107. *Aromatic Reactivity. Part XIV.*[1] *Cleavage of Aryltricyclohexyl- and Aryltrimethyl-stannanes by Aqueous-ethanolic Perchloric Acid.*

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We have measured the rates of cleavage of some tricyclohexyl- and trimethyl-phenylstannanes and of *p*-methoxyphenyltriphenylstannane by a mixture of ethanol (50 vol.) and aqueous perchloric acid (2 vol.) at 50·0°. As expected for an electrophilic aromatic substitution, electron-releasing substituents in the phenyl group increase the ease of cleavage and electron-withdrawing substituents decrease it (the *p*-methoxy- and *p*-trimethylammonio-derivative are 63 and 0·0068 times, respectively, as reactive as tricyclohexylphenylstannane). The $+E$ effects of substituents appear to operate less effectively in this reaction than in most electrophilic aromatic substitutions, including the analogous cleavages of aryl-silicon and aryl-germanium bonds.

It has been shown that cleavages of Ar–Si and Ar–Ge bonds by electrophilic reagents are electrophilic aromatic substitutions, analogous to those in which Ar–H bonds are broken, and that the effects of substituents in the aryl groups can be correlated with those in more familiar electrophilic aromatic substitutions such as nitration, halogenation, or hydrogen-exchange.[2-7] Electrophilic reagents, such as acids, halogens, and mercuric, silver, or thallium salts, cleave Ar–Sn bonds even more readily than Ar–Si and Ar–Ge bonds, and we now report a kinetic study of the cleavage at 50·0° of substituted tricyclohexylphenylstannanes by a mixture of ethanol (50 vol.) and aqueous perchloric acid (2 vol.):

$$(C_6H_{11})_3Sn{\cdot}C_6H_4{\cdot}X + MOH \xrightarrow{H^+} (C_6H_{11})_3Sn{\cdot}OM + C_6H_5{\cdot}X \ (M = Et \text{ or } H)$$

$$(C_6H_{11})_3Sn{\cdot}OM + HClO_4 \rightleftharpoons (C_6H_{11})_3SnClO_4 + MOH$$

The reactions were studied spectrophotometrically.

We chose tricyclohexyl compounds for the main study because, being solids, they could be purified by recrystallization, but their relative insolubility in the aqueous-methanolic mixtures used for silicon and germanium compounds [3,6] caused us to use ethanol containing only a little water. We examined *p*-methoxyphenyltriphenylstannane and a few trimethylphenylstannanes for comparison with the tricyclohexyl compounds.

The results for the tricyclohexylphenylstannanes are shown in Table 1. Observed first-order rate constants, k, are listed, along with the rate, k_{rel} for each compound relative

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[1] Part XIII, Eaborn and Taylor, *J.*, 1961, 247.

[2] Eaborn, " Organosilicon Compounds," Butterworths Sci. Publ., London, 1960, pp. 146—156.

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

[4] Eaborn and Webster, *J.*, 1957, 4449; 1960, 179.

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

[6] Eaborn and Pande, *J.*, 1961, 297.

[7] Benkeser, Hoke, and Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5294.

to that of the unsubstituted compound, tricyclohexylphenylstannane. The rates were not all measured at the same acid concentration (and thus the same ethanol–water ratio), and the values of k_{rel} are derived by the overlap procedure previously used.[3,5,6] Slightly different values might be obtained for some of the compounds if all were measured directly in, say, the medium containing 0·6M(added)-perchloric acid. It will be noticed that at the lowest acid concentrations the rate increases only a little faster than the concentration of acid, but rises more steeply at higher concentrations, behaviour which seems to be normal for acid-catalysed reactions in alcohols or in aqueous alcohols of low water content.[8]

Derivation of the value of k_{rel} for the *p*-dimethylamino-compound requires explanation. The fact that the rate of cleavage for this compound is doubled by doubling the acid concentration indicates that it is mainly present as the free base at the acid concentrations used. (Spectrophotometric measurements show this to be true for dimethylaniline, which probably has a comparable base strength.) If a substantial proportion of the compound were present as the unreactive protonated base, then additional protonation would counteract the normal increase in rate associated with increase in acid concentration. (For a discussion of the behaviour of an analogous silicon compound see ref. 3.) If proportionality between rate and acid concentration is assumed for the *p*-methoxy-compound at the low acid concentrations involved, then k for this compound would be 0·62 min.$^{-1}$ for 0·0020M(added)-acid, and thus k_{rel} for the *p*-dimethylamino-compound would be 63(161/0·62), *i.e.*, $1{\cdot}6 \times 10^4$. Since, in fact, the rate for the *p*-methoxy-compound probably falls off somewhat more steeply than the acid concentration, the figure of 2×10^4 which we assign to k_{rel} for the *p*-dimethylamino-compound in Table 1 may be slightly low, but it is probably within 50% of the correct value.

