# Aromatic Reactivity. Part LV.[1] Solvent Isotope Effects in the Base Cleavage of Aryltrimethylstannanes in Methanol: Evidence for Electrophilic Assistance by the Solvent

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Values of the product isotope-effects. corresponding to the product ratios $XC_6H_5/XC_6H_4D$ obtained in 1 :1 MeOH–MeOD mixtures for cleavage of $X{\cdot}C_6H_4{\cdot}SnMe_3$ compounds by sodium methoxide in methanol at 21°, have been found to be as follows: (X =) *p*-OMe. 5·2; *p*-Me. 5·1: H. 4·9: *m*-OMe. 4·9: *p*-Cl. 4·5; *m*-$CF_3$, 4·3; *p*-$NO_2$, 3·8. For the compounds with X = *p*-OMe and *m*-$CF_3$ values of 2·45 and 2·00 for the overall solvent effects. $(k_{MeOH}/k_{MeOD})_S$. have been determined by measurement of the separate rates at 50° in MeOH and in MeOD. It is concluded that proton transfer from the solvent to the carbon atom of the Sn–aryl bond is involved in the rate-determining step, which is probably the conversion of the $Sn^V$ intermediate $(MeO)Me_3Sn^-{\cdot}C_6H_4{\cdot}X$ into the Wheland-intermediate $(MeO)Me_3Sn^-{\cdot}C_6H_5{}^+{\cdot}X$.

THE cleavage of aryltrimethylstannanes, $X{\cdot}C_6H_4{\cdot}SnMe_3$, by aqueous-methanolic alkali has been shown to give rise to a most unusual pattern for the effects of the substituents X.[2,3] In brief, the effects of *m*-substituents correlate with σ-constants, with a ρ value of 2·2, but for *p*-substituents, not only electron-withdrawing groups such as *p*-$CF_3$, but also the strongly electron-supplying *p*-OMe and *p*-$NMe_2$ groups increase the reaction rate. This behaviour has been interpreted in terms of a rate-determining process in which the cleavage of the aryl–Sn bond, which will be generally facilitated by electron-withdrawing groups as electrons are transferred to the carbon atom of the bond, is accompanied by proton donation to this carbon atom, such electrophilic attack being specifically assisted by substituents capable of conjugative electron release.[3]

TABLE 1

Solvent isotope effects on the cleavage of $X{\cdot}C_6H_4{\cdot}SnMe_3$ compounds by sodium methoxide in methanol

| X | PIE [a] 1 : 2 MeOH–MeOD [b] | PIE [a] 1 : 1 MeOH–MeOD [c] | $\left(\frac{k_{MeOH}}{k_{MeOD}}\right)_S$ [d] | $(k_{MeOH}/k_{MeOD})_S$ / PIE | $k_{rel}$ [e] | $\sigma^+$ |
|---|---|---|---|---|---|---|
| *p*-OMe | 5·2 | 5·5 | 2·45 | 0·46 | 1·64 | −0·78 |
| *p*-Me | 5·1 | 4·8 | | | 0·86 | −0·31 |
| H | 4·9 | 4·5 | | | 1·00 | 0·00 |
| *m*-OMe | 4·9 | | | | 1·78 | 0·05 |
| *p*-Cl | 4·5 | 3·9 | | | 4·65 | 0·11 |
| *m*-$CF_3$ | 4·3 | 4·0 | 2·0 | 0·50 | 10·25 | 0·52 |
| *p*-$NO_2$ | 3·8 | | | | | 0·79 |

[a] ArH/ArD product ratio at 21° after any correction for solvent composition. The probable error limits are based on reproducibility and assessment of the uncertainty arising from allowance for the $^{13}C$ content. [b] ±0·2. [c] ±0·3. [d] At 21°: see Table 2. [e] Relative rates of cleavage by a 2 : 3 v/v mixture of aqueous alkali and methanol at 50°.[2]

To provide direct evidence for the importance of the proton transfer by the solvent we have now examined the effects of replacing a methanol solvent wholly or partly by methan[$^2$H]ol.[4]

