35. *Aromatic Reactivity. Part VIII.* Bromo- and Chloro-desilylation in Acetic Acid.*

By C. Eaborn and D. E. Webster.

In bromodesilylation in 1·5% water–acetic acid the order of reaction has been found to increase with increasing bromine concentration. Relative reactivities of several substituted phenyltrimethylsilanes have been measured in this reaction, and a similarity in the pattern of substituent effects to that in aromatic bromination by a positive species is discussed.

Phenyltrimethylsilanes have been shown to undergo chlorodesilylation on treatment with chlorine in 1·5% water–acetic acid. They are cleaved by chlorine only a little faster than by bromine.

We report below some extensions of our study of the cleavage by bromine of substituted phenyltrimethylsilanes (bromodesilylation) in acetic acid containing 1·5% of water.[1] Concentrations of halogen and aromatic compound were initially equal throughout the work.

Order of Reaction.—We previously showed that bromodesilylation of phenyltrimethylsilane in 1·5% water–acetic acid is approximately of second order (first order in each reactant) for initial bromine concentrations of $<0{\cdot}01$M, whereas the bromination of anisole, which has a comparable rate, is of markedly higher order.[1] In molecular bromination the order is known to increase with initial concentration of bromine,[2] and Table 1 shows this to be true also of bromodesilylation. The order of bromodesilylation can even exceed 3, but at all concentrations studied it is lower than that of bromination. The order is independent of which aryltrimethylsilane is involved for the limited variety examined.

Table 1. *Orders of reaction of* $ArSiMe_3$ *or* ArH *with bromine at* 25·0°.†

Aromatic compd.	Concn. (M)	Order	Aromatic compd.	Concn. (M)	Order
$C_6H_5{\cdot}SiMe_3$	0·0005—0·001	1·9	p-$Cl{\cdot}C_6H_4{\cdot}SiMe_3$	0·03—0·06	2·9
m-$Me{\cdot}C_6H_4{\cdot}SiMe_3$	0·0015—0·003	1·9	p-$Cl{\cdot}C_6H_4{\cdot}SiMe_3$	0·10—0·20	3·1
$C_6H_5{\cdot}SiMe_3$	0·002—0·004	2·0	$MeO{\cdot}C_6H_5$	0·001—0·002	2·5
p-$Cl{\cdot}C_6H_4{\cdot}SiMe_3$	0·002—0·004	2·0	2,4,6-$Me_3C_6H_3$	0·001—0·002	2·4
$C_6H_5{\cdot}SiMe_3$	0·01—0·02	2·4	p-$Br{\cdot}C_6H_4{\cdot}OMe$	0·025—0·050	3·2
p-$Cl{\cdot}C_6H_4{\cdot}SiMe_3$	0·01—0·02	2·4			

† The order was determined from the change in times required for 5, 10, and 20% of reaction on doubling the initial concentrations of both reactants, as in the second and fifth columns (see ref. 1).

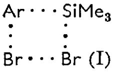
The occurrence of orders greater than 2 in molecular bromination means that there are concurrent reactions of the second, third, and possibly higher order as in eqn. (1).[2] It is

$$-d[\mathrm{ArH}]/dt = k_2[\mathrm{ArH}][\mathrm{Br_2}] + k_3[\mathrm{ArH}][\mathrm{Br_2}]^2 + k_4[\mathrm{ArH}][\mathrm{Br_2}]^3 + \ . \quad . \qquad (1)$$

suggested [2] that an electrophil, E, is needed to remove the bromide ion from the attacking bromine molecule:

$$\mathrm{HAr\cdots Br\cdots Br\cdots E} \xrightarrow{\text{slow}} \mathrm{ArHBr^+ + BrE^-} \xrightarrow{\text{fast}} \mathrm{ArBr + H^+ + BrE^-}$$

The electrophil may be a solvent molecule or an additional bromine molecule (or more than one such molecule when orders higher than three are involved). For this discussion it does not matter whether the rate-determining step in the third-order reaction involves attack of an additional bromine molecule on the intermediate $ArHBr_2$[2,3,4] or attack of a Br_4 complex on the compound ArH. It seems that the greater availability of electrons in the Ar–$SiMe_3$ bond compared with that in an Ar–H bond leads to a smaller need for the additional electrophil in bromodesilylation



(I)

---

* Part VII, *J.*, 1959, 3640.

