ORGANOSILICON COMPOUNDS

XXXII[a]. THE CLEAVAGE OF ARYL-SILICON BONDS BY SULPHUR TRIOXIDE

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INTRODUCTION

Cleavages of aryl-silicon bonds by electrophilic reagents are electrophilic aromatic substitutions, analogous to those in which aryl-hydrogen bonds are broken[1], and cleavages by acids[2,3], halogens[4,5,6], nitrating agents, and mercuric salts[7] have been studied in some detail. We now report the results of a qualitative study of cleavage of aryl-silicon bonds by sulphur trioxide[d]. This reagent does not cleave alkyl-silicon bonds, and has been used, for example, to convert poly(dimethyl)siloxane into dimethylsilyl sulphate[10] (97 %), and chlorotrimethylsilane into the trimethylsilyl ester of chlorosulphonic acid[11] (83 %).

RESULTS AND DISCUSSION

Aryltrimethylsilanes react readily with sulphur trioxide in carbon tetrachloride, in the absence of water, to give goods yields (generally 80–90 %) of esters of the type $ArSO_2OSiMe_3$, which are hydrolysed rapidly by water at room temperature to the free sulphonic acids:

$$ArSiMe_3 + SO_3 \longrightarrow ArSO_2OSiMe_3 \xrightarrow{H_2O} ArSO_3H \quad (+Me_3SiOH)$$

This reaction sequence may be of value in synthesis as a means of introducing the sulpho group into an aromatic compound at a specific position under relatively mild conditions (*cf.* nitrodesilylation[12]). For example, *m*-tolyltrimethylsilane gives *m*-toluenesulphonic acid in good yield.

With bis(triorganosilyl)benzenes, replacement of one silyl group by the strongly deactivating SO_2OSiMe_3 group retards cleavage of the other aryl-silicon bond, and esters of (triorganosilyl)benzenesulphonic acids can be obtained in good yields; for example, the compound *m*-$Me_3SiC_6H_4SiMe_3$ gives the ester *m*-$Me_3SiC_6H_4SO_2OSiMe_3$ in 88 % yield. The esters may be quantitatively hydrolysed to the free sulphonic acids, and these may then be converted to the usual derivatives (see Table) without

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loss of the second silyl group. The acids *m*- and *p*-$HSO_3C_6H_4SiMe_3$ are the first reported compounds containing a sulphoaryl group attached to silicon; they are unusual organosilicon compounds in that they are water soluble*.

The esters formed by cleavage of the compounds *m*- and *p*-$Ph_3SiC_6H_4SiMe_3$ could not be purified because of their high boiling points, and the analyses of the derived sulphonic acids were poor, but various derivatives, $Ph_3SiC_6H_4SO_2X$, were obtained in good yields, indicating that the Ar–$SiMe_3$ bond is cleaved in preference to the Ph–$SiAr_3$ or Ar–$SiPh_3$ bonds (*cf.* ref. 1, p. 152). This is consistent with the observation[15] that the *p*-$MeOC_6H_4$–$SiMe_3$ bond is cleaved about 60 times as readily as the *p*-$MeOC_6H_4$–$SiPh_3$ bond by aqueous methanolic perchloric acid at 50°, and about 1100 times as readily by bromine in aqueous acetic acid at 25°.

Benzyl–silicon bonds are not cleaved under the conditions used, and *o*-, *m*-, and *p*-[(trimethylsilyl)methyl]benzenesulphonic acids were obtained from the [(trimethylsilyl)benzyl]trimethylsilanes; the *p*-isomer was identical with that prepared from benzyltrimethylsilane and chlorosulphonic acid[16].

Hydrolysis of the product (assumed to be the ester *p*-$MeF_2SiC_6H_4SO_2OSiMe_3$) of the reaction of the compound *p*-$MeF_2SiC_6H_4SiMe_3$ with sulphur trioxide gave a water-soluble, very viscous, highly hygroscopic oil which was presumably a polysiloxane, $[Me(p\text{-}HSO_3C_6H_4)SiO]_n$. An attempt to obtain this polymer by hydrolysing the ester [assumed to be $Me_3SiOSO_2C_6H_4SiMe(OSO_2OEt)_2$]** obtained by treating diethoxy(methyl)[*p*-(trimethylsilyl)phenyl]silane with three equivalents of sulphur trioxide gave a product contaminated with ethyl sulphate.

