

ORGANOSILICON COMPOUNDS. XCIV.*

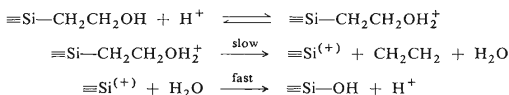
ACID-CATALYSED SOLVOLYSIS
OF (2-HYDROXYETHYL)ARYLDIMETHYLSILANESJ. VENCL^a, J. HETFLÉŠ^b, P. KUČERA^b, J. ČERMÁK^a and V. CHVALOVSKÝ^b^a Research Institute of Organic Syntheses, Pardubice - Rybitví and^b Institute of Chemical Process Fundamentals,

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Rate constants of the solvolysis of (2-hydroxyethyl)aryldimethylsilanes of the type $\text{XC}_6\text{H}_4(\text{CH}_3)_2\cdot\text{SiCH}_2\text{CH}_2\text{OH}$ ($\text{X} = p\text{-CH}_3\text{O}, p\text{-CH}_3, m\text{-CH}_3, \text{H}, p\text{-F}, p\text{-Cl}, m\text{-Cl}, m\text{-CF}_3$) in 50% aqueous methanol were measured at 40° and 50°C. The reaction was catalysed with 4·15M- H_2SO_4 . The dependence of the rate constants on the structure of studied compounds was discussed in terms of the earlier proposed mechanisms of the reaction.

Within the framework of a broader study of organofunctional silicon derivatives^{1,2} in the present work we deal with the acid catalysed solvolysis of (2-hydroxyethyl)aryldimethylsilanes. This reaction was first studied by Miller³ who suggested that it proceeds via the rate determining formation of siliconium ion (Scheme 1). While the equilibrium protonation of the substrate was proved by the observed linear dependence of solvolysis rate on the H_0 function of the medium,



SCHEME 1

no evidence in favour of the second step proposed has been presented. On the basis of the stereochemical and kinetic study of elimination reactions of related organofunctional derivatives it was suggested⁴ that a carbonium ion, rather than a siliconium one, is formed during the reaction.

We believed that a study of the relationship between the structure of (2-hydroxyethyl)-substituted silanes and their reactivity could provide further information concerning this problem. We started from the assumption that if the formation of a siliconium ion were rate determining, the rate data should be linearly correlated with σ^+ constants⁵, derived from the rates of solvolyses of the carbon analogues, *p*-substituted cumyl chlorides, rather than with Hammett σ constants. This assumption

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was based on two presumptions: 1. Substituent constants derived for carbon derivatives are generally applicable also to structure-reactivity correlations for organosilicon compounds and 2. silicon atom possesses a similar ability to delocalize the positive charge on the aromatic system as does carbon atom. The first presumption was verified by a number of workers (*cf.*⁶ and references therein). Also the other presumption is not unreasonable, since in a mass spectroscopic study of fragmentation of substituted phenyldimethylethoxysilanes the ionisation potentials of the formation of aryldimethylsilylium ions were found to be well correlated with σ^+ substituent constants.* The effect of the structure of the 2-hydroxyethyl derivatives on their reactivity has already been studied by Miller³. Unfortunately, the minimum number of the derivatives investigated (phenyl- and *m*-trifluoromethylphenyldimethyl(2-hydroxyethyl)silane), which did not make possible to draw any convincing conclusions on the validity of any correlation, and also the choice of the substituents were inappropriate with regard to the aim of the present work (for both substituents σ constant is identical with σ^+ constant). For this reason we prepared series of (2-hydroxyethyl)aryldimethylsilanes of the type $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{OH}$ and studied their solvolysis under experimental conditions reported by Miller³.

EXPERIMENTAL

Temperature data are uncorrected. The purity of prepared compounds was checked by g.l.c., their structure by IR and NMR spectroscopy.

Aryldimethylchlorosilanes and *aryldimethyl(chloromethyl)silanes* were prepared in the usual way^{6,7}.