TABLE 1. *Cleavage of* $X{\cdot}C_6H_4{\cdot}Sn(C_6H_{11})_3$ *compounds at* 50·0°.

X	$[HClO_4]$ [a] (M)	10^3k (min.$^{-1}$)	k_{rel}
p-NMe_2	0·0010	77	—
	0·0020	161	*ca.* 2×10^4
p-MeO	0·0283	8·75	—
	0·099	34·0	63
p-Bu^t	0·313	12·6	—
	0·571	24·4	6·9
	2·35	128	7·2
p-Pr^i	0·313	12·2	—
	0·571	24·0	6·9
	2·35	124	7·0
p-Et	0·313	10·2	—
	2·35	94	5·3
p-Me	0·099	2·97	5·5
	0·313	10·4	—
	0·571	20·4	5·8
	2·35	95·5	5·4
m-Me	0·571	6·49	1·84
	2·35	33·0	1·85
o-Ph	0·571	7·02	1·99
p-Ph	0·571	6·24	1·77
H	0·099	0·54	1
	0·571	3·53	
	2·35	17·8	
	3·41	29·2	
	4·48	46·0	
m-MeO	2·35	15·9	0·89
	4·48	37·8	0·82
p-F	4·48	28·5	0·62
p-Cl	4·48	8·63	0·187
p-Br	4·48	6·68	0·145
m-Cl	4·48	1·78	0·039
	9·15	5·92	—
p-CO_2H	9·15	4·60	0·030
p-NMe_3^+ [b]	9·15	1·04	0·0068

[a] Concn. of aqueous acid, 2 vol. of which was mixed with 50 vol. of an ethanolic solution of the organostannane. [b] The methiodide of *p*-dimethylaminophenyltricyclohexylstannane was used.

Comparison of the values of k_{rel} for destannylation of the $(C_6H_{11})_3Sn{\cdot}C_6H_4{\cdot}X$ compounds with those which apply in desilylation of $Me_3Si{\cdot}C_6H_4{\cdot}X$ compounds,[3] and degermylation of $Et_3Ge{\cdot}C_6H_4{\cdot}X$ compounds,[6] both in aqueous methanol, reveals that, while the substituents lie in much the same order with respect to their activating or deactivating effects, there are differences in detail. The most striking difference is in the overall spread of rates; thus the *p*-methoxy-group, which activates 1500 and 540 times, respectively, in desilylation and degermylation, activates only 63 times in the destannylation,

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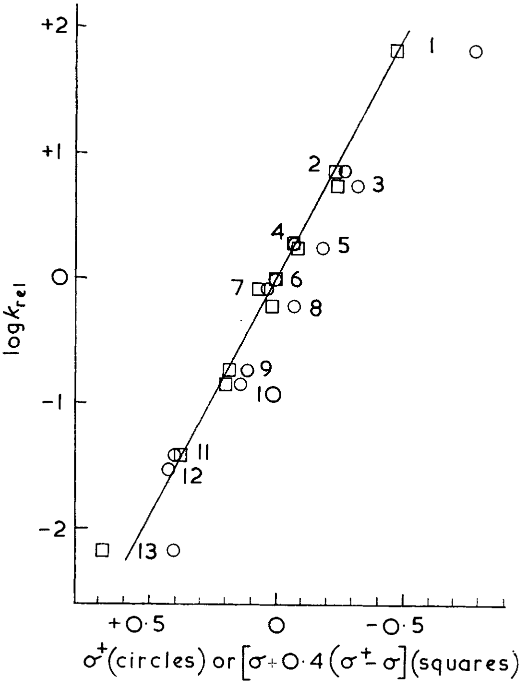
[8] Long and Paul, *Chem. Rev.*, 1957, **57**, 935; Satchell, *J.*, 1957, 2878; Baines and Eaborn, *J.*, 1956, 1436.

while the *m*-chloro-atom deactivates 26 times, compared with 60 times in degermylation. A linear free-energy relation, such as applies between the substituent effects in desilylation and degermylation,[6] does not apply between the effects in either of these reactions and those in destannylation. Neither is a straight line obtained when log $k^{\mathrm{Sn}}_{\mathrm{rel}}$ (the superscript denotes which demetallation is involved) is plotted against the electrophilic substituent constants, σ^+,[9] which apply approximately to degermylation and desilylation, as to a wide variety of electrophilic aromatic substitutions and related reactions (see Figure). A plot of log $k^{\mathrm{Sn}}_{\mathrm{rel}}$ against the Hammett substituent constant, σ,[10] is also unsatisfactory.



