

SOME RECENT STUDIES OF THE CLEAVAGE OF CARBON-SILICON AND RELATED BONDS

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This brief review will be concerned with heterolytic cleavages of carbon-silicon and related bonds, and will concentrate on some more recent investigations by the author and his co-workers.

The C—Si bond is fairly stable towards homolytic fission, and under free radical conditions the C—H bonds of organosilicon compounds are usually more readily attacked than the C—Si bonds¹. The C—Si bond is moderately polar, however, (Pauling electronegativities indicate that there is 12% ionic character in the direction C—Si⁺), and is relatively easily attacked by ionic reagents. Since C—H bonds break heterolytically in the same direction, C—H⁺, a good indication of the behaviour of an R—Si bond can be obtained by considering the reactions of the corresponding R—H bond². For example, just as the C—H bond of chloroform, HCCl₃, is readily broken by attack of hydroxide ion on the hydrogen atom, so the Si—C bond of the compound Me₃SiCCl₃ is broken, even more readily, in alkali, by nucleophilic attack at silicon. Again, just as aryl—H bonds are broken readily by electrophilic reagents such as bromine or sulphur trioxide, so aryl—SiMe₃ bonds are also broken readily by these reagents. It is usually but not always true that an R—SiMe₃ bond is more reactive than the corresponding R—H bond towards ionic reagents.

NUCLEOPHILIC CLEAVAGE OF BENZYL—SILICON AND RELATED BONDS

Unsubstituted alkyl groups are cleaved from silicon with difficulty by common nucleophilic reagents, although even tetraalkylsilanes are cleaved by powerfully-basic reagents such as potassium *tert*-butoxide in dimethylsulphoxide³. With benzyl-silicon bonds, the separating carbanion is stabilized by resonance, and cleavage occurs much more readily. The rates of cleavage of XC₆H₄CH₂SiMe₃ compounds by aqueous methanolic alkali can be conveniently measured by the change in the ultra-violet absorption,⁴ and a few of the results provided by such studies are shown in *Table 1* in which k_{rel} is the rate of cleavage of the substituted compound XC₆H₄CH₂SiMe₃ relative to that of the parent compound C₆H₅CH₂SiMe₃. It will be seen that the cleavage is markedly facilitated by electron-withdrawal in the substituent X; the activating effect of a *p*-NO₂ group is so large that *p*-nitrobenzyltrimethylsilane is cleaved by aqueous methanol alone about as rapidly as is benzyltrimethylsilane by 2M sodium hydroxide in this medium.

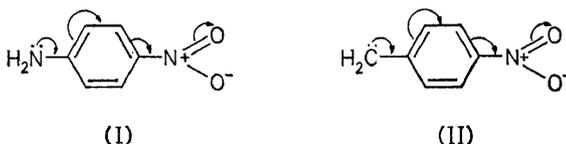
The substituent effects fit very well the Hammett free energy relationship

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Table 1. Relative rates of cleavage of $\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{X}$ compounds by alkali in 39 wt.-% water-methanol at 50°.

X	k_{rel}	X	k_{rel}
<i>p</i> -NO ₂	1.8×10^6	<i>m</i> -CF ₃	1.0×10^2
<i>o</i> -NO ₂	5.0×10^5	<i>o</i> -Cl	8.0×10
<i>p</i> -PMe ₃ ⁺	4.2×10^5	<i>m</i> -Cl	6.3×10
<i>p</i> -COPh	1.6×10^5	<i>p</i> -Cl	1.4×10
<i>p</i> -SO ₂ Ph	1.5×10^5	<i>p</i> -SiMe ₃	9.6
<i>p</i> -P(O)Ph ₂	1.5×10^4	<i>m</i> -CO ₂ ⁻	2.1
<i>m</i> -PMe ₃ ⁺	4.6×10^3	H	1.0
<i>p</i> -CONH ₂	6.3×10^2	<i>p</i> -Me	0.20
<i>o</i> -I	1.4×10^2	<i>p</i> -OMe	~0.02

$\log k_{\text{rel}} = \rho\sigma$, with a high value of ρ of 4.9. For substituents such as *p*-NO₂, *p*-CO₂H, and *p*-SO₂Ph, which can withdraw electrons by a conjugative mechanism, the ("exalted") σ^- -constants have to be used⁴. These constants are derived from strengths of phenols and amines, in which lone pairs of electrons are available for conjugation with the *para*-substituent, as in (I), and it is understandable that they should apply to the cleavage of benzylsilicon compounds since the separating carbanion is stabilized by similar conjugation, as in (II). Because of the considerable sensitivity of the cleavage to effects of substituents, the reaction provides a useful means of measuring the extent of this kind of conjugation for various substituents. For example,



the effects of some phosphorus-containing substituents have recently been studied⁵, and the values of k_{rel} shown in Table 2 reveal that these substituents have markedly larger activating effects from the *para*- than from the *meta*-position, which is consistent with the existence of conjugative electron-withdrawal resulting from (*p*→*d*)_π bonding between the ring and the phosphorus atom.

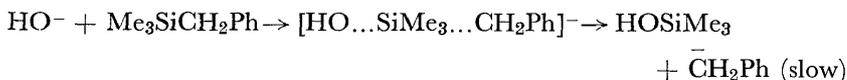
Table 2. Relative rates of cleavage of some phosphorous-containing $\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{X}$ compounds in 39 wt.-% water-methanol at 50°

X	k_{rel}	X	k_{rel}
<i>p</i> -PMe ₃ ⁺	4.2×10^5	<i>m</i> -PMe ₃ ⁺	4.6×10^3
<i>p</i> -P(O)Ph ₂	1.5×10^4	<i>m</i> -P(O)Ph ₂	2.6×10^2
<i>p</i> -P(O)Me ₂	4.0×10^3	<i>m</i> -P(O)Me ₂	1.4×10^2
<i>p</i> -P(O)(OEt) ₂	1.25×10^4		

Interesting in this connection is the 9.6-fold activation by the *p*-Me₃Si group (Table 1)⁴. With this group the electron-supplying inductive effect is opposed by the electron-withdrawing (*p*→*d*)_π-bonding effect, and overall

the group is usually slightly electron supplying but sometimes slightly electron withdrawing, depending on the nature of the electron demand, but in the reaction under discussion the ($p \rightarrow d$) $_{\pi}$ -bonding effect very clearly dominates.