(*Carboxymethyl*)phenyldimethylsilanes were prepared *A.* by the procedure worked out in our laboratory⁷, *B.* by the procedure reported by Fessenden and Fessenden⁸, and *C.* by the procedure reported by Gold and coworkers⁹. The yields and physical properties of the products are presented in Table I. *A.* A mixture of 26 g (0.4 g-atom) of the zinc powder activated by heating with iodine *in vacuo*, 44 g (0.26 mol) of ethyl bromoacetate, 30 ml of dry diethyl ether, and a small amount of an aryldimethylchlorosilane was brought to boil. After few iodine crystals had been added, strongly exothermic reaction started, which was controlled by cooling the reaction mixture with water. After the exothermic reaction had subsided, a solution of 0.25 mol of aryldimethylsilane in 20 ml of dry diethyl ether was added such that the reaction mixture was kept under reflux. Then the reaction mixture was refluxed for another 2 h, filtered, the filtrate was diluted with the ether to the total volume of 500 ml and washed twice with 200 ml of water. After drying the ether layer over magnesium sulphate and removal of the solvent, the residue was distilled through a 20 τP column. *B.* A mixture of 31.7 g (0.5 g-atom) of the zinc activated by iodine and 500 ml of dry benzene was brought to boil and then 75 ml of the solvent was removed by distillation while stirring. To the refluxed mixture, several drops of a solution of 83.5 g (0.5 mol) of ethyl bromoacetate and 0.4 mol of aryldimethylchlorosilane in 200 ml of diethyl ether-benzene (1 : 1) were added, and the reaction was further carried out as described in paragraph *A.* After the

* Communicated to us by Dr C. Shorr, Institut für Physikalische Chemie, DAW, Berlin, DDR.

reaction was complete, the reaction mixture was decomposed by pouring into a mixture of 400 ml of 1M-HCl and crushed ice and worked up in the usual fashion. C. To a warmed mixture of 13.2 g (0.55 mol) of magnesium turnings, several iodine crystals and 50 ml of dry diethyl ether, 0.5 mol of (chloromethyl)dimethylarylsilane was added and the mixture was refluxed for another 1 h. The solution of the so prepared Grignard reagent was filtered and added in one portion to a solution of 60 g (0.55 mol) of ethyl chloroformate in 400 ml of dry diethyl ether and the mixture was refluxed for 18 h. Then it was cooled and decomposed by pouring onto crushed ice, the ether layer was separated, washed with 100 ml of saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulphate. The product was obtained by distillation.

(2-Hydroxyethyl)aryldimethylsilanes were obtained by reduction of (carboethoxymethyl)aryldimethylsilanes with lithium aluminium hydride, following the procedure reported by Miller³,

TABLE I

Preparation and Properties of (Carboethoxymethyl)aryldimethylsilanes $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{COO}\cdot\text{C}_2\text{H}_5$

