108. *Aromatic Reactivity. Part XXIII.*[1] *Cleavage of Aryl–Tin Bonds by Iodine in Carbon Tetrachloride.*
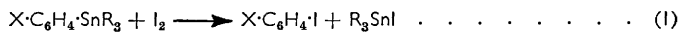
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We have measured the rates of cleavage of some $R_3Sn \cdot C_6H_4 \cdot X$ compounds (where R = cyclohexyl, Et, Me, or Ph) by iodide in carbon tetrachloride at 25°. This reaction, which is an electrophilic aromatic substitution, is of second order in iodine and first order in organostannane, and appears to be homogeneous and chain-free.

The effects on the rate of substituents, X, in the series mainly studied, *viz.*, compounds in which R is cyclohexyl, are not in accord with substituent effects in other electrophilic aromatic substitutions, and possible reasons for this are considered. The preferred explanation is that the transition state of the rate-determining step has some π-complex character.

The relative reactivities of some $R_3Sn-C_6H_5$ bonds are: (R =) C_6H_{11}, 5·4; Et, 5·1; Me, 1·0; Ph, 0·018.

It is well known that carbon–tin bonds are broken easily by halogens, aryl–tin being broken much more easily than alkyl–tin bonds,[2] and we have now studied kinetically the reaction between some aryltriorganostannanes and iodide in carbon tetrachloride. This reaction (1), is an electrophilic aromatic substitution, and formally resembles aromatic halogenation and, more obviously, cleavage of trialkylarylsilanes by bromine, a reaction which was described earlier in this series.[3] Mainly we have used aryltricyclohexyl-stannanes, because, being solids, they can be obtained pure fairly easily, but we have also used some aryltrimethylstannanes and some tetra-arylstannanes.

$$X \cdot C_6H_4 \cdot SnR_3 + I_2 \longrightarrow X \cdot C_6H_4 \cdot I + R_3SnI \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

Characteristics of the Reaction.—Detailed examination in the case of one compound, tricyclohexyl-*p*-fluorophenylstannane, showed that the reaction is homogeneous, being unaffected by addition of glass wool. It probably does not involve radicals, since the rate was unaffected by illumination during the first 50% of reaction; a slightly lower rate of iodine disappearance in the later stages of reaction probably originates in some decomposition of the products. (A similar effect was observed in the iodination of trialkyl-silanes in carbon tetrachloride.[4]) Unlike uncatalysed bromination of aromatic compounds in carbon tetrachloride,[5] but like iodination of trialkylsilanes,[4] iododestannylation is unaffected by the presence of water in the carbon tetrachloride.

The reaction is of third order, as shown by the satisfactory constancy of third-order rate constants during runs involving equal initial concentrations of the reactants and carried to 60—70% of completion, and, more conclusively, by the non-dependence of the third-order rate constant on the initial concentrations (see the Table). Because of the high order, any one compound can be conveniently studied only over a small concentration range, but use of a range of compounds of different reactivities permitted rate measurements to be made for initial reactant concentrations in the range 4×10^{-4} to 50×10^{-4}M, and no departure from third-order behaviour was observed. Outside this range the order might possibly be dependent on the halogen concentration, as in aromatic halogenation [6,7]

[1] Part XXII, Baker, Eaborn, and Sperry, *J.*, 1962, 2382.
[2] Luijten and van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford. 1955. pp. 4, 19; Manulkin, *Zhur. obshchei Khim.*, 1943, **13**, 42; 1944, **14**, 1047; Grüttner and Krause, *Ber.*, 1917, **50**, 1802; Krause, *Ber.*, 1918, **51**, 912.
[3] Eaborn and Webster, *J.*, 1957, 4449; 1960, 179.
[4] Deans and Eaborn, *J.*, 1954, 3169.
[5] Keefer, Blake, and Andrews, *J. Amer. Chem. Soc.*, 1954, **76**, 3062.
[6] Robertson, *Sci. Progr.*, 1955, **43**, 418.
[7] de la Mare and Ridd, "Aromatic Substitution: Nitration and Halogenation," Butterworths Scientific Publns., London, 1959, pp. 123—125.

and in aromatic bromodesilylation in acetic acid.[3] (In some aromatic halogenations in carbon tetrachloride the integrated high-order rate constants were also found to vary with the concentration of the aromatic compound,[5,8] but at concentrations much higher than those we used.)

