BASE-CATALYSED SOLVOLYSIS OF ACYLSILANES

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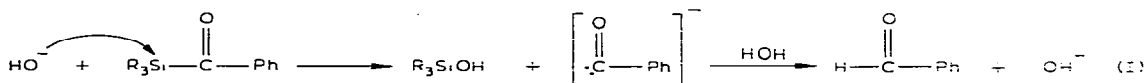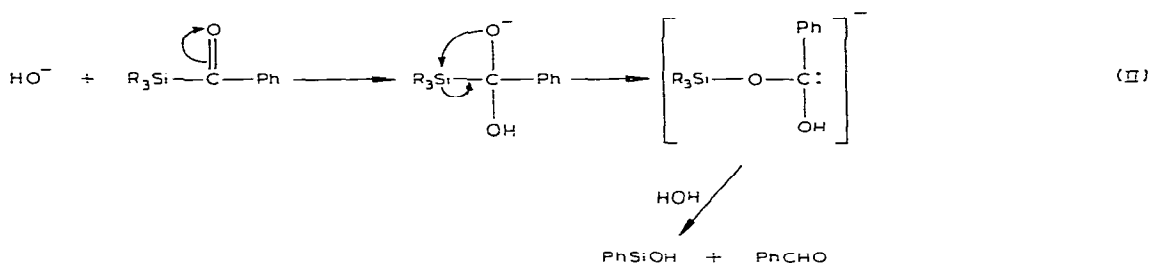
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Summary

Kinetic studies have been made of the hydrolysis of $XC_6H_4COSiR_3$ compounds (R = Me, Et, Ph) in a mixture of THF (3 vol.) and aqueous sodium hydroxide (1 vol.). The rates of cleavage of $p\text{-}NO_2C_6H_4CH_2SiMe_3$, $C_6H_5COSiMe_2C_6H_5$ and $C_6H_5COSiMe_2C_6H_4Cl\text{-}p$ compounds under the same conditions have also been measured. Electron-attracting substituents on either side of the bond being broken lead to an increase in the rate. For the $XC_6H_4COSiR_3$ compounds, the effects of the substituents X correlate excellently with their Hammett σ constants ($\rho = 3.5$ and 2.5 for R = Me and Ph, respectively). The data are consistent with a mechanism in which the attack of the hydroxide ion occurs at the carbonyl C atom.

Introduction

The reactions of the acylsilanes, first prepared by Brook [1] have been the subject of extensive investigations [2,3a—d]. Whereas with alkoxides two distinct reactions, rearrangement and cleavage occur, only the cleavage is found [4] in hydrolysis by aqueous bases. Two pathways are conceivable for this latter reaction, vz.: (I) nucleophilic attack on silicon followed by displacement, and (II) nucleophilic attack on the carbonyl carbon atom followed by rearrangement.

$$HO^- + R_3Si{-}\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}{-}Ph \longrightarrow R_3Si{-}\underset{\displaystyle OH}{\overset{\displaystyle O^-}{C}}{-}Ph \longrightarrow \left[R_3Si{-}O{-}\underset{\displaystyle OH}{\overset{\displaystyle Ph}{C}}{:} \right]^- \tag{II}$$

$$\xrightarrow{\;HOH\;} \quad PhSiOH + PhCHO$$

The aim of this study was to get a clearer understanding of the route taken by the cleavage reaction in basic aqueous media, and especially to decide on the site of the nucleophilic attack by the base. To this end, a detailed kinetic analysis has been carried out on (a) the efficiency of the transmission of the electronic effects of the substituents to the silicon and carbonyl carbon atoms, and (b) the influence of the nature of the R groups on the ease of cleavage of $PhCOSiR_3$ compounds.

Results and discussion

Aqueous THF (1 : 3, v/v) was used for all the kinetic experiments. Our results for the cleavage of $XC_6H_4COSiMe_3$, $XC_6H_4COSiPh_3$, $C_6H_5COSiEt_3$, and $C_6H_5COSiMe_2C_6H_4X$, are shown in Table 1, in which are listed the observed first-order rate constants k, at the specified concentration of sodium hydroxide, the value of the specific rate constants k_s, and the values of k_{rel}, the reactivity relative to that of $C_6H_5COSiMe_3$.