The majority of the measurements involved cleavage of an $X{\cdot}C_6H_4{\cdot}SnMe_3$ compound at *ca.* 21° in either 1 : 1 MeOH–MeOD containing 2·0M-sodium methoxide or 1 : 2 MeOH–MeOD containing 1·35M-NaOMe, followed by determination of the $X{\cdot}C_6H_5/X{\cdot}C_6H_4{\cdot}D$ product ratio. For the 1 : 1 mixture this ratio gives directly the product isotope effect (PIE) which is a measure of the preference of the reaction for cleavage of H–OMe rather than D–OMe bonds, and is for practical purposes, the primary solvent isotope effect, $(k_{MeOH}/k_{MeOD})_I$ for the product-determining step. With the 1 : 2 mixture the $X{\cdot}C_6H_5/X{\cdot}C_6H_4{\cdot}D$ ratio has to be multiplied by 2 to give the PIE; the results for this medium are more accurate than those for the 1 : 1 medium because the

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[1] Part LIV, C. Eaborn, Z. Salih, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **36**, 47.

[2] C. Eaborn, H. L. Hornfeld, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1967, 1036.

[3] A. R. Bassindale, C. Eaborn, R. Taylor, A. R. Thompson, D. R. M. Walton, J. Cretney, and G. J. Wright, *J. Chem. Soc.* (*B*), 1971, 1155.

[4] For a brief account of a rather less accurate preliminary study see R. Alexander, C. Eaborn, and T. G. Traylor, *J. Organometallic Chem.*, 1970, **21**, P65.

latter leads to rather small $X{\cdot}C_6H_4{\cdot}D$ contents. The measured PIE values are shown in Table 1.

For two compounds, *viz.* those with X = *p*-OMe and *m*-$CF_3$, we also determined the ratio, $(k_{MeOH}/k_{MeOD})_S$, of the rates of reaction in MeOH and in MeOD. (The overall solvent isotope effects were also measured for methanol–water mixtures, and found not to be significantly different from those in methanol alone.) The results are given in Table 2.

TABLE 2

Overall solvent isotope effects for $X{\cdot}C_6H_4{\cdot}SnMe_3$ compounds at 50·0°

| X | Medium [a] | $10^5k$ ($s^{-1}$) | $k_{SH}/k_{SD}$ |
|---|---|---|---|
| *p*-OMe | MeOH | 10·1 | 2·45 |
| | MeOD | 4·12 | |
| | MeOH–$H_2O$ (18 mol %) | 10·45 | 2·39 |
| | MeOD–$D_2O$ (18 mol %) | 4·37 | |
| *m*-$CF_3$ | MeOH | 58·1 | 2·00 |
| | MeOD | 29·0 | |
| | MeOH–$H_2O$ (25 mol %) | 61·5 | 2·00 |
| | MeOD–$D_2O$ (25 mol %) | 30·7 | |

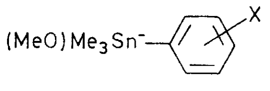
[a] With 2·0M-NaOMe or 2·0M-(NaOMe + NaOH) present in each case.

The main features of the results are as follows: (*a*) The PIE values are fairly large. This rules out the possibility that a free carbanion is produced and then destroyed by reaction with the solvent, since this reaction would be effectively unselective.*

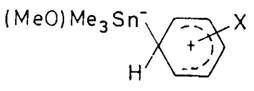
(*b*) The PIE value shows a significant variation as the group X is changed. It is especially significant that the sequence of values does not follow the sequence of overall reactivity, as established for cleavage in aqueous-methanolic alkali (see Table 1). The PIE sequence does follow the ability of the group X to facilitate electrophilic attack on the relevant position of the aromatic ring; *e.g.*, it follows the sequence of $\sigma^+$-constants for the X groups (Table 1).