The magnitude and nature of the substituent effects indicate that the benzyl carbanion is separating in the rate-determining step I, though it may never be wholly free; the simplest mechanism consistent with the facts involves a rate-determining synchronous attack of base and separation of the carbanion, which subsequently rapidly abstracts a proton from the solvent:



In this mechanism the silicon atom bears more negative charge in the transition state of the slow step than in the initial state, and thus electron-withdrawal in the non-cleaved R groups attached to silicon in $\text{R}_3\text{SiCH}_2\text{-C}_6\text{H}_4\text{X}$ compounds should also facilitate cleavage. The results in *Table 3* show that this is indeed the case¹, although the effects are much smaller than those observed for substituents in the cleaved group. *Table 3* also shows that as methyl groups are replaced by phenyl groups the rate rises and then falls again, presumably as steric hindrance to nucleophilic attack on silicon counteracts the increased electron-withdrawal.

Table 3. Approximate effects of R on the relative reactivities of $p\text{-R}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CO}_2^-$ and $p\text{-R}_3\text{SiC}_6\text{H}_2\text{C}_6\text{H}_4\text{Cl}$ compounds in cleavage by aqueous methanolic alkali at 50°

R_3	$p\text{-R}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{Cl}$ <i>Rel. React.</i>	R_3	$p\text{-R}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CO}_2^-$ <i>Rel. React.</i>
PhMe ₂	100	Me ₃	100
$p\text{-MeC}_6\text{H}_4\text{Me}_2$	60	Et ₃	20
$p\text{-MeOC}_6\text{H}_4\text{Me}_2$	45	Pr ₃ ⁿ	12
$p\text{-ClC}_6\text{H}_4\text{Me}_2$	300	PhMe ₂	480
MePh ₂	100	Ph ₂ Me	480
Me ₃	17	Ph ₃	230

Additional stabilization of the charge on the separating carbanion by attachment of further phenyl groups to the α -carbon atom also increases the reactivity⁶:

Compound	PhCH ₂ SiMe ₃	Ph ₂ CHSiMe ₃	Ph ₃ CSiMe ₃
Rel. Rate	1.0	1400	1800

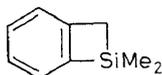
Even greater stabilization is present in the 9-fluorenyl anion, and 9-fluorenyl trimethylsilane is cleaved some 2×10^6 times as readily as benzyltrimethylsilane.

Surprisingly large effects are found for change from Me₃Si to Et₃Si groups in the reactive systems⁶:

System	$\text{R}_3\text{SiCHPh}_2$	9-R ₃ Sifluorene
Rel. Reactivity Me ₃ Si/Et ₃ Si	440	960

These effects seem too large to be the result of simple polar influences, and it must be assumed that steric hindrance is mainly responsible.

Steric effects of another kind account for the very great ease of cleavage (with ring-opening) of the aryl—CH₂Si bond in 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene (III), which occurs rapidly in methanol alone, the reactivity being at least 10¹⁰ times as great as that of benzyltrimethylsilane.



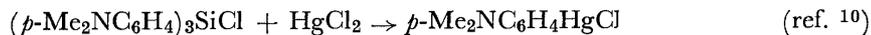
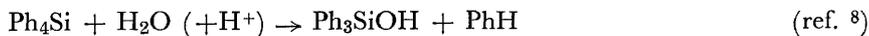
(III)

(It is noteworthy that while addition of alkali greatly accelerates the ring-opening, as expected, addition of a trace of acid completely inhibits it. This indicates that methoxide ion produced by autoprotolysis is responsible for the neutral cleavage, not methanol itself.) The high reactivity arises from the strain in the four-membered ring; this strain would be relieved in the transition state not only by stretching of the C—Si bond undergoing cleavage but also by the change from a tetrahedral angle at silicon towards the 90° angle available for the Ar—SiMe₂—CH₂ angle in a transition state approximating to that of a five-coordinate, *sp*³*d* hybridized, silicon intermediate⁷.

It is of interest to compare the reactivities of corresponding silicon, germanium, and tin compounds in cleavage of benzyl—MR₃ and similar bonds. Relative reactivities of *m*-ClC₆H₄CH₂MMe₃ compounds towards alkali in 80 per cent methanol are⁶: (M=) Si, 1; Ge, ~10⁻³; Sn, 17. It seems to be fairly generally true that C—Ge bonds are broken less readily than corresponding C—Si bonds by nucleophilic reagents, but there are exceptions. Thus 9-fluorenyltrimethylsilane is 2.5 times as reactive as 9-fluorenyltrimethylgermane, but change to Et₃M groups causes a larger fall in reactivity for the silicon than for the germanium system, with the result that the germanium is three times as reactive as the silicon compound⁶.

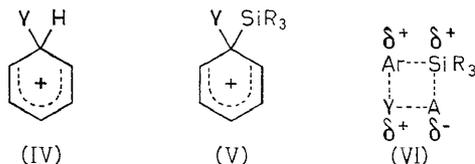
CLEAVAGE OF ARYL-SILICON AND RELATED BONDS

Aryl groups are removed from silicon by electrophilic reagents, and there are several examples of such cleavages in the early literature: e.g.



