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## Aromatic Reactivity. Part XXXV.<sup>1</sup> Alkali Cleavage of Aryltrimethylstannanes: an Unusual Electrophilic Aromatic Substitution

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We have measured spectrophotometrically the rates of cleavage by aqueous methanolic alkali of the aryl-tin bonds in a series of  $X \cdot C_6H_4 \cdot SnMe_3$  compounds. In this reaction, the rate-determining step of which probably involves separation of the carbanion  $X \cdot C_6 H_4^-$ , the effects of *meta* substituents are in accord with the Hammett  $\sigma$  constants  $(\rho = 2.18)$ , but the effects of *para* substituents show an abnormal pattern. For example, there is rate-acceleration not only by electron-withdrawing groups such as  $\rho$ -CF<sub>3</sub> and  $\rho$ -CI, but also by normally electron-releasing groups such as p-OMe and p-NMe<sub>2</sub>. For the *para* substituents, the effects are roughly in line with their  $\sigma_1$  constants.

The analogy with base-catalysed aromatic hydrogen-exchange is discussed, and substituent effects in the two reactions are compared. An explanation previously advanced for the abnormalities in the hydrogen exchange is examined in the light of the results for the cleavage.

In previous Parts we described effects of nuclear substituents in cleavage of phenyltrimethylstannanes, X·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub>, and their organosilicon and organogermanium analogues, by electrophilic reagents, notably acids and halogens, and have shown that these effects. can be satisfactorily correlated with those in familiar electrophilic aromatic substitutions in which arylhydrogen bonds are broken (cf. ref. 2). We have now examined a very different kind of electrophilic aromatic substitution, viz., the cleavage of substituted phenyltrimethylstannanes by aqueous methanolic alkali, which is represented by equation (1), in which M = Me or H.

$$X \cdot C_6 H_4 \cdot SnMe_3 + MOH \xrightarrow{MO^-} X C_6 H_5 + Me_3 SnOM$$
(1)

This is, by definition, an electrophilic substitution at carbon, since the carbon atom retains the electrons of the C-Sn bond, but the dominant driving force is provided by the nucleophilic attack of hydroxide and methoxide ion on the tin atom, electrophilic attack by the solvent at carbon being of secondary importance, and probably occurring only in a subsequent fast step. The analogous reaction in which a C-H bond is broken is base-catalysed hydrogen exchange in substituted benzenes.<sup>3-8</sup>

The cleavage was studied spectrophotometrically, as for the corresponding acid cleavage,<sup>9</sup> the medium being a mixture of 2 vol. of aqueous 7.61M-sodium hydroxide and 3 vol. of methanol. Reactions were of first order up to more than 80% completion. Reactions of halflife greater than about 90 min. could not be studied in this medium because some decomposition occurs of one or more of the trimethyltin products, Me<sub>3</sub>SnOH, Me<sub>3</sub>SnOMe, and (Me<sub>3</sub>Sn)<sub>2</sub>O, to give species which absorb at the wavelengths used. For this reason a rate constant could not be obtained, for example, for the compound p-HO·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub>, which would be effectively completely converted into the very unreactive phenoxide ion in the reaction medium.

The effect of varying the concentration of the alkali was briefly studied with the relatively reactive compound m-CF<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub>. Over the range 3.75—7.61 m (added) alkali the rate increases less than would be expected for first-order dependence on the base concentration, in contrast with the linearity observed at lower base some concentrations in cleavage of benzyltrimethyl-silanes and -stannanes.<sup>10</sup> The departure from non-linearity in the present cleavage is qualitatively in accord with the expected salt effect.

For determination of relative reactivities, one alkali concentration was used; Table 1 lists the concentration, C, of the methanolic solution of the organostannane, the wavelength used, the value of the observed (pseudo-)first-order rate constant, k, and the value of  $k_{rel}$ , the rate relative to that of phenyltrimethylstannane.