(*c*) For the two compounds for which the overall solvent isotope effect at 50° was measured, the ratio $(k_{MeOH}/k_{MeOH})_S$ : PIE has values of 0·46 and 0·50.† This result is of considerable importance, since it shows that the breaking of the H–OMe bond cannot follow the rate-determining step. In principle, substantial PIE values could arise from a step after the rate-determining process, provided this required sufficient activation energy to discriminate between MeOH and MeOD molecules. If this were the case, however, the value of $(k_{MeOH}/k_{MeOD})_S$ would be similar to that of the secondary isotope effect, $(k_{MeOH}/k_{MeOD})_{II}$, which arises from the less effective solvation of methoxide ions in methan[$^2$H]ol than in methanol,[6] *i.e.* $(k_{MeOH}/k_{MeOD})_S$ would have a value in the range 0·44—0·50.[6] We can thus rule out, for example, a mechanism involving rate-determining formation of a $Sn^V$ intermediate $[(MeO)Me_3Sn^-{\cdot}C_6H_4{\cdot}X]$ (I), confirming the conclusion reached on other grounds.[2,3] We can also rule out a rate-determining formation of a so-called 'ion-pair' $[(MeO)Me_3Sn \cdots R^-]$, which has been suggested as a general possibility for base-cleavage of $Me_3M$–R bonds.[7] Values of 0·46—0·50 for the $(k_{MeOH}/k_{MeOD})_S$ : PIE ratio are just what would be expected for a reaction in which, at the highest-energy transition state, the attacking methoxide ion is strongly bound to the metal atom but the methoxide ion being generated by the proton transfer is not free enough to be effectively solvated (see below). (Corresponding ratios of 0·49, 0·42, and 0·46 respectively, have been observed for base-catalysed methanolyses of triphenylsilane, *m*-trifluoromethylbenzyltrimethylstannane, and *m*-trifluoromethylbenzyltrimethylsilane, for each of which a highest-energy transition state of this nature has been proposed.[8])

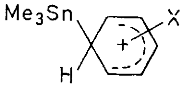
We are still left with a wide range of possibilities, which we can outline in general terms as follows: (i) Rapid reversible formation of the $Sn^V$ intermediate (I) is followed by a rate-determining attack of the proton at the aryl–Sn bond. In such a step, either the aryl–Sn bond breaks as the C–H bond forms, or the Wheland-intermediate (II) is produced, the aryl–Sn bond then being broken in a subsequent fast step.



(I)



(II)



(III)

(ii) The formation of the MeO–Sn bond could be synchronous with the attack of the proton on the Sn–C bond, and once again this process could either involve breaking of the aryl–Sn bond or give the Wheland-intermediate (II).

The mechanism which leads to the simplest interpretation of the results is the sequence shown in equations (1)—(3), in which a rapid and reversible formation of the $Sn^V$ intermediate (I) is followed by rate-determining formation of the Wheland-intermediate (II), which is then destroyed in a fast step. In this mechanism the PIE values would be determined in step (2). Such a step is closely analogous to the rate-determining step in the cleavage of $Me_3Sn{\cdot}C_6H_4{\cdot}X$ compounds by acids, which is a simple electrophilic aromatic substitution,

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* The first use of product isotope ratios to rule out the formation of free carbanions in the cleavage of organic groups from a Group IVb metal was made by Dr. D. L. Stiggall in association with Professor T. G. Traylor.[5]

† The difference between the temperatures of measurement of the two isotope effects is neglected. We found, in fact, that PIE values at 50° were not significantly different from those at 21°.

[5] D. L. Stiggall, *Diss. Abs.*, 1968, **29**, *B*, 1991.

[6] R. A. More O'Ferrall, *Chem. Comm.*, 1969, 114; C. G. Mitton, M. Gressner, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1969, **91**, 2045.

[7] I. P. Beletskaya, K. B. Butin, and O. A. Reutov, *Organometallic Chem. Rev.*, 1971, **7**, 51.

[8] C. Eaborn and I. D. Jenkins, *J. Organometallic Chem.*, 1974, in the press; R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, in the press.

and is believed to involve rate-determining formation of a Wheland-intermediate of type (III).[9] While reaction

$$\mathrm{MeO^- + Me_3Sn{\cdot}C_6H_4X \rightleftharpoons \underset{(I)}{(MeO)Me_3Sn^-{\cdot}C_6H_4{\cdot}X}} \quad (1)\ (\text{fast})$$

$$\mathrm{(MeO)Me_3Sn^-{\cdot}C_6H_4{\cdot}X + MeOH \longrightarrow \underset{(II)}{(MeO)Me_3Sn^-{\cdot}C_6H_5{}^+{\cdot}X} + MeO^-} \quad (2)\ (\text{slow})$$

$$\mathrm{(MeO)Me_3Sn^-{\cdot}C_6H_5{}^+{\cdot}X \longrightarrow MeOSnMe_3 + C_6H_5X} \quad (3)\ (\text{fast})$$

(3) involves a much less reactive electrophile, methanol, the effect of this will be countered by the greater reactivity of $[\mathrm{(MeO)Me_3Sn{\cdot}C_6H_4{\cdot}X}]^-$ than of $\mathrm{Me_3Sn{\cdot}C_6H_4{\cdot}X}$.

