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ORGANOSILICON COMPOUNDS
XLVII.* THE SUBSTITUENT EFFECTS AND LEAVING GROUP ABILITIES OF MONO-, BIS- AND TRIS-(TRIMETHYLSILYL)SILYL GROUPS IN ELECTROPHILIC AROMATIC SUBSTITUTION

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SUMMARY

The rates of cleavage at 50° by a mixture of ethanol (5 vol) and aqueous perchloric acid (2 vol) of the aryl–$SnMe_3$ bonds of p-$[(Me_3Si)_xMe_{(3-x)}Si]C_6H_4SnMe_3$ compounds relative to that of phenyltrimethylstannane have been found to be 0.93 ($x=0$), 1.31 ($x=1$), 1.67 ($x=2$) and 1.76 ($x=3$). The increase in rate with the increasing magnitude of x can be attributed to inductive and hyperconjugative electron release from the Si–Si bonds.

The rates of cleavage at 50° by a mixture of methanol (5 vol) and aqueous perchloric acid (2 vol) of the aryl–Si bonds of the compounds $[(Me_3Si)_xMe_{(3-x)}Si]Ph$ are 1.0 ($x=0$), 2.1 ($x=1$), 0.35 ($x=2$), and 0.056 ($x=3$). The reactivity sequence as x is increased is attributed to opposition between a rate enhancement associated with the increasing electron release and a rate retardation associated with increasing steric hindrance, especially hindrance to solvation of the transition state.

INTRODUCTION

We recently investigated the nature of the electronic effects of $(Me_3Si)_xH_{(3-x)}C$ groups ($x=0$–3) by examining their influences as m- and p-substituents in aromatic protodetrimethylsilylation, an electrophilic aromatic substitution; this involved measurement of the rate of acid cleavage of the aryl–silicon bonds in $[(Me_3Si)_xH_{(3-x)}C]C_6H_4SiMe_3$ compounds[2]. We have now studied the effects of the analogous $[(Me_3Si)_xMe_{(3-x)}Si]$ groups; for this acid cleavage of the aryl–Sn bonds[3] of p-$[(Me_3Si)_xMe_{(3-x)}Si]C_6H_4SnMe_3$ compounds has been utilized, there being no interference from cleavage of the aryl–silicon bonds under the conditions employed.

We have also examined the relative ease of acid cleavage of the aryl–silicon bonds in $[(Me_3Si)_xMe_{(3-x)}Si]Ph$ compounds in order to provide information on the relative leaving-powers of the several $[(Me_3Si)_xMe_{(3-x)}Si]$ groups in electrophilic aromatic substitution.

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* For Part XLVI see ref. 1.

RESULTS AND DISCUSSION

Data on the rates of cleavage by aqueous-ethanolic perchloric acid of the aryl–Sn bonds of p-$XC_6H_4SnMe_3$ compounds, where $X=H$ or $[(Me_3Si)_xMe_{(3-x)}Si]$ ($x=0$–3), are listed in Table 1, which shows the first-order rate constant, k, at the acid-concentration used, the rates, k_{rel}, relative to that of the parent compound with $X=H$, and the wave-length, λ, used to follow the progress of the reaction. Corresponding information on the cleavage by aqueous-methanolic perchloric acid of the various $[(Me_3Si)_xMe_{(3-x)}Si]Ph$ compounds (which required much stronger acid) are given in Table 2.

TABLE 1

CLEAVAGE OF p-$XC_6H_4SnMe_3$ COMPOUNDS IN AQUEOUS-ETHANOLIC PERCHLORIC ACID[a] AT 49.9°

X	$10^3 k$ (min^{-1})	k_{rel}	λ (mμ)
H	75	1.0	260
$SiMe_3$	70	0.93	268.5
$SiMe_2SiMe_3$	98	1.31	241
$SiMe(SiMe_3)_2$	125	1.67	249
$Si(SiMe_3)_3$	132	1.76	250

[a] A mixture of aqueous perchloric (0.235 M) (2 vol) with an ethanolic solution of the organostannane (5 vol).

TABLE 2

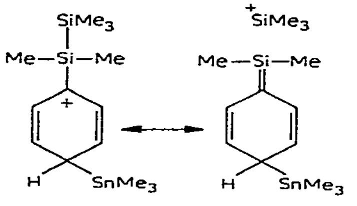
CLEAVAGE OF C_6H_5X COMPOUNDS IN AQUEOUS-METHANOLIC PERCHLORIC ACID[a] AT 50.0°

X	$10^3 k$ (min^{-1})	k_{rel}	λ (mμ)
$SiMe_3$	6.27	1.0	264
$SiMe_2SiMe_3$	13.0	2.1	232
$SiMe(SiMe_3)_2$	2.20	0.35	241
$Si(SiMe_3)_3$	0.35	0.056	240

[a] A mixture of aqueous perchloric acid (12.0 M) (2 vol) with a methanolic solution of the organosilane (5 vol).