X	Procedure	Yield %	B.p., °C/Torr n_D^{25}	Formula m. w.	Calculated/Found	
					% C	% H
H	A	35.0	84/1	$\text{Si}_1\text{C}_{12}\text{H}_{18}\text{O}$	64.84	8.16
	B	39.5	1.4944 ^a	222.3	64.79	8.15
<i>m</i> -CF ₃	A	40.0	95—97/2	$\text{Si}_1\text{C}_{13}\text{H}_{17}\text{O}_2\text{F}_3$	53.77	5.90
	B	49.0	1.4590 ^b	290.4	53.70	6.07
<i>m</i> -Cl	B	25.7	112—115/3	$\text{Si}_1\text{C}_{12}\text{H}_{17}\text{O}_2\text{Cl}_1$	56.13	6.67
	C	48.6	1.5099	256.8	55.76	6.65
<i>p</i> -Cl	A	42.0	107/1	$\text{Si}_1\text{C}_{12}\text{H}_{17}\text{O}_2\text{Cl}_1$	56.13	6.67
	B	46.1	1.5098	256.8	55.76	6.71
<i>p</i> -F	A	42.0 ^c	92—93/1	$\text{Si}_1\text{C}_{12}\text{H}_{17}\text{O}_2\text{F}_1$	59.95	7.13
	B	72.1	1.4820	240.4	59.87	7.07
<i>m</i> -CH ₃	A	0.0	111—114/3	$\text{Si}_1\text{C}_{13}\text{H}_{20}\text{O}_2$	66.05	8.52
	C	54.1	1.4978	236.4	65.68	8.38
<i>p</i> -CH ₃	A	0.0	112—115/4	$\text{Si}_1\text{C}_{13}\text{H}_{20}\text{O}_2$	66.05	8.52
	B	15.3	1.4970	236.4	65.73	8.37
	C	55.8				
<i>p</i> -CH ₃ O	B	6.0	96—98/3	$\text{Si}_1\text{C}_{13}\text{H}_{20}\text{O}_3$	61.86	7.98
	C	60.2	1.5060 ^d	252.4	61.60	7.86

^a n_D^{25} 1.4947 (lit.⁸), ^b n_D^{20} (lit.³ records 1.4590), ^c reaction time 10 h, ^d n_D^{20} (lit.³ records 1.5060).

except that the unreacted lithium aluminium hydride was decomposed by adding water in small portions to the reaction mixture until the hydroxides formed quickly set down. The filtrate was then worked up in the usual fashion. The yields, elemental analyses and physical properties of prepared compounds are presented in Table II.

Kinetic measurements. A solution of 4.15M-H₂SO₄ in 50% aqueous methanol was used as the reaction medium. The concentration of sulphuric acid was determined titrimetrically on phenolphthalein. With regard to the fact that the concentration of the acid changed on standing (by c. 0.008M per day), fresh solutions were prepared every third day. In kinetic measurements the volume of the ethylene evolved was followed in dependence on time by a manometric method on Warburg apparatus provided with modified reaction vessels. This apparatus was already used in a kinetic study of solvolysis of organosilicon hydrides¹⁰ and described in detail elsewhere¹¹. To the shorter arm of the two-armed reaction vessel were weighed 3–17 mg of 0.5–2.0M solution of a (2-hydroxyethyl)aryldimethylsilane in dry methanol, and to the longer arm were pipeted

TABLE II
Yields and Properties of (2-Hydroxyethyl)aryldimethylsilanes XC₆H₄(CH₃)₂SiCH₂CH₂OH

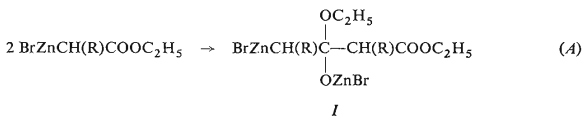
X	Yield %	B.p., °C/Torr <i>n</i> _D ²⁵	Formula m. w.	Calculated/Found	
				% C	% H
H	80.0	120–122/8 1.5185 ^a	Si ₁ C ₁₀ H ₁₆ O ₁ 180.3	66.70 66.59	8.96 8.85
<i>m</i> -CF ₃	85.0	110–112/7 1.4720 ^b	Si ₁ C ₁₁ H ₁₅ O ₁ F ₁ 248.3	53.25 53.20	6.11 6.05
<i>m</i> -Cl	56.8	114–116/3 1.5340	Si ₁ C ₁₀ H ₁₅ O ₁ Cl ₁ 214.8	55.91 56.01	7.04 7.04
<i>p</i> -Cl	86.0	107/1 1.5302	Si ₁ C ₁₀ H ₁₅ O ₁ Cl ₁ 214.8	55.91 56.26	7.04 6.92
<i>p</i> -F	90.0	116–117/4 1.5020	Si ₁ C ₁₀ H ₁₅ O ₁ F ₁ 198.3	60.72 60.64	7.63 7.51
<i>m</i> -CH ₃	53.1	94–96/1 1.5180	Si ₁ C ₁₁ H ₁₈ O ₁ 194.4	67.96 67.74	9.33 9.34
<i>p</i> -CH ₃	41.0	110–111/2 1.5192	Si ₁ C ₁₁ H ₁₈ O ₁ 194.4	67.96 68.14	9.33 9.25
<i>p</i> -CH ₃ O	76.0	115–116/3 1.5248 ^c	Si ₁ C ₁₁ H ₁₈ O ₂ 210.4	62.79 62.69	8.62 8.57