Such cleavages are electrophilic aromatic substitutions, and have been reviewed in the general context of such substitutions¹¹. It is usually assumed that the reactions proceed through a σ -complex (Wheland-intermediate) such as (V), analogous to the complexes of type (IV) involved in familiar aromatic substitutions in which C—H bonds are broken, but it is possible that four-centre processes of type (VI) are sometimes involved. There is no clear evidence, however, that they do occur, and the observation that reac-

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tion is accompanied by inversion at the silicon atom rules out such a mechanism for cleavage by bromine in carbon tetrachloride¹², in which a process of type (VI) should be highly favoured, since it would avoid separation of ions at any stage. In the cleavage which has been most studied, *viz.* that by acids (protodesilylation), the similarity to hydrogen-exchange, the corresponding reaction involving replacement of hydrogen, is so close that a four-centre mechanism seems unlikely¹³, and the evidence points to a slow attachment of a proton to form an intermediate of type (V), followed by rapid loss of the silyl group^{13,14}.

Effects of varying the structure of the aryl group of Me_3SiAr compounds have been extensively investigated^{15,16}. Aqueous methanolic perchloric acid and (usually for less reactive compounds) sulphuric acid in acetic acid have been mainly used as media, and the cleavages can again be conveniently followed by the change in the ultra-violet absorption.

As *Tables 4 and 5* show, electron-releasing substituents accelerate and electron-withdrawing substituents retard the cleavage. The effects of the substituents X in $\text{Me}_3\text{SiC}_6\text{H}_4\text{X}$ compounds correlate fairly well with σ^+ -constants, and very well with a combination of σ^- and σ^+ -constants

Table 4. Relative rates of cleavage of $\text{XC}_6\text{H}_4\text{SiMe}_3$ compounds in $\text{HClO}_4/\text{MeOH}/\text{H}_2\text{O}$ at 50°

X	k_{rel}	X	k_{rel}	X	k_{rel}
<i>p</i> -NMe ₂	$\sim 3 \times 10^7$	<i>p</i> -Me	21	<i>m</i> -Me	2.5
<i>p</i> -OH	10,700	<i>o</i> -Me	17	<i>p</i> -SiMe ₃	2.5
<i>p</i> -OMe	1,500	<i>p</i> -Bu ^t	15.6	H	1.00
<i>o</i> -OMe	335	<i>p</i> -SPh	10.7	<i>p</i> -F	0.75
<i>p</i> -OPh	88	<i>p</i> -OPh	8.7	<i>m</i> -OMe	0.5
<i>p</i> -SMe	78	<i>m</i> -CH ₂ SiMe ₃	6.5	<i>m</i> -OPh	0.36
<i>p</i> -(CH ₂) ₂ SiMe ₃	28	<i>m</i> -Bu ^t	3.8	<i>p</i> -Cl	0.13
<i>p</i> -(CH ₂) ₄ SiMe ₃	24	<i>p</i> -Ph	3.5	<i>p</i> -Br	0.10

Table 5. Relative rates of cleavage of $\text{XC}_6\text{H}_4\text{SiMe}_3$ compounds in $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ at 50°

X	k_{rel}	X	k_{rel}	X	k_{rel}
<i>p</i> -OMe	1000	<i>m</i> -Cl	0.012	<i>p</i> -NMe ₃ ⁺	4×10^{-4}
<i>p</i> -Me	18	<i>m</i> -CO ₂ H	9×10^{-3}	<i>m</i> -NO ₂	3×10^{-4}
<i>p</i> -Ph	2.8	<i>p</i> -CO ₂ H	2×10^{-3}	<i>p</i> -NO ₂	1×10^{-4}
H	1.0	<i>p</i> -CO ₂ Me	2×10^{-3}	<i>p</i> -PMe ₃ ⁺	$\sim 0.7 \times 10^{-4}$
<i>p</i> -F	0.95	<i>m</i> -CF ₃	2×10^{-3}	<i>p</i> -P(O)Ph ₂	$\sim 0.4 \times 10^{-4}$
<i>p</i> -Cl	0.19	<i>p</i> -SO ₃ H	1×10^{-3}		

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which is used in the Yukawa-Tsuno relationship, $\log k_{\text{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$ (with $r = 0.7$). The spread of rates, *i.e.* the value of ρ , is somewhat higher in $\text{HClO}_4/\text{H}_2\text{O}/\text{MeOH}$ than in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$; e.g. the *p*-OMe group activates 1500 and 1000 times, respectively, in these media.

In *Table 6* are shown the effects of changing the non-cleaved R groups on the ease of cleavage of $\text{R}_3\text{SiC}_6\text{H}_4\text{OMe-}p$ compounds¹⁷, and it will be seen that electron-withdrawal in R hinders the reaction, as would be expected since there is more positive charge in the neighbourhood of the silicon atom in the transition state than in the initial state. Steric hindrance also seems to be important, as revealed by the low reactivity of the $(o\text{-MeC}_6\text{H}_4)_3\text{SiC}_6\text{H}_4\text{OMe-}p$ compared with that of the isomeric $(p\text{-MeC}_6\text{H}_4)_3\text{SiC}_6\text{H}_4\text{OMe-}p$. This hindrance cannot be to nucleophilic attack on silicon if the above mechanism is correct, since this occurs only in a fast process after the rate-determining step, but it may arise from interference with the solvation of the positively charged transition state.

Table 6. Effects of the R groups on the rate of cleavage of $\text{R}_3\text{SiC}_6\text{H}_4\text{OMe-}p$ compounds in $\text{HClO}_4/\text{MeOH}/\text{H}_2\text{O}$ at 50°

R ₃	Rel. React.	R ₃	Rel. React.
Me ₃	1000	$(p\text{-MeOC}_6\text{H}_4)_3$	ca. 75
Et ₃	490	$(p\text{-MeC}_6\text{H}_4)_3$	36
Pr ⁿ ₃	420	$(p\text{-ClC}_6\text{H}_4)_3$	5.4
Pr ¹ ₃	55	$(o\text{-MeC}_6\text{H}_4)_3$	~0.075
Me ₂ Ph	330	Me ₂ (ClCH ₂) ₂	120
MePh ₂	74	Me(ClCH ₂) ₂	40
Ph ₃	16		

Change of the metal from silicon to germanium, tin, and lead leads to increasing ease of reaction. Thus the relative reactivities of the PhMMe_3 compounds towards aqueous methanolic perchloric acid are as follows¹⁸:

M	Si	Ge	Sn	Pb
Rel. Rate	1	36	2.5×10^5	2×10^8

It seems to be generally true that, contrary to the behaviour towards nucleophilic reagents, Si—C are less reactive than Ge—C bonds towards electrophilic reagents.