Runs involving different initial concentrations of organostannane and iodine revealed that the reaction was of the first order in organostannane and of the second-order in halogen. The order in halogen is lower than might have been expected from observations on aromatic halogenation; for example, iodination of mesitylene by iodine monochloride in carbon tetrachloride is of the third order in halogen,[9] as in iodine-catalysed bromination,[10] and generally the order seems to increase with decreasing reactivity of the halogen.[6] The lower order of the iododestannylation is consistent with the fact that bromine cleavage of aryltrimethylsilanes in acetic acid is of lower order than aromatic bromination under the same conditions.[3] The high orders in aromatic halogenation have been attributed [6,7,9] to the need for extra halogen molecules to assist heterolysis of the molecule, X_2, engaged in electrophilic attack on the aromatic ring, presumably by stabilising the separating anion, X^-, through complex-formation (*e.g.*, Br_3^-). Because of the high reactivities of

Interaction of $R_3Sn\cdot C_6H_4\cdot X$ compounds with iodine in carbon tetrachloride at 25°.

X	Concn. (10⁻⁵ᴍ)	$10^{-4}k_3$ *	k_{rel}	X	Concn. (10⁻⁵ᴍ)	$10^{-4}k_3$ *	k_{rel}
		R = Cyclohexyl.				R = Cyclohexyl.	
p-OMe	42	687	69	*p*-Br	83	0·80	0·080
p-Sn(C₆H₁₁)₃	42	198	20		111	0·79	—
	50	199	—	*m*-Cl	170	0·39	0·039
p-Buᵗ	42	142	13·9 †		250	0·38	—
	50	136	—	*p*-CO₂H	250	0·145	0·0145
p-Prⁱ	42	124	12·1 †				
	50	119	—			R = Me.	
p-Et	42	101	10·1	*p*-Me	41	14·1	7·5
	50	102	—		50	13·9	—
p-Me	42	75	7·5	H	50	1·87	1·0
	50	75	—		83	1·86	—
m-Me	42	42	4·2	*p*-Cl	330	0·124	0·067
	50	42	—		500	0·127	—
p-Ph	42	28·7	2·9	*m*-Cl	500	0·031	0·016
	50	28·6	—				
m-OMe	42	22·3	2·2			R = Et.	
H	42	10·0	1·0				
	83	10·1	—	H	42	9·3	—
	111	9·8	—		50	9·7	—
o-Ph	42	3·4	0·34				
	50	3·5	—			R = Ph.	
p-F	83	2·25	0·22 †	H	33	0·034	1·0
	111	2·20	—		50	0·035	—
p-Cl	83	1·02	0·10	*p*-OMe	110	0·72	21·0
	111	0·98	—		170	0·71	—
	167	0·99	—				

* In l.² mole⁻² min.⁻¹. † Average for two initial concentrations.

aryl-metal compounds (compared with corresponding aryl-H compounds) less assistance from such anion stabilisation is required during the reactions with halogens. (Equivalently, we could say that because of the high reactivity of the aryl–metal bond the transition state of the rate-determining step resembles the reactants more in the cleavages than in aromatic halogenation, so that the X–X bond is less polarised in the transition state of the cleavage.)

Effects of Substituents in the Aromatic Ring.—In the Table the effect of a substituent, X, on the rate of reaction is shown by the value of k_{rel}, the rate for the compound

[8] Blake and Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 3707.
[9] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1957, **79**, 1412.
[10] Robertson, Allan, Haldane, and Simmers, *J.*, 1949, 933.

X·C$_6$H$_4$·SnR$_3$ relative to that for the corresponding parent compound C$_6$H$_5$·SnR$_3$. In this section we discuss the effects for the case in which R is cyclohexyl.