As shown in the Table, the acylsilanes are very reactive species, the Si—CO bond being cleaved rapidly even at low sodium hydroxide concentrations: $C_6H_5COSiMe_3$ is in fact only 3 times less reactive than $p\text{-}NO_2C_6H_4CH_2SiMe_3$ whose rate of cleavage corresponds at 25°C, in 1 : 3 (v/v) aqueous THF at 0.0033 M NaOH, to a k of 1.28×10^{-3} s^{-1}. For the small range of substituents examined, the effect of the X group in $XC_6H_4COSiR_3$ compounds correlates well with their Hammett σ constants, with ρ values of 3.5 and 2.5 for R = Me

TABLE 1

RATE CONSTANTS FOR CLEAVAGE OF $XC_6H_4COSiR_2R'$ BY SODIUM HYDROXIDE (0.0033 M IN THF/WATER (3 : 1, v/v), AT 25°C)

R	R'	X	$10^4 k^a$ (s^{-1})	$10^2 k_s{}^b$ (l mol^{-1} s^{-1})	$k_{rel.}$
CH$_3$	CH$_3$	p-OCH$_3$	0.505	1.53	0.12
		H	4.10	12.4	1
		p-Cl	25.4	76.96	6.2
		m-Cl	79.4	240.6	19.40
C$_2$H$_5$	C$_2$H$_5$	H	0.13	0.39	0.03
C$_6$H$_5$	C$_6$H$_5$	p-OCH$_3$	79.4	240.6	19.40
		H	316	958	77.25
		p-Cl	1554	4709	379.8
		m-Cl	3090	9363	755.1
CH$_3$	C$_6$H$_5$	H	9.3	28.18	2.27
CH$_3$	p-ClC$_6$H$_4$	H	40.96	124.12	10

^{a} Observed first-order rate constants. ^{b} Specific rate constants, i.e. $k/[NaOH]$

and R = Ph, respectively. This indicates a very great sensitivity of the cleavage to the substituents, and shows that a substantial negative charge develops on the carbonyl carbon during formation of the transition state, which is stabilized by electron-withdrawing and destabilized by electron-releasing substituents. The data for $PhCOSiMe_2C_6H_4X$, are less complete, and the rates at 0.0033 M NaOH in 1 : 3 (v/v) aqueous THF show that the p-chlorophenyl derivative is 4.4 times as reactive as the unsubstituted parent compound, corresponding to a rough value of ρ ca. 2.8. These values are somewhat smaller than the ρ of 4.9 for the alkali cleavage [5] of $XC_6H_4CH_2SiMe_3$ in aqueous methanol but it must be remembered that for two set of analogous compounds it is usual for substituent effects to be smaller in the more reactive set, and also that the carbonyl group in α-silyl ketones is highly polarized [6] and can tolerate a given degree of negative charge more readily that the benzylic carbon, so that less delocalization of charge into the aromatic ring will take place than in the $C_6H_5CH_2SiMe_3$ system. The smaller ρ value (2.8) for the $PhCOSiMe_2C_6H_4X$ solvolysis as compared with that (3.5) for $XC_6H_4COSiMe_3$ series, does suggest, however, that in the transition state less negative charge develops at the silicon atom than at the carbonyl carbon atom. Furthermore in contrast to the observations in the $PhCH_2SiR_3$ series, where as Me groups are replaced by phenyl groups the rate rises and then falls again [7], due to a conflict between electronic facilitation and steric retardation of nucleophilic attack at silicon, in the $PhCOSiR_3$ series the rate increases stepwise with successive replacement of the mehtyl groups, suggesting that steric effects play a minor role compared with inductive effects. A steric effect is revealed, on the other hand by the low reactivity of $PhCOSiEt_3$ in comparison with $PhCOSiMe_3$. It has been previously suggested [8] that such a ratio should increase with the reactivity of the substrates in those cases where the rate-determining step moves closer to the Si^V intermediate, a Me_3Si/Et_3Si quotient of only 31, appears surprisingly low compared with a ratio of ca. 450 observed for the less reactive $Ph_2CHSiMe_3$ compounds [9] and of 960 for $9-R_3M$-fluorene pairs [9] which have reactivities rather similar to those of $PhCOSiMe_3$.

