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ORGANOSILICON COMPOUNDS

LII*. A COMPARISON OF THE BASE CLEAVAGE OF 2-BENZOFURYL— AND *p*-CHLOROBENZYL—SILICON BONDS

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Summary

Rates of cleavage have been measured for $XC_6H_4Me_2Si$—$CH_2C_6H_4Cl$-*p* bonds in aqueous methanolic alkali and 2-($XC_6H_4Me_2Si$)—C_8H_5O bonds (C_8H_5O = benzofuryl) in this medium and in 1/6 H_2O/DMSO containing borax. The benzyl—silicon and benzofuryl—silicon bonds have fairly similar reactivities, and show similar sensitivities to variation in the nature of X (in the range X = *m*-Cl, *p*-Cl, H, *m*-Me, *p*-Me, *p*-OMe), and it is concluded that the nature of the highest energy transition state is much the same in both systems. This is consistent with a mechanism in which the rate-determining step is the cleavage of the Si—C bond within a pentacoordinate silicon intermediate.

Introduction

We recently showed that in the cleavage of Me_3M—$CH_2C_6H_4X$ (M = Si or Sn) and Me_3Sn—C_6H_4X bonds by methanolic alkali, transfer of a proton from the solvent to the separating carbon atom provides electrophilic assistance in the bond-breaking process, which is the rate-determining step of the reaction [2,3]. The extent of the C—H bond formation in the highest energy transition state was found to be much smaller for the cleavage of the $Me_3MCH_2C_6H_4X$ compounds than for the $Me_3SnC_6H_4X$ compounds (and thus probably also than for the $Me_3SiC_6H_4X$ compounds, which are not cleaved rapidly enough for study in the medium concerned). This implied a substantial difference in the distribution of the excess of negative charge in the (highest energy) transition states in the two cases, but it was not clear whether this originated in a fundamental difference between the two systems (such as the much greater ease of electrophilic attack on an aromatic than on a benzylic carbon atom) or simply in the much greater reactivity

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[*] For part LI see ref. 1.

of the benzyl than of the aryl compounds studied. To obtain information about the degree of negative charge developed on the silicon atom during alkali cleavage of Si—benzyl and Si—aryl bonds of fairly similar reactivities we have examined the cleavage of $XC_6H_4Me_2SiCH_2C_6H_4Cl$-*p* and $XC_6H_4Me_2SiC_8H_5O$ compounds (where C_8H_5O denotes the 2-benzofuryl group).

Results and discussion

The rates of cleavage were measured spectrophotometrically, mainly in ca. 7.5% aqueous methanol containing 0.82 *M* potassium hydroxide. The results are shown in Tables 1 and 2, in which k represents the observed pseudo first-order constant, and k_{rel} the rate relative to that of the appropriate parent compound with X = H. It will be seen that the parent 2-benzofuryl compound, $PhMe_2SiC_5H_8O$, is some 20 times as reactive as the parent *p*-chlorobenzyl compound, $PhMe_2SiCH_2C_6H_4Cl$-*p*, and that the (approximate) activation energies are much the same in the two systems, possibly being slightly lower in the benzofuran series, in line with the higher rates of reaction in this series.

A plot of values of log k_{rel} for the $XC_6H_4Me_2SiCH_2C_6H_4Cl$-*p* compounds (where k_{rel} is the rate at 50° relative to that for the parent compound with X = H) against values of log k_{rel} for the $XC_6H_4Me_2SiC_5H_8O$ compounds is a good straight line with a slope close to unity, as shown in Fig. 1. (The line shown is drawn by inspection with a slope of 0.97.) Thus we conclude the excess of negative charge developed on the silicon atoms in the highest energy (rate-determining) transition state is similar in the two systems. Since the activation energies, and thus the activation entropies, are also much the same in the two systems, it seems likely the highest energy transition states are rather similar. This implies that the degree of proton transfer to the benzofuran group is as small as that to the benzyl group, but this will have to be established by measurement of the product isotope effects for the appropriate benzofuran compounds.