[1] Eaborn and Webster, *J.*, 1957, 4449.

[2] Robertson, *Science Progr.*, 1955, **43**, 418.

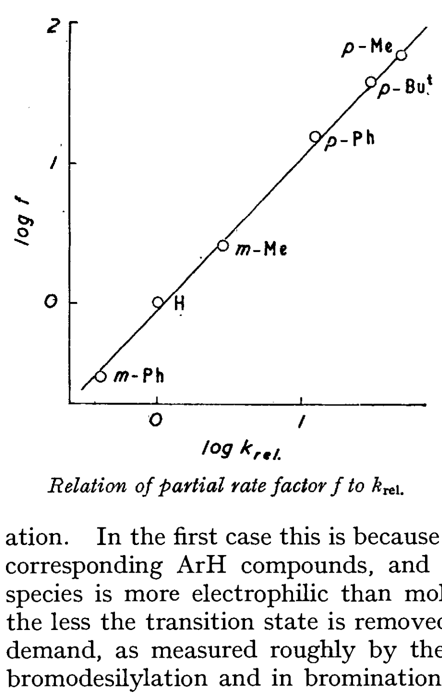
[3] de la Mare, in "Progress in Stereochemistry," Ed. by W. Klyne, Vol. II, Butterworths Scientific Publications, London, 1958, p. 72.

[4] Keefer, Blake, and Andrews, *J. Amer. Chem. Soc.*, 1954, **76**, 3062; Blake and Andrews, *ibid.*, 1955, **77**, 3707; Keefer, Ottenberg, and Andrews, *ibid.*, 1956, **78**, 255; Keefer and Andrews, *ibid.*, 1956, **78**, 3637; Andrews, *Chem. Rev.*, 1954, **54**, 713.

even when the $ArSiMe_3$ and ArH compounds are of comparable reactivity. [We do not wish to complicate the discussion at this stage by enlarging on the possibility of a cyclic transition state in the second-order bromodesilylation, *viz.*, (I), but in view of the probable ease of " flank " attack at silicon [5] such a possibility cannot be discounted. We hope to explore it through stereochemical studies.]

Increase in the water content of the medium raises the rate of reaction, as for molecular bromination.[2] For example, compared with reactions in 1·5% water–acetic acid, *p*-chlorophenyltrimethylsilane (initially 0·04M) reacts *ca.* 2·4 times as fast in 5% water–acetic acid, and phenyltrimethylsilane (initially 0·003M) reacts *ca.* 40 times as fast in 20% water–acetic acid. This is partly because water enters into the reaction as an electrophil more effectively than acetic acid, but mainly because a reaction involving formation of charge in the transition state from initially neutral reactions is facilitated by increasing the solvating power of the medium.

The order did not fall below 2 under a combination of conditions favouring low orders, *viz.*, low initial bromine and *p*-chlorophenyltrimethylsilane concentrations (0·0004 and 0·0008M), high water content (20%) in the solvent, and a temperature of 40°.