In general, electron-releasing substituents facilitate and electron-withdrawing substituents hinder the reaction, as expected for an electrophilic aromatic substitution, but a more detailed analysis shows clear anomalies. Outstanding is the 2·2-fold activation by a *m*-methoxy-group; this substituent normally deactivates in electrophilic aromatic substitution,[11] and while it activates aromatic bromination in acetic acid [11,12] this could be attributed to an unusually high electron-demand in the reaction (for example, a *p*-Me group activates 2420 times),[13] whereas in iododestannylation the overall electron-demand is small. Further, a large electron-demand normally results in activation by a *p*-fluoro-substituent (for example, in chlorination,[14] bromodeboronation,[15] and detritiation [16]), whereas in iododestannylation this substituent has a rather large deactivating effect in relation to the fairly small general spread of rates.

The effects of substituents in a variety of electrophilic aromatic substitutions, including cleavage of aryl–silicon,[17] –germanium,[18] and –tin bonds [19] by acids, and of aryl–silicon bonds by bromine in acetic acid,[3] can be qualitatively accounted for in terms of the σ$^+$-constants [20] of the substituents, or better, in terms of a combination of these constants with the Hammett σ-constants, by means of the Yukawa–Tsuno equation,[21] log k_{rel} = ρ[σ + r(σ$^+$ − σ)], where r is a measure of the demand on electron-releasing polarisability effects of substituents. With the values of log k_{rel} listed for iododestannylation in the Table, however, no value of r leads to even approximate agreement with the Yukawa–Tsuno equation. Even the points for *meta*-substituents do not fall on a straight line; indeed, they show a greater scatter than do points for *para*-substituents. The substituent effects could reasonably be expected to be related to those in cleavage of the same aryltri-cyclohexylstannanes by aqueous-ethanolic perchloric acid,[19] particularly since the overall spread of rates is much the same in both reactions (for example, a *p*-methoxy-group activates 69 times in the iodine cleavage and 63 times in the acid cleavage), but a plot of log k_{rel} against corresponding values, log k'_{rel}, for acid cleavage (see Figure) does not even approximate to a straight line. We have nevertheless, for reference purposes, drawn a line rather arbitrarily passing through the point for the unsubstituted compound and between those for the *p*-alkyl-compounds, and it will be seen that the points for the *meta*-substituted compounds deviate from this line in a direction which shows these compounds to be, relative to *para*-substituted compounds, more reactive in iodine cleavage than in acid-cleavage (and it should be remembered that substituent effects in the acid cleavage can be correlated, through the Yukawa–Tsuno equation, with those in other electrophilic aromatic substitutions [19]). On the other hand, the reactivities of the *p*-methoxy- and *p*-fluoro-compounds appear to be relatively low in the iodine cleavage.

We shall consider three possible explanations for the anomalous effects of substituents in the iodine cleavage, *viz.*, (*a*) the non-polar nature of the solvent, (*b*) the effects of the substituents on the stabilisation of the aryltricyclohexylstannanes by p_π–d_π-bonding between the aromatic ring and the tin atom, and (*c*) a significant proportion of interaction of the π-complex type between the aromatic compound and the attacking iodine molecule in the highest-energy transition state of the reaction.

Explanation (*a*) is superficially attractive because of its simplicity, and because a

[11] Stock and Brown, *J. Amer. Chem. Soc.*, 1960, **82**, 1942.
[12] de la Mare and Vernon, *J.*, 1951, 1764.
[13] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421.
[14] Ref. 7, p. 140.
[15] Kuivila and Benjamin, *J. Amer. Chem. Soc.*, 1955, **77**, 4834.
[16] Eaborn and Taylor, *J.*, 1961, 2388.
[17] Eaborn, *J.*, 1956, 4858; Deans and Eaborn, *J.*, 1959, 2299.
[18] Eaborn and Pande, *J.*, 1961, 297, 5082.
[19] Eaborn and Waters, *J.*, 1961, 542.
[20] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
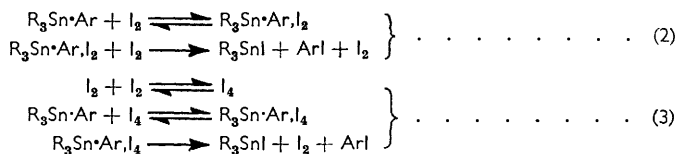[21] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