The nature of the variation of the PIE values is explicable in terms of the position of the transition state of reaction (2) along the path from the reactants, *viz.* the $\mathrm{Sn^V}$ intermediate and methanol, to the products, *viz.* the Wheland-intermediate (II) and the methoxide ion. The energy of activation for this step will be smaller the greater the stability of the Wheland intermediate (II), and so the transition state will be further from this intermediate the greater the ability of X to facilitate aromatic substitution, and thus, the greater the negative value of the $\sigma^+$-constant.* The degree of proton transfer will thus rise progressively in the sequence of the $\sigma^+$-constants from the compound X = *p*-OMe to that with X = *p*-$\mathrm{NO_2}$. The values of PIE will also fall in this sequence provided that the proton transfer has passed the point of maximum isotope effect, *i.e.*, roughly the point of half transfer, in all cases, and this is reasonable in view of the low reactivity of the electrophile, MeOH, even though the aromatic compound (I) is highly reactive. The degree of proton transfer cannot be such as to lead to liberation of substantially free methoxide ion at the transition state, since this would be incompatible with the values of the overall solvent isotope effect; this is because generation of free methoxide ion would cancel out the secondary isotope effect arising from the removal from its solvent shell of the methoxide ion which attacks the tin atom.[6] It is reasonable to assume that the methoxide ion generated from the methanol will not be available for effective solvation until it is almost fully liberated from the proton.

The formation of the intermediate (I) in reaction (1) would be favoured by electron-withdrawal by the groups X, and the linear relationship $\log K_1 = \rho_1\sigma$, where $K_1$ is the equilibrium constant for step (1), would be expected to apply, with a positive value of $\rho_1$. For the electrophilic aromatic substitution step (2), on the other hand, a Yukawa–Tsuno relationship $\log k_2 = \rho_2[\sigma^+ + r(\sigma^+ - \sigma)]$ would be expected to apply, with a value of $\rho_2$ which is negative and numerically smaller than that of $\rho_1$, and with a positive value of *r*. (In the cleavage of aryltricyclohexylstannanes by aqueous ethanolic perchloric acid, values of *ca.* 3·8 and +0·4 are observed for $\rho$ and *r*, respectively.[10]) Since the overall rate constant, *k*, is proportional to $k_2K_1$, the relationship $\log k_{\mathrm{rel}} = \rho'[\sigma + r'(\sigma^+ - \sigma)]$ should apply, where $\rho'$ has a positive value and $r'$ has a negative value.† This is reasonably close to the observed effects in this type of reaction, which can be satisfactorily expressed in terms of the relationship $\log k_{\mathrm{rel}} = \rho'[\sigma + r'\Delta]$, where $\rho$, based on *meta*-substituents, has a value of 2·2, and $\Delta$ is a quantity related to the ability of the group X to release electrons by a conjugative effect, and which shows a pattern very similar to that of the quantity $-(\sigma^+ - \sigma)$, although it is not accurately proportional to the latter.[3]

While we favour the sequence (1)—(3), we cannot completely rule out a process in which reactions (2) and (3) are synchronous (the Wheland intermediate being by-passed), or one in which (1) and (2) are synchronous (the $\mathrm{Sn^V}$ intermediate being by-passed), or, indeed, one in which all three stages are synchronous. It is very difficult with any of these possibilities, however, to account for the fact that the PIE values follow the sequence of activation by X towards electrophilic attack. For example, if the rate-determining step were the conversion of the $\mathrm{Sn^V}$ intermediate directly into the final products [*i.e.*, reaction (1) were followed by a synchronous (2) and (3)], then this step would be strongly exothermic, and the transition state would be expected to lie much closer to the reactant (I) than to the products. The H–OMe bond would then be less than half-broken, and the fall in the value of the PIE on going from the *p*-methoxy- to the *p*-nitro-compound would have to be associated with a *decrease* in the extent of H–OMe bond-breaking, which would then be associated with a *decreasing* activation energy for this step in the order of decreasing PIE values. This order would not necessarily show any simple relationship to that of the activation energy for the overall process (*i.e.*, to the reactivity), since some opposing effects could operate on the free energy for equilibrium (1) and the activation energy of step [(2) + (3)]. That the order of the PIE values follows so well that of $\sigma^+$ would thus have to be regarded as coincidental, and this makes us favour the participation of a Wheland-intermediate. Furthermore, since the destruction of (I) is an electrophilic aromatic substitution, there seems no reason, in the absence of contrary evidence, to believe that a Wheland-intermediate would be avoided.

