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AROMATIC REACTIVITY
XXXIV*. THE ACID CLEAVAGE OF (PENTAFLUOROPHENYL)-TRIMETHYL-STANNANE AND -SILANE

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INTRODUCTION

There is much interest in pentafluorophenyl derivatives of metals (*cf.* ref. 2), and from reports of work on these derivatives and on pentafluorophenyl compounds generally, one receives the impression that many authors think that the pentafluorophenyl group shows abnormal behaviour which goes beyond what would be expected from the separate operation of the electronic effects of the five fluorine atoms. We have now measured the rates of acid cleavage of (pentafluorophenyl)trimethylsilane and -stannane, and conclude, on the contrary, that the combined effect of the five fluorine atoms in each case is smaller than that expected for separate operation of the effects of the individual fluorine atoms, and markedly so for the tin compounds.

RESULTS AND DISCUSSION

The rates of cleavage of the compounds $C_6F_5SnMe_3$, *o*-, *m*-, and *p*-FC_6H_4-$SnMe_3$, and $C_6H_5SnMe_3$ were measured in aqueous methanolic perchloric acid by the spectrophotometric method previously described[3,4]. The results are shown in Table 1, as observed first order rate constants *k*, and as rates k_{rel}, relative to that of

TABLE 1

CLEAVAGE OF (FLUOROPHENYL)TRIMETHYLSTANNANES IN METHANOL/WATER/PERCHLORIC ACID AT 50.0°

Compound	$[HClO_4]^a$ (*M*)	$10^3 k$ (*min*$^{-1}$)	k_{rel}	λ^b (*mμ*)
$C_6H_5SnMe_3$	0.60	300	1.0	264
	0.48	228		
p-$FC_6H_4SnMe_3$	0.60	276	0.93	270
	0.48	215		
o-$FC_6H_4SnMe_3$	0.60	119	0.41	269
	0.48	93.2		
m-$FC_6H_4SnMe_3$	0.60	64.9	0.22	270
	0.48	51.0		
$C_6F_5SnMe_3$	0.60	126	0.43	270
	0.48	101		

[a] Strength of aqueous perchloric acid, 2 vol. of which was mixed with 5 vol. of a methanolic solution of the organostannane. [b] Wavelength at which the spectral change was recorded.

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* For Part XXXIII see ref. 1.

phenyltrimethylstannane. It will be seen that the pentafluorophenyl compound is cleaved at practically the same rate as the *o*-fluoro compound, and it is, in fact, cleaved some 57 times as fast as would be expected if the effects of the two *ortho*-, two *meta*- and one *para*-fluorine atoms were simply additive. This unexpectedly high reactivity of the pentafluorophenyl compound is not due to cleavage by the solvent concurrent with that by acid; the compound is indeed cleaved by aqueous methanol alone, but addition of a trace of acid suppresses the cleavage completely, which indicates that the "neutral" cleavage is not by solvent molecules but by hydroxide and methoxide ions produced by autoprotolysis.

The acid cleavage of the $C_6F_5SiMe_3$ compound is much slower, and had to be studied in a mixture of acetic acid and aqueous sulphuric acid (*cf.* ref. 5). The results are shown in Table 2. Because the effects of substituents are much greater in this reaction, all the compounds concerned cannot be compared in one medium, and the rate of cleavage of the $C_6F_5SiMe_3$ compound was measured relative to that of the p-$Me_3N^+C_6H_4SiMe_3$ compound, for which the value of k_{rel} (relative to that of phenyltrimethylsilane) is approximately known[5]. The value of k_{rel} thus derived from the pentafluorophenyl compound is some 6 times as great as that expected from additive operation of the separate effects of the five fluorine atoms*. There is, however, a considerable uncertainty in the value of k_{rel} for the p-Me_3N^+ compound, arising from the assumption that relative rates are unaffected by the change in the composition of the medium as the proportion of acid is increased. The error is most unlikely to be greater than a factor of 10, and it seems safe to conclude that the reactivity of the pentafluorophenyl compound is not significantly less than would be expected from additivity of effects of the separate fluorine atoms, and is probably greater.

TABLE 2

CLEAVAGE OF SUBSTITUTED PHENYLTRIMETHYLSILANES IN ACETIC ACID/WATER/SULPHURIC ACID AT 50.0°

Compound	$[H_2SO_4]$[a] *(M)*	$10^3\,k$ *(min^{-1})*	k_{rel}	λ[b] *(mμ)*
$C_6H_5SiMe_3$	10.0	130	1.0	269
p-$FC_6H_4SiMe_3$	10.0	125	0.96	273
m-$FC_6H_4SiMe_3$			0.0215[c]	
o-$FC_6H_4SiMe_3$	10.0	9.44	7.26×10^{-2}	271
p-$Me_3N^+C_6H_4SiMe_3$	18.3	48.6	3.84×10^{-4}[d]	269
$C_6F_5SiMe_3$	18.3	1.86	1.47×10^{-5}	268

[a] Strength of aqueous sulphuric acid, 1 vol. of which was added to 2 vol. of a glacial acetic solution of the silane. [b] Wavelength at which the spectral change was recorded. [c] Calculated value (see footnote to main text). [d] Value of k_{rel} taken from ref. 5.