In all cleavages, slightly less than one equivalent of sulphur trioxide was used and no evidence was found of normal sulphonation, *i.e.* attack at an Ar–H bond. It has been estimated that the Ar–$SiMe_3$ bond is approximately 10^8 times as reactive as the Ar–H bond towards bromine in acetic acid[4] and 10^4 times as reactive towards aqueous sulphuric acid[2] but a lower factor would be expected in cleavage by the more reactive, less selective, sulphur trioxide***. In the compounds studied, the most reactive Ar–H bond relative to the Ar–$SiMe_3$ bond in the same compound would be that *para* to the (trimethylsilyl)methyl group in [*m*-(trimethylsilyl)benzyl]trimethylsilane, but Ar–$SiMe_3$ cleavage accounted for at least 85 % of the reaction in this case.

Cleavage of aryl–silicon bonds may frequently or generally proceed through intermediates of type (I) (where E is an electrophile)[1]. In acid cleavage, the simplest mechanism consistent with the facts is one in which the intermediate (I) (E = H) is formed in the slow step, and destroyed by nucleophilic attack by a solvent molecule on silicon, in a subsequent fast step[3]. If the intermediate (II) is involved in cleavage by sulphur trioxide in the weakly-polar carbon tetrachloride, it is unlikely that the Me_3Si group ever leaves the vicinity of the SO_3^- group. The ion Me_3Si^+ might separate and migrate to the SO_3^- group within an ion-pair, or attack of an oxygen atom of the SO_3^- group on silicon might be synchronous with the breaking of the C–$SiMe_3$ bond

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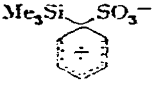
* The preparation of water-soluble sulphoarylsilicon compounds having aliphatic carbon atoms between the silicon and the sulphoaryl group have been described[13,14].

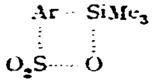
** Reaction of $Me_2Si(OEt)_2$ with one equivalent of sulphur trioxide gives the easily hydrolysable $Me_2Si(OEt)OSO_2OEt$.

*** Little information on the effects of substituents in reactions with sulphur trioxide is available (*cf.* ref. 17) but in competitive sulphonation at 25°, toluene is about 10 times as reactive as benzene[18].

of the intermediate (II). Even more attractive is a fully-concerted four-centre process, (III)[2,4,*], but a similarly attractive analogous process for cleavage by bromine in carbon tetrachloride has been ruled out by a stereochemical study[6].


(I)


(II)


(III)

EXPERIMENTAL

Preparation of compounds

*[m-(Trimethylsilyl)phenyl]triphenylsilane***. A solution of (*m*-chlorophenyl)-trimethylsilane (18.5 g, 0.1 mole) and fluorotriphenylsilane (27.8 g, 0.1 mole) in toluene (50 ml) was added dropwise (during 30 min) to molten sodium (5.5 g, 0.24 g-atom) in boiling toluene (100 ml), and the mixture refluxed for 1 h and then cooled. Sodium salts and unchanged sodium were removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallised from benzene–methanol to give [*m*-(trimethylsilyl)phenyl]triphenylsilane (31 g, 76 %), m.p. 115–116°. (Found: C, 79.0; H, 6.6. $C_{27}H_{28}Si_2$ calcd.: C, 79.4; H, 6.9 %.)

*[o-(Trimethylsilyl)benzyl]trimethylsilane***, b.p. 76–77°/1 mm, n_D^{25} 1.4992 (Found: C, 66.3; H, 10.2. $C_{13}H_{24}Si_2$ calcd.: C, 66.0; H, 10.3 %.) was similarly obtained (86 g, 70 %) from (*o*-chlorobenzyl)trimethylsilane (103.5 g, 0.52 mole), chlorotrimethylsilane (56.7 g, 0.52 mole), and sodium (29 g, 1.26 g-atom).