change to carbon tetrachloride from the fairly polar hydroxylic solvents usually employed in the study of substituent effects in electrophilic aromatic substitution could be expected to result in a different balance between space- and bond-transmitted polar effects and also between effects of substituents on electron distribution and on steric interference with solvation; such effects would be additional to any specific solvent effects on the inherent electronic effects of substituents.[22]   But there are several reactions (not including electrophilic aromatic substitution) in carbon tetrachloride, hydrocarbons, or similar solvents in which substituent effects are satisfactorily or roughly in accord with the Hammett σ-constants,[23] or with the Yukawa–Tsuno equation,[21] while effects of substituents on the
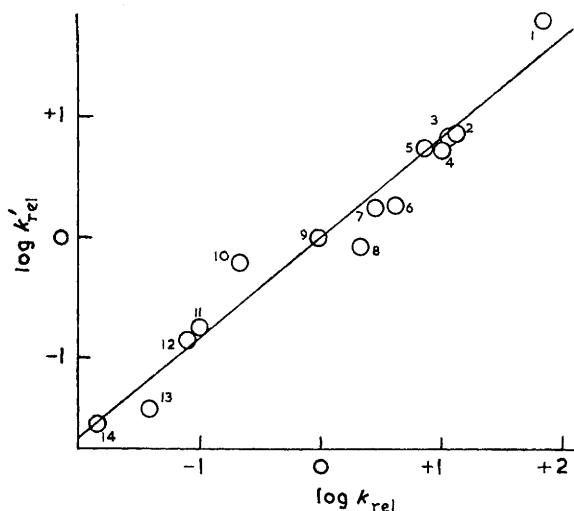
Plot of log k_{rel} in iodine cleavage against log k'_{rel} in acid cleavage of $X \cdot C_6H_4 \cdot Sn(C_6H_{11})_3$ compounds.

X = 1, p-OMe; 2, p-Bu^t; 3, p-Pr^i; 4, p-Et; 5, p-Me; 6, m-Me; 7, p-Ph; 8, m-OMe; 9, H; 10, p-F; 11, p-Cl; 12, p-Br; 13, m-Cl; 14, p-CO$_2$H.

thermal decomposition of a wide variety of 1-aryl- or 1,2-diaryl-ethyl acetates in the gas phase can be correlated closely with σ^+-constants,[24] and it thus seems that solvent effects on the factors mentioned above must be of secondary importance.

$$\left. \begin{array}{l} R_3Sn \cdot Ar + I_2 \rightleftharpoons R_3Sn \cdot Ar, I_2 \\ R_3Sn \cdot Ar, I_2 + I_2 \longrightarrow R_3SnI + ArI + I_2 \end{array} \right\} \quad \cdots \cdots \cdots \quad (2)$$

$$\left. \begin{array}{l} I_2 + I_2 \rightleftharpoons I_4 \\ R_3Sn \cdot Ar + I_4 \rightleftharpoons R_3Sn \cdot Ar, I_4 \\ R_3Sn \cdot Ar, I_4 \longrightarrow R_3SnI + I_2 + ArI \end{array} \right\} \quad \cdots \cdots \cdots \quad (3)$$

In considering explanation (b) we note that substituents must affect the extent of d_π–p_π-bonding in the aryl-tin compounds, and that those electronic effects which stabilise a transition state of the type normal in electrophilic aromatic substitutions will also stabilise the initial aryl-tin compounds.   There is thus a possibility of complex differential effects, but we discard this as a correct, or at least as a complete, explanation of the observed anomalies for the following reasons: (i) The effects of substituents on the initial state are the same for acid cleavage as for iodine cleavage, so that the absence of a free-energy relation denoted by the Figure would have to arise from substantially different transition-state configurations in the two reactions [and thus we should have to look to an explanation of type (c)].   (ii) Substituents could be expected to influence the extent of d_π–p_π-bonding in accord with their σ- or σ^+-constants, or some combination of the two, so that, if the transition state is of the usual type, the free-energy change from initial state

