Cl}_1$ 198.8	60.42	7.61
		1.5188		60.52	7.63
<i>p</i> -CH ₃	47.2	99—102/2	$\text{Si}_1\text{C}_{11}\text{H}_{17}\text{Cl}_1$ 212.8	62.09	8.05
		1.5182		62.27	8.00
<i>p</i> -F	42.0	72—74/1	$\text{Si}_1\text{C}_{10}\text{H}_{14}\text{Cl}_1\text{F}_1$ 216.8	55.40	6.51
		1.5053		55.65	6.43
<i>p</i> -Cl	26.0	111—112/2	$\text{Si}_1\text{C}_{10}\text{H}_{14}\text{Cl}_2$ 233.2	51.51	6.05
		1.5316		51.86	6.14
<i>m</i> -Cl	32.5	84—87/0.5	$\text{Si}_1\text{C}_{10}\text{H}_{14}\text{Cl}_2$ 233.2	51.51	6.05
		—		51.22	6.07
<i>m</i> -CF ₃	53.3	71—72/1 ^b	$\text{Si}_1\text{C}_{11}\text{H}_{14}\text{Cl}_1\text{F}_3$ 266.8	49.52	5.29
		1.4740		49.80	5.32

^a Lit.³ records b.p. 85—90°C/3 Torr. ^b Lit.³ records b.p. 69—71°C/0.7 Torr.

TABLE II
Correlations of $\log k_1$ of Solvolysis of (2-Chloroethyl)aryldimethylsilanes $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{Si}\cdot\text{CH}_2\text{CH}_2\text{Cl}$ at 50°C with Y Values

X	95.0—50.0% C ₂ H ₅ OH		96.8—60.0% CH ₃ OH	
	<i>m</i>	$\log k_0$	<i>m</i>	$\log k_0$
<i>p</i> -CH ₃	0.73	—3.892	0.64	—3.530
H	0.80	—4.187	0.75	—3.861
<i>p</i> -F	0.94	—4.497	0.90	—4.163
<i>p</i> -Cl	0.98	—4.627	0.90	—4.391
<i>m</i> -CF ₃	0.87	—5.076	0.89	—4.804

used. Dependence of rate constants k_1 on structure is graphically represented in Figs 1 and 2. From the figures it is obvious that with the exception of 95% ethanol and 96.8% methanol the effect of substituents on solvolysis rate can be well described by Hammett relation, which shows that all members of the series are solvolysed by the same mechanism. A similar situation has been found by us also in the acid catalysed solvolysis of (2-hydroxyethyl)aryldimethylsilanes¹. From the reasons discussed in the previous work¹ such a correlation indicates that not the silicon-carbon bond (to give a silicon ion⁵), but the carbon-chlorine bond is cleaved in the rate determining step of the reaction. A relatively high reaction constant, ρ , is indicative of the interaction of the silicon with the electron-deficient carbon of the C—Cl bond, since so large effects of substituents could hardly be expected if they were transferred to the reaction centre through the alkylene chain. A more complex situation arises, however, in the media with low content of water (Fig. 1, curve 5, and Fig. 2, curve 4). The curvature of the $\log k - \sigma$ plots indicates that here solvolysis proceeds through two independent paths. As we have not found any change in the kinetics of the reaction, both paths should be first order in the substrate.

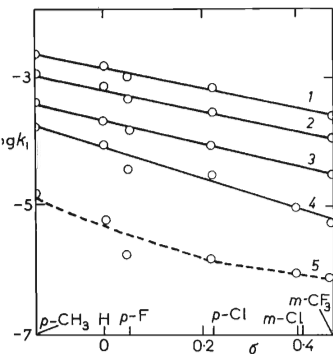


FIG. 1

Dependence of $\log k_1$ of Solvolysis of 2-Chloroethylsilanes of the Type $\text{XC}_6\text{H}_4\text{.}(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ in Aqueous Ethanol on σ

Aqueous ethanol (Y value¹¹); 1 50% (1.72), 2 60% (1.12), 3 70% (0.60), 4 80% (0.00), 5 95% (-1.29).

