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CLEAVAGE OF BENZYLTRIMETHYLSTANNANES BY AQUEOUS METHANOLIC PERCHLORIC ACID

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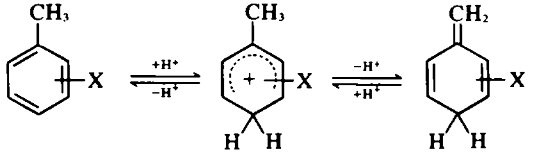
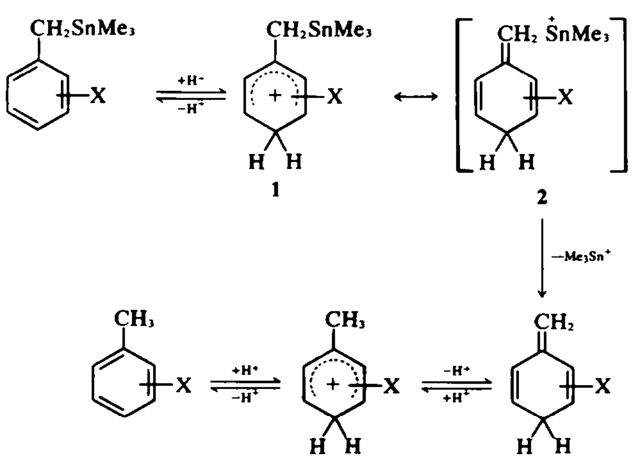
Abstract—The rates of cleavage of some $XC_6H_4CH_2$-$SnMe_3$ bonds by aqueous-methanolic perchloric acid have been measured spectrophotometrically, and the rate of cleavage of the Me–Sn bonds of $PhCH_2SnMe_3$ and Me_4Sn by monitoring the methane evolution. The results indicate that for X = H, *p*-Me, *o*-Me, *p*-Bu^t, *o*-, *m*- and *p*-F and -Cl, and *o*-Br, the cleavage of the CH_2–$SnMe_3$ bond involves attack of the acid at the benzylic atom, and is not much faster than that of the Sn–Me bonds, but that a mechanism involving ring-protonation is important for X = *m*-Me, and greatly predominant for X = *m*-OMe.

INTRODUCTION

A few years ago we observed acid-catalysed exchange of hydrogen between trifluoroacetic acid and Me groups attached to aromatic rings, and attributed this to the reaction sequence outlined in Scheme 1[1]. It seemed to us likely that an analogous reaction, but involving loss of the Me_3Sn group instead of a proton, would occur on treatment of a suitable Me_3SnCH_2Ar compound with acid. Such a process, represented in Scheme 2 for the simplest case of $XC_6H_4CH_2SnMe_3$ compounds,† would be favoured by (a) the large hyperconjugative stabilisation of the Wheland intermediate (1) by the Me_3SnCH_2 substituent[2] (for which an approximate σ^+-constant of $-1{\cdot}3$ has been derived[3]), (b) the location on the tin atom of a substantial proportion of the positive charge of this intermediate as a result of the hyperconjugation [see, *e.g.*, structure (2)], which will render the tin atom very susceptible to the attack of



SCHEME 1



SCHEME 2

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†It will be appreciated that the initial protonation can also take place ortho- to the CH_2SnMe_3 substituent.

nucleophiles, and (c) the usually much greater ease of cleavage of C–$SnMe_3$ than of C–H bonds by nucleophiles. (Related cleavages of other benzyl–metal bonds have been observed previously.[4]) We thus examined the cleavage of a series of $XC_6H_4CH_2SnMe_3$ compounds by aqueous methanolic perchloric acid, a medium we have previously used for studying the cleavage of aryl–MMe_3 bonds (M = Si, Ge, Sn).[5] The results presented some ambiguities, and we have delayed publication in the hope of being able to make further studies. There is, however, no realistic prospect that these can be carried out in the near future, and since our work does provide clear evidence that a cleavage process of the type depicted in Scheme 2 can, indeed, operate, we thought it appropriate to place the results briefly on record.[6]

