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ALKALINE CLEAVAGE OF SUBSTITUTED PHENYLTRIMETHYLSILANES IN AQUEOUS DIMETHYLSULPHOXIDE

J. CRETNEY AND G. J. WRIGHT
Department of Chemistry, University of Canterbury, Christchurch 1 (New Zealand)

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SUMMARY

The rates of cleavage of nineteen *meta*- and *para*-substituted phenyltrimethylsilanes by hydroxide ion in aqueous dimethyl sulphoxide have been measured. The reaction is sensitive to substituents (ρ 6.0); the relative rates for the *meta*-substituents correlate well with Hammett σ values, but *para*-substituents capable of conjugative electron release are more activating or less deactivating than predicted by the σ-constants.

INTRODUCTION

Eaborn, Hornfeld and Walton measured the rates of cleavage of some XC_6H_4-$SnMe_3$ compounds by aqueous methanolic alkali and observed a most unusual pattern of substituent effects[1]. It was of interest to see whether the corresponding arylsilicon compounds would show similar behaviour, but these are not cleaved at a measurable rate by aqueous methanolic alkali[2]. We have now found that they are cleaved at a convenient rate by hydroxide ion in 1/9 v/v water/dimethyl sulphoxide (H_2O/DMSO) at 40.0°, and we set out below the results for a wide range of XC_6H_4-$SiMe_3$ compounds.

RESULTS AND DISCUSSION

The results for the range of $XC_6H_4SiMe_3$ compounds are shown in Table 1 as observed first order rate constants, k, and as values of the rates k_{rel}, relative to those of the parent compound with X = H. (Not all the compounds could be examined at one alkali concentration and rates were not proportional to the base concentration. In the derivation of k_{rel} values we have assumed that relative rates are independent of the alkali concentration in the range used.) The plot of log k_{rel} against Hammett σ-constants, presented in Fig. 1, shows some features similar to those in the corresponding plot for the cleavage of aryltrimethylstannanes[1]; thus the points for *meta*-substituents generally lie satisfactorily about a straight line but many of the points for *para*-substituents deviate from this line, groups possessing substantial electron-releasing resonance effects, such as *p*-NMe_2, *p*-OMe, *p*-Me, *p*-Et, *p*-Ph and *p*-F, being either more activating or less deactivating than would be expected from the σ-constants. The de-

TABLE 1

CLEAVAGE OF $XC_6H_4SiMe_3$ COMPOUNDS BY HYDROXIDE ION IN 1/9 V/V H_2O/DMSO AT 40.0°

X	λ (nm)	$10^2 \times [OH^-]$ (M)	$10^2 k$ (min^{-1})	k_{rel}
m-NO_2	313	2.0	572	12960
p-NO_2	290	2.0	446	10120
m-Br	270.5	2.0	32	
m-Br		5.0	90	726
m-CF_3	274	5.0	59	480
m-Cl	270	5.0	49	
m-Cl		10	80	400
m-F	271.8	10	21.8	108
p-Br	272	10	10.2	
p-Br		20	15.2	50.5
p-Cl	274	20	10.4	34.5
p-F	270.2	20	2.4	8.0
m-Ph	290	20	1.15	3.84
p-Ph	276	20	0.75	2.49
m-OMe	285	20	0.65	2.17
H	270.5	20	0.300	1.00
m-Me	275	20	0.137	0.45
p-Et	274	20	0.121	0.40
p-Me	274	20	0.079	0.265
p-OMe	285	20	0.071	0.24
m-NMe_2	274	20	0.0395	0.131
p-NMe_2	290	20	0.0078	0.026

viations are much smaller than those observed for the cleavage of $XC_6H_4SnMe_3$ compounds in aqueous methanol, and, in particular, the p-NMe_2 and p-OMe substituents deactivate, as would be expected for groups which are normally electron-releasing, whereas they activate in the cleavage of the tin compounds in aqueous methanol. It is noteworthy that the p-NO_2 group activates markedly less than would be expected from its σ-constant, since large deviations in the same direction were observed for the strongly electron-withdrawing p-CF_3 and p-NMe_3^+ groups in the aryl–tin cleavages. The spread of rates is much larger in the aryl–silicon cleavage in H_2O/DMSO (ρ 6.0) than for the aryl–tin cleavage in H_2O/MeOH (ρ 2.2). This may be due in part to transfer of a greater degree of charge from the hydroxide ion to the aromatic ring, but even more important may be the poorer solvation of the negatively charged transition state, relative to that of the initial $XC_6H_4SiMe_3$ compound, by the H_2O/DMSO medium; the less effective this solvation, the greater the amount of charge left to interact with the substituents. On the other hand, the very much greater rate of alkali cleavage of the aryl–silicon compounds in H_2O/DMSO than in H_2O/MeOH is to be attributed to the much greater nucleophilicity of the hydroxide ion in the former medium, arising from its much less effective solvation[3].