[22] Ritchie and Lewis, *J. Amer. Chem. Soc.*, 1962, **84**, 591; Taft, *J. Phys. Chem.*, 1960, **64**, 1805.
[23] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[24] G. G. Smith and R. Taylor, personal communication.

to transition state should also be correlated, at least roughly, with some combination of σ- and σ$^+$-constants (cf. ref. 25). (iii) It would be difficult to interpret the effects of some individual substituents; for example, the 2·2-fold activation by the *m*-methoxy-group would imply a surprisingly large destabilisation of the aryl-tin compound.

Explanation (*c*) involves the assumption that a π-complex between the arylstannane and iodine participates in the rate-determining step, the reaction sequence being either (2) or (3). (There is evidence for the existence of I$_4$ complexes in carbon tetrachloride solutions of iodine.[26]) It is unnecessary, in fact, to distinguish between these sequences because the same highest-energy transition state is involved in both cases, and for simplicity we shall use sequence (2) in our discussion below.

Aromatic compounds are known to form π-complexes with halogens in carbon tetrachloride,[27,28] and it has been suggested that such complexes are involved in aromatic halogenations in this and other media,[8,9] that π-complexes are, in general, intermediates in electrophilic aromatic substitutions,[29] and that their significant participation in the reaction mechanism will lead to abnormal substituent effects.[11,30,31] In molecular halogenation of ordinary aromatic compounds, however, it seems that the free-energy of the rate-determining transition state for substitution is so much higher than that of the complex that no significant degree of π-complex character persists in this transition state, and, as far as substituent effects are concerned, it is irrelevant whether or not the reaction proceeds through such a complex (cf. ref. 32). An aryl–tin bond is, however, very much more reactive than the corresponding aryl–hydrogen bond (a factor of *ca.* 10^{10} applies in cleavage of the bonds by acid,[33] and a larger factor will apply in cleavage by iodine, which is a less reactive and more selective electrophile), and thus in the reaction involving arylstannanes the rate-determining transition state will not be so far removed from the π-complex, and it is possible that influences which stabilise the complex also contribute significantly to stabilisation of the transition state.*

The complex it is relevant to consider is that in which the iodine molecule lies over one bond of the ring, not necessarily perpendicularly to the ring, and this is possibly not the complex of lowest energy (cf. ref. 34). The stability of this complex is determined by the general electron-availability in the 1–2 bond, and a substituent X has the same effect on the bond from the 5- as from the 4-position (any interaction between the X and R$_3$Sn groups being neglected). Thus in the rate-determining transition state a *meta*-substituent will appear to have some *para*-character, and *vice-versa*, and consequently, as observed in iododestannylation, the difference between the effects of *m*-X and *p*-X substituents will be smaller (the overall spread of rates being taken into account) than is usual in electrophilic aromatic substitution. The *m*-methoxy-group, for example, having some of the effect normally associated with a *p*-methoxy-group, increases the reaction rate, while the

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* The moderately large effect of ring substituents, which is as great as that in cleavage of the arylstannanes by aqueous-ethanolic perchloric acid, might seem to conflict with the suggestion that the transition state is not far removed from the π-complex. But the degree of development of positive charge on the ring could be much smaller in the iodine than in the acid cleavage, and the influence of substituents on this charge still be as great because of the lack of solvent stabilisation of the charge in carbon tetrachloride.

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

[26] Kortüm and Friedheim, *Z. Naturforsch.*, 1947, **2a**, 20; Keefer and Allen, *J. Chem. Phys.*, 1956, **25**, 1059.

[27] Andrews and Keefer, " Advances in Inorganic Chemistry and Radiochemistry," ed. Eméleus and Sharpe, Academic Press, New York, 1961, Vol. III, p. 91.