Protodesilylation has been extensively used in studies of substituent effects in electrophilic aromatic substitution^{15,16}. For example, the effects of *ortho*-substituents have recently been investigated for $o\text{-XC}_6\text{H}_4\text{SiMe}_3$ compounds, with the results shown in *Table 7*¹⁹. Since steric effects are probably small in most cases, the results provide quantitative information about the electronic effects of *ortho*-substituents, about which there is relatively little known from studies of other electrophilic aromatic substitutions. If the transition state coincided with the Wheland intermediate one would expect a linear free energy relationship to exist between the effects of *ortho*- and *para*-substituents, and in a plot of $\log k_{\text{rel}}$ for *ortho*-substituted compounds the points lie roughly about a straight line¹⁹. But since the transition state is, in fact, between the initial state and the Wheland intermediate, a substantial amount of charge will reside near the reaction site, mainly on the incoming proton, and

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 Table 7. Effects of *ortho*-substituents on cleavage of $\text{XC}_6\text{H}_4\text{SiMe}_3$ compounds in $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ at 50°

X	k_{rel}	X	k_{rel}	X	k_{rel}
<i>o</i> -OMe	335	H	1.00	COOH	5.2×10^{-3}
<i>o</i> -CH ₂ SiMe ₃	31	F	7.3×10^{-2}	SO ₃ H	2.6×10^{-3}
<i>o</i> -Me	18	I	3.8×10^{-2}	NO ₂	6.8×10^{-5}
<i>o</i> -Bu ^t	8.0	Cl	3.4×10^{-2}	NMe ₃ ⁺	6.8×10^{-5}
<i>o</i> -Ph	5.85	Br	2.5×10^{-2}		

inductive effects (including direct electrostatic effects) of the nearby *ortho*-substituents will have a greater influence than those of the more remote *para*-substituents. In the Yukawa-Tsuno relationship, $\log k_{\text{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$, the value of r is a measure of the importance of the resonance effect relative to that of the inductive effect of the substituents; for *para*-substituents the best value of r is about 0.7, while for *ortho*-substituents a surprisingly good plot is obtained with a smaller for value of r , *viz.* 0.3, corresponding with a greater relative contribution from inductive effects¹⁹.

Another recent study was concerned with the possibility that together the five fluorine atoms of the pentafluorophenyl group have, as is often implicitly assumed in discussions, a combined effect which is markedly greater than that expected for simple additivity of the effects of the separate fluorine atoms. The relative reactivities of the compounds PhSiMe₃, *o*-, *m*-, and *p*-F-C₆H₄SiMe₃, and C₆F₅SiMe₃ towards H₂SO₄-H₂O-CH₃CO₂H were determined, with the results shown in Table 8²⁰. The k_{rel} value for the pentafluorophenyl compound, *viz.* 1.47×10^{-5} , is some 6 times greater than that expected [*viz.* $0.96 \times (0.0215)^2 \times (0.073)^2 = 0.24 \times 10^{-5}$] for separate operation of the five fluorine atoms, indicating that their combined electron withdrawal is, if anything, less than expected for simple additivity.

 Table 8. Cleavage of fluoro-phenyl-trimethylsilanes in $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ at 50°

Compound	k_{rel}
C ₆ H ₅ SiMe ₃	1.00
<i>p</i> -FC ₆ H ₄ SiMe ₃	0.96
<i>m</i> -FC ₆ H ₄ SiMe ₃	0.0215
<i>o</i> -FC ₆ H ₄ SiMe ₃	7.26×10^{-2}
C ₆ F ₅ SiMe ₃	1.47×10^{-5}

Protodesilylation has also been used in a study of the electronic effects of the groups Me₃SiCH₂, (Me₃Si)₂CH, and (Me₃Si)₃C²¹. The relevant values of k_{rel} for cleavage of the *m*- and *p*-(Me₃Si)_xCH_{3-x}C₆H₄SiMe₃ compounds with $x = 0-3$ are shown in Table 9. Replacement of one hydrogen atom of a methyl group by a Me₃Si group causes a large increase in electron release, as revealed by the activating effects of the *m*- and *p*-Me₃SiCH₂ groups. This is normally attributed to the large electron-releasing inductive effect of the Me₃Si group (although the probable importance of hyperconjugation from the Me₃Si—CH₂ bond has been pointed out¹⁵), and one would expect

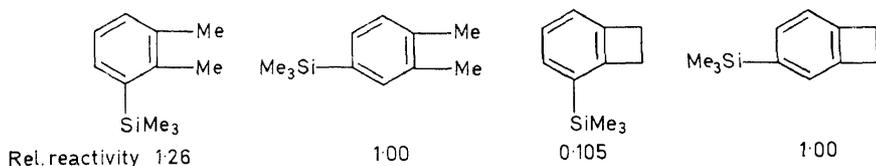
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Table 9. Substituent effects of $(\text{Me}_3\text{Si})_x\text{CH}_{3-x}$ groups in cleavage of $\text{XC}_6\text{H}_4\text{SiMe}_3$ compounds by aqueous methanolic perchloric acid at 50°

