Journal of Organometallic Chemistry, 82 (1974) 17—20

THE UNCATALYSED ETHANOLYSIS OF $(XC_6H_4)Me_2SiNMePh$ COMPOUNDS

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(Received June 21st, 1974)

Summary

Rates of uncatalysed cleavage of the compounds $(XC_6H_4)Me_2SiNMePh$ where X = H, *p*-OMe, *p*-Me, *m*-Me, *m*-Cl, or *p*-Cl, have been measured for solvolysis by solutions of sodium acetate in ethanol. Electron release by X increases the rate of the reaction, and there is an excellent correlation with the σ-constants of the X groups ($\rho = -0.96$). The mechanism is discussed in the light of this.

Introduction

Previous studies of the solvolysis of *N*-triorganosilylanilines have concentrated on the acid- and base-catalysed reactions, but a significant contribution by the spontaneous process, involving the neutral solvent molecules, has been demonstrated [1—3]*. To obtain information about the nature of the transition state in this process, we have studied the rates of solvolysis of some $XC_6H_4Me_2SiNMePh$ compounds in ethanol containing sodium acetate.

Results and discussion

For two representative $XC_6H_4Me_2SiNMePh$ compounds, viz. those with X = H and *p*-Cl, the rates of solovolysis were measured over a wide range of sodium acetate concentrations (the ionic strength being maintained constant with lithium perchlorate). The results are shown in Table 1, and it will be seen that acid-catalysed process (i.e. catalysis by ethoxonium ions produced by autoionization of the solvent) is marked at the lowest sodium acetate concentrations, but is insignificant at concentrations in the 8×10^{-4} to 16×10^{-4} *M* range. The base-catalysed process appears to make a small contribution at much higher concentrations.

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* In Table 1 of ref. 2, the formula $m\text{-}ClC_6H_4NEtSiEt_3$ should read $m\text{-}ClC_6H_4NHSiEt_3$.

TABLE 1

DEPENDENCE ON THE SODIUM ACETATE CONCENTRATION OF THE OBSERVED FIRST ORDER RATE CONSTANTS FOR THE SOLVOLYSIS OF $(XC_6H_4)Me_2SiNMePh$ COMPOUNDS IN ETHANOL CONTAINING SODIUM ACETATE AT 50.2°

10^4 $[NaO_2CCH_3]$ (*M*)[a]	0.50	0.92	2.00	4.00	8.00	16.00	54	100
$10^3 k(X = H)$ (s^{-1})	40	18.4	11.5	10.2	8.10	8.5	9.3	11.5
$10^3 k(X = p\text{-Cl})$ (s^{-1})	28	15.7	9.5	7.3	5.3	4.9	6.0	6.1

[a] Ionic strength maintained at 0.05 with $LiClO_4$.

For the other $XC_6H_4Me_2SiNMePh$ compounds, the rates were measured only at 8 × 10^{-4} and 16 × 10^{-4} *M* sodium acetate concentrations; the results are shown in Table 2 as first order rate-constants, k, and as rates k_{rel}, relative to that of the parent compound with X = H. The absence of significant differences between the rates at the two concentrations confirmed that for all of them only the spontaneous process was contributing at these concentrations. Values of log k give an excellent straight line when plotted against the Hammett σ-constants, the slope, ρ, being -0.96 and the correlation coefficient, r, being 0.998. (A plot against σ^0 is as good within the limits of uncertainty, and has $\rho = -1.03$, $r = 0.988$.) For the compounds with X = *m*-Me or *p*-Me the rates were measured at 30.1° as well as at 50.2°; the temperature coefficient corresponds with a very small activation energy of ca. 2 kcal $mole^{-1}$.

The spontaneous process can be represented most simply as involving the two-step sequence shown in eqns. 1 and 2, with step 2 rate-determining.

$$ArMe_2SiNMePh + EtOH \rightleftarrows ArMe_2Si\overset{+}{N}HMePh + EtO^- \qquad (1)$$

$$ArMe_2Si\overset{+}{N}HMePh + EtO^- \rightarrow ArMe_2SiOEt + NHMePh \qquad (2)$$

The very low activation energy implies a highly unfavourable entropy of activa-

TABLE 2

OBSERVED FIRST ORDER RATE CONSTANTS, k, FOR THE SOLVOLYSIS OF $(XC_6H_4)Me_2SiNMePh$ COMPOUNDS IN ETHANOL CONTAINING SODIUM ACETATE AT 50.2°

X	$10^4[NaO_2CCH_3]$[a] (*M*)	10^3k (s^{-1})	Mean 10^3k (s^{-1})	k_{rel}
m-Cl	8	3.9	3.8	0.46
	16	3.7		
p-Cl	8	5.3	5.1	0.61
	16	4.9		
H	8	8.1	8.3	1.00
	16	8.5		
m-Me	8	10.4[b]	10.7	1.29
	16	11.0		
p-Me	8	12.0[c]	12.3	1.48
	16	12.6		
p-OMe	8	15.3	15.3	1.84
	16	15.3		

[a] Ionic strength maintained at 0.05 with $LiClO_4$. [b] At 30.1°, $10^3k = 8.5\ s^{-1}$ ($E_{act} \approx 2$ kcal mol^{-1}).
[c] At 30.1°, $10^3 k = 9.8\ s^{-1}$ ($E_{act} \approx 2$ kcal mol^{-1}).

tion (i.e. a very low frequency factor), which is consistent with the proposed sequence, since effectively three component species ($ArMe_2SiNMePh$, H^+, and EtO^-) are concerned in the transition state of the rate-determining step, which involves a high degree of charge separation and thus a considerable solvent orientation. [An equivalent statement is that the highly unfavourable entropy of reaction of step 1, associated with solvation of the ions formed, is only slightly offset by the favourable entropy of activation of step 2.]