[28] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 4500; 1955, **77**, 2164.

[29] Dewar, " The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, pp. 168—172.

[30] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323, 5621.

[31] Olah, Kuhn, and Flood, *J. Amer. Chem. Soc.*, 1961, **83**, 4571.

[32] Cf. ref. 7, pp. 40—41, 46.

[33] Eaborn and Pande, *J.*, 1960, 1566.

[34] Murrell, *J. Amer. Chem. Soc.*, 1959, **81**, 5037; Mulliken, *J. Chem. Phys.*, 1955, **23**, 397.

p-fluoro-substituent, acting as though it were partly m-fluoro, deactivates more than would be expected.

We represent the structure of the highest-energy transition state as (II) (the aromatic electrons being omitted for simplicity). We show the Ar–Sn bond as breaking in the rate-determining step because this accounts for the much higher reactivity of Ar–Sn than of the stronger Ar–Si bonds towards iodine (Cottrell [35] lists values of 60 and 54 kcal./mole,
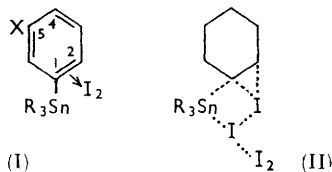
respectively, for C–Si and C–Sn bonds), whereas there is no reason to expect much difference in the ease of formation of the intermediates $[Me_3Sn\cdot Ar\cdot I]^+$ and $[Me_3Si\cdot Ar\cdot I]^+$, since Me_3Sn and Me_3Si groups differ little in their power of electron-release towards aromatic [36] or saturated [37] carbon atoms. We furthermore prefer a cyclic transition state, involving some interaction between the forming iodide and the tin atom, because the formation of free R_3Sn^+ and I^- (or I_3^-) ions is unlikely in carbon tetrachloride. The second iodine molecule required by the kinetics is shown as stabilising the forming iodide ion, and indeed the immediate product could be the complex R_3SnI,I_2 [cf. the known [38] complex $(C_6H_{11})_3SiI,I_2$], which subsequently dissociates.

Because of the complications noted, it would be pointless to discuss individual substituent effects in detail, but we draw attention to the 10-fold activating effect of a p-$(C_6H_{11})_3Sn$ substituent [the value of k_{rel} for the compound p-$(C_6H_{11})_3Sn\cdot C_6H_4\cdot Sn(C_6H_{11})_3$ has to be halved in considering the substituent effect, because two equivalent aryl–Sn bonds are available for reaction]. This factor is greater than that for a p-methyl substituent, whereas a p-Me_3Si group activates only 1·58 times in bromodesilylation,[3] in which p-Me and m-Me groups activate 49 and 2·9 times, respectively. As measured by the strengths of the acids p-$Me_3M\cdot C_6H_4\cdot CO_2H$, the electron-releasing effects of Me_3Si and Me_3Sn groups are roughly equal.[36]

Variation of R in $R_3Sn\cdot C_6H_4\cdot X$ *Compounds.*—The relative reactivities of the tin–aryl bonds in the $R_3Sn\cdot C_6H_5$ compounds examined are: (R =) C_6H_{11}, 5·4; Et, 5·1; Me, 1·0; Ph, 0·018. (The reactivity of tetraphenylstannane has to be divided by four for the comparison because it has four equivalent Sn–Ph bonds available for reaction. The satisfactory third-order kinetics observed for this compound indicate that only one bond is cleaved.) The low reactivity of the Ph_3Sn–Ph bond can be attributed to the $-I$ effects of the non-cleaved phenyl groups, the return of electrons by d_π–p_π-bonding not being sufficient to outweigh them. Tetra-arylsilanes are similarly unreactive, compared with trialkylarylsilanes, towards electrophilic reagents.