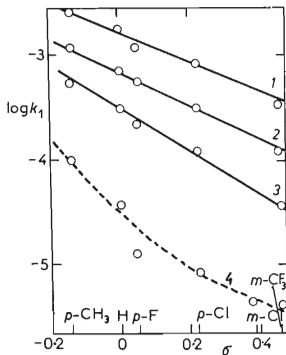


FIG. 2

Dependence of $\log k_1$ of Solvolysis of 2-Chloroethylsilanes of the Type $\text{XC}_6\text{H}_4\text{.}(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ in Aqueous Methanol on σ

Aqueous Methanol (Y value¹¹); 1 60% (1.49), 4 69.5% (1.02, ref.¹²), 3 80.0% (0.38), 4 96.8% (-0.72, ref.¹⁰).

One of the processes might be the formation of a non-classical carbonium ion¹³⁻¹⁶. As to the other process, it seems highly improbable that it would involve the formation of a carbonium ion or the ion pair¹⁷. Such assumption would not account for the fact that the sensitivity of the reaction toward polar effects of substituents decreases in the case of the derivatives substituted by electron-attracting groups (e.g. the ρ constant for *p*-chloro, *m*-chloro, and *m*-trifluoromethyl derivatives is roughly -1.2 in 95% ethanol and -1.5 in 96.8% ethanol, whereas in 80% ethanol it is -2.3 , and in 80% methanol -2.0).

The reaction constant increases with decreasing ionizing power of the medium, quite in harmony with the generally accepted assumption that the sensitivity of a reaction toward polar effects of substituents increases with decreasing polarity of medium. This trend is followed by the *p*-methyl derivative and the parent compound even in the media in which the curvature of the $\log k - \sigma$ plot is observed. This indicates that not these derivatives, but the derivatives containing electron-attracting groups behave „anomalously“. The small ρ constant for the latter derivatives shows that their solvolysis proceeds predominantly *via* transition state of low polarity. This could be either a four-centre state⁴ or a transition state in which the cleavage of the C—Cl bond is accompanied by more or less simultaneous formation of the bond between the silicon and the solvent.

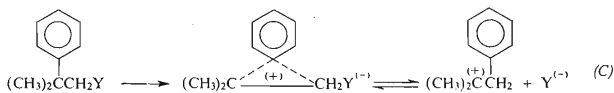
Both possibilities fulfil the experimentally found first order in the substrate and cannot be thus distinguished kinetically. The formation of both transition states would be facilitated by electronegative substituents. Based on the current knowledge, the reaction with nucleophilic participation of the solvent seems to be more probable in this case than a four-centre process. The latter has so far been observed only for gas-phase reactions of organosilicon compounds and reactions in nonpolar solvents⁴. Furthermore, another factor which, along with substituent effects, determines the proportion of the solvent-assisted process, is the nucleophilicity of the solvent. It is to be expected that this process will be more important in more nucleophilic solvents, *i.e.* its proportion will increase with decreasing ionizing power of the solvolytic medium. Our results agree with this assumption. As follows from Table II, rate constants of solvolysis of all the compounds studied decrease with decreasing ionizing power of the medium in accordance with Grunwald–Winstein equation¹⁰ (*I*)

$$\log(k_1/k_0) = mY, \quad (I)$$

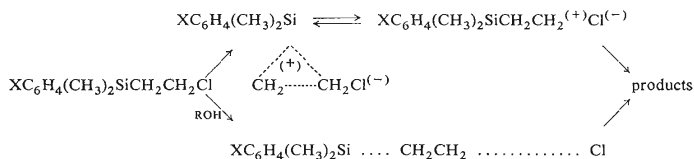
where *Y* is the measure of ionizing power of the solvent and *m* is the constant characterizing sensitivity of the reaction toward the change in the ionizing power of the medium.

It is noteworthy that solvolysis of 2-chloroethyl derivatives studied is less sensitive to changes in polarity of the reaction medium than the solvolysis of tert-butyl chloride ($m = 1$), and the *m* values are close to these observed in solvolysis of neophyl chloride,

which proceeds *via* formation of a non-classical phenonium ion^{18,19} (in aqueous methanol at 50°C $m = 0.833$ and in aqueous ethanol $m = 0.790$, equation (C)).



In conclusion, our results can be best interpreted in terms of a mechanism involving two independent solvolytic paths. Both proceed *via* rate-determining cleavage of the C—Cl bond, former with and the latter without participation of the solvent (Scheme 2). The proportion of the solvent-assisted process increases with increasing nucleo-



R = H, alkyl

SCHEME 2

phily of a solvent and with increasing electronegativity of the substituents attached to the aromatic ring. Nearly in all media studied, owing to their high ionizing power, the first process plays a predominant role. The solvent-assisted process becomes important only in media of low ionizing power, especially in the solvolysis of the compounds substituted by electronegative groups.

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