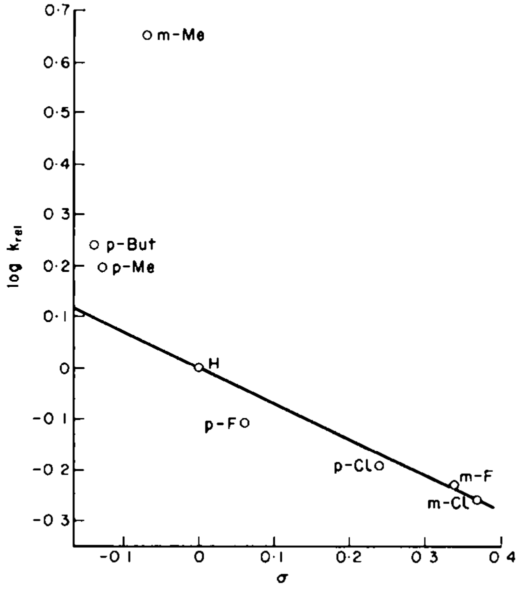

Fig 1. Plot of log k_{rel} for the cleavage of $XC_6H_4CH_2$-$SnMe_3$ compounds against σ.

RESULTS AND DISCUSSION

The progress of the cleavage of the benzyl-tin bond was followed spectrophotometrically at wavelengths corresponding with absorption by the aromatic ring. (Base cleavage of benzyltrimethylstannanes were successfully studied by this method.[7]) Excellent first-order rate plots were derived from the change in optical density, with the reading after ten half-lives used as the 'infinity' value. The results are shown in Table 1, which lists, in addition to the observed first-order rate constant, k, the rate, k_{rel}, relative to that for benzyltrimethylstannane itself, the concentration of the aqueous acid used (2 vol of which were mixed with 5 vol of a methanolic solution of the organostannane), and the wavelength employed.

The relative rates for the alkyl-substituted compounds vary with the concentration of the acid (see below). Fig. 1 shows a plot of log k_{rel} against σ for k_{rel} values determined in the highest acid concentrations, and it will be seen that the points lie moderately well about a straight line (of slope, ρ, = −0·70) for X = *m*-Cl, *m*-F, *p*-Cl, *p*-F, and H, but that there is an appreciable deviation for X = *p*-Bu^t and *p*-Me and a large deviation for X = *m*-Me. The point for X = *m*-OMe, (for which k_{rel} was measured only at much lower acid concentrations) would lie so far above the line that it cannot be shown on the plot. (The *m*-methoxy-compound is some 90 times as reactive as expected from the ρσ relationship represented by the line in Fig 1.) Now the *m*-Me and *m*-OMe substituents are just those which, by facilitating ring protonation at positions *ortho*- and *para*- to themselves, should greatly increase the ease of the sequence in Scheme 2, and we conclude that the cleavage of the *m*-$MeOC_6H_4CH_2$–$SnMe_3$ bond proceeds almost exclusively, and that of the *m*-$MeC_6H_4CH_2$–$SnMe_3$ bond predominantly by this mechanism. The cleavage of 3,5-$Me_2C_6H_3CH_2$–$SnMe_3$ bond must also proceed very predominantly by this mechanism.

The implication of this conclusion is that the cleavage of the other $XC_6H_4CH_2$–$SnMe_3$ bonds does not proceed by this special mechanism, but involves direct electrophilic attack at the benzylic carbon. If this were so, there would be no reason why the cleavage of these bonds should be greatly different from that of the Sn–Me bonds in the same molecules, and we found that cleavages of the Sn–Me bonds were, indeed, occurring at comparable rates in these cases. The evolution of gas (assumed to be exclusively methane) from benzyltrimethylstannane was monitored, and found to give a good first-order plot, with a first-order rate constant of about half that for the $PhCH_2$–$SnMe_3$ cleavage (Table 2), implying that a single Sn–Me bond was cleaved about one-sixth as readily as the $PhCH_2$–$SnMe_3$ bond; this is consistent with the results of studies of $PhCH_2$–Sn and Me–Sn bonds by other electrophiles.[8] The gas evolution from tetramethylstannane gave a rate constant about twice as large as that for benzyltrimethylstannane in the same medium (Table 2). (The volume of gas evolved was that expected for cleavage of one Sn–Me bond of the tetramethylstannane; but the first-order plot showed some curvature after 70% of reaction.) Allowing for the availability of four Sn–Me bonds in tetramethyl- and three in benzyltrimethyl-stannane, this means that a single such bond is cleaved about 1·5 times as rapidly in the former as in the latter. We did not measure the rate of gas evolution from the substituted $XC_6H_4CH_2SnMe_3$ compounds, but