From the results some conclusions can be drawn about the mechanism of the base-catalysed Si—CO bond cleavage in the aqueous medium. While the effects of the substitutents do not distinguish unambiguously between mechanisms I and II, since from the ρ_{CO} (3.5) and ρ_{Si} (2.8) values it is evident that both the carbonyl carbon and the silicon atoms carry a partial negative charge in the transition state, other features are revealing. The effect of replacing Me groups at silicon with Ph groups and the low Me_3Si/Et_3Si ratio, appear in fact to be unusual for a cleavage mechanism involving nucleophilic attack at silicon. Finally the reactivities of $PhCOSiMe_3$ and $p-NO_2C_6H_4\,CH_2SiMe_3$ do not fit the Brønsted relationship [10] between log k with the pK_a of the corresponding carbon acids *; since the compounds corresponding to carbon acids of

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* The pK_a of PhCO—H is not available to our knowledge, but the very low acidity of this compound can be deduced from the pK_a of ca. 35 found for CH_3OCO—H by polarographic methods [11]. In contrast a pK_a value for $p-NO_2C_6H_4\,CH_3$ of approximately 22 can be derived from the rate of cleavage of $p-NO_2C_6H_4CH_2SiMe_3$ [12], and this is consistent with the value of 20.4 observed in Me_2SO [16].

markedly different acidities exhibit very similar reactivity, it seems likely that the mechanism of cleavage is different for $XC_6H_4CH_2SiR_3$ and $XC_6H_5COSiR_3$ compounds.

The base-catalysed cleavage of the acylsilanes in aqueous medium is thus best explained interms of an initial nucleophilic attack of the base at the carbonyl carbon atom, as in mechanism II; this would be consistent with the abnormally high polarity of the carbonyl group in these organometallic derivatives [6] and with the most recent results of Brook [3d], showing that the cleavage pathway for the reaction of alkoxides with acylsilanes involves attack at the carbonyl group, followed by subsequent rearrangement. From the substituent effects, which show that a substantial degree of charge is present on both the carbon of the CO group and the Si atom, we concluded that the rate-determining step is the migration of the R_3Si group from carbon to oxygen.

Experimental

The commercial materials used for the syntheses were carefully purified before use. The ^1H NMR spectra were recorded on Varian ME-390 and Jeol C-60 instruments.

Preparation of compounds

The acylsilanes $R_3SiCOC_6H_4X$ were made by the method described by Brook [2,4] involving bromination of the corresponding trialkyl- and triarylbenzyl-silanes with n-bromosuccinimide. The dibromo derivatives were converted into the corresponding acylsilanes by treatment with silver acetate, and the product was purified by vacuum distillation or crystallization. The purity of the acyl-silanes was checked by IR and ^1H NMR spectroscopy and by elemental analysis. The properties were consistent with those previously reported for R = Me, X = H [6], R = Et, X = H [13], R = Ph, X = H [1], X = p-Cl [14], X = p-OMe [14]. The new compounds had the following physical constants and analyses: boiling points ($^\circ$C/mmHg), R = Me, X = p-Cl, 81/0.1 (Found: C, 56.1; H, 6.07. $C_{10}H_{13}OClSi$ calcd.: C, 56.45; H, 6.16%), X = m-Cl, 74/0.1 (Found: C, 56.8; H, 6.02. $C_{10}H_{13}OClSi$ calcd.: C, 56.45; H, 6.16%), X = p-OMe 85/0.1 (Found: C, 63.1; H, 7.88. $C_{11}H_{16}O_2Si$ calcd.: C, 63.4; H, 7.74%); melting point ($^\circ$C), R = Ph, X = m-Cl 88 (Found: C, 75.8; H, 4.81. $C_{25}H_{19}OClSi$ calcd.: C, 75.28; H, 4.80%). The synthesis of $C_6H_5Me_2SiCOPh$ was described previously [6]; p-ClC$_6$H$_4$Me$_2$Ph, prepared by treatment of the appropriate halide with benzyl-magnesium bromide, gave, following the general procedure (see above), p-ClC$_6$H$_4$Me$_2$SiCOPh (60% yield), b.p. ($^\circ$C) 123/0.1 mmHg. (Found: C, 65.43; H, 5.47. $C_{15}H_{15}OClSi$ calcd.: C, 65.55; H, 5.50%). p-NO$_2$C$_6$H$_4$ CH$_2$SiMe$_3$ was prepared as previously described [15].

Rate studies

The cleavages were monitored by observing the changes of the optical density at 355 and 420 nm with a Perkin Elmer 323 spectrophotometer. To 2 ml of the acylsilane solutions (2-8 × 10^{-4} M) in THF contained in a thermostatted 1 cm quartz cell was added 1 ml of the aqueous NaOH solution of the appro-

priate concentration, and the spectrum was recorded at intervals. The final spectrum exactly matched that of the corresponding benzaldehyde, showing the quantitative nature of the reaction. For the most reactive compounds, a stopped-flow technique was used. Pseudo-first order rate constant were evaluated in the usual way. Kinetic runs were normally carried out in duplicate, and the agreement was usually within 2%.

Acknowledgement

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