For $XC_6H_4NHSiEt_3$ compounds, the spontaneous process is known to be facilitated by electron-releasing groups in the aromatic ring of the aniline [3], and this is as expected, since on any reasonable representation of the mechanism the nitrogen atom is likely to be more positively charged in the highest energy transition state [e.g. the transition state of reaction 2] than in the original neutral silylaniline. The facilitation of the reaction by electron release from the X groups of $XC_6H_4Me_2SiNMePh$ compounds could not be so confidently foreseen, because such electron release should hinder the nucleophilic attack at silicon while facilitating the attachment of the proton to the nitrogen atom. The observed behaviour is consistent with the sequence proposed above, however, since in step 2 a positively charged silicon-containing species, in which some of the positive charge will be relayed to the silicon, is converted into a neutral silicon-containing species, and so in the transition state between them it is likely that the silicon atom will bear a slightly greater degree of positive charge than it does in the original reactant, $XC_6H_4Me_2SiNMePh$; in such a case, electron release in X will decrease the overall activation energy. However, reaction 2 need not be a quantitatively synchronous process, and the Si—OEt bond in the transition state could, in principle, be formed to a greater extent than the Si—N bond is broken, so that the silicon atom could bear a significant excess of negative charge, and the overall reaction thus be hindered by electron release to silicon. The observed result can be understood in terms of the marked exothermicity of step 2, which means that the transition state will lie close to the reactants, with the Si—O bond little formed.

The accelerating effect of electron release to the silicon atom also argues against the possibility that reaction 2 might itself be a two-step process, represented by eqns. 2'a and 2'b. If 2'a were the rate-determining step, the transition

$$\mathrm{ArMe_2Si\overset{+}{N}HMePh + EtO^- \rightarrow ArMe_2\overset{-}{Si}(OEt)\overset{+}{N}HMePh} \qquad (2'a)$$

$$\mathrm{ArMe_2\overset{-}{Si}(OEt)\overset{+}{N}HMePh \rightarrow ArMe_2SiOEt + NHMePh} \qquad (2'b)$$

state would necessarily lie over towards the product, the pentacoordinate silicon species, since this would be a relatively high-energy species and the reaction clearly endothermic; in this case the silicon would bear a greater degree of negative charge than in the original reactant species, and the overall reaction would be facilitated by electron-withdrawal from silicon. If (as seems very unlikely) step 2'b were rate-determining, the silicon atom would again bear a substantial degree of negative charge in the transition state, and the overall reaction would once more be facilitated by electron withdrawal from silicon. Thus in this reaction it seems likely that the penta-coordinate silicon intermediate is avoided.

TABLE 3

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR $(XC_6H_4)Me_2SiNMePh$ COMPOUNDS

X	B.p. (°C/mm)	n_D^{20}	Found (calcd.) (%)		
			C	H	N
H	90/0.1	1.5376	74.0 (74.6)	8.1 (7.9)	5.8 (5.8)
p-Me	114/0.2	1.5682	74.9 (75.2)	8.5 (8.3)	5.3 (5.5)
m-Me	110/0.1	1.5672	75.0 (75.2)	8.7 (8.3)	5.5 (5.5)
p-OMe	157/1.0	1.5738	70.2 (70.8)	7.9 (7.8)	5.1 (5.2)
p-Cl	165/3.5	1.5712	65 8 (65.3)	6.9 (6.7)	4.7 (5.1)
m-Cl	136/0.6	1.5782	65 6 (65.3)	6.9 (6.7)	4.9 (5.1)

If the reaction sequence 1 + 2 is correct, an equivalent interpretation of the accelerating effect of electron release by the X groups must be that the negative ρ factor (say −2.0) for equilibrium 1 outweighs the positive ρ factor (say +1.0) for reaction 2.

Experimental

N-(Aryldimethylsilyl)-N-methylanilines

A solution of butyllithium (1.05 molar proportion) in ether was added dropwise with stirring to *N*-methylaniline in ether. The mixture was refluxed for 1 h, then the aryldimethylchlorosilane (1.0 molar proportion) in benzene was added. The ether was distilled off, and the mixture refluxed for 3 h, then cooled and filtered. The filtrate was fractionally distilled, to give the required product in 70-85% yields. Analyses and some physical constants are listed in Table 3.

Rate measurements

Ethanol distilled from calcium oxide was used as solvent. Solutions of sodium acetate and lithium perchlorate were made up so as to maintain a constant ionic strength of 0.05.

Rates were measured spectrophotometrically as previously described [1,2], a wave-length of 259 nm being used. The UV spectra after 10 half-lives were identical with those of *N*-methylaniline in the relevant region of the spectrum, and good first-order kinetics were observed.

Acknowledgements

We thank the Royal Norwegian Council for Scientific and Industrial Research for the award of a Fellowship to B.B.

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