Relations between substituent constants and rates of cleavage of $X{\cdot}C_6H_4{\cdot}Sn(C_6H_{11})_3$ *compounds, where* X *is*: 1, *p*-MeO; 2, *p*-Bu^t; 3, *p*-Me; 4, *m*-Me; 5, *p*-Ph; 6, H; 7, *m*-MeO; 8, *p*-F; 9, *p*-Cl; 10, *p*-Br; 11, *m*-Cl; 12, *p*-CO_2H; 13, *p*-NMe_3^+.

It is rewarding to analyse the substituent effects using Yukawa and Tsuno's method.[11] As they have pointed out, the quantity $(\sigma^+ - \sigma)$ is a measure of the potential ability of a group to stabilize by resonance effects (mainly, presumably, by its $+E$ effect) a centre of excess of positive charge with which it is conjugated, and the extent to which the resonance effects operate differs from reaction to reaction. For a large number of electrophilic reactions, Yukawa and Tsuno showed that the relation $\log k_{\mathrm{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$ is more satisfactory than either of the relations $\log k_{\mathrm{rel}} = \rho\sigma$ or $\log k_{\mathrm{rel}} = \rho\sigma^+$.* By definition, $r = 1$ for solvolysis of αα-dimethylbenzyl chlorides in 90% aqueous acetone, and $r = 0$ for ionization of benzoic acids in water, and can have a range of values above zero, for example: 2·29 in brominolysis of benzeneboronic acids ($\rho = -3{\cdot}84$), 1·66 in halogenation of substituted benzenes in acetic acid ($\rho = -8{\cdot}82$), 0·897 for nitration of substituted benzenes in nitromethane or acetic acid ($\rho = -6{\cdot}38$), and 0·436 for the Beckmann rearrangement of acetophenone oximes in 94·5% sulphuric acid ($\rho = 1{\cdot}98$). It

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* For a related analysis of substituent effects see ref. 12. A treatment equivalent to Yukawa and Tsuno's, but applicable to reactions in which there is a *loss* of resonance stabilization on going from initial state to transition state, has been proposed by Dickinson and Eaborn.[13]

[9] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[10] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420; Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[11] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[12] Bekhum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[13] Dickinson and Eaborn, *J.*, 1959, 3036.

should be noted that from reaction to reaction, r, which measures the extent to which the "resonance potential" of the substituents is brought into play, does not necessarily increase with ρ, which measures the general demand for electrons at the reaction site.

Desilylation [3,9] and degermylation [6] give fairly good straight line log $k_{\rm rel}$–σ^+ plots, but there are significant deviations from the line, and plots of log $k_{\rm rel}^{\rm Si}$ against $[\sigma + 0{\cdot}7(\sigma^+ - \sigma)]$ ($\rho = 5{\cdot}0$) and of log $k_{\rm rel}^{\rm Ge}$ against $[\sigma + 0{\cdot}65\ (\sigma^+ - \sigma)]$ ($\rho = 4{\cdot}6$) are distinctly better.* For destannylation, the appropriate relation is log $k_{\rm rel}^{\rm Sn} = 3{\cdot}8\ [\sigma + 0{\cdot}4(\sigma^+ - \sigma)]$ (see Figure). (The deviation for the *p*-$\rm NMe_3{}^+$ group is not significant in view of the uncertainty of the σ constant,[9,10] but real deviation for this positively charged group in a reaction involving a positively charged electrophilic species would not be surprising.[5]) The value of ρ is quite large in destannylation, though markedly smaller than in the other two demetallations, and the relatively small effect of a *p*-methoxy-group is largely associated with a low value of the resonance factor, r.

The relative unimportance of the resonance effects of substituents enables us to understand several differences between the substituent effects in destannylation and those in desilylation or degermylation. Thus although the *p*-methoxy-group has such a small effect in destannylation, the *m*-chloro-atom, which operates mainly through its $-I$ effect, has a deactivating effect (26-fold) not very far removed from that in degermylation (60-fold). Again, the inductive order of activation *p*-$\rm Bu^t$ > *p*-Me applies in destannylation, while the Baker–Nathan order *p*-Me > *p*-$\rm Bu^t$, which may reflect the greater hyperconjugative effect of the methyl group, applies in desilylation and degermylation, as in most electrophilic substitutions (the only exceptions noted previously being detritiation in some media [14] and nitration [15]).