X	k _{rel}	log k _{rel}	X	k _{rel}	log k _{rel}
H	1.00	0.00	<i>p</i> -CH ₃	21	1.32
<i>m</i> -CH ₃	2.43	0.39	<i>p</i> -CH ₂ SiMe ₃	280	2.44
<i>m</i> -CH ₂ SiMe ₃	6.48	0.81	<i>p</i> -CH(SiMe ₃) ₂	670	2.82
<i>m</i> -CH(SiMe ₃) ₂	8.42	0.92	<i>p</i> -C(SiMe ₃) ₃	200	2.30
<i>m</i> -C(SiMe ₃) ₃	3.46	0.54			

further substantial increases in the activating effect on going to the $(\text{Me}_3\text{Si})_2\text{-CH}$ and $(\text{Me}_3\text{Si})_3\text{C}$ substituents. In fact there is only a small increase on going from the Me_3SiCH_2 to the $(\text{Me}_3\text{Si})_2\text{CH}$ group, and then there is a substantial fall on going to the $(\text{Me}_3\text{Si})_3\text{C}$ group, which activates less than the Me_3SiCH_2 group. It seems that other large influences, such as hyperconjugation, are in operation in addition to inductive effects; steric hindrance to solvation must be of significance, but it is unlikely that this could account for the observed results.

The high reactivity of the aryl-SiMe₃ bond has also been utilized in a study of the reactivities of the 3- and 4-positions in the benzocyclobutene system²². Benzocyclobutene is known to undergo electrophilic substitution dominantly at the 4-position, clearly as a consequence of strain in the four-membered ring^{23,24}. One explanation, based on consideration of the changes in tensions and compressions of the bonds in the aromatic ring on going to the transition state²³, would require that the 4-substitution would result from enhanced reactivity of the 4- and normal reactivity of the 3-position. A second, based on a consideration of the increase or decrease in strain in the four-membered ring consequent on the change in the length of the bond common to both rings on going to the transition state, would require enhanced reactivity at the 4- and reduced reactivity at the 3-position²⁴. Yet a third, based on consideration of the influence of the four-membered ring on the hybridization and thus electronegativity, of the carbon atoms common to both rings, would require reduced reactivity at the 3- and slightly reduced reactivity at the 4-position²⁵. It is difficult to measure these reactivities in common electrophilic substitutions such as nitration and acetylation because considerable opening of the 4-membered ring takes place²³. The 3- and 4-trimethylsilyl derivatives, however, can be cleaved under mild acid conditions in which no ring-opening occurs, and the reactivities compared with those of the analogous 3- and 4-trimethylsilyl xylenes are as follows²²:



It will be seen that there is marked reduction in reactivity at the 3-position and a normal reactivity at the 4-position in the benzocyclobutene system. The first of the explanations²³ listed above is thus ruled out. The

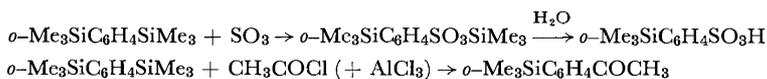
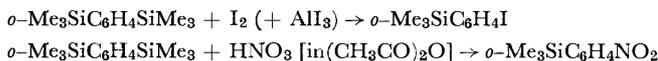
hybridization effect²⁵ probably contributes most to the lowering of the reactivity at the 3-position, but the fact that the reactivity at the 4-position is normal suggests that there may be a significant contribution from the strain effect²⁴ of the second explanation.

The even greater reactivity of the aryl—SnMe₃ bond has been utilized to provide information about the effects of the ethynyl substituent on electrophilic aromatic substitution. This information would be very difficult to obtain for the more familiar electrophilic aromatic substitutions on phenylacetylene because the ethynyl group itself is more reactive than the benzene ring towards electrophiles. Acid cleavage of HC≡CC₆H₄SnMe₃ compounds occurs in aqueous methanolic perchloric acid at 50° under conditions in which there is no significant hydration of the triple bond, and the following relative reactivities have been recorded²⁶:

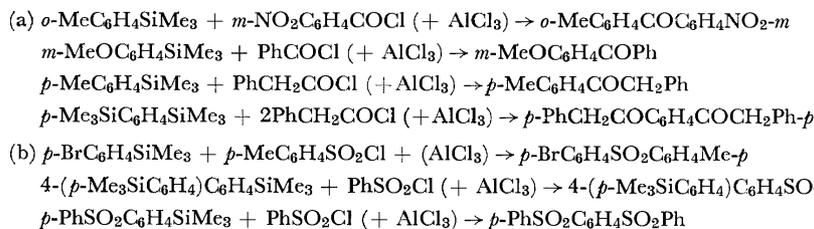
X in XC ₆ H ₄ SnMe ₃ <i>k</i> _{rel}	H 1.00	<i>m</i> -C≡CH 0.28	<i>p</i> -C≡CH 0.43
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The fact that the ethynyl group deactivates less from the *para*- than from the *meta*-position suggests that a small conjugative return of electrons to the ring can, at the demand of the reaction, operate to oppose the inductive withdrawal.

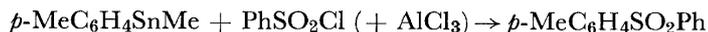
Desilylation also offers a useful means of introducing functional groups into aromatic rings at specific positions¹. The preparations of some of the *ortho*-substituted phenyltrimethylsilanes needed for the rate studies mentioned above provide some illustrative examples¹⁹:



Desilylation under Friedel Crafts conditions has been used recently to provide useful new routes to unsymmetrical ketones and sulphones^{27,28}: *e.g.*



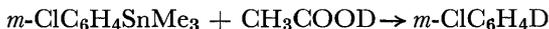
Destannylation sometimes offers advantages in that it can be carried out under even milder conditions. The following reaction, for example, was carried out in methylene dichloride at -25°²⁸:



Nitrodestannylation can be effected under usefully mild conditions. For example, the first (nitroaryl)tin compound has been prepared by treatment of *p*-bistrimethylstannylbenzene with copper nitrate trihydrate in acetic anhydride at -40°²⁷:



Cleavage of aryl-SnMe₃ bonds by deuterioacetic acid (sometimes with addition of a little deuteriosulphuric acid) provides a convenient method of introducing deuterium into a specific position of an aromatic system²⁹: e.g.