Table 1. Rates of cleavage of $XC_6H_4CH_2$–$SnMe_3$ bonds by a mixture of MeOH (5 vol) and aqueous $HClO_4$ (2 vol) at 50°

X	$10^3 \times$ [Stannane][a]/M	[$HClO_4$][b]/M	λ/nm	$10^4 k/s^{-1}$	k_{rel}
H	1·3	12·35	275	24·8	1
	1·5	12·00		21·9	
	1·5	11·10		12·9	
	1·5	9·50		7·2	
	2·1	8·00		3·55	
	2·1	4·08		1·08	
o-Me	1·3	12·35	275	21·8	0·87
	1·4	11·10		10·95	0·85
m-Me	2·3	12·35	277	110·8	4·4
	3·2	11·10		58·15	4·5
	2·6	9·50		24·6	3·4
	1·6	8·00		11·35	3·2
	0·9	4·08		1·85	1·7
p-Me	1·2	12·35	280	39·15	1·57
	1·5	11·10		19·2	1·48
	1·2	9·5		9·0	1·25
	1·5	8·0		4·27	1·20
p-Bu^t	1·2	12·00	276	37·95	1·73
o-F	0·6	12·35	272	10·8	0·43
m-F	0·9	12·35	274	14·9	0·60
	1·0	11·1		7·7	0·59
p-F	0·8	12·35	284	19·25	0·77
o-Cl	1·9	12·35	277·5	10·2	0·41
m-Cl	1·9	12·35	279	13·65	0·55
	0·8	11·1		6·97	0·54
p-Cl	1·5	12·35	284	15·9	0·64
o-Br	2·3	12·35	279	10·4	0·42
m-OMe	1·3	4·08	279	64·8	60
3,5-Me_2[c]	1·8	4·08	276	27·8	26

[a] Concentration of the initial methanolic solution of the organostannane.
[b] Concentration of the initial aqueous perchloric acid.
[c] Refs to 3,5-$Me_2C_6H_3CH_2SnMe_3$.

it is unlikely that the group X will have much influence on the ease of cleavage of the Sn–Me bonds.

In view of the above results, it would appear that about two-thirds of the benzyltrimethylstannane should react to give toluene and one-third to give methane. In accord with this, GLC analysis indicated that toluene was produced from this compound in a yield of about 60%. With the other $XC_6H_4CH_2SnMe_3$ compounds the corresponding yields were not determined, but in each case the spectrum of the solution when cleavage was complete was compared with that of a solution of the $XC_6H_4CH_3$ of the same concentration as the initial $XC_6H_4CH_2SnMe_3$ compound. The spectrum of the cleaved material corresponded in shape in each case to that of the expected product, but the optical densities were significantly lower than for the latter, as expected for incomplete formation of the $XC_6H_4CH_3$ due to concomitant cleavage of the Sn–Me bond. However, in the case of the *m*-$MeOC_6H_4CH_2SnMe_3$ compound, the optical density of the solution of the cleavage product was > 80% of that of the *m*-$MeOC_6H_4CH_3$ solution.

Table 2. Rates of CH_4 evolution from methylstannanes in a mixture of MeOH (5 vol) and aqueous $HClO_4$ (2 vol) at 50°

Compound	Wt/g	$[HClO_4]^a$/M	$10^4 k/s^{-1}$	Exptal Vol^b/ml	Calcd Vol^{b,c}/ml
$PhCH_2SnMe_3$	0·1109	9·5	4·12	10·8	9·7
	0·1519	12·0	13·9	15·6	13·3
	0·2685	9·5	3·97	23·3	23·6
Me_4Sn	0·0760	9·5	8·80	10·1	9·5
	0·1609	9·5	8·88	20·9	20·1
	0·2356	9·5	9·03	28·7	29·5

[a] Concentration of the initial aqueous acid.
[b] Corrected to NTP.
[c] Calculated assuming cleavage of one Sn-Me bond only.