^a *n*_D²⁵ 1.5184 (lit.³), ^b *n*_D²⁵ 1.4724 (lit.³), ^c *n*_D²⁵ 1.5245 (lit.³).

3 ml of 4·15M-H₂SO₄ in 50% aqueous methanol saturated with ethylene. The solutions were warmed to the reaction temperature, then mixed and shaken (120 swings per min). The reaction temperature was maintained within $\pm 0\cdot5^\circ\text{C}$, the time was read with the accuracy of ± 1 s. The reaction was usually followed to 100% conversion of the silane. The pseudo-first order rate constants k_1 were calculated from the slope of the linear dependence of $\log v_\infty/(v_\infty - v_t)$ on time, where v_∞ and v_t is the experimental volume of the ethylene evolved at 100% conversion and at time t , respectively. The experimental v_∞ value differed from the theoretical value (calculated from the weighed amount of the corresponding (2-hydroxyethyl) derivative) less than 5%. Rate constants are averages of at least three measurements. The relative error in determination of rate constant k_1 did not exceed ± 3 per cent.

RESULTS AND DISCUSSION

For preparing (carboxymethyl)silanes several routes have been reported⁷⁻⁹, each being employed in a very limited number of cases. For this reason we were first interested in the scope and limitations of these methods. As it is obvious from Table I, of the three methods employed in this work, the most general one is by Gold and coworkers⁹, which is based on the reaction of dimethylarylsilylmethylmagnesium chlorides with ethyl chloroformate. The procedure used earlier in our laboratory⁷ as well as that reported by Fessenden and Fessenden⁸ gave good yields only with the derivatives substituted by electronegative groups (*p*-F, *m*- and *p*-Cl, and *m*-CF₃). We have found that the course of the reaction depends here not only on the way of the activation of the zinc, but also on the amount of the iodine used. Neither efficient activation did make it possible to obtain *p*- and *m*-tolyl and *p*-anisyl derivatives in satisfactory yields, obviously because of the low reactivity of starting chlorosilanes toward the organozinc reagent. This assumption is supported by the fact that on preparation of these compounds by the method by Fessenden and Fessenden⁸ we obtained, along with symmetrical tetramethyldisiloxane, the product of solvolysis of the starting chlorosilane during work-up of the reaction mixture, also a substance, which on the basis of elemental analysis and IR and NMR spectra was identified with the corresponding dimethylarylethoxysilane. So, for example, on preparation of (carboxymethyl)dimethyl(*m*-tolyl)silane we obtained dimethyl(*m*-tolyl)ethoxysilane in 16% yield. Similarly, Fessenden and Fessenden⁸ observed the formation of the ethoxy derivative (14%) in the preparation of (carboxymethyl)triphenylsilane. This fact was regarded as surprising⁸, since the ethyl bromoacetate used did not contain ethanol. The formation of this compound during the reaction has not been explained. It is likely that the ethoxy derivative is formed as a consequence of the coupling reaction between two molecules of the organozinc reagent (reaction (A)), which leads to the formation of intermediate *I*, the structure of which was proved by Dippy and Parkins¹². The alkoxy silane then arises from the reaction of the starting chlorosilane with this intermediate; a similar displacement of the halogen by the alkoxy group was already observed in the reaction of dimethyl-dichlorosilane with ethyl orthoformate¹³. This assumption is further supported



by the fact that in the preparation of (carboethoxymethyl) (*p*-methoxyphenyl)dimethylsilane we found the product to be contaminated with a small amount of ethyl ester of β -ketobutyric acid, the structure of which was confirmed by NMR spectroscopy.