*Diethoxy(methyl)[p-(trimethylsilyl)phenyl]silane***. Triethoxymethylsilane (88 g, 0.49 mole) was added (at −70 to −80°) to the Grignard reagent from (*p*-bromophenyl)-trimethylsilane (124 g, 0.54 mole) and magnesium (14 g, 0.57 g-atom) in ether (200 ml). The mixture was then allowed to warm to room temperature and refluxed for 7 h. The ether was replaced by benzene, the magnesium salts were filtered off under dry nitrogen, and the solution was fractionated to give diethoxy(methyl)-[*p*-(trimethylsilyl)phenyl]silane (80 g, 57 %), b.p. 100–102°/1.5 mm, n_D^{25} 1.4739. (Found: C, 59.6; H, 9.6. $C_{14}H_{26}O_2Si_2$ calcd.: C, 59.5; H, 9.3 %.)

*Difluoro(methyl)[p-(trimethylsilyl)phenyl]silane***. Hydrofluoric acid (40 % w/w, 35 ml) was added to diethoxy(methyl)[*p*-(trimethylsilyl)phenyl]silane (25 g, 0.088 mole) in ethanol (250 ml) and the mixture refluxed for 5 h and poured into water (1 l). The non-aqueous layer was dissolved in ether, dried (Na_2SO_4) and fractionated, to give difluoro(methyl)[*p*-(trimethylsilyl)phenyl]silane (15.5 g, 76 %), b.p. 46°/0.6 mm, n_D^{25} 1.4622. (Found: C, 51.9; H, 7.3; $C_{10}H_{16}F_2Si_2$ calcd.: C, 52.1; H, 7.0 %.)

Sulphodesilylation and the preparation of sulphonic acids and derivatives

(*i*) A freshly prepared solution of sulphur trioxide (4.0 g, 0.05 mole) (obtained by heating 65 % oleum) in anhydrous carbon tetrachloride (40 ml) was added dropwise, with exclusion of moisture, during 10 min to a stirred solution of *p*-bis(trimethyl-

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[*] The order of the reaction is not known and possibly more than one molecule of sulphur trioxide is involved (sulphonation of aromatic compounds in nitrobenzene is second order in sulphur trioxide[17]), but additional molecules could be incorporated in processes of the general type postulated.

[**] New compound.

silyl)benzene (17 g, 0.077 mole) in carbon tetrachloride (70 ml) cooled with ice–water. The mixture was refluxed gently for 15 min and then fractionally distilled through a precision-made Vigreux column (20 plates) to give bis(trimethylsilyl)benzene (5.1 g, 30 %), b.p. 79°/2 mm, m.p. 96–97°, and trimethylsilyl *p*-(trimethylsilyl)benzenesulphonate* [12.1 g, 80 % (allowing for recovered starting material)], b.p. 150–151°/2 mm, 130–131°/0.6 mm, m.p. 83–86° (sealed tube). (Found: C, 47.4; H, 7.15. $C_{12}H_{22}O_3SSi_2$ calcd.: C, 47.6, H, 7.3 %.)

(*ii*) The sulphonate (3 g) was dissolved in water (15 ml), and after 15 min the excess water and hexamethyldisiloxane were evaporated below 50° under reduced pressure, and the residue (2.4 g) recrystallised from benzene to give *p*-(trimethylsilyl)benzenesulphonic acid monohydrate* (2.1 g, 85 %), m.p. 89–90° (sealed tube). (Found: C, 43.4; H, 6.45. $C_9H_{16}O_4SSi$ calcd.: C, 43.5; H, 6.5 %.) The *S*-benzylthiouronium salt*, m.p. 212–213° (from chloroform), was prepared in the normal way. (Found: C, 52.1; H, 5.8; N, 6.7. $C_{17}H_{24}N_2O_3S_2Si$ calcd.: C, 51.5; H, 6.1; N, 7.0 %.)

(*iii*) A solution of the sulphonate (7 g) in water (30 ml) was neutralized (to phenolphthalein) with 5 % aqueous sodium hydroxide and the water removed at reduced pressure. The residue was taken up in a little water and re-precipitated by addition of ethanol, to give sodium *p*-(trimethylsilyl)benzenesulphonate monohydrate* (5.7 g, 91 %). (Found: C, 39.4; H, 5.95. $C_9H_{15}NaO_4SSi$ calcd.: C, 39.9; H, 5.6 %.)