The pattern of substituent effects is very unusual. As would be expected for attack of a negatively charged ion on the organotin compound, substituents which are unambiguously electron-withdrawing, such as *m*-F, p-CF<sub>3</sub>, and p-NMe<sub>3</sub><sup>+</sup>, raise the rate. The weakly electronreleasing m- and p-Me groups correspondingly lower the rate, but the p-OMe and p-NMe<sub>2</sub> groups, which are normally strongly electron-releasing, raise it.

In Figure 1, values of log  $k_{\rm rel}$  are plotted against the Hammett  $\sigma$  constants. The points for the meta substituents lie satisfactorily about a straight line which passes not far from the origin. (The value of  $\rho$  for the line shown is 2.18.) The points for the *para* substituents lie well away from this line and show a large scatter. It is apparent that the p-NMe<sub>2</sub> and p-OMe groups are acting as if their electron-supplying resonance effects are largely suppressed, so that their inductive effects render them electron-withdrawing overall, and, indeed,

<sup>&</sup>lt;sup>1</sup> Part XXXIV, C. Eaborn, J. A. Treverton, and D. R. M.

<sup>Walton, J. Organometallic Chem., 1967, 9, 259.
<sup>2</sup> R. O. C. Norman and R. Taylor, "Electrophilic Substitution</sup> in Benzenoid Compounds," Elsevier Publ. Co., Amsterdam, 1965,

ch. 9. <sup>3</sup> A. I. Shatenshtein, *Tetrahedron*, 1962, **18**, 95, and references therein.

<sup>&</sup>lt;sup>4</sup> G. E. Hall, R. Piccolini, and J. D. Roberts, J. Amer. Chem. Soc., 1955, 77, 4540. <sup>5</sup> G. E. Hall, E. M. Libby, and E. L. James, J. Org. Chem.,

<sup>1963, 28, 311.</sup> 

<sup>&</sup>lt;sup>6</sup> A. Streitwieser, R. G. Lawler, and C. Perrin, J. Amer. Chem. Soc., 1965, 87, 5383; A. Streitwieser and R. A. Caldwell, ibid., p. 5394.

A. Streitwieser and R. G. Lawler, J. Amer. Chem. Soc., 1965, **87**, 5388.

<sup>8</sup> A. Streitwieser, R. A. Caldwell, R. G. Lawler, and G. R. Ziegler, J. Amer. Chem. Soc., 1965, 87, 5399.

C. Eaborn and J. A. Waters, J. Chem. Soc., 1961, 542.

<sup>&</sup>lt;sup>10</sup> C. Eaborn and S. H. Parker, J. Chem. Soc., 1955, 126; R. W. Bott, C. Eaborn and T. W. Swaddle, ibid., 1963, 2342.

all the para substituents which have a substantial electron-releasing resonance component, viz., p-NMe<sub>2</sub>, p-OMe, p-SMe, p-F, p-Br, and p-Cl, lie above the line defined by the *meta* groups, the extent of the individual

### TABLE 1

Effects of substituents on the rate of cleavage of X·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub> compounds