The log k_{rel} values for the *p*-chlorobenzyl series correlate fairly well with σ-constants ($\rho = 1.72$; $r = 0.986$), and apparently rather better with σ^0-constants ($\rho = 1.89$; $r = 0.999$), but the difference in the correlation coefficients, r, is within the limits of uncertainty. Similar correlations are observed for the benzofuran compounds between the log k_{rel} values at 50° and σ- ($\rho = 1.85$;

TABLE 1

SOLVOLYSIS OF $XC_6H_4Me_2SiCH_2C_6H_4Cl$-*p* COMPOUNDS IN CA. 7.5% AQUEOUS METHANOL CONTAINING 0.82 *M* KOH

X	10^5k (s^{-1})		k_{rel}	*E*
	30.1°	50.2°	(50°)	(kcal mol^{-1})
m Cl	0.91	10.4	4.95	24
p-Cl	0.54	7.4	3.5	25
H		2.10	1.00	
m Me		1.66	0.79	
p-Me		1.12	0.53	
p-OMe		1.05	0.50	

TABLE 2

SOLVOLYSIS OF 2-($XC_6H_4Me_2Si$)C_8H_5O COMPOUNDS IN CA. 7.5 % AQUEOUS METHANOL CONTAINING 0.82 *M* KOH

X	10^5k(s^{-1})		k_{rel}		*E*
	30.1°	50.2°	30.1°	50.2°	(kcal mol^{-1})
m-Cl	10.7	120	6.6	5.8	23
p-Cl	6.6	67	4.1	3.25	22
H	1.62	20.6	1.00	1.00	25
m-Me	1.55	15.7	0.96	0.76	22
p-Me	1.09	10.1	0.67	0.49	22
p-OMe	0.94	9.3	0.58	0.45	22

r = 0.991) or σ^0-constants (ρ = 2.03; r = 0.999). (The corresponding log k_{rel} values at 30° give comparable correlations; viz. with σ, ρ = 1.77, r = 0.981; with σ^0, ρ = 1.95, r = 0.995.)

We also examined the cleavage of the benzofuryl compounds in aqueous DMSO (dimethyl sulphoxide) containing borax, in order to ascertain whether the change to the much more nucleophilic medium causes a change in the nature of the transition state. The results are shown in Table 3. The plot (not shown) of the log k_{rel} values at 30° against those at 30° in aqueous methanolic alkali is a good straight line of slope 1.22, and the log k_{rel} values thus correlate fairly well with σ-constants (ρ = 1.91; r = 0.960 at 50°; ρ = 2.14; r = 0.979 at 30°) and apparently rather better with σ^0-constants (ρ = 2.14, r = 0.995 at 50°; ρ = 2.35, r = 0.993 at 30°). Thus even though the activation energies are distinctly lower than those for aqueous methanolic alkali, there is only a fairly small difference between the degrees of negative charge developed at the silicon atom in the two media in the highest energy transition states. This can be easily understood if the rate-determining step is indeed the breaking of the

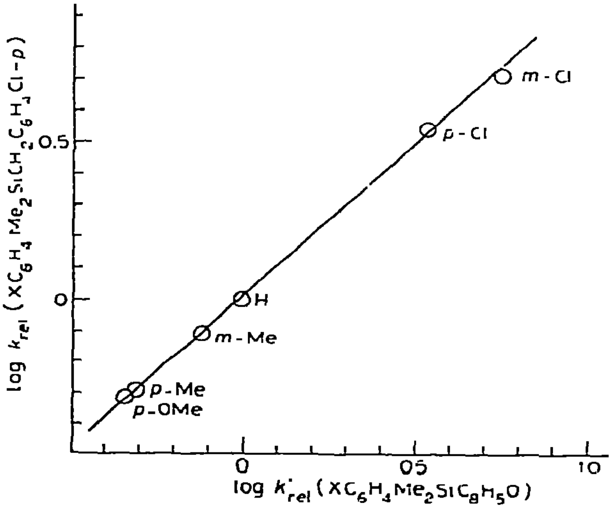

Fig. 1.

TABLE 3

SOLVOLYSIS OF 2-($XC_6H_4Me_2Si$)C_8H_5O COMPOUNDS IN A MIXTURE OF DIMETHYL SULPHOXIDE (6 VOL) AND 0.01 M AQUEOUS BORAX (1 VOL)

X	$10^3k(s^{-1})$		k_{rel}	E
	30.1°	50.2°	30.1°	(kcal mol^{-1})
m-Cl	67		8.9	
p-Cl	44	(ca. 250)	5.9	
H	7.5	55	1.00	19
m-Me	6.2	40	0.83	18
p-Me	5.1	33	0.68	18
p-OMe	3.6	28	0.48	20