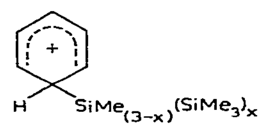
It will be seen from Table 1 that the p-Me_3Si group has a small deactivating influence on the aryl–tin cleavage. With this group the electron-releasing inductive effect is almost exactly counterbalanced by an electron-withdrawing conjugative effect, usually ascribed to $(p\rightarrow d)\pi$-bonding; thus the value of the σ-constant for the group is near zero[4], and a similar value has been reported even for the σ^+-constant as measured by the carbonyl stretching frequency of p-$Me_3SiC_6H_4COCH_3$ in carbon tetrachloride solution[5]. The group does, however, activate slightly in nitration[6], and also in acid cleavage of the compound p-$Me_3SiC_6H_4SiMe_3$[7]. It deactivates, however, in acid cleavage of the biphenyl derivative[8] 4-$Me_3SiC_6H_4C_6H_4SiMe_3$-4′, in which there is a smaller overall influence of substituents, and this is consistent with the small deactivation in the detrimethylstannylation in which overall substituent influences are very small.

The $(Me_3Si)_xMe_{(3-x)}Si$ groups with $x = 1$–3 all have an activating influence, the size of which increases slightly with the increasing magnitude of x. There are several electronic effects in operation in these systems, but the overall result is what one might expect from the simplest analysis in that replacement of Me groups by the more electropositive Me_3Si groups leads to increase in activation. The inductive electron-release of these additional Me_3Si groups should be supplemented to some extent by hyperconjugative (σ–π conjugative) electron-release from the Me_3Si–Si bonds, illustrated for a Wheland intermediate in (I), though this would be expected to be smaller than the hyperconjugative release from Me_3Si–C bonds previously discussed[2,9]. The influence of the hyperconjugation should be greatest for the introduction of the first Me_3Si group, smaller for that of the second, and very small or zero for that of the third (*cf.* ref. 2). The observed results are reasonably consistent with this expectation, but enhanced $(p\rightarrow d)\pi$-bonding between the aromatic ring and the attached silicon atom in the reactant molecule as additional Me_3Si groups are attached must also play some part; it has been shown, for example, that the conjugative electron-withdrawal by the $Me_3SiSiMe_2$ group, as indicated by σ- and σ^--constants, is greater than that of the Me_3Si group[5].



(I)

Increasing electron release should by itself lead to an increase in the ease of cleavage of the aryl–silicon bonds of $Ph[SiMe_{(3-x)}(SiMe_3)_x]$ compounds as x is increased and the Wheland intermediates (II) are increasingly stabilized. The expected increase is observed on introducing the first Me_3Si in place of an Me group, but after that the ease of cleavage falls substantially. This effect is reminiscent of the 18-fold decrease (again in face of increasing electron-release) in the ease of cleavage of the aryl–Si bond on going from p-$MeOC_6H_4SiMe_3$ to p-$MeOC_6H_4Si(CHMe_2)_3$[10], and can be plausibly attributed to steric effects, particularly hindrance to solvation of the positively charged transition state.



(II)

EXPERIMENTAL

(*p-Bromophenyl*)*trimethylstannane*

A solution of chlorotrimethylstannane (60.0 g, 0.30 mole) in ether (100 ml) was added to the Grignard reagent prepared from p-dibromobenzene (60 g, 0.25 mole) and magnesium (6.0 g, 0.25 g-atom) in ether (300 ml). The mixture was subsequently refluxed for 6 h, then treated with ice-water. The ether layer was separated, dried ($MgSO_4$), and fractionally distilled to give (*p*-bromophenyl)trimethylstannane (52 g, 68%), b.p. 85°/1.0 mm, n_D^{25} 1.5679 (lit.[11], b.p. 64°/0.2 mm, n_D^{25} 1.5669).

[*p*-(*Trimethylsilyl*)*phenyl*]*trimethylstannane*

A mixture of (*p*-bromophenyl)trimethylstannane (6.4 g, 0.020 mole), chlorotrimethylsilane (5.5 g, 0.050 mole), and magnesium (1.0 g, 0.041 g-atom) in tetrahydrofuran (THF) (50 ml) was boiled under reflux for 6 h and then treated with ice-water. Organic products were extracted with ether, and the extracts were dried and then evaporated to leave a solid, which was recrystallized successively from benzene and ethanol to give [*p*-(trimethylsilyl)phenyl]trimethylstannane (5.0 g, 80%), m.p. 103.5°–104.5° (lit.[11], m.p. 104°). The ^1H NMR spectrum had the correct integration and aromatic hydrogen pattern, with τ values as follows: Me_3Si 9.83, Me_3Sn 9.81, C_6H_4 2.65 (s).