It would not be surprising to find the combined electron-withdrawing effect of the five fluorine atoms to be less than the sum of their separate effects, because as the overall inductive electron withdrawal from the ring is progressively increased so

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* The value of k_{rel} for the m-$FC_6H_4SiMe_3$ compound was calculated from the value for the compounds m-$FC_6H_4GeEt_3$[6] [denoted m-F(Ge)], m-$ClC_6H_4GeEt_3$[6] [denoted m-Cl(Ge)], and m-$ClC_6H_4SiMe_3$[5] [denoted m-Cl(Si)], by use of the linear free energy relation [log k_{rel} m-Cl(Ge)]/[log k_{rel} m-Cl(Si)] = [log k_{rel} m-F(Ge)]/[log k_{rel} m-F(Si)][7]. The value is unlikely to be in error by more than 10%.

one would expect a compensatory increase in the extent of p_π–p_π bonding between each fluorine atom and the ring. However, the departure from additivity in the case of the pentafluorophenyltin compound seems too great to be attributed to this effect alone, and it is possible that there is some steric acceleration of the cleavage in this case, analogous to that observed in cleavage of (polymethylphenyl)trimethylsilanes[8]. For this, the buttressing effect of the *m*-F atoms, themselves buttressed by the *p*-F atom, would have to cause compression between *o*-F atoms and the $SnMe_3$ group; the compression would be relieved as the configuration of the 1-carbon atom changes towards the tetrahedral as a proton attaches. A similar effect, but probably larger, would then be expected for the silicon compound, and may, indeed, be present, but obscured by the uncertainty in the value of k_{rel}.

It is also possible that some mechanistic change, either of type or emphasis, occurs on passing from the mono- to pentafluorophenyltin compound, but in the absence of supporting evidence it would be unwise to complicate the discussion by postulating it.

EXPERIMENTAL

(*o-Fluorophenyl*)*trimethylstannane*

o-Fluoroiodobenzene (21.8 g, 0.10 mole) was added at 0° to trimethylstannyllithium[9] (0.10 mole) in tetrahydrofuran (65 ml). The mixture was refluxed for 1 h, and then treated with saturated aqueous ammonium chloride. Organic products were extracted with ether, and the ethereal extract was dried and fractionally distilled to give (*o*-fluorophenyl)trimethylstannane (18%), b.p. 63–64°/7 mm, n_D^{25} 1.5221 (lit.[10] b.p. 65°/4 mm, n_D^{25} 1.5180).

(*m- and p-Fluorophenyl*)*trimethylstannane*

The Grignard reagent prepared from *m*-bromofluorobenzene (34.5 g, 0.20 mole) and magnesium turnings (7.3 g, 0.30 g-atom) in ether (50 ml) was treated with bromotrimethylstannane (36.4 g, 0.15 mole). After 2 h reflux, the reaction mixture was worked up as described above to give (*m*-fluorophenyl)trimethylstannane (91%), b.p. 55–57°/1.8–2.4 mm, n_D^{25} 1.5172. (Found: C, 42.0; H, 5.1. $C_9H_{13}FSn$ calcd.: C, 41.6; H, 5.1%.)

A similar preparation from *p*-bromofluorobenzene gave (*p*-fluorophenyl)-trimethylstannane (84%), b.p. 50–51°/0.7–0.8 mm, n_D^{25} 1.5160 (lit.[11] b.p. 88°/10 mm, n_D^{20} 1.5176).

(*Pentafluorophenyl*)*trimethyl-silane and -stannane*

Pentafluorophenylmagnesium bromide, prepared in ether from pentafluorobromobenzene[12], was treated (*i*) with chlorotrimethylsilane to give (pentafluorophenyl)trimethylsilane (72%), b.p. 56°/9.0 mm, n_D^{25} 1.4307 (lit.[13] b.p. 170–172°), and (*ii*) with bromotrimethylstannane to give (pentafluorophenyl)trimethylstannane (60%), b.p. 97.5°/20 mm, n_D^{25} 1.4726 (lit.[12] 118–119°/50 mm, n_D^{20} 1.4744).

Other compounds

The preparation of these has been described previously[3,5,14].

Rate studies

The rates of cleavage of aryl–silicon and –tin bonds were measured spectrophotometrically as previously described[4,5].

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SUMMARY

The rates of acid cleavage of (pentafluorophenyl)trimethyl-stannane and -silane have been measured. For the first compound the rate is markedly larger than would be expected for additivity of the deactivating effects of the five fluorine atoms separately. For the second, the rate is not significantly less than that expected for such additivity, and is probably somewhat greater.

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