Aryl-silicon bonds can be cleaved by nucleophilic reagents, but with most simple substituted phenyltrimethylsilanes the cleavages do not occur under conditions most convenient for rate studies¹. (Correspondingly, abstraction of protons from benzene requires very basic conditions). Cleavage of aryl-tin bonds by basic reagents takes place much more readily, and the rates of cleavage of a range of XC₆H₄SnMe₃ compounds by aqueous methanolic alkali have been measured³⁰:



It is likely that the carbanion XC₆H₄⁻ is partly formed in the slow step of the reaction, so that the observed effects of substituents are related to those on the ease of formation of the free carbanions.

Values of k_{rel} are shown in *Table 10*. The effects of *meta*-substituents follow a normal pattern in that they correlate very well with the appropriate Hammett σ -constants. With *para*-substituents, however, the pattern is quite abnormal; the reaction is facilitated not only by clearly electron-withdrawing group such as *p*-NMe₃⁺, *p*-CF₃, and *p*-Cl, but also by groups such as *p*-OMe and *p*-NMe₂ which are normally electron-releasing; the effects do not correlate satisfactorily with the σ -constants of the groups but show a rough correlation with the (inductive) σ_1 -constants³⁰. The pattern of substituent effects, which is consistent with that observed in base-catalysed hydrogen-exchange, has not been satisfactorily explained.

Table 10. Effects of substituents on the rate of cleavage of XC₆H₄SnMe₃ compounds in aqueous methanolic alkali at 50°

X	k_{rel}	X	k_{rel}	X	k_{rel}
<i>o</i> -F	29	<i>p</i> -Br	4.6	<i>m</i> -SiMe ₃	1.39
<i>p</i> -NMe ₃ ⁺	10.3	<i>p</i> -C≡CH	3.9	<i>p</i> -SiMe ₃	1.13
<i>m</i> -CF ₃	10.25	<i>m</i> -C≡CH	3.8	H	1.00
<i>m</i> -Br	9.1	<i>p</i> -F	2.9	<i>p</i> -Bu ^t	0.95
<i>p</i> -CF ₃	8.2	<i>p</i> -SMe	2.4	<i>p</i> -Me	0.86
<i>m</i> -Cl	8.1	<i>p</i> -Ph	1.80	<i>m</i> -Me	0.83
<i>o</i> -Cl	7.55	<i>m</i> -OMe	1.78	<i>m</i> -NH ₂	0.66
<i>o</i> -CF ₃	7.05	<i>m</i> -Ph	1.69	<i>o</i> -OMe	0.61
<i>m</i> -F	5.45	<i>p</i> -NMe ₂	1.63	<i>o</i> -Me	0.25
<i>p</i> -Cl	4.65	<i>p</i> -OMe	1.64		

CLEAVAGE OF ALKYNYL-SILICON AND RELATED BONDS

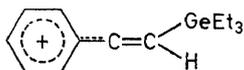
A proton is readily abstracted from an acetylene by nucleophilic reagents and acetylenic carbon atoms are readily attacked by electrophiles. Correspondingly, alkynyl—Si bonds are readily cleaved by both nucleophilic

and electrophilic reagents. Towards acid, cleavage of the compounds $\text{ArC}\equiv\text{CSiMe}_3$ is not very much faster than the hydration of the cleavage products $\text{ArC}\equiv\text{CH}$, so that rate studies are inconvenient, but the corresponding $\text{ArC}\equiv\text{CGeEt}_3$ compounds are cleaved in acid too weak to cause significant hydration, and some relative rates of cleavage of $\text{XC}_6\text{H}_4\text{C}\equiv\text{CGeEt}_3$ compounds are shown in *Table 11*³¹. In this reaction it is likely that the rate-determining step is protonation to give the ion (VII), and close analogy would be expected between the effects of substituents in this reaction and

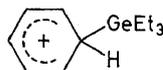
Table 11. Cleavage of $\text{XC}_6\text{H}_4\text{C}\equiv\text{CGeEt}_3$ compounds by aqueous methanolic perchloric acid at 29.05°

X	k_{rel}	X	k_{rel}	X	k_{rel}
<i>p</i> -OMe	110	<i>p</i> -F	0.89	<i>m</i> -Cl	0.059
<i>p</i> -Bu ^t	5.4	<i>m</i> -OMe	0.67	<i>o</i> -Cl	0.059
<i>p</i> -Me	5.3	<i>o</i> -OMe	0.63	<i>o</i> -Br	0.076
<i>o</i> -Me	2.1	<i>p</i> -I	0.29	<i>m</i> -Br	0.057
<i>m</i> -Me	1.7	<i>p</i> -Cl	0.27	<i>m</i> -CF ₃	0.022
H	1.00	<i>p</i> -Br	0.23		

those in cleavage of the corresponding $\text{XC}_6\text{H}_4\text{GeEt}_3$ compounds, in which the ion (VIII) is thought to be formed in the rate-determining step. There is, indeed, an excellent linear free-energy relationship between the substituent effects in the two reactions³¹. It follows that the substituent effects in the cleavage of the $\text{XC}_6\text{H}_4\text{C}\equiv\text{CGeEt}_3$ compounds fit the Yukawa-Tsuno equation.



(VII)



(VIII)

Alkynyl-SiMe₃ compounds are very readily cleaved by aqueous methanolic alkali:



In keeping with the very high acidity of phenylacetylene relative to that of toluene, the compound $\text{PhC}\equiv\text{CSiMe}_3$ is cleaved some 10⁷ times as fast as the benzyl compound $\text{PhCH}_2\text{SiMe}_3$ ³². In spite of the high reactivity of the $\text{RC}\equiv\text{C-SiMe}_3$ bond, it is broken much less readily by alkali than the corresponding $\text{RC}\equiv\text{C-H}$ bond; a factor of *ca.* 10³-10⁴ applies between the $\text{PhC}\equiv\text{CSiMe}_3$ and $\text{PhC}\equiv\text{CH}$ systems. This constitutes a clear exception to the useful generalization made in the first paragraph of this review; it is noteworthy that the analogous $\text{Me}_3\text{Si-C}\equiv\text{N}$ and $\text{H-C}\equiv\text{N}$ pair almost certainly constitute another exception.