[*p*-(*Trimethylstannyl*)*phenyl*]*pentamethyldisilane*

To the Grignard reagent prepared from (*p*-bromophenyl)trimethylstannane (31.9 g, 0.10 mole) and magnesium (2.9 g, 0.12 g-atom) in THF (200 ml) was added a solution of chloropentamethyldisilane[12] (20.0 g, 0.14 mole) in THF (50 ml). The mixture was refluxed for 12 h then treated with ice-cold aqueous ammonium chloride. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic phases were dried and distilled to give [*p*-(trimethylstannyl)-phenyl]pentamethyldisilane (nc) (11.1 g, 29%), b.p. 101–103°/0.2 mm, n_D^{25} 1.5265. (Found: C, 45.1; H, 7.7. $C_{14}H_{28}Si_2Sn$ calcd.: C, 45.3; H, 7.6%.) The ^1H NMR spectrum showed τ values as follows: Me_3Sn 9.75, Me_3Si 9.96, $SiSiMe_2$ 9.71, C_6H_4 2.65 (s).

Bromotris(*trimethylsilyl*)*silane*

Tetrakis(trimethylsilyl)silane, prepared from silicon tetrachloride, chlorotrimethylsilane and lithium chippings in THF[13], was converted into tris(trimethylsilyl)silane by treatment with methyllithium followed by dilute aqueous sulphuric acid[14]. Tris(trimethylsilyl)silane and excess of 1-bromobutane were refluxed for 12 h and the mixture was distilled to give bromotris(trimethylsilyl)silane (85%), m.p. 84–86° (sealed tube) (lit.[15], m.p. 80–85°).

2-*Phenyl- and* 2-*chloro-heptamethyltrisilane*

An *in situ* reaction[16] between phenylmethyldichlorosilane, chlorotrimethylsilane, and sodium/potassium alloy in xylene gave 2-phenylheptamethyltrisilane (37%), b.p. 133–135°/20 mm, n_D^{25} 1.5230 (lit.[16], b.p. 133°/19 mm, n_D^{20} 1.5236.) The ^1H NMR spectrum for $C_6H_5SiMe(SiMe_3)_2$ showed τ values as follows: Me_3Si 9.85, $(Me_3Si)_2Si\mathit{Me}$ 9.58, C_6H_5 multiplet centered at 2.71. Treatment of the 2-phenylheptamethyltrisilane with aluminium chloride and dry hydrogen chloride gave 2-chloroheptamethyltrisilane (83%), b.p. 80°/20 mm, n_D^{25} 1.4700 (lit.[16], b.p. 80.5°/20 mm, n_D^{20} 1.4727).

2-[*p*-(*Trimethylstannyl*)*phenyl*]*heptamethyltrisilane*

The Grignard reagent, prepared from (*p*-bromophenyl)trimethylstannane

(22 g, 0.070 mole) and magnesium (3.0 g, 0.12 g-atom) in THF (100 ml) was treated with 2-chloroheptamethyltrisilane (16.0 g, 0.070 mole) in THF (50 ml). The reaction mixture was subsequently refluxed overnight then treated with ice-water. Work-up in the usual way, culminating in distillation followed by refractionation, gave 2-[*p*-(trimethylstannyl)phenyl]heptamethyltrisilane (nc) (9.5 g, 32%), b.p. 113–114°/0.1 mm, n_D^{25} 1.5370. (Found: C, 44.3; H, 7.8. $C_{16}H_{34}Si_3Sn$ calcd.: C, 44.7; H, 7.9%.) The ^1H NMR spectrum showed τ values as follows: Me_3Sn 9.76, Me_3Si 9.91, SiSiMe 9.65, C_6H_4 2.71 (s).

[*p*-(*Trimethylstannyl*)*phenyl*]*tris*(*trimethylsilyl*)*silane*

The Grignard reagent prepared from (*p*-bromophenyl)trimethylstannane (31.0 g, 0.10 mole) and magnesium (3.5 g, 0.15 g-atom) in THF (150 ml) was filtered under nitrogen and added to a solution of bromotris(trimethylsilyl)silane (30.0 g, 0.091 mole) in THF (100 ml). The reaction mixture was stirred for 12 h, then treated with ice-water. The organic layer was separated and dried, and the products distilling up to a temperature equivalent to 350° at atmospheric pressure were removed *in vacuo*. The residue solidified on cooling and was successively recrystallized from ethanol and light petroleum (b.p. 40–60°) to give [*p*-(trimethylstannyl)phenyl]tris(trimethylsilyl)silane (nc) (6.3 g, 15%), m.p. 55°. (Found: C, 44.5; H, 8.2. $C_{18}H_{40}Si_4Sn$ calcd.: C, 44.4; H, 8.2%.) The ^1H NMR spectrum showed τ values as follows: Me_3Sn 9.77, Me_3Si 9.81, C_6H_4 2.73 (s).