Relation of partial rate factor f to $k_{rel.}$

Substituent Effects.—The relative reactivities of some substituted phenyltrimethylsilanes, determined as previously described,[1] are listed in Table 2.* (Where they differ slightly from those previously given, the present figures are the more accurate.) We need not add to our earlier discussions of these reactivities,[1,7] except to point out the remarkable similarity of the pattern of substituent effects in bromodesilylation to that in bromination by a positive species [8] over the (admittedly restricted) range of substituents in common. This is revealed by the plot of log $k_{rel.}$ for the former reaction against log *f* for the latter (see Figure), where *f* is the partial rate factor. There is smaller demand on the electrons of the ring both in bromodesilylation and in ionic bromination than in molecular bromination. In the first case this is because $ArSiMe_3$ compounds are more nucleophilic than the corresponding ArH compounds, and in the second it is because the positive bromine species is more electrophilic than molecular bromine. (The more reactive the reactants the less the transition state is removed from them.) By chance, we believe, the electron demand, as measured roughly by the activation factor for a *p*-Me group, is similar in bromodesilylation and in bromination by a positive species and thus the patterns agree for other *meta*- and *para*-substituents. (This discussion implies that in substitution in benzene the substituent effects depend more on the reactivity of the electrophilic reagent than on its charge type.)

It is noteworthy that the similarity in substituent effects in ionic bromination and in

* Since there are two identical bonds to be broken in the compound *p*-$Me_3Si{\cdot}C_6H_4{\cdot}SiMe_3$ the relative rate of 3·05 must be halved to give the effect of one *p*-Me_3Si group on the reactivity of the other aryl–$SiMe_3$ bond. Appropriate correction should be made to the log $k_{rel.}$–σ^+ plot for bromodesilylation [1] and, analogously, to that for protodesilylation.[6]

[5] Eaborn, " Organosilicon Compounds," Butterworths Scientific Publications, London, 1959, pp. 107—110.

[6] Eaborn, *J.*, 1956, 4858.

[7] Deans, Eaborn, and Webster, *J.*, 1959, 3031; Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.

[8] (*a*) de la Mare and Harvey, *J.*, 1956, 36; (*b*) *idem*, *J.*, 1957, 131; (*c*) de la Mare and Hassan, *J.*, 1957, 3004.

bromodesilylation extends to the *o*-Me group, which activates 76 times in the former reaction [8a] and 81·5 times in the latter. This suggests that steric effects are relatively small in both cases (such effects would hinder bromination and facilitate bromodesilylation) and that the polar effect of the *o*-Me group is larger than that of the *p*-Me group, at least in these reactions in which the electron-demand is fairly small (cf. refs. 8*b* and 9).

We have also examined the effect of increasing the size of the alkyl groups attached to silicon by comparing the rates of reaction of phenyltri-isopropyl- and phenyltrimethylsilane with bromine in 1·5% water–acetic acid. The rate is *ca.* 158 and 330 times greater for the latter compound at initial reactant concentrations of 0·0118 and 0·067M respectively. Polar effects alone would make the tri-isopropyl compound, with its additional inductive release of electrons to the reaction site, the more reactive, and it is clear that steric hindrance seriously reduces its reactivity, the effect apparently being greater for the higher-order components of the reaction. The steric hindrance is markedly greater than in protodesilylation in aqueous-methanolic perchloric acid at 50°, for which the trimethyl compound is only 25 times more reactive than the tri-isopropyl.[10] We postpone discussion of these effects until we have additional results.

TABLE 2. *Relative reactivities of* $R\cdot C_6H_4\cdot SiMe_3$ *compounds in bromodesilylation.*

R	$k_{rel.}$	R	$k_{rel.}$	R	$k_{rel.}$	R	$k_{rel.}$
$2,3-C_4H_3$ [a]	195	*p*-Bu^t	29·2	*o*-Ph	1·81	*p*-Cl	0·092
o-Me	81·5	*p*-Ph	12·5	*p*-Me_3Si	3·05	*p*-I	0·088
p-Me	48·8	$3,4-C_4H_3$ [b]	11·5	H	1·00	*p*-Br	0·071
p-Et	45·4	*m*-$Me_3Si\cdot CH_2$	8·5	*p*-F	0·68	*m*-Cl	0·0030
p-Pr^i	32·5	*m*-Me	2·9	*m*-Ph	0·41		

[a] 1-Naphthyltrimethylsilane. [b] 2-Naphthyltrimethylsilane.