		λ	104C	$10^{3}k$	
No.	X	(mµ)	(M)	(min1)	$k_{rel}$
1	o-F	269.5	17	349	29
2	p-NMe <sub>2</sub> +	258	19	125	10.3
3	m-CF <sub>3</sub>	271	33	124	10.25
4	m-Br	268	<b>27</b>	110	9.1
5	p-CF <sub>3</sub>	270	14	99	8.2
6	m-Cl	268	<b>26</b>	98	8.1
7	o-C1	276	<b>28</b>	91	7.55
8	0-CF3	<b>274</b>	29	85	7.05
9	m-F	<b>275</b>	10	66	5.45
10	p-Cl	266	44	56	4.65
11	p-Br	267	<b>27</b>	55	4.6
12	$p$ -C $\equiv$ CH	281.5	<b>27</b>	47	3.9
13	m-CECH	274.5	<b>34</b>	46	$3 \cdot 8$
14	<b>⊅</b> -F	<b>270</b>	19	35.0	$2 \cdot 9$
15	p-SMe	259	4	29.3	$2 \cdot 4$
16	p-Ph	257	0.5	$21 \cdot 8$	1.80
17	m-OMe	$283 \cdot 5$	$4 \cdot 5$	21.5	1.78
18	m-Ph	<b>281</b>	0.5	20.4	1.69
19	p-NMe <sub>2</sub>	<b>270</b>	0.2	19.7	1.63
<b>20</b>	p-OMe	283.5	15	19.8	1.64
<b>21</b>	m-SiMe <sub>3</sub>	240, 242	10	16-8	1.39
<b>22</b>	p-SiMe <sub>3</sub>	<b>240</b>	2	13.7	1.13
<b>23</b>	H	265	8	$12 \cdot 1$	1.00
<b>24</b>	p-Bu <sup>t</sup>	261, 263	4	11.5	0.95
<b>25</b>	2,3-C4H4 ª	293	0.8	11.2	0.93
<b>26</b>	p-Me	<b>272</b>	<b>42</b>	10.4	0.86
<b>27</b>	m-Me	271	17	10.0	0.83
<b>28</b>	$m - NH_2$	288	4	7.95	0.66
<b>29</b>	o-OMe	275	3	7.36	0.61
30	o-Me	271	<b>24</b>	3.00	0.25

<sup>α</sup> Refers to α-naphthyltrimethylstannane.

deviations decreasing roughly in line with the proportion of the resonance component. The deviations are not confined to this type of substituent, however; for example, the p-CF<sub>3</sub> activates less effectively than the m-CF<sub>3</sub> group, while the contrary would be clearly expected on the basis of  $\sigma$  constants. Use of  $\sigma_n$ <sup>11</sup> or  $\sigma^\circ$ constants,12 in which the inductive component is emphasised, leads to somewhat better plots (not shown), but again the activating influence of the p-OMe and p-NMe<sub>2</sub> groups is unaccounted for. Use of the inductive constants,  $\sigma_I$ ,<sup>13</sup> for the *para* substituents (Figure 2) puts the points for the p-OMe and p-NMe<sub>2</sub> groups on the right side of the origin, but serious deviations now appear for groups such as p-F, p-CF<sub>3</sub>, and p-C=CH. It seems safe to conclude, however, that electron-supplying resonance effects of *para* substituents are effectively largely inoperative in the transition state of the rate-determining step of the cleavage.

We consider now the nature of this step. The possible mechanisms seem to be: (i), synchronous attack of the MO<sup>-</sup> ion at tin and breaking of the aryl-Sn bond, (ii)

rapid formation of a pentaco-ordinate tin intermediate, [MOMe<sub>3</sub>SnPh]<sup>-</sup>, followed by rate-determining breaking of the aryl-Sn bond, and, (iii) rate-determining formation of a pentaco-ordinate tin intermediate, followed by fast breaking of the aryl-Sn bond. In all three cases the phenylcarbanion could separate as such, and then react rapidly with the solvent, or it could interact with the solvent, to acquire a proton, as it separated.



Plot of log  $k_{rel}$  against  $\sigma$  for alkali cleavage of FIGURE 1  $X \cdot C_6 H_4 \cdot Sn Me_3$  compounds. The numbering of the substituents is shown in Table 1

Squares denote meta and circles para substituents



FIGURE 2 Plot of log  $k_{rel}$  against  $\sigma_I$  for alkali cleavage of X·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub> compounds

Possibly (iii) can be ruled out, because the analogous mechanism has been ruled out for base cleavage of benzyltrimethylstannane,<sup>10</sup> which is a much faster reaction, and there is no reason to believe that formation of the pentaco-ordinate intermediate would be much slower for phenyl- than benzyl-trimethylstannane, as it would have to be for mechanism (iii) to apply in the present case; indeed, the contrary would be expected, in view of the extra stabilisation of the negative charge on tin by the

<sup>&</sup>lt;sup>11</sup> H. van Bekkum, P. E. Verkade, and B. M. Wepster, Rec. Trav. chim., 1959, **78**, 815. <sup>12</sup> R. W. Taft, jun., J. Phys. Chem., 1960, **64**, 1805.