Phenylpentamethyldisilane

A similar reaction between phenylmagnesium bromide and chloropentamethyldisilane gave phenylpentamethyldisilane (66%), b.p. 113–115°/24 mm n_D^{25} 1.5005 (lit.[17], b.p. 113–114.5°/25 mm, n_D^{20} 1.5056). The ^1H NMR spectrum showed τ values as follows: Me_3Si 9.88, $SiSiMe_2$ 9.61, C_6H_5 multiplet centered at 2.65.

Phenyltris(*trimethylsilyl*)*silane*

A solution of [*p*-(trimethylstannyl)phenyl]tris(trimethylsilyl)silane (1.0 g) in a mixture of methanol (5 ml) and aqueous (5*M*) perchloric acid (2 ml) was maintained at 50° for 10 min. (The progress of the reaction was followed by withdrawing samples, diluting them with methanol, and observing the change in the UV spectrum.) The mixture was subsequently neutralised with aqueous alkali and the organic products were extracted with ether. The ether extracts were dried, the ether was removed under reduced pressure, and the residue was transferred to an alumina column and eluted with light petroleum (b.p. 40–60°). The first fractions, which contained the desired products, were evaporated to dryness and the residue was taken up in methanol/ethanol. On cooling this solution to −40°, phenyltris(trimethylsilyl)silane precipitated as a waxy solid, m.p. 88–90°. (Found: C, 55.8; H, 9.9. $C_{15}H_{32}Si_4$ calcd.: C, 55.5; H, 9.9%.) The ^1H NMR spectrum showed a singlet ($SiMe_3$) resonance at τ 9.81, and a multiplet C_6H_5 centered at τ 2.75.

Proton NMR measurements

These were recorded on a Varian HA100 spectrometer; 10% solutions in carbon tetrachloride with acetone as internal standard were used.

Rate measurements

The acid cleavage of aryl–tin and –silicon bonds was followed by the spectrophotometric method previously described[3,7] sealed ampoules being used for the aryl–silicon cleavages. The spectra of the solutions produced by cleavage of the aryltin compounds were in quantitative agreement with those solutions of the appropriate arylsilanes in the reaction medium. The latter spectra were shown to be unchanged during a period of 10 times that of the half-life of the corresponding cleavage. The spectra of the solutions produced by cleavage of the aryl silanes in the stronger acid medium agreed quantitatively with those of solutions of benzene in the medium.

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REFERENCES

1 A. G. Beaumont, C. Eaborn and R. A. Jackson, *J. Chem. Soc. B*, in press.
2 A. R. Bassindale, C. Eaborn, D. R. M. Walton and D. J. Young, *J. Organometal. Chem.*, 20 (1969) 49.
3 C. Eaborn and J. A. Waters, *J. Chem. Soc.*, (1961) 542.
4 R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, London, 1965, p. 287.
5 H. Sakurai, S. Deguchi, M. Yamamoto, S.-I. Morimoto, M. Kira and M. Kumada, *J. Organometal. Chem.*, 18 (1969) 285.
6 J. L. Speier, *J. Amer. Chem. Soc.*, 75 (1953) 2930.
7 C. Eaborn, *J. Chem. Soc.*, (1956) 4858.
8 R. Baker, R. W. Bott, C. Eaborn and P. M. Greasley, *J. Chem. Soc.*, (1964) 627.
9 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 485–486.
10 R. W. Bott, C. Eaborn and P. M. Jackson, *J. Organometal. Chem.*, 7 (1967) 79.
11 C. Eaborn, H. L. Hornfeld and D. R. M. Walton, *J. Chem. Soc. B*, (1967) 1036.
12 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Lett.*, (1966) 5493.
13 H. Gilman and C. L. Smith, *J. Organometal. Chem.*, 8 (1967) 245.
14 H. Gilman and C. L. Smith, *J. Organometal. Chem.*, 14 (1968) 91.
15 H. Gilman and R. L. Harrell, *J. Organometal. Chem.*, 5 (1966) 199.
16 M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, 2 (1964) 478.
17 H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 80 (1958) 608.