The reasonably satisfactory picture presented above is complicated by the puzzling finding that the volume of gas evolved from benzyltrimethylstannane was very close to that expected for cleavage of one Sn–Me bond per molecule of starting material, which is three times as much as would be expected from the analysis above. The possibility that more than one Sn–Me bond is cleaved seems unlikely in view of the observations that the gas evolution from Me_4Sn corresponds with cleavage of one such bond per molecule, and that when chlorotrimethylstannane is dissolved in the medium, gas evolution is much slower, and effectively ceases after evolution of only 20% of that expected for cleavage of one Sn–Me bond per molecule. Possible explanations can be devised (*e.g.*, it is conceivable that disproportionation of Me_3SnX species to Me_2SnX_2 and Me_4Sn occurs in the medium and is facilitated by the presence of the more mobile $PhCH_2$–Sn bonds), but there is little point in such speculation until additional experiments can be carried out.

The absence of a significant contribution by the process of Scheme 2 to the cleavage of the $PhCH_2$–$SnMe_3$ bond was confirmed in the following ways. First benzyltrimethylstannane was cleaved in an aqueous methanolic perchloric acid medium of high O-*d* content. The toluene produced contained no D_2 species, indicating that exchange of ring hydrogen was not accompanying the cleavage. Secondly, samples of *o*- and *p*-deuteriotoluenes were converted into the *o*- and *p*-$DC_6H_4CH_2SnMe_3$ compounds by a method which would not disturb the deuterium. These compounds were then subjected to the acid cleavage, and in each case the toluene obtained was found to have the same deuterium content as the original deuteriotoluene. (As a further check, the toluene obtained by base-cleavage was also examined, and found to have the same deuterium content.) If the reaction followed the course of Scheme 2 to any significant extent, loss of deuterium would be observed. This result also indicates that the absence of contribution by this mechanism can be attributed to the smallness of the rate of ring protonation, to give Wheland-intermediates of type (1), rather than to the failure of this intermidiate to lose the Me_3Sn group, since the ring-protonation would necessarily be reversible under these conditions, and hydrogen-exchange, with loss of deuterium, would result, and would show up in a low deuterium content of the toluene subsequently produced by direct electrophilic attack at the benzylic C atom. That the contribution of the mechanism of Scheme 2 becomes substantial for the *m*-Me compound is understandable, since the ring-protonation is probably about 300–1000 times as rapid for this compound as for benzyltrimethylstannane itself; this follows from the fact that the *m*-Me group probably facilitates protonation of positions *ortho*- and *para*- to it by a factor of about 100–300. (In hydrogen-exchange in toluene in trifluoroacetic acid at 70° the Me group activates the *ortho*- and *para*- positions by factors of 220 and 450 respectively,[9] and factors of about 250 apply to both positions in aqueous sulphuric acid,[10] but the activating effect will probably be rather smaller in the presence of the strongly releasing Me_3SnCH_2 group.) The value of k_{rel} for *m*-methylbenzyltrimethylstannane falls significantly with the strength of the acid (Table 1), and it is possible that the ring-protonation mechanism is increasingly favoured over the direct side chain attack as the acid concentration is raised. If this is so, the small increase in k_{rel} observed for the *p*-methyl-compound over a smaller range of acid concentration suggests that there might be a significant contribution from the ring-protonation mechanism in this case also, and, by extension, for the *p*-t-butyl compound. The k_{rel} value of 26 for 3,5-$Me_2C_6H_3$-CH_2SnMe_3 indicates that introduction of the second *m*-Me group in the less concentrated acid has about the same effect as the introduction of a single such group in the media of highest acid concentration.

We also examined the rate of cleavage of the benzyl–Sn bonds in the compounds $PhCHMeSnMe_3$ and $PhCMe_2SnMe_3$, since elimination of the $SnMe_3$ group, to give the transient olefinic species of type (2) (Scheme 2), should be facilitated by stabilisation of the olefins by the pendant methyl groups. In fact, as shown in Table 3, the introduction of the first C-methyl group had no significant influence, and that of the second caused a 2·4-fold rate reduction. Again, these results are consistent with cleavage by direct electrophilic attack at the benzylic C atom. A rather greater rate reduction was caused by the change from $PhCH_2SnMe_3$ to $PhCH_2Sn(CH_2Cl)Me_2$, the electron-withdrawing CH_2Cl group lowering the rate of cleavage of the $PhCH_2$-Sn bond by a factor of about 11. The cleavage of the benzyl-Sn bond of $PhCH_2SnEt_3$ was about 5·6 times lower than that of $PhCH_2SnMe_3$ (Table 3).