<sup>&</sup>lt;sup>13</sup> R. W. Taft, jun., J. Amer. Chem. Soc., 1957, **79**, 1045; 1958, **80**, 2436; 1959, **81**, 5343, and in "Steric Effects in Organic Chemistry" (ed. M. S. Newman), Wiley, New York, 1956, p. 556.

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-*I* effect of the phenyl group and possibly also by some delocalisation of this charge from the *d*-orbitals of tin into the p-orbitals of the ring.

No decision can yet be made between possibilities (i) and (ii), but this is unimportant for a discussion of substituent effects. We note that the unusual trends in these effects in the cleavage are present also, though less exaggerated, in base-catalysed aromatic hydrogen exchange (see below) and thus are not to be primarily ascribed to a special mechanism involving the tin atom. [We also do not consider in detail the possibility of some stabilisation of the initial state by  $(p \rightarrow d)_{\pi}$  interaction between the ring and the tin atom, since the expected consequences would be in the opposite direction to the abnormalities observed; for example, the p-OMe and p-NMe<sub>2</sub> groups would deactivate by this effect.] The similarity to the hydrogen-exchange, in which breaking of the aryl-H bond must be synchronous with the attack of the base, is close enough for us to favour a synchronous mechanism for the cleavage. The much smaller effect of *meta* substituents in the cleavage than in the exchange, indicating that markedly less negative charge is generated on the ring in the rate-determining transition state, is consistent with the much greater reactivity of the tin compounds, for which the transition state would lie closer to the reactants. (This would be true whether the effective reactant were the ArSnMe3 compound or the ion [ArSnMe<sub>3</sub>OM]<sup>-</sup>.)

Irrespective of whether mechanism (i) or (ii) operates, the aryl group in the transition state will have some of the character of the free phenyl carbanion (I). The un-



shared electron pair in this carbanion is in an orbital in the plane of the ring, and thus cannot be delocalised by resonance effects, but the electrostatic effect of these  $\sigma$  electrons would be expected to distort the  $\pi$ -electron cloud. By such a  $\pi$ -polarisation effect a fraction of the negative charge would be located on the para and ortho carbon while a slight positive charge would be generated at the meta positon (though this would be outweighed, of course, by the normal  $\sigma$ -inductive effect to this position). The presence of excess of  $\pi$ -electron density at the *para* position would be expected to inhibit to some extent the operation of the electron-releasing resonance effects of para substituents, but it is difficult to see why the inhibition should be so great on the cleavage under discussion, since the phenyl carbanion must be far from fully formed in the transition state. Further, no abnormal effect of the p-OMe group is observed on the acid strength of phenols, although the effect is largely on the stability of the phenoxide ion, such as p-MeO·C<sub>6</sub>H<sub>4</sub>·O<sup>-</sup>, in which a substantial degree of excess  $\pi$ -electron density must, by a quite different delocalisation mechanism, be placed on the carbon para to the negatively-charged oxygen atom. Streitwieser and Lawler concluded that the  $\pi$ -polarisation effect in the aryl carbanion was relatively unimportant in base-catalysed hydrogenexchange in polynuclear aromatic hydrocarbons, and that an inductive field effect greatly predominated.<sup>7</sup> Streitwieser and his co-workers also concluded, however, that the  $\pi$ -polarisation effect was of some significance in the hydrogen-exchange for substituted benzenes, such as toluene.<sup>8</sup>