Si–aryl bond within a Si^V intermediate $[R_3Si(OH)Ar]^-$, formed rapidly and reversibly in a pre-equilibrium step. For a given base concentration, the rate will be much greater (and the activation energy markedly lower) in the aqueous DMSO because of the much higher activity of the hydroxide ion and hence a larger equilibrium constant for formation of the Si^V intermediate. But the nature of the rate-determining step, the breaking of the Si—aryl bond, will be much the same in the two media, except for any difference between the extents of the electrophilic assistance by proton transfer from the solvent. If the extent of such assistance is in any case relatively small, then little difference in the nature of the transition states would be expected between the two media, at least as long as the aqueous DMSO contains a fairly high proportion of water, as does that we used. (In H_2O/DMSO containing very small amounts of water the proton-availability would be seriously reduced.) Different considerations might apply if the electrophilic assistance made a markedly greater contribution, or if the O—Si bond-making and the Si—C bond-breaking were synchronous.

Experimental

Preparation of $XC_6H_4Me_2SiCH_2C_6H_4Cl$-*p* *compounds*

These were made by refluxing the appropriate aryl(chloro)dimethylsilane

TABLE 4

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR $XC_6H_4Me_2SiCH_2C_6H_4Cl$-*p* COMPOUNDS

X	M.p.	Found (calcd.) (%)	
	(°C)	C	H
H	56	69.5 (69.1)	6.2 (6.6)
p-Me	[a]	71.5 (69.9)	7.3 (7.0)
p-OMe	71	66.4 (66.1)	6.2 (6.6)
p-Cl	68	60.8 (61.0)	6.0 (5.5)
m-Cl	[b]	61.3 (61.0)	5.7 (5.5)
m-Me	[a]	71.4 (69.9)	7.1 (7.0)

[a] Solid melting below room temp. [b] B.p. 158°/2 mm.

TABLE 5

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR 2-($XC_6H_4Me_2Si$)C_8H_5O COMPOUNDS

X	B.p.	n_D^{20}	Found (calcd.) (%)	
	(°C/mm)		C	H
H	124/0.2	1.5475	76.5 (76.1)	6.6 (6.4)
m-Me	142/0.3	1.5908	77.5 (76.9)	7.1 (6.8)
p-Me	158/0.5	1.5862	77.1 (76.9)	7.2 (6.8)
p-OMe	157/1.0	1.5690	72.4 (72.3)	6.7 (6.4)
p-Cl	166/0.5	1.5858	66.7 (67.0)	5.5 (5.3)
m-Cl	172/2.0	1.5850	66.9 (67.0)	5.3 (5.3)

with the Grignard reagent prepared from *p*-chlorobenzyl chloride in diethyl ether. After addition of dilute hydrochloric acid, separation, drying (Na_2SO_4) and evaporation of the ethereal layer, the residue was fractionally distilled. A sample was purified by crystallization from light petroleum (b.p. 60-80°) (X = H, *p*-OMe, and *p*-Cl) or by preparative GLC (X = *p*-Me, *m*-Cl, and *m*-Me). Analyses and some physical constants are shown in Table 4.

Preparation of 2-(aryldimethylsilyl)benzofurans, 2-($XC_6H_4Me_2Si$)C_8H_5O

Benzofuran was treated with n-butyllithium in diethyl ether or hexane at room temperature, and the mixture was refluxed for 1 h then cooled. A solution of the appropriate aryl(chloro)dimethylsilane in diethyl ether was added dropwise with stirring, and the mixture was subsequently refluxed for 4 h. Water was added, and the ethereal layer separated, dried (Na_2SO_4) and evaporated, and residue was fractionally distilled. Physical constants and analyses are shown in Table 5. The fact that the kinetics of the cleavage were uncomplicated, and that the products in each case had a UV absorption spectrum in the relevant range, identical with that of benzofuran, provides confirmation of the identity of the compounds, and of the absence of any serious contamination by the 3-isomer.

Rate studies

Rates were measured spectrophotometrically on samples contained in stoppered quartz absorption cells kept in a thermostat in the cell compartment of the spectrophotometer [4].

The media used were as follows:

(a). A mixture of methanol (50 vol.) with ca. 10 *M* aqueous potassium hydroxide (4 vol.); the concn. of base in the mixture was found by titration to be 0.82 *M*.

(b). A mixture of dimethyl sulphoxide (6 vol.) with 0.01 *M* aqueous borax (1 vol.). A wave-length of 288 nm was used to follow the progress of the cleavage of the benzofuran compounds; the absorption spectra after 10 half-lives were identical with that of benzofuran. A wave-length of 242 nm was used for the *p*-chlorobenzyl compounds. Good first order kinetics were obtained in all cases.

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