The substituent effects in the cleavages of $XC_6H_4SnMe_3$ compounds in H_2O/MeOH were discussed in terms of formation of the free carbanion, $XC_6H_4^-$, in a rate-determining step, although it was appreciated that transfer of a proton from the solvent to carbon might be synchronous with the breaking of the C–$SnMe_3$ bond[1]. Subsequently by analysis of the isotopic content of the XC_6H_5 obtained on cleavage of

$XC_6H_4MR_3$ compounds Alexander, Eaborn, and Traylor showed that such electrophilic attack at carbon is of importance in the rate-determining step[4]. The abnormal influences of *para*-substituents with electron-releasing resonance effects can be associated with assistance to this electrophilic attack, and a forthcoming publication will present a detailed analysis of the results we describe above along with those of other workers for some related reactions[5].

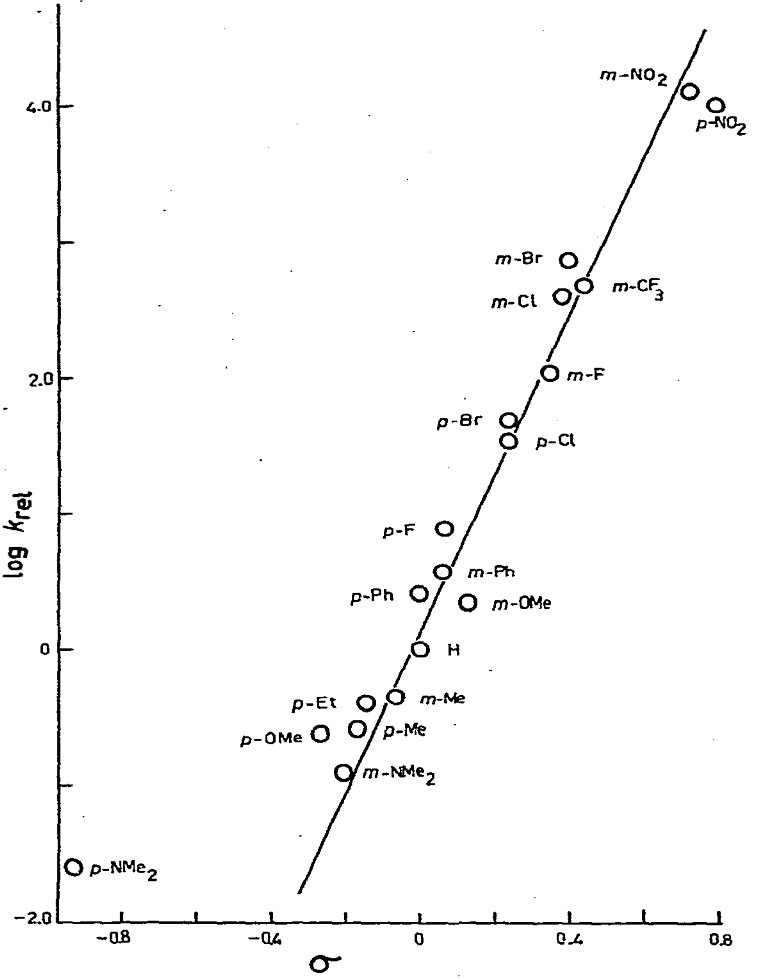

Fig. 1. Cleavage of $XC_6H_4SiMe_3$ compounds by hydroxide ion in aqueous dimethylsulphoxide. Plot of log k_{rel} *vs.* Hammett σ-values; the line is the least squares line through the points for *m*-NO_2, Br, Cl, F, Me and the unsubstituted compound.

EXPERIMENTAL

Materials

The aryltrimethylsilanes, all known compounds, were prepared by literature methods. Solids were purified by recrystallization, and liquids by fractionation through a spinning band column. GLC analysis on two columns revealed no impurities in the samples used. Dimethyl sulphoxide (Koch–Light) was distilled under reduced pressure (at ca. 80°) from calcium hydride.

Rate measurements

A mixture of 2 vol. of aqueous potassium hydroxide (of the concentration specified in Table 1) with 17 vol. of DMSO was set aside at room temperature for two days, during which an initial cloudiness disappeared. This mixture (2 ml) was pipetted into a 1 cm silica absorption cell, and brought to 40.0°; 105 μl of a solution of the aryltrimethylsilane in DMSO, of such a concentration that the optical density would be in a suitable range, were then added from a microsyringe, and the mixture was rapidly shaken. The optical densities were recorded at appropriate times with a Shimadzu M.P.S. 502 spectrophotometer. The cell was left within the thermostatted cell compartment, at $40 \pm 0.05°$ for faster reactions and the optical density was continuously recorded at the wave-length indicated in Table 1. For slow reactions the cell was kept in a constant temperature bath at 40° and rapidly transferred to the cell compartment at appropriate intervals for measurement. Checks revealed the optical density of the medium did not change by more than 1% during the reaction time.

Excellent first-order plots were obtained. Runs were carried out in triplicate, and readings were taken during at least 3–4 half-lives, except for the least reactive compounds with $X = p\text{-NMe}_2$ and $m\text{-NMe}_2$, which were studied for only 2 half lives. Rate constants were derived by use of a least squares computer programme, and were reproducible to within ±3%. Use of the overlap technique for deriving k_{rel} values can give rise to cumulative errors in these values; the greatest uncertainty arises with the most reactive compounds, and we estimate the k_{rel} values for the *m* and *p*-nitro compounds be in error by as much as ±15%.

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