Another difficulty arises for the fully-concerted process with (1), (2), and (3) all synchronous; the reaction would again be exothermic [though less so than for conversion of the intermediate (I) into the final products], and the transition state would be expected

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* More strictly, the greater the negative value of the quantity $[\sigma + r(\sigma^+ - \sigma)]$, but the latter follows the same sequence as $\sigma^+$ except for very small values of *r*. The sequence of the decreasing PIE values in Table 1 agrees with that of the decreasing reactivity of $\mathrm{Me_3Sn{\cdot}C_6H_4{\cdot}X}$ compounds towards aqueous-methanolic perchloric acid.[10]

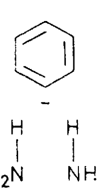
† Reasonable values for $\rho_1$ and $\rho_2$, as given by *meta*-substituents (for which $\sigma \simeq \sigma^+$), would be +4 and −2, giving rise to an overall $\rho'$ of +2.

[9] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804.

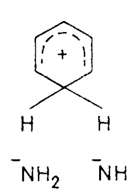
[10] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542.

to lie on the reactant side, whereas the overall solvent isotope effect indicates that the methoxide ion is fairly fully transferred from its solvent shell to the tin atom in the highest-energy transition-state. Such an objection would not apply to the process with reactions (1) and (2) synchronous in the rate-determining step; since the product of this step would be the high-energy intermediate (II), the transition state would lie over towards this intermediate, and the methoxide ion would be fairly fully transferred to the tin atom in this transition state. Again, however, no simple explanation of the sequence of PIE values could be offered.

A disadvantage of sequence (1)—(3) is that it does not immediately account for the close analogy, amounting to a reasonably quantitative correlation,[3] between the effects of substituents in the cleavage and those in hydrogen-exchange between $C_6H_5X$ compounds and liquid ammonia catalysed by potassium amide, since no intermediates analogous to (I) and (II) can be involved in the latter reaction. However, all that is necessary to give rise to the observed pattern of substituent effects is that the substituents should (i) stabilise in proportion to their $\sigma$-constants, *either* a real intermediate before the highest energy transition state *or* a structure which contributes importantly to that transition state, and (ii) stabilise in inverse proportion to their $\sigma^+$-constants another such real intermediate *or* another such contributing structure. As previously proposed, for the hydrogen-exchange this corresponds with stabilisation of the contributing structures (IVa) and (IVb), respectively, in the transition state.[3]

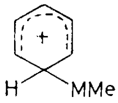


(IVa)

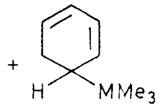


(IVb)

Whatever the detailed nature of the mechanism of the cleavage of the $X\cdot C_6H_4\cdot SnMe_3$ compounds, it is clear that there is a substantial degree of proton transfer to the aryl group in the highest-energy transition state. The existence of this electrophilic assistance nicely accounts for the fact that the $Me_3Sn$–Ph bond is cleaved by aqueous methanolic alkali very much more readily than is the $Me_3Si$–Ph bond (the factor is at least $10^3$, and probably $>10^4$) [3] even though there is relatively little difference between the ease of cleavage of $Me_3Sn$–$CH_2Ph$ and $Me_3Si$–$CH_2Ph$ bonds under similar conditions (the tin- is *ca.* 29 times as reactive as the silicon-compound in 1 : 5 v/v $H_2O$–MeOH at 50°).[11] It is well established that while the $R_3Sn$ and $R_3Si$ groups both greatly facilitate the attack of an electrophile at the carbon atom of the aryl–$MR_3$ bond, the effect of the $R_3Sn$ groups is much greater; *e.g.*, the rate of attack of oxonium ion on Ph–H, Ph–$SiEt_3$, and Ph–$SnEt_3$ bonds in aqueous methanolic perchloric acid rises in the ratio $1 : 10^4 : 10^{10}$.[12] This effect can now be confidently associated with the $\sigma$–$\pi$ (hyperconjugative) electron release from the $Me_3M$–C bonds in the Wheland-intermediate (V), which is most clearly visualised in terms of stabilisation of the β-carbonium ion structure (Va),[9,13] and the ease of this electron release is known to be greater for $Me_3Sn$–C than for $Me_3Si$–C bonds.[14] Still greater electron release can be expected from the $(MeO)Me_3Sn^-$–C bonds in the Wheland-intermediate (II).