Another substituent whose effect reflects strongly the demand on $+E$ effects is the *para*-phenyl group; [16,17] the following rate factors show how activation, $f_p^{\rm Ph}$, by this group varies compared with activation, $f_m^{\rm Me}$, by the *m*-methyl group for which $+E$ effects must be negligible: molecular chlorination, $f_p^{\rm Ph} = 595$, $f_m^{\rm Me} = 4{\cdot}95$; [16,18,19] ionic bromination, $f_p^{\rm Ph} = 15{\cdot}6$, $f_m^{\rm Me} = 2{\cdot}5$; [16] nitration, $f_p^{\rm Ph} = 11{\cdot}0$, $f_m^{\rm Me} = 2{\cdot}5$; [15,16] desilylation, $f_p^{\rm Ph} = 2{\cdot}8$, $f_m^{\rm Me} = 2{\cdot}2$; [17] degermylation, $f_p^{\rm Ph} = 2{\cdot}69$, $f_m^{\rm Me} = 2{\cdot}1$.[6] In destannylation the *p*-phenyl group actually activates to only about the same extent as the *m*-methyl group ($f_p^{\rm Ph} = 1{\cdot}77$; $f_m^{\rm Me} = 1{\cdot}84$).

TABLE 2. *Cleavage of* $\rm X{\cdot}C_6H_4{\cdot}SnMe_3$ *compounds and of* *p*-$\rm MeO{\cdot}C_6H_4{\cdot}SnPh_3$.

Compound	[Acid] (M)	10^3k (min.$^{-1}$)	$k_{\rm rel}$	Compound	[Acid] (M)	10^3k (min.$^{-1}$)	$k_{\rm re}$
$\rm C_6H_5{\cdot}SnMe_3$	2·35	90	1	*p*-$\rm Cl{\cdot}C_6H_4{\cdot}SnMe_3$ ...	2·35	34·5	0·38
	0·099	3·1	1	*m*-$\rm Cl{\cdot}C_6H_4{\cdot}SnMe_3$ ...	2·35	15·8	0·18
p-$\rm Me{\cdot}C_6H_4{\cdot}SnMe_3$ ...	0·099	10·7	3·4	*p*-$\rm MeO{\cdot}C_6H_4{\cdot}SnPh_3$	2·35	31·5	—

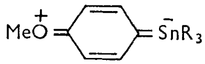
It has been suggested that the large increase in the ease of acid cleavage on going from Ar–Si and Ar–Ge bonds to Ar–Sn bonds may indicate a change of mechanism.† The fall in ρ and, more particularly, in r, may be associated with such a change in mechanism, but for the present we infer only that the electrons of the weak, highly polarizable, Ar–Sn

* Where r has a value in the range 0·7—1·3, log $k_{\rm rel}$–σ^+ plots approximate reasonably to straight lines.[11]

† One possibility tentatively suggested by Eaborn and Pande for the mechanism of destannylation involved assumption of rapid co-ordination of a solvent molecule to the tin atom in $\rm ArMR_3$ compounds.[20] This assumption, which was not well based and may be incorrect, is being tested.

[14] Eaborn and Taylor, *Chem. and Ind.*, 1959, 949.
[15] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **162**, 291.
[16] de la Mare and Hassan, *J.*, 1957, 3004.
[17] Deans, Eaborn, and Webster, *J.*, 1959, 3031.
[18] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.
[19] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.
[20] Eaborn and Pande, *J.*, 1960, 1566.

bond are probably readily available to help in the formation of the Ar–HOM bond, so that only a small excess of positive charge is concentrated on the central carbon in the highest-energy transition state, and there is only a small demand on the electrons of the ring, and particularly on the $+E$ effects of substituents. Another factor which may lead to low r values in demetalations of Ar·MR$_3$ compounds is resonance stabilization of the initial states, involving d_π–p_π bonding of the type indicated, for example, in structure (I), for resonance effects which stabilize the transition state will be to some extent obscured by this stabilization of the initial state. It is impossible at present to decide how the importance of d_π–p_π bonding in Ar·MR$_3$ compounds varies in the series M = Si, Ge, Sn; Chatt and Williams concluded that there was probably little change in the degree of such bonding for the three elements,[21] but this conclusion depends on assumptions about the electronegativities of the elements which may be incorrect.[6,22]



(I)

The trimethylphenylstannanes (see Table 2) are more readily cleaved than the corresponding tricyclohexyl compounds, the factor being *ca.* 5·4 for the unsubstituted compounds. The effects of substituents are smaller for the trimethyl compounds. These differences may originate in steric effects, the cyclohexyl groups not only hindering any nucleophilic attack at the tin atom, but, what is probably more important, also hindering solvation around the reaction site in the transition state. Since the excess of positive charge on the central carbon is less stabilized by solvation, not only will the tricyclohexyl compounds be less reactive but there will also be a greater demand on the electrons of the ring.