Tricyclohexyl- and triethyl- are more reactive than trimethyl-phenylstannane, probably because the $+I$ effect of a cyclohexyl or ethyl group is larger than that of a methyl group. In proto-desilylation, -degermylation,[33] and -destannylation,[19] all in aqueous-alcoholic media, a tricyclohexylmetal group is cleaved from an aromatic ring less readily than a trimethylmetal group, and this can be attributed to steric hindrance by the cyclohexyl groups, possibly towards any nucleophilic attack on the metal atoms, but probably towards solvation of the positive charge at the reaction centre in the transition state.[19] In iododestannylation nucleophilic attack on tin is probably relatively

[35] Cottrell, " The Strengths of Chemical Bonds," Butterworths Scientific Publns., London, 1958, 2nd edn., pp. 275—278.
[36] Chatt and Williams, *J.*, 1954, 4403.
[37] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269; Eaborn and Walton, unpublished results.
[38] Eaborn, *J.*, 1953, 4154.

unimportant [that is, the Sn–I bond in (II) is little formed in the transition state], while solvation effects must be very small in carbon tetrachloride.

As usual, the effect of a nuclear substituent is larger in a less reactive system; thus a *p*- and a *m*-chloro-substituent reduce the rate of cleavage of trimethylphenylstannane 15 and 60 times, respectively, but cleavage of tricyclohexylphenylstannane only 10 and 26 times. Again, a *p*-methoxy-group accelerates the cleavage of a $Ph_3Sn–C_6H_5$ bond 84 times, but the cleavage of a $(C_6H_{11})_3Sn–C_6H_5$ bond only 69 times.

EXPERIMENTAL

Preparation of Materials.—The preparations of the organotin compounds have been described.[39]

Carbon tetrachloride (May and Baker's " Reagent Grade ") was dried over phosphorus pentoxide and fractionated, with exclusion of moisture, from a fresh batch of the same reagent, the first and the last tenth of the distillate being discarded.

Iodine was ground with potassium iodide, sublimed from the mixture, resublimed, and stored in a desiccator ($CaCl_2$).

Rate Measurements.—The solution of iodine in carbon tetrachloride was standardised by titration against aqueous sodium thiosulphate (see below), and a solution of organostannane in carbon tetrachloride was prepared to be exactly of the same molarity. The solutions were stored in a thermostat-bath at $25 \cdot 0° \pm 0 \cdot 02°$, and usually equal volumes of each were transferred quickly by pipette to a 150-ml. conical flask fitted with a long neck and ground-glass stopper, coated with black paint, and contained in the thermostat-bath. The flask was shaken during the mixing, and the zero time of the reaction was taken to be the point at which half of the second solution had been added. Aliquot parts (5 ml.) were removed at suitable times by means of a rapid-transfer pipette (that used for standardisation of the iodine solution), and each was added to a cold mixture of an excess of standard aqueous thiosulphate and 10% aqueous potassium iodide (10 ml.) in a separatory funnel. The mixture was shaken thoroughly, the lower layer was discarded, the aqueous layer was flushed into a titration vessel, and the excess of sodium thiosulphate was titrated against standard solution of iodine in aqueous potassium iodide, the dead-stop end-point method [40] being used.

For fast runs the reactant solutions (5 ml. of each) were placed in separate limbs of an inverted-Y shaped vessel, contained in the thermostat-bath, and after a few minutes the vessel was tilted to and fro so that mixing was complete in a few seconds. After a suitable time the contents of the vessel were added rapidly to a sodium thiosulphate–potassium iodide solution, as above, and subsequent procedure was as below. Eight to ten such experiments were carried out for each run.

The third-order rate constant, k_3, is given by

$$k_3 t = (2T^2/M^2)[(T - T_t)^{-2} - (T - T_0)^{-2}],$$

where T_0 and T are the (calculated) aqueous iodine titres at zero and infinite time, respectively, T_t the titre at time t, and M the molarity of the aqueous iodine solution. Normally rate constants were determined from the slope of a plot of $1/(T_0 - T_t)^2$ against t, but in the following typical runs rate constants are calculated for each point.