An additional abnormality, which is out of keeping with the other abnormalities noted above, is that the m- and p-SiMe<sub>3</sub> groups, which would be regarded as electron-releasing in terms of  $\sigma$  or  $\sigma_I$  constants, both activate, though by a small amount. The SiMe<sub>3</sub> group can withdraw electrons from the ring by  $p_{\pi}-d_{\pi}$  interaction (see, for example, refs. 10 and 14), but the fairly large electron-releasing inductive effect of this group would be expected to dominate. The activating effect of the p-SiMe<sub>a</sub> group could conceivably be attributed to delocalisation (by  $p_{\pi}$ - $d_{\pi}$  interaction) of the negative charge induced at the *para* position by the  $\pi$ -polarisation effect mentioned above (the greater activation by the p-Ph than by the *m*-Ph group could be similarly interpreted), but no such explanation could apply to the effect of the *m*-SiMe<sub>3</sub> group.

We have noted that the main trends of abnormalities in the effects of substituents on the cleavage are present for hydrogen-exchange in substituted benzenes in liquid ammonia containing potassium amide. Substituent effects,  $k^{\rm H}_{\rm rel}$ , for the hydrogen-exchange for those substituents which we have also studied are shown in Table 2; unfortunately they were not all determined

TABLE 2

Effects of substituents on the rate of hydrogen-exchange of  $X \cdot C_g H_4 \cdot ^2 H$  compounds in liquid ammonia containing potassium amide <sup>a</sup>

x	$k^{\mathbf{H}}_{\mathbf{rel}}$	Ref.	х	$k^{H}_{rel}$	Ref.	
o-F	$>4 imes10^{6}$	4	<i>m</i> -Ph	3.3	3	
o-CF <sub>3</sub>	$6  imes 10^5$	4	<i>p</i> -Ph	$2 \cdot 9$	3	
<i>m</i> -CF <sub>3</sub>	104	4	Ĥ	1.00		
p-CF <sub>3</sub>	104	4	<i>p</i> -OMe	0.20	3	
<i>m</i> -F	$4 imes 10^3$	4	p-Me	0.44	5	
o-OMe	500	4	o-Me	0.41	5	
<i>ν</i> -F	200	4	<i>m</i> -Me	0.36	<b>5</b>	
2,3-C <sub>4</sub> H <sub>4</sub>	9.7	3	p-Bu <sup>t</sup>	0.21	5	
			<i>p</i> -NMe <sub>2</sub>	0.07	3	
			/ 000 1	1		

 $^a$  Values from ref. 4 refer to  $-33^\circ\!,$  and those from ref. 5 to  $0^\circ\!.$ 

under the same reaction conditions, but this does not affect our conclusions. The spread of rates for the *meta* substituted compounds is very much greater than in the cleavage, indicating that for the exchange there is more negative charge on the phenyl group in the transition state, which presumably thus has more phenylcarbanion character. In spite of this, the p-OMe and p-NMe<sub>2</sub> groups deactivate, though much less than would be expected for normal operation of the electronreleasing resonance effects of these substituents. The

<sup>14</sup> C. Eaborn, "Organosilicon Compounds," Butterworths, 1960, pp. 97-103.

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o-OMe group, on the other hand, has a large activating influence, although this group deactivates slightly in the cleavage.

A plot of log  $k_{\rm rel}$  for the cleavage against log  $k^{\rm H}_{\rm rel}$  for the exchange approximates to a straight line for a good proportion of *meta* and *para* groups (see Figure 3), but there are marked deviations for the *p*-OMe and *p*-NMe<sub>2</sub> groups. The very large activating effect of the *o*-F atom in the exchange is fairly accurately reflected in the cleavage, and that of the *o*-CF<sub>3</sub> groups rather less so. Except for the fluoro-compound, the *ortho*-substituted compounds, including the  $\alpha$ -naphthyl compound, are less reactive in the cleavage than would be expected by analogy with the hydrogen-exchange. This would be



FIGURE 3 Plot of  $\log k_{rel}$  for the cleavage of  $X \cdot C_6 H_4 \cdot SnMe_3$ compounds against  $\log k_{rel}^{H}$  for hydrogen-exchange of  $X \cdot C_6 H_4 \cdot [^2H]$  compounds

consistent with the operation of some steric hindrance by the larger *ortho* groups in the cleavage, but it is not easy to see how such hindrance would arise.