In the alkali cleavage of $\text{XC}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$ compounds the effect of the substituents, some of which are shown in *Table 12*, correlate reasonably well with σ -constants³². Change from Me₃Si to Et₃Si groups causes a 280-fold reduction in rate for $\text{PhC}\equiv\text{CSiR}_3$ compounds; other effects of changes in

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Table 12. Cleavage of $\text{XC}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$ compounds by aqueous methanolic alkali at 29.4°

X	k_{rel}	X	k_{rel}
<i>m</i> -Br	4.4	<i>o</i> -Mc	0.58
H	1.00	<i>p</i> -OMe	0.425
<i>p</i> -OMe	0.60		

the non-cleaved groups attached to silicon are shown in Table 13, and it will be seen that increased electron withdrawal leads to a quite large rate increase.

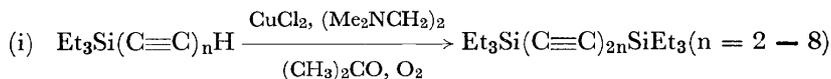
The ease of reaction of $\text{ArC}\equiv\text{CMR}_3$ compounds rises in the order $(\text{M}=\text{C}) \text{Ge} < \text{Si} \ll \text{Sn}$; the difference between the silicon and germanium compounds is smaller than with benzyl- MR_3 compounds; a factor of 34 applies for $\text{PhC}\equiv\text{CMR}_3$ compounds³².

Table 13. Cleavage of $(\text{XC}_6\text{H}_4)_3\text{SiC}\equiv\text{CPh}$ compounds by aqueous methanolic alkali at 30°

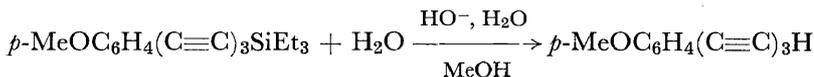
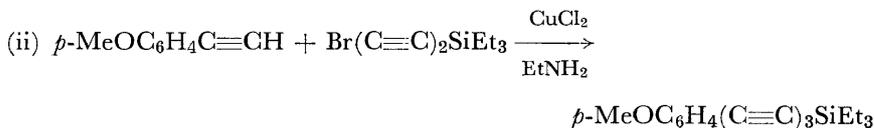
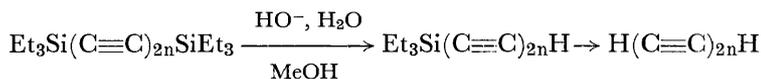
X	k_{rel}	X	k_{rel}
<i>p</i> -OMe	0.24	<i>p</i> -F	13.7
<i>p</i> -Me	0.26	<i>p</i> -Cl	98
H	1.00	<i>m</i> -Cl	320
<i>m</i> -Me	0.35		

The knowledge gained in these quantitative studies has enabled important advances to be made in the preparation of polyacetylenes, especially of those bearing one or two terminal hydrogen atoms^{33,34}. The established methods of preparation of polyacetylenes involve either (i) treatment of $\text{R}(\text{C}\equiv\text{C})_n\text{H}$ compounds with oxygen in presence of cuprous chloride and tetramethylethylenediamine in acetone to give $\text{R}(\text{C}\equiv\text{C})_{2n}\text{R}$ compounds (the Glaser Reaction), or (ii) the coupling of $\text{R}(\text{C}\equiv\text{C})_n\text{H}$ and $\text{Br}(\text{C}\equiv\text{C})_m\text{R}'$ compounds in the presence of cuprous chloride and ethylamine, to give $\text{R}(\text{C}\equiv\text{C})_n(\text{C}\equiv\text{C})_m\text{R}'$ compounds (the Cadiot-Chodkiewicz Reaction). Basic media are involved in both cases, and the ease of reaction increases with the acidity of the acetylene which means that coupling of $\text{R}(\text{C}\equiv\text{C})_n\text{H}$ occurs more readily the larger is n , and hence it is difficult to control the couplings in the case of terminal acetylenes.

Alkynyl- SiR_3 bonds are stable in the media used (use is here being made of the observation that such bonds are less reactive than the corresponding alkynyl-H bonds towards nucleophiles), but can be broken when required by use of slightly more basic media, and so MR_3 groups can with great advantage be used to protect terminal ethynyl groups in the Glaser and Cadiot-Chodkiewicz couplings³³. The rather greater stability of alkynyl- SiEt_3 than of alkynyl- SiMe_3 bonds, mentioned above, makes the Et_3Si more generally useful protecting group, and some examples of its use are given below^{33,34}:



CLEAVAGE OF CARBON-SILICON BONDS



It will be seen that polyacetylenes containing up to sixteen ethynyl groups have been made by method (i)³⁴.

Triethylgermyl groups have also been satisfactorily used in these reactions.

Interesting information on substituent effects can be obtained from quantitative studies on the linear polyacetylene-silicon and -germanium compounds made by these new processes³⁵. For example, the ease of alkali cleavage of $\text{Ph}(\text{C}\equiv\text{C})_n\text{SiEt}_3$ compounds increases with increasing length of n as follows:

n	1	2	3
Rel. Reactivity	1.0	80	1440

The effects of the substituents, X, on alkali cleavage of $\text{XC}_6\text{H}_4(\text{C}\equiv\text{C})_n\text{SiEt}_3$ compounds with $n=2$, or 3 correlate well with σ -constants³⁵, as they do when $n=1$, as noted above. (Values of ρ in 1:5 vol/vol water-methanol are $n=1$, + 1.68; $n=2$, + 1.16; $n=3$, + 0.73). The importance of this observation is that it casts doubts on the validity of some important current interpretations of substituent effects which are based on the postulate that inductive effects are predominantly space-transmitted, and have influences dependent on the through-space distance between the substituent and the reaction site, whereas resonance effects are transmitted through π -bonds, and have influences dependent upon the efficiency of conjugation between the substituent and the reaction site. If these postulates were correct, it is difficult to see how the balance of inductive and resonance effects of the substituent X in the $\text{XC}_6\text{H}_4(\text{C}\equiv\text{C})_n\text{SiEt}_3$ systems could remain unchanged as n increases, except by improbable coincidence.