In harmony with the observation by Miller³ the solvolysis of the studied series of 2-hydroxyethyl derivatives in 4.15M-H₂SO₄ – 50% aqueous methanol proceeds as a first order reaction, with most derivatives over more than three half-times (*i.e.* over 85% conversion of the silanes to the products). The pseudo-first order rate constants were independent of the initial concentration of the substrate. So, for example, the change of the initial concentration of (2-hydroxyethyl)phenyldimethylsilane from $5.78 \cdot 10^{-6}$ mol/l to $1.72 \cdot 10^{-5}$ mol/l (threefold increase) brought about the change in the rate constant of only 7% (k_1 was $1.03 \cdot 10^{-1} \text{ s}^{-1}$ and $0.96 \cdot 10^{-3} \text{ s}^{-1}$, respectively).

A different situation arises in solvolysis of *p*-anisyl- and *p*-tolyl derivatives at both temperature chosen (40°C and 50°C) and for *m*-tolyl derivative at the higher temperature. Here, the satisfactory agreement between the calculated and the experimental volume of the evolved ethylene has not been found. Furthermore, even when the experimental value was used to calculate k_1 , deviations from the first order dependence were observed already after 1–2 half-times. The great difference between the calculated and the experimental volume (50%) made it impossible to determine k_1 for solvolysis of *p*-anisyl derivative for both temperatures and for *p*-tolyl derivative for the temperature of 50°C.

The rate constants k_1 are presented in Table III. In an attempt to correlate them

TABLE III

Rate Constants k_1 of Solvolysis of (2-Hydroxyethyl)aryldimethylsilanes of the Type XC₆H₄·(CH₃)₂SiCH₂CH₂OH in 4.15-M H₂SO₄–50% Aqueous Methanol

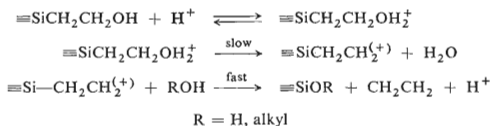
X	$k_1 \cdot 10^4 \text{ (s}^{-1}\text{) at}$		X	$k_1 \cdot 10^4 \text{ (s}^{-1}\text{) at}$	
	40°C	50°C		40°C	50°C
<i>p</i> -CH ₃	11.11	—	<i>p</i> -Cl	5.04	17.20
<i>m</i> -CH ₃	12.86	26.01	<i>m</i> -Cl	2.85	9.20
<i>H</i>	9.96	37.87	<i>m</i> -CF ₃	1.84	5.26
<i>p</i> -F	7.41	21.99			

with σ^+ constants we found that there is virtually no correlation between these two quantities. The rate constants can be correlated, however, with Hammett σ substituent constants, deviations being observed only with both tolyl derivatives. These deviations cannot be accounted for by the greater error in determination of the rate constants for these compounds (10%). It seems likely that they can be attributed to the easy dearylation of these compounds in the acid medium used, which leads to the formation of the less reactive, symmetrical bis(2-hydroxyethyl)tetramethyldisiloxane. A similar situation was already observed with the *p*-anisyl derivative by Miller³ who found that the reactivity of this derivative is comparable to that of the bis-(2-hydroxyethyl)disiloxane. The rate of this cleavage reaction, which competes with solvolysis, strongly depends on the kind of the substituent on the aryl group and increases with increasing electropositivity of substituents, the reaction constant ρ being -4 up to -5 , cf.¹⁴.