p-Methoxyphenyltriphenylstannane is about 35 times less reactive than the corresponding tricyclohexyl compound. This deactivating effect of phenyl groups attached to the metal is paralleled in cleavages of Ar–SiPh$_3$ and Ar–GePh$_3$ bonds, and presumably arises mainly from the electron-withdrawing effect of phenyl compared with alkyl groups

Failure of Linear Free-energy Relations in Electrophilic Aromatic Substitution.—We wish to stress a more general aspect of our results, *viz.*, the demonstration that the effects of substituents in an electrophilic aromatic substitution cannot necessarily be interpreted, even approximately, directly in terms of their σ^+ constants. Further, our work demonstrates that certain other observations associated with application of the analysis of substituent effects in terms of σ^+ constants do not extend to all electrophilic aromatic substitutions. For example, it was demonstrated that for those electrophilic aromatic substitutions for which accurate data were available, the ratio $(\log f_p^{\mathrm{Me}})/(\log f_m^{\mathrm{Me}})$ had a value in the range 3·18—4·72.[23] The value of this ratio in destannylation is 2·8, and there seems no reason why even lower values should not be found. (A value of 2·9 has been noted in detritiation.[1,14]) It has indeed been envisaged by H. C. Brown and his co-workers [24] that exceptions to their generalizations may be found for reactions which differ seriously in detailed mechanism from that accepted for the more familiar aromatic substitutions such as nitration or bromination.

EXPERIMENTAL

Materials.—The preparation of the organotin compounds will be described elsewhere.

Ethanol was dried [25] and fractionally distilled.

Rate Measurements.—The general procedures have been described.[3,6,20] To 50 ml. of a solution of the organotin compound in ethanol, of concentration noted in Table 3, 2 ml. of aqueous perchloric acid were added from a microburette. The rate of change of the optical density of the solution at the wavelength(s), λ, noted in the Table, was measured, the mixture

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[21] Chatt and Williams, *J.*, 1954, 4404.

[22] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

[23] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323.

[24] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 5621.

[25] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

being kept either in a 1 cm. cell at 50·0° ± 0·04° (thermostat) in the Unicam S.P. 500 spectrophotometer or, in the one case of the unreactive methiodide of *p*-dimethylaminophenyltricyclohexylsilane, in sealed tubes in a bath at 50·0° ± 0·02°.

While (with the exception of the *p*-dimethylamino-compound, discussed below) rate constants could be duplicated to within ±2%, the random variations in the relative rates of reactions of some pairs of compounds at two or more acid concentrations suggest that the rate constants recorded in Tables 1 and 2 are somewhat less accurate than those obtained in desilylations and degermylations, and we do not feel confident that they are accurate to better than ±3%. We did not attempt to improve on this because the errors involved are unimportant for our purposes.

TABLE 3. *Concentration of* $X\cdot C_6H_4\cdot SnR_3$, *and wavelength used.*

R	X	10^3 × Concn. (M)	λ (mμ)	R	X	10^3 × Concn. (M)	λ (mμ)
C_6H_{11}	H	1·67	254, 262	C_6H_{11}	*p*-F	1·67	265, 272
	m-Me	1·67	257, 267		*m*-MeO	0·42	276, 284
	p-Me	1·67	257, 267		*p*-MeO	0·83	284
	p-Et	1·67	256, 263		*p*-NMe_2	0·042	262
	p-Pr^i	1·67	255, 262		*p*-$\overset{+}{N}Me_3$	0·167	249
	p-Bu^t	1·67	255, 262		*p*-CO_2H	0·167	253
	p-Ph	0·042	275	Me	H	1·67	259
	o-Ph	0·167	264, 268		*p*-Me	1·67	273
	m-Cl	0·83	262, 269		*m*-Cl	5·0	276
	p-Cl	0·83	259, 269		*p*-Cl	5·0	276
	p-Br	1·67	259, 264	Ph	*p*-MeO	0·83	284

In the sole case of the *p*-dimethylamino-compound, the concentration of acid in the reaction medium is comparable with the concentration of organostannane, and the tricyclohexyltin hydroxide produced in the cleavage removes a significant proportion of the acid. Consequently, first-order rate constants fall throughout each run, and the values of *k* given for this compound in Table 1 are obtained by studying the first 20% of reaction carefully and deriving the rate at zero time by extrapolation. The rate constants could be duplicated within ±5%, and are believed to be accurate to within ±10%.

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