CONCLUSION

Cleavage studies of the type described above are leading to advances in three main directions:

- An increase in understanding of the mechanisms of the reactions concerned, and thus of the factors governing the stability of C—Si and related bonds under various conditions.
- The provision of precise data on substituent effects, valuable for the understanding of the theory of these effects in organic chemistry generally.
- The development of new synthetic methods, which depend on the replacement of MR_3 groups at carbon by hydrogen atoms or functional groups under optimal conditions.

The support of the following organizations for the researches reviewed above is gratefully acknowledged: The United States Army and United States Office of Aerospace Research (both through their European Offices), the Science Research Council, the Nobel Division of Imperial Chemical Industries Ltd., Midland Silicones Ltd., and the International Tin Research Council.

References

- 1 R. W. Bott and C. Eaborn, in *Organometallic Compounds of the Group IV Elements* (Ed. A. G. MacDiarmid); Vol. 1, Marcel Dekker, New York, 1968, Chapter 2.
- 2 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, Chapter 4.
- 3 C. C. Price and J. R. Sowa, *J. Org. Chem.* **32**, 4126 (1967);
J. R. Sowa, *Dissertation Abstr.* **26**, 5046 (1966); *Chem. Abstr.* **65**, 2339 (1966).
- 4 C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 126 (1955);
R. W. Bott, C. Eaborn and B. M. Rushton, *J. Organometal. Chem.* **3**, 448 (1963).
- 5 R. W. Bott, B. F. Dowden and C. Eaborn, *J. Chem. Soc.* 4994 (1965).
- 6 R. W. Bott, C. Eaborn and T. W. Swaddle, *J. Chem. Soc.* 2342 (1963).
- 7 C. Eaborn, D. R. M. Walton and M. Chan, *J. Organometal. Chem.* **9**, 251 (1967).
- 8 F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.* **74**, 449 (1901).
- 9 A. Ladenburg, *Ber. Deut. Chem. Ges.* **40**, 2274 (1907).
- 10 C. Combes, *C.R. Acad. Sci. Paris* **122**, 622 (1896).
- 11 R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965.
- 12 C. Eaborn and O. W. Steward, *J. Chem. Soc.* 521 (1965).
- 13 C. Eaborn, P. M. Jackson and R. Taylor, *J. Chem. Soc.*, 613 (1966).
- 14 R. W. Bott, C. Eaborn and P. M. Greasley, *J. Chem. Soc.* 4804 (1964).
- 15 C. Eaborn, *J. Chem. Soc.* 4858 (1956).
- 16 F. B. Deans and C. Eaborn, *J. Chem. Soc.* 2299 (1959);
F. B. Deans, C. Eaborn and D. E. Webster, *J. Chem. Soc.* 3031 (1959);
C. Eaborn, Z. Lasocki and D. E. Webster, *J. Chem. Soc.* 2034 (1959);
C. Eaborn and R. C. Moore, *J. Chem. Soc.* 4921 (1961);
R. Baker, C. Eaborn and J. A. Sperry, *J. Chem. Soc.* 2382 (1962);
R. Baker, R. W. Bott, C. Eaborn and P. M. Greasley, *J. Chem. Soc.* 627 (1964);
R. W. Bott, C. Eaborn and K. Leyshon, *J. Chem. Soc.* 1971 (1964);
C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.* **3**, 169 (1965).
- 17 R. W. Bott, C. Eaborn and P. M. Jackson, *J. Organometal. Chem.* **7**, 79 (1967).
- 18 C. Eaborn and K. C. Pande, *J. Chem. Soc.* 1566 (1960).
- 19 C. Eaborn, D. R. M. Walton and D. J. Young, *J. Chem. Soc. (B)*, 15 (1969).
- 20 C. Eaborn, J. A. Treverton and D. R. M. Walton, *J. Organometal. Chem.* **9**, 259 (1967).
- 21 A. R. Bassingdale, C. Eaborn, D. R. M. Walton and D. J. Young, unpublished work.
- 22 A. R. Bassingdale, C. Eaborn and D. R. M. Walton, *J. Chem. Soc. (B)*, 12 (1969).
- 23 J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964); **21**, 245 (1965).
- 24 J. Vaughan, G. J. Welch and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).
- 25 A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis and R. G. Lawler, *J. Amer. Chem. Soc.* **90**, 1357 (1968).
- 26 C. Eaborn, A. R. Thompson and D. R. M. Walton, *J. Chem. Soc. (B)* 1969.
- 27 K. Dey, C. Eaborn and D. R. M. Walton, unpublished work.
- 28 S. B. Bhattacharya, C. Eaborn and D. R. M. Walton, *J. Chem. Soc. (C)*, 1969
- 29 W. A. Asomaning, C. Eaborn and D. R. M. Walton, unpublished work.
- 30 C. Eaborn, H. L. Hornfield and D. R. M. Walton, *J. Chem. Soc. (B)*, 1036 (1967).
- 31 R. W. Bott, C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.* **1**, 420 (1964).
- 32 C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.* **4**, 217 (1965).
- 33 R. Eastmond and D. R. M. Walton, *Chem. Communications*, 204 (1968).
- 34 R. Eastmond and D. R. M. Walton, unpublished work.
- 35 C. Eaborn, R. Eastmond and D. R. M. Walton, unpublished work.