Reaction of m-*Methoxyphenyltrimethylsilane with Bromine.*—In the interaction of *m*-methoxyphenyltrimethylsilane with bromine in 1·5% water–acetic acid, not only was the rate relative to that for phenyltrimethylsilane much higher than expected but fell markedly as reaction proceeded, indicating that a higher-order reaction was involved with the methoxy-compound. For an initial-concentration pair of 0·00076 and 0·00152M, the order for the *m*-methoxy-compound is, in fact, 2·5, similar to that for anisole, and it is clear that the large activation *para* to the MeO group causes ring bromination to occur rather than bromodesilylation. Isolation of bromotrimethylsilylanisole but no bromoanisole from a larger-scale reaction confirms this; the product is probably 4-bromo-3-trimethylsilylanisole, but small amounts of other isomers may be present.

The *m*-methoxy-compound reacts with bromine some 200 and 6 times faster than do phenyltrimethylsilane and anisole, respectively, as measured by the times for the initial 10 or 20% of reaction. Assuming that bromination occurs exclusively *para* to the MeO group, we can conclude that the *o*-Me_3Si group activates some 6 times in molecular bromination.

Neglecting the fact that reactions of different orders are involved, we can also derive an approximate figure for the reactivity of Ar–H and Ar–$SiMe_3$ bonds towards bromine. Anisole reacts with bromine in acetic acid *ca.* $1\cdot 2 \times 10^9$ times as fast as benzene,[11] and so phenyltrimethylsilane reacts *ca.* $(6 \times 1\cdot 2 \times 10^9)/200$, *i.e.*, $3\cdot 6 \times 10^7$ times as fast as benzene. Since there are six Ar–H bonds to be broken in benzene compared with one Ar–$SiMe_3$ bond in phenyltrimethylsilane, the reactivity of the latter type of bond is *ca.* 2×10^8 greater than that of the former. A smaller difference in reactivity between the Ar–H and Ar–$SiMe_3$ bonds is to be expected when electrophils of higher reactivity are involved (*e.g.*, nitronium ion).

Chlorodesilylation.—From chlorination of phenyltrimethylsilane in 1·5% water–acetic acid we isolated hexamethyldisiloxane and chlorobenzene; no higher-boiling material was

---

[9] de la Mare, Harvey, and Varma, *J.*, 1958, 2756.
[10] Miss P. M. Greasley, unpublished work.
[11] de la Mare, *J.*, 1954, 4451.

produced. The absence of chlorotrimethylsilylbenzene (which would not undergo significant protodesilylation in this medium) shows that chlorodesilylation occurs to the exclusion of ring chlorination.

Chlorination of benzene derivatives in acetic acid is of lower order than bromination at the higher halogen concentrations, and is of second order at the concentrations commonly employed.[2] Since orders lower than 2 are unlikely we were not surprised to find that the rate of chlorodesilylation of phenyltrimethylsilane relative to that of chlorination of *p*-bromoanisole remained constant (at 1·8) during 25—85% of reaction, showing that the reactions have the same order. The second-order rate constants in both cases rise slightly during a run, no doubt because of catalysis by the hydrogen chloride formed.[2]

Chlorine in acetic acid halogenates aromatic compounds much more rapidly than does bromine; thus in second-order halogenation of *m*-xylene or naphthalene in acetic acid, chlorination is faster by a factor of 10^4.[12] For *p*-chlorophenyltrimethylsilane and halogen both initially 0·01M, the first 10% of chlorine is removed only 2·5 times as fast as that of bromine, and the first 20% some 3·2 times as fast. (The factor rises because the order of the bromodesilylation is slightly higher than 2.) For phenyltrimethylsilane and halogen initially 0·02M, 30% and 70% of the halogen are removed 1·3 and 2·0 times faster for chlorine than for bromine.