(*iv*) The sodium salt (5 g, 0.019 mole) was heated at 130° for 20 min with phosphorus pentachloride (7 g, 0.034 mole) and the mixture was added to ice–water (40 ml). Extraction with benzene, followed by separation, drying (Na_2SO_4) and fractional distillation of the extract gave *p*-(trimethylsilyl)benzenesulphonyl chloride* (3.9 g, 78 %), b.p. 160–162°/11 mm, m.p. 56–57° (from light petroleum). (Found: C, 43.5; H, 5.45. $C_9H_{13}ClO_2SSi$ calcd.: C, 43.45; H, 5.3 %.)

(*v*) The sulphonyl chloride (1 g) was added with stirring to a few ml of aqueous ammonia (*d* 0.88). The solid which separated was dried and recrystallised from benzene–light petroleum, to give *p*-(trimethylsilyl)benzenesulphonamide*, m.p. 115–116°. (Found: C, 47.2; H, 6.8; N, 5.9. $C_9H_{15}NO_2SSi$ calcd.: C, 47.1; H, 6.6; N, 6.1 %.)

(*vi*) Aniline (2 g) was added to a solution of the sulphonyl chloride (1 g) in benzene (20 ml), the mixture was refluxed for 5 min, cooled and washed with 0.5 *N* hydrochloric acid and then with water. The benzene layer was evaporated and the residue (1.2 g) was recrystallized from benzene–light petroleum, to give *p*-(trimethylsilyl)benzenesulphonanilide*, m.p. 122–123°. (Found: C, 58.7; H, 6.45; N, 4.65. $C_{15}H_{19}NO_2SSi$ calcd.: C, 59.0; H, 6.3; N, 4.6 %.)

A number of aryltrimethylsilanes were treated similarly and details of the products are given in Table 1.

Difluoro(methyl)[*p*-(trimethylsilyl)phenyl]silane (13 g, 0.056 mole) in carbon tetrachloride (100 ml) and sulphur trioxide (4.5 g, 0.056 mole) in carbon tetrachloride (180 ml) were reacted in the usual way. The residue (16 g) {assumed to be trimethylsilyl *p*-[difluoro(methyl)silyl]benzenesulphonate} was dissolved in water (100 ml) and refluxed for 2 h with excess barium carbonate. Insoluble barium salts were filtered from the cold solution which was then passed through a column of Amberlite IR-

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* New compound.