(V)



(Va)

The importance of the proton transfer process also accounts for effects which arise on changing the medium from aqueous methanol to water in dimethyl sulphoxide. In the latter media the hydroxide ion is much more strongly nucleophilic and at the same time the proton availability is greatly reduced, so that the electrophilic attack at the aryl–$MMe_3$ bond plays a smaller part. Thus it is understandable that the compounds $Me_3SnPh$ and $Me_3SiPh$ show almost identical reactivities in alkaline 1 : 6 v/v $H_2O$–$Me_2SO$,[3] and that in dimethyl sulphoxide containing only 3% (w/w) of water the silicon compound should be the more reactive (by a factor of 5·5).[15]

## EXPERIMENTAL

*Materials.*—The preparation of *p*-nitrophenyltrimethylstannane will be described elsewhere.[16] The other $X\cdot C_6H_4\cdot SnMe_3$ compounds were made from the appropriate Grignard reagents and chlorotrimethylstannane, and purified by fractional distillation; the physical constants agreed with those previously reported.[17] Care was taken to ensure that no traces of $X\cdot C_6H_5$ were present, since these would lead to inaccurate product isotope effects.

*Measurement of Product Isotope Effects.*—The two solvent systems were made up as follows: (*a*) A 3·80M-solution (10·00 ml) of sodium methoxide in methanol was mixed with methan[$^2$H]ol (18·00 ml; Ryvan >99% MeOD) to give 1 : 2 MeOH–MeOD containing 1·35M-sodium methoxide, (*b*) A 10·0 : 9·0 mixture of the same components gave 1 : 1 MeOH–MeOD containing 2·0M-sodium methoxide.

A mixture of the $X\cdot C_6H_4\cdot SnMe_3$ compound (*ca.* 0·8 mmol) with 4·0 ml of one of the above media was sealed in a 10 ml Pyrex ampoule, which was shaken at room temperature

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[11] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Chem. Soc.*, 1963, 2342.

[12] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566.

[13] C. Eaborn, *J.C.S. Chem. Comm.*, 1972, 1255; see H. J. Berwin, *ibid.*, p. 237.

[14] W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 829, 7476, and references therein.

[15] C. Eaborn, A. A. Najam, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **46**, 255.

[16] C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin I*, in the press.

[17] C. Eaborn, H. L. Hornfeld. and D. R. M. Walton, *J. Organometallic Chem.*, 1967, **10**, 529.

(21 ± 1°) for 7 days. The mixture was then added to water (5·0 ml) at 0° and aromatic material extracted with n-pentane (2 × 3 ml). The extract was washed with water (3 × 2 ml) and dried ($Na_2SO_4$); the solvent was removed by distillation (bath temperature up to 70°) from a small pear-shaped flask fitted with a 1 in Vigreux column. A sample of the residual droplet of liquid was injected into a Pye model 64 gas chromatograph linked with an Edwards E606 fast scanning spectrometer operating at 9—14 eV, and the average taken of 30 scans of the $m/(m + 1)$ mass ratio (where $m$ refers to the parent ion from $X{\cdot}C_6H_5$). After correction for the $^{13}C$ content, this gives the $X{\cdot}C_6H_5/C_6H_4{\cdot}D$ ratio.

*Overall Solvent Isotope Effects.*—Rates were measured spectrophotometrically by the method previously described.[2] For *m*-trifluoromethylphenyltrimethylstannane the mixture was contained throughout in a stoppered quartz absorption cell kept at 50·0 ± 0·1° in a thermostatted cell-compartment of a Unicam SP 500 spectrophotometer, and the change in optical density at 272 nm was recorded. For the less reactive *p*-methoxyphenyltrimethylstannane, the mixture was placed in a flask fitted with a serum cap, which was kept in a thermostat bath at 50 ± 0·02°. Aliquot portions were withdrawn at suitable intervals and added to methanol (4·0 ml), and the optical density of the resulting solution was measured at 282 nm. The infinity value of the optical density was recorded after about 10 half-lives in each case. The first order rate constants obtained are shown in Table 2.

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