The small difference between the rates of chloro- and bromo-desilylation is another consequence of the greater nucleophilic power of the phenyltrimethylsilanes than of simple aromatic compounds; for the more reactive a nucleophil, the less it discriminates between two electrophils. Again, the reactivity difference between corresponding Ar–H and Ar–$SiMe_3$ bonds is smaller towards chlorine than bromine because the more reactive electrophil discriminates less between the two nucleophils, as mentioned in the previous section.

If one wishes to make derivatives of arylsilicon compounds by direct halogenation then chlorination is likely to be more profitable than bromination.

EXPERIMENTAL

General.—Methods used for rate studies have been described.[1] The solvent was 1·5 wt. % water–acetic acid [1] and the temperature was 25·0° ± 0·02° for the runs described.

Materials.—The preparation or purification of most of the compounds has been described.[1,7,13]

m-*Methoxyphenyltrimethylsilane* was prepared from *m*-chloroanisole, trimethylchlorosilane, and sodium in boiling toluene. Fractionation gave material of b. p. 214°, n_D^{20} 1·5025, in 65% yield (Found: C, 66·2; H, 8·7. $C_{10}H_{16}OSi$ requires C, 66·6; H, 8·9%).

m-Tolyltrimethylsilane was prepared from trimethylchlorosilane, *m*-chlorotoluene, and sodium in boiling toluene. The product, b. p. 187°, n_D^{20} 1·4930, contained impurities reactive towards bromine (even though the *m*-chlorotoluene had been purified by progressive freezing and fractionation). These were removed by treating a solution of the compound (20 g.) in pyridine (20 ml.) with bromine (3 g.) and fractionating; the fraction of b. p. 180—190° was taken up in ether, and the solution was filtered, washed with 10% sulphuric acid and then water, dried (Na_2SO_4), and fractionated. A fraction of b. p. 187°, n_D^{20} 1·4962, which probably contained a little bromotoluene, was used for rate studies.

Relative Rates.—Solutions of two organosilanes in 1·5% water–acetic acid were prepared of exactly the same concentration as a standardized bromine solution. The times for disappearance of definite fractions of bromine were compared for 10—70% of reaction. [The ratio of these times normally remained constant; we previously found [1] that it varied for a *m*-tolyltrimethylsilane–phenyltrimethylsilane pair, but when a sample of the *m*-tolyl compound from which reactive impurities (probably *o*- and *p*-isomers) had been removed, as above, was used the ratio was satisfactorily constant at 2·9 ± 0·1 for 10—70% of reaction.]

Relative rates in Table 2 are based on such direct comparisons, previously listed [1] or as follows. For each pair of $R{\cdot}C_6H_4{\cdot}SiMe_3$ compounds (substituents *para* unless otherwise

---

[12] Personal communication from Professor P. W. Robertson.

[13] Deans and Eaborn, *J.*, 1959, 2299.

indicated) the average inverse ratio of times for disappearance of specific fractions of bromine is given, along with the limits of variation in this ratio during 20—70% of reaction: *o*-Me/Me, 1·67 ± 0·04; 2,3-C_4H_3/Me, 4·0 ± 0·2; H/*m*-Ph, 2·4 ± 0·1; 3,4-C_4H_3/H, 11·5 ± 0·5; 3,4-C_4H_3/*m*-Me_3SiCH_2, 1·35 ± 0·02; Ph/Me_3Si, 4·11 ± 0·06; *m*-Me_3SiCH_2/H, 8·5 ± 0·5; *o*-Ph/H, 1·84 ± 0·03; Ph/H, 12·4 ± 0·2; Cl/*m*-Cl, 31 ± 2.