TABLE 1

SULPHONIC ACIDS AND THEIR DERIVATIVES OBTAINED FROM ARYLSILANES

X	*b.p.* °/*mm* (*m.p.*)	n_D^{25}	*Yield*[a] (%)	*Found* %[b]		*Required* %	
				C	*H*	*C*	*H*
Products m-$\mathrm{Me_3SiC_6H_4SO_2}X$ *from* m-$\mathrm{Me_3SiC_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	135–6/1.5	1.4966	88[c]	47.6	7.4	47.6	7.3
$\mathrm{OH \cdot H_2O}$	(65–6)			43.2	6.8	43.5	6.5
$\mathrm{O^-[PhCH_2SC(NH_2)_2]^+}$	(161–2)			51.6	6.3	51.5	6.1
Cl	146–7/10	1.5304	80	43.8	5.5	43.45	5.3
$\mathrm{NH_2}$	(112–3)			47.2	6.9	47.1	6.6
NHPh	(83–4)			59.0	6.5	59.0	6.3
Products o-$\mathrm{Me_3SiCH_2C_6H_4SO_2}X$ *from* o-$\mathrm{Me_3SiCH_2C_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	111–2/0.5	1.4958	50[c]	49.2	7.5	49.3	7.6
$\mathrm{OH \cdot H_2O}$	(87–8)			45.3	6.9	45.8	6.9
$\mathrm{O^-Na^+}$	—			41.9	5.7	42.2	6.0
Cl	89–90/0.3	1.5361	72	45.5	5.8	45.7	5.75
$\mathrm{NH_2}$	(74–5)			49.7	7.2	49.35	7.0
NHPh	(102–3)			60.0	6.7	60.1	6.6
Products m-$\mathrm{Me_3SiCH_2C_6H_4SO_2}X$ *from* m-$\mathrm{Me_3SiCH_2C_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	133–4/0.6	1.4922	85	49.7	7.2	49.3	7.6
OH	dec.	1.5207		48.65	6.6	49.1	6.6
$\mathrm{O^-Na^+}$	—			44.5	5.7	45.0	5.7
Cl	111–2/0.6	1.5280	73	45.9	5.8	45.7	5.75
$\mathrm{NH_2}$	(75–6)			49.7	6.9	49.35	7.0
NHPh	(79–80)			59.1	6.6	60.1	6.6
Products p-$\mathrm{Me_3SiCH_2C_6H_4SO_2}X$ *from* p-$\mathrm{Me_3SiCH_2C_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	151–2/1(114-5)		80	49.1	7.6	49.3	7.6
OH	(115–6)[d]						
Products m-$\mathrm{MeC_6H_4SO_2}X$ *from* m-$\mathrm{MeC_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	124–5/1	1.4916	80	49.1	6.75	49.15	6.6
Cl	(10.5–11.5)[e]						
$\mathrm{NH_2}$	(111)[f]						
Products m-$\mathrm{Ph_2SiC_6H_4SO_2}X$ *from* m-$\mathrm{Ph_3SiC_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	(127 dec.)		89	(not purified)			
OH	(143 dec.)			(impure)			
$\mathrm{O^-Na^+ \cdot H_2O}$	—			63.9	4.4	63.2	4.4
Cl	(123–4)		96	66.3	4.4	66.2	4.4
NHPh	(154–5)			73.6	4.9	73.3	5.1
Products p-$\mathrm{Ph_3SiC_6H_4SO_2}X$ *from* p-$\mathrm{Ph_3SiC_6H_4SiMe_3}$							
$\mathrm{OSiMe_3}$	(132 dec.)		90	(not purified)			
OH	(138 dec.)			(impure)			
$\mathrm{O^-Na^+ \cdot H_2O}$	—			63.2	4.4	63.2	4.4
Cl	(185–6)		84	65.8	4.6	66.2	4.4
NHPh	(196–7)			73.3	5.1	73.3	5.1

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[a] Yields of acids and sodium salts from the esters, and of amides and anilides from the chlorides, were nearly quantitative. [b] Analyses given for new compounds. [c] Allowing for 30% recovery of starting material. [d] M.p. undepressed when mixed with sample made by the method of Bygden[18]. [e] Lit.[13] m.p. 11.7°. [f] Lit.[19] m.p. 108°.

120(H) ion-exchange resin, and evaporated to dryness under reduced pressure to give a highly hygroscopic, very viscous oil, assumed to be poly(methyl-*p*-sulphophenyl)-siloxane (10.5 g, 87%). [Found: C, 38.9; H, 3.9. $(C_7H_8O_4SSi)_n$ calcd.: C, 38.9; H, 3.7%.]

Treatment of diethoxydimethylsilane (9.0 g, 0.06 mole) with sulphur trioxide (4.0 g, 0.05 mole) by the general method gave ethyl ethoxydimethylsilyl sulphate* (5.2 g, 46%), b.p. 66–67°/0.6 mm, n_D^{25} 1.4085. (Found: C, 31.6; H, 7.0. $C_6H_{16}O_5SSi$ calcd.: C, 31.6; H, 7.0%.)

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SUMMARY

Aryltrimethylsilanes, $ArSiMe_3$, react with sulphur trioxide in carbon tetrachloride to give the sulphonic esters, $ArSO_2OSiMe_3$, which undergo hydrolysis readily to the sulphonic acids $ArSO_3H$. The reaction provides a means of introducing a sulpho group at a specific position of the aromatic ring; thus from *m*-tolyltrimethylsilane, *m*-toluenesulphonic acid is obtained in 80% yield.

The reaction has been used to prepare from the compounds *m*- or *p*-$R_3SiC_6H_4SiMe_3$, where R = Me or Ph, the acids *m*- or *p*-$R_3SiC_6H_4SO_3H$ and their derivatives, the first examples of compounds containing sulphoaryl groups attached directly to silicon.

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* New compound.