With the exclusion of the data influenced by the above reason, the dependence of the reactivity on the structure of the studied compounds can be expressed by the following equations which were obtained by the least squares method: for 40°C $\log k_1 = -3.02 - 1.44\sigma$; for 50°C $\log k_1 = -2.47 - 1.60\sigma$. Theoretically unexpected¹⁵ increase of the reaction constant with temperature is too small to be discussed.

These results do not comport with the mechanism proposed by Miller³, which involves a siliconium ion in the rate determining step (Scheme 1). In such a case the correlation of the rate data with σ constants would indicate that the positive charge is localised on the silicon and is not transferred in an appreciable extent to the aromatic ring. This is however highly improbable, since the phenyl-silicon bond shows significant (*p-d*) π character^{16,17}. The low value of the constant could at first sight be taken as further support for this assumption, since for the formation of dimethylbenzylcarbonium ion its value is usually within the range of -4 to -5 . The situation here is however less straightforward, since the rate determining step of the solvolysis is preceded by the equilibrium protonation of the substrate³. Although the reaction constants of both processes could be expected to have the negative signs (both processes are facilitated by substituents enhancing electron density on the reaction centre), their magnitude is at the moment difficult to estimate. A number of other indirect observations⁴ are at variance with the idea on the formation of a siliconium ion in solvolytic reactions, the most important being the α -deuterium isotope effect in the solvolysis of (2-hydroxyethyl)trimethylsilane^{18,19}.

In conclusion, our results indicate that the reaction proceeds *via* rate determining formation of a silyl-substituted carbonium ion, which in the subsequent step undergoes fast solvolytic cleavage by the solvent (Scheme 2). It cannot be ruled out (in view of a relatively small magnitude of the ρ constant) that the cleavage of the C—OH bond is facilitated by a partial delocalization of the positive charge on the carbon of this bond to the silicon, similarly as in the case of solvolytic eliminations of 2-halo-enoethyl-substituted silanes²⁰.



SCHEME 2

REFERENCES

1. Pola J., Bažant V., Chvalovský V.: This Journal 38, 1055 (1973).
2. Hetflejš J., Svoboda L., Jakoubková M., Chvalovský V.: This Journal 38, 717 (1973).
3. Miller R. A.: *Thesis*. Pennsylvania State University, Philadelphia 1957.
4. Jarvie A. W. P.: *Organometal. Chem. Rev. A*, 6, 153 (1970).
5. Okamoto Y., Brown H. C.: *J. Am. Chem. Soc.* 79, 1913 (1957).
6. Mareš F., Hetflejš J., Chvalovský V.: This Journal 35, 2831 (1970).
7. Kučera P.: *Thesis*. Institute of Chemical Technology, Prague 1967.
8. Fessenden R. S., Fessenden J. S.: *J. Org. Chem.* 32, 3535 (1967).
9. Gold J. R., Sommer L. H., Whitmore F. C.: *J. Am. Chem. Soc.* 70, 2874 (1948).
10. Čermák J.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1963.
11. Hetflejš J., Mareš F., Chvalovský V.: This Journal 30, 1643 (1965).
12. Dippy J. F. J., Parkins J. C.: *J. Chem. Soc.* 1951, 1570.
13. Shorr L. M.: *J. Am. Chem. Soc.* 76, 1390 (1954).
14. Nasielski J., Planchon M.: *Bull. Soc. Chim. Belges* 69, 123 (1960).
15. Jaffé J. J.: *Chem. Rev.* 53, 191 (1953).
16. Chatt J., Williams A. A.: *J. Chem. Soc.* 1954, 4103.
17. Chvalovský V.: *Pure Appl. Chem.* 13, 231 (1966).
18. Exner O.: *Chem. listy* 53, 1302 (1959).
19. Jarvie A. W. P., Holt A., Thompson J. J.: *J. Chem. Soc. B*, 746 (1970).
20. Jarvie A. W. P., Holt A., Thompson J. J.: *J. Chem. Soc. B*, 852 (1969).

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