(i) Initial reactant concns.: $[p\text{-Et}\cdot C_6H_4\cdot Sn(C_6H_{11})_3] = [I_2] = 4\cdot167 \times 10^{-4}M$; $[Na_2S_2O_3] = 11\cdot39 \times 10^{-4}M$; [Aqueous I_2] $= 2\cdot525 \times 10^{-4}M$.

t (min.)	0	1·4	3·0	6·0	10	17	36	50	92	∞
T (ml.)	(3·02)	4·48	5·50	6·57	7·36	8·16	9·03	9·30	9·80	(11·25)
$10^{-2}k_3$ (l.^{2} mole^{-2} min.$^{-1}$)	—	1·03	1·01	1·05	1·05	1·08	1·07	1·04	1·03	—

(ii) Initial reactant concns.: $[m\text{-Cl}\cdot C_6H_4\cdot Sn(C_6H_{11})_3] = [I_2] = 25\cdot00 \times 10^{-4}M$; $[Na_2S_2O_3] = 52\cdot08 \times 10^{-4}M$; [Aqueous I_2] $= 11\cdot13 \times 10^{-4}M$.

t (min.)	0	1·25	6·0	14	21·5	37	54	68	82	98
T (ml.)	(0·47)	0·80	1·80	2·98	3·82	4·83	5·76	6·15	6·54	6·93	(11·70)
$10^{-3}k_3$ (l.^{2} mole^{-2} min.$^{-1}$)	—	3·96	3·90	3·84	3·85	3·64	3·79	3·66	3·64	3·71	—

Runs were normally taken to 60—75% of completion, but occasionally to 85% of completion. All runs were duplicated, and the mean rate constant was reproducible within $\pm 2\%$. Rate

[39] Eaborn and Waters, *J.*, 1962, 1131.
[40] Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

constants at two or more initial reactant concentrations usually agreed within 3%, and in all cases within 5%.

While anhydrous carbon tetrachloride was normally used, for some typical runs it was found that shaking the iodine and organostannane solutions with a little water beforehand had no significant effect on the rates. Runs in clear vessels under illumination from a 150-w tungsten lamp did not differ during the first 30—50% of reaction from those kept in the dark, but subsequent iodine disappearance was slightly slowed, probably because decomposition of the products returned iodine to the solution (cf. ref. 4). Packing the reaction vessel with glass wool had no effect.

In a run involving m-methoxyphenyltrimethylstannane, the rate of removal of iodine was unchanged by addition of 10 equivalents of anisole, indicating that no ring iodination occurred along with the cleavage.

Order of Reaction.—That the reaction is of second order in iodine and first in organostannane was confirmed in the case of tricyclohexyl-p-fluorophenylstannane by taking unequal concentrations of the stannane and iodine, finding (from tangents to the plot of iodine titre against time) the instantaneous rates, $d[I_2]/dt$ at various percentages of reaction, and comparing these with the values calculated from the equation $[dI_2]/dt = k_3[I_2]^2[Ar \cdot SnR_3]$, where k_3, determined separately in runs involving equal initial reactant concentrations (see Table), has a value of $2 \cdot 20 \times 10^4$ l.^{2} mole^{-2} min.$^{-1}$ Examples are:

(i) Initial concns.: $[I_2]$, $8 \cdot 33 \times 10^{-4}$M; $[Ar \cdot SnR_3]$, $11 \cdot 11 \times 10^{-4}$M.

% of reaction	10	20	30
$10^5 \times d[I_2]/dt$ (l.$^{-1}$ mole min.$^{-1}$) (obs.)	1·25	0·93	0·65
$10^5 \times d[I_2]/dt$ (l.$^{-1}$ mole min.$^{-1}$) (calc.)	1·27	0·92	0·64

(ii) Initial concns.: $[I_2]$, $11 \cdot 11 \times 10^{-4}$M; $[Ar \cdot SnR_3]$, $5 \cdot 55 \times 10^{-4}$M.

% of reaction	10	20	30
$10^5 \times d[I_2]/dt$ (l.$^{-1}$ mole min.$^{-1}$) (obs.)	1·22	0·98	0·77
$10^5 \times d[I_2]/dt$ (l.$^{-1}$ mole min.$^{-1}$) (calc.)	1·19	0·98	0·76

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