For the hydrogen-exchange, Roberts and his colleagues have argued that since attack on the aromatic proton by base does not involve the  $\pi$ -electron system of the ring in an important way, resonance effects of substituents will be of negligible importance.<sup>4</sup> This explanation seems to us unsatisfactory; there can be no direct involvement of the  $\pi$ -electrons of the ring in, for example, the ionisation of phenylacetic acids, X·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, and yet the p-OMe group behaves in this case as an electron-releasing, acid-weakening substituent, which stabilises the negatively-charged carboxylate ion less than it stabilises the undissociated acid. One assumes that this is because of repulsion between the negative charge in the side-chain and the excess of electron density at the 1-carbon atom of the ring arising from tautomeric effect of the 4-OMe group. (Alternative descriptions of the interaction are possible, but they are mainly equivalent to the one we use, and lead to the same conclusions.) A similar but larger repulsion would be expected when the negative charge is placed directly on the 1-carbon atom as in the hydrogen-exchange and in

<sup>15</sup> M. L. Crossley, R. H. Kienle, and C. H. Benbrook, J. Amer. Chem. Soc., 1940, **62**, 1400.

the cleavage we have studied. That the Hammett  $\sigma$  constants, or, where appropriate,  $\sigma_n$  or  $\sigma^\circ$  constants, which apply satisfactorily to effects of substituents in the ionisation of phenylacetic acid, and in other reactions in which there is no conjugative interaction between the substituent and the reaction centre, should fail so completely to apply to the reactions generating phenyl carbanions seems to us much more surprising than Roberts *et al.* imply, and reveals how little understood is the nature of the interaction between nuclear substituents and non-conjugated reaction centres in a sidechain.

A possibility to be considered is that the differential resonance effects of substituents on initial state and transition state are not unimportant in an absolute sense in the reactions generating phenylcarbanions but are obscured by a powerful operation of the direct field effect, which is so strong not only because the forming negative charge is much closer to the substituent than it is in side-chain reactions, but also because the electrostatic interaction is entirely through the substrate cavity. On this picture the p-OMe group might reasonably activate, though the smallness of the activation by the p-NMe<sub>3</sub><sup>+</sup> group would be difficult to explain.

The very serious difficulty with this explanation is that the observed abnormalities are confined to para (and possibly ortho) substituents. Field effects would be expected to be larger and even more dominant for *meta* substituents, while the results show not only that there is little difference between, for example, the effects of m-OMe and p-OMe groups, but also that the effects of meta groups relative to one another show little correlation with  $\sigma_I$  constants, and are, on the contrary, remarkably in agreement with their ordinary  $\sigma$  constants. In other words, for these substituents the balance of resonance and inductive effects is the same as it is for common side-chain reactions. The most impressive single illustration of the importance of the resonance effects for a *meta* substituent is that the m-NH<sub>2</sub> group deactivates, in accord with the sign of its  $\sigma$  constant. There are fewer results available for meta substituents in the hydrogen-exchange, but for them also there is a good correlation with  $\sigma$  constants.

Another difficulty is that the abnormality of substituent effects is greater in the cleavage than in the hydrogen-exchange, in the sense that p-OMe and p-NMe<sub>2</sub> groups activate in the former but not the latter, in spite of the fact that the degree of charge developed in the transition state, and thus the magnitude of any electrostatic interaction, is much smaller in the cleavage.