With $[PhSiR_3] = [Br_2] = 0{\cdot}0118$M, the reaction times for tri-isopropylphenylsilane relative to those for the trimethyl compound were as follows:

Reaction (%)	20	30	40	50	60
Relative time	163	160	154	152	162

With $[ArSiR_3] = [Br_2] = 0{\cdot}0670$M, the reaction times for tri-isopropyl compounds relative to those for *p*-chlorophenyltrimethylsilane were as follows:

Reaction (%)	20	30	40	50	60	70
Relative time	33	29	27	29	32	31

Bromination of m-*methoxyphenyltrimethylsilane.*—Bromine (2·80 ml.) was added to a solution of the organosilane (10 g.) in 1·5% water–acetic acid. After 12 hr. at 25° the solution was added to water. Extraction with ether, followed by washing (aqueous sodium sulphite, aqueous sodium hydrogen carbonate, and water) drying (Na_2SO_4), and fractionation of the extract under reduced pressure gave 4-*bromo*-3-*trimethylsilylanisole* (60%), b. p. *ca.* 150°/10 mm., 260°/760 mm., n_D^{20} 1·5462 (Found: C, 46·3; H, 5·7. $C_{10}H_{15}OSiBr$ requires C, 46·3; H, 5·8%). No bromoanisole was obtained.

Chlorodesilylation.—(i) A solution of phenyltrimethylsilane (20 g.) and chlorine (0·93M) in 1·5% water–acetic acid (100 ml.) was kept at 25° for 48 hr. and then added to water. Extraction with light petroleum (b. p. $<40°$), followed by drying (Na_2SO_4) and fractionation of the extract, gave hexamethyldisiloxane, b. p. 100°, n_D^{20} 1·3901, chlorobenzene (7 g., 60%), b. p. 133°, n_D^{20} 1·5212, and phenyltrimethylsilane (4·5 g.), b. p. 167°, n_D^{20} 1·4918, leaving no residue.

(ii) *Comparison of chloro- and bromo-desilylation.*

(*a*) $[PhSiMe_3] = 0{\cdot}0177$M; $[Br_2] = 0{\cdot}01175$M.

Time (sec.)	0	45	205	665	1325	2440	3600	5680	7565	11,460
Titre (ml.)	3·240	3·130	2·905	2·480	2·060	1·660	1·375	1·070	0·865	0·625

(*b*) $[PhSiMe_3] = 0{\cdot}0177$M; $[Cl_2] = 0{\cdot}01175$M.

Time (sec.)	0	75	185	385	780	1395	2710	3300	4705	7710
Titre (ml.)	3·250	2·910	2·750	2·500	2·140	1·665	1·070	0·930	0·625	0·370

Reaction (%)	30	40	50	60	70
Relative rate (chloro-/bromo-desiln.)	1·55	1·60	1·75	1·88	2·10

(*c*) With $[PhSiMe_3] = [Hal_2] = 0{\cdot}0118$M, the relative rates of reaction with chlorine and and bromine were as follows:

Reaction (%)	30	40	50	60	70
Relative rate (chloro-/bromo-desiln.)	1·21	1·35	1·58	1·85	1·98

With $[p\text{-}Cl{\cdot}C_6H_4{\cdot}SiMe_3] = 0{\cdot}0130$M acid $[Hal_2] = 0{\cdot}0114$M the relative rates of reaction with chlorine and bromine were as follows:

Reaction (%)	5	10	20
Relative rate (chloro-/bromo-desiln.)	2·5	2·5	3·2

(iii) *Comparison of chlorodesilylation of phenyltrimethylsilane* (0·0300M) *and chlorination of* p-*bromoanisole* (0·0300M); $[Cl_2] = 0{\cdot}0130$M.

Reaction (%)	23	39	54	70	85
Relative rate (chlorinatn./chlorodesiln.)	2·2	1·8	1·8	1·8	1·8

We thank the Department of Scientific and Industrial Research for a maintenance grant to one of us (D. E. W.), and Professor P. W. Robertson for helpful comments and suggestions.

THE UNIVERSITY, LEICESTER. [*Received, June* 11*th*, 1959.]