We think it is probably not coincidental that a rather similar, but inverted, pattern of substituent effects is observed in the solvolysis of substituted phenyldiazonium ions,<sup>15</sup> in which the phenylcarbonium ion (II), is believed to be formed in the rate-determining step.<sup>16</sup> In that

<sup>&</sup>lt;sup>16</sup> C. K. Ingold, "Structure and Mechanism in Organic Chemistry," C. Bell and Son, London, 1953, pp. 799-802; J. F. Bunnett and E. Zahler, *Chem. Rev.*, 1951, **49**, 273; E. S. Lewis and E. B. Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 429.

reaction *meta* substituents behave normally, with electron-withdrawing groups deactivating, but all the para substituents studied including p-Me, p-OMe, p-OH, p-Ph, and p-NO<sub>2</sub> deactivate. The suggested explanations,<sup>16</sup> which can be put on to an apparently satisfactory semiquantitative basis,<sup>17,18</sup> cannot be modified in any straightforward way to apply to the cleavage reaction we have studied. (The outstanding difference between the two types of reaction, is that in the aryldiazonium solvolysis there is substantial resonance interaction between the para substituents and the sidechain in the initial state which has largely disappeared in the transition state, whereas no significant resonance into the side-chain is involved in either the initial or the transition state for the cleavage or the hydrogenexchange.) The explanations do, however, involve the assumption that inductive effects of para substituents are greatly dominant in the phenylcarbonium ion, the electron-releasing resonance effect of the p-OMe group, for example, being largely inoperative. A  $\pi$ -inductive effect of the type mentioned above from the phenyl carbanion should in this case lead to a substantial deficiency of  $\pi$ -electrons at the *para*-carbon atom, and by the reverse of the reasoning used in the case of the phenyl carbanion above, one might have expected that the resonance effect of a methoxyl group at this carbon atom would respond to this deficiency, and so lead to some stabilisation of the carbonium ion. It thus seems that  $\pi$ polarisation effects are of little importance in substituted phenylcarbonium ions and phenylcarbanions.

### EXPERIMENTAL

Preparation of Aryltrimethylstannanes.-Previously reported aryltrimethylstannanes, X·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub>, were prepared from bromotrimethylstannane and the appropriate aryl-lithium or Grignard reagent in diethyl ether, and had the following physical properties: (X =) H, b. p. 198°/ 760 mm.,  $n_{\rm D}^{25}$  1.5329; *p*-Br, b. p. 64°/0.2 mm.,  $n_{\rm D}^{25}$  1.5669; *m*-Cl, b. p.  $84^{\circ}/3.5$  mm.,  $n_{D}^{25}$  1.5491; *p*-F, b. p.  $45^{\circ}/1$  mm.,  $n_{\rm p}^{25}$  1.5149; *m*-Me, b. p. 55°/0.9 mm.,  $n_{\rm p}^{25}$  1.5309; *p*-Me, b. p.  $69^{\circ}/1.2$  mm.,  $n_{\rm p}^{25}$  1.5294; *p*-NMe<sub>2</sub>, m. p. 38°; *p*-OMe, b. p.  $102^{\circ}/4$  mm.,  $n_{\rm p}^{25}$  1.5392; *p*-Ph, m. p. 52°; *p*-SiMe<sub>3</sub>, m. p. 104°; *o*-F, b. p. 32°/0·5 mm.,  $n_{\rm D}^{25}$  1·5227; *o*-Cl, b. p. 47°/0·5 mm.,  $n_{\rm D}^{25}$  1·5977. Trimethyl-*α*-naphthyl-stannane (prepared by J. L. Bennett) had b. p. 120°/1·0 mm., (lit., 19 121°/1.0 mm.). The preparations of new  $X \cdot C_6H_4 \cdot SnMe_3$  compounds are described elsewhere.<sup>20</sup>

<sup>17</sup> J. D. Dickinson and C. Eaborn, J. Chem. Soc., 1959, 3036.
 <sup>18</sup> R. W. Taft, jun., S. Ehrenson, I. C. Lewis, and R. E. Glick, J. Amer. Chem. Soc., 1959, 81, 5352.
 <sup>19</sup> O. Buchmann, M. Grossjean, and J. Nasielski, Bull. Soc. chim. belges, 1962, 71, 467.

# J. Chem. Soc. (B), 1967

Cleavage Products .--- The aromatic products were shown to be the expected  $X \cdot C_6 H_5$  compounds by comparing the ultraviolet spectra of the reaction mixtures at the end of the runs with those of mixtures obtained by acid cleavage 9 of the aryltrimethylstannanes in a similar medium. For the compounds  $X \cdot C_6 H_4 \cdot Sn Me_3$  with X = p - F, p-Me, p-Cl, and H, analysis of aromatic products by gas-liquid chromatography revealed only the expected  $X \cdot C_6H_5$  compounds.

Rate Measurements.-An ice-cold methanol solution (3 vol.) of the organostannane, of concentration, C (Table 1), was mixed with aqueous 7.61M-sodium hydroxide (2 vol.). A sample was transferred to a stoppered quartz cell and the change in optical density, D, was recorded at the wavelength specified in Table 1 by the method previously described.<sup>9,10</sup> For slower runs, viz., those for X = o-OMe, o-Me, and p-Bu<sup>t</sup>, rate constants were evaluated by the Guggenheim method.21 (For phenyltrimethylstannane this method was found to give a rate constant within 2% of that obtained by the usual method.)

Rate constants were determined graphically, but in the specimen runs given in Table 3 rate constants calculated throughout the runs are given.

TABLE	3
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(i) C <sub>6</sub> H <sub>5</sub> ·SnMe <sub>3</sub> t (min.) 10 <sup>3</sup> D	$\frac{6}{580}$	$\begin{array}{c} 10 \\ 561 \end{array}$	$\begin{array}{c} 20 \\ 515 \end{array}$	$\begin{array}{c} 45\\ 423\end{array}$	60 389	105 286	
$10^{3k}$ (min. <sup>-1</sup> )		11.5	12.0	12.0	12.2	12.2	
(11) $m$ -CF <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ·SI	nMe <sub>3</sub>						
t (min.)	6	8	10	12	14	16	8
$10^{3}D$	709	593	502	<b>430</b>	376	332	180
$10^{3}k$ (min. <sup>-1</sup> )	_	123	124	125	125	125	
(iii) $p$ -Me·C <sub>6</sub> H <sub>4</sub> ·Snl	$Me_3$						
t (min.) 10 <sup>3</sup> D 10 <sup>3</sup> k (min. <sup>-1</sup> )	8 569 —	$15 \\ 543 \\ 12{\cdot}5$	$30 \\ 501 \\ 11\cdot 3$	$45 \\ 468 \\ 10.4$	$60 \\ 439 \\ 10.5$	$112 \\ 363 \\ 10.6$	$\frac{\infty}{260}$

Dependence of Rate on Alkali Concentration.-The following values of  $10^{3}k$  at  $50 \cdot 0^{\circ}$  were obtained for the compound m-CF<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·SnMe<sub>3</sub> in mixtures of methanol (6 ml.) with aqueous sodium hydroxide (4 ml.) of the concentration shown: 3.805M, 89 min.<sup>-1</sup>; 5.33M, 104 min.<sup>-1</sup>; 7.61M, 124 min.-1.

This work was supported by the International Tin Research Council. We thank Dr. E. S. Hedges of the Tin Research Institute for his interest and advice, and the Royal Society for the loan of apparatus.

[7/481 Received, April 21st, 1967]

<sup>20</sup> C. Eaborn, A. R. Thompson, and D. R. M. Walton, J. Chem. Soc. (C), 1967, 1364; C. Eaborn, H. L. Hornfeld, and D. R. M. Walton, J. Organometallic Chem, in the press. <sup>21</sup> E. A. Guggenheim, Phil. Mag., 1926, 7, 538.