Further study of cleavage by the process of Scheme 2 could profitably be concentrated on *m*-methoxybenzyltin compounds.

EXPERIMENTAL

Proton NMR spectra were recorded on a Varian A60 instrument using 10% solns in CCl_4 with TMS as internal standard.

α,α-Dimethyl- and α-methyl-benzyltrimethylstannane, $PhCMe_2SnMe_3$ *and* $PhCHMeSnMe_3$. A soln of Me_3SnBr (27 g, 0·11 mole) in ether (150 ml) was added to $PhCMe_2K$ [prepared from $PhCMe_2OCH_2Ph$ (16 g, 0·11 mole) and K (7·8 g, 0·2 g-atom) in AnalaR heptane (100 ml)[11]] and the mixture was boiled under reflux for 2 h. After cautious addition of MeOH (10 ml) followed by satd aqueous NH_4Cl (100 ml), the ether layer was separated and washed with H_2O (50 ml). The aqueous layer and washings were re-extracted with ether (2 × 50 ml) and the combined ether-extracts were dried (Na_2CO_3) and distilled to give $PhCMe_2SnMe_3$ (20 g, 65%) b.p. 80°/2 mmHg, $[n]^{25}_{D}$ 1·5389 (Found: C, 50·5; H, 7·1. $C_{12}H_{20}Sn$ requires: C, 50·8; H, 5·1%). An ^1H NMR spectrum had the correct integration and showed resonances as follows: ($\tau =$) C_6H_5(m) centered at 2·87, $C(CH_3)_2$ 8·48(s) and $(CH_3)_3Sn$ 10·06(s). In the same way, starting from PhCHMeK[11] was prepared $PhCHMeSnMe_3$ (68%) b.p. 50°/0·4 mmHg, $[n]^{25}_{D}$ 1·5386 (Found: C, 48·7; H, 6·6. $C_{11}H_{18}Sn$ requires: C, 49·0; H, 6·7%). ^1H NMR ($\tau =$) C_6H_5(m) centered at 2·87, $CH(CH_3)$(m) centered at 8·43, and $(CH_3)_3Sn$ 10·10(s).

Benzyl (chloromethyl) dimethylstannane, $PhCH_2Sn(CH_2Cl)Me_2$. A soln of $Me_2Sn(CH_2Cl)Cl$[12] (23·5 g, 0·1 mole) in ether (100 ml) was added to $PhCH_2MgCl$ made from $PhCH_2Cl$ (13 g, 0·1 mole) and Mg turnings (2·5 g, 0·1 g-atom) in ether (100 ml) and the mixture was boiled under reflux for 3 h. After treatment with aqueous 10% HCl, organic products were extracted with ether and the ether layer was separated, dried (Na_2SO_4) and distilled to give $PhCH_2Sn(CH_2Cl)Me_2$ (20 g, 65%) b.p. 49°/1·0 mmHg, $[n]^{25}_{D}$ 1·5645 (Found: C, 41·8; H, 5·2. $C_{10}H_{15}ClSn$ requires: C, 41·4; H, 5·1%). ^1H NMR: C_6H_5(m) centred at 2·90, CH_2Cl 7·01 (s), CH_2-benzyl 7·56(s) and $(CH_3)_2Sn$ 9·85(s).

Details of $XC_6H_4CH_2SnMe_3$ compounds prepared analogously from $XC_6H_4CH_2MgBr(Cl)$ reagents and Me_3SnCl in ether are given in Table 4. The compound $PhCH_2SnEt_3$, also prepared in this way in 72% yield from $PhCH_2MgCl$ and Et_3SnBr, had b.p. 80°/0·4 mmHg, $[n]^{25}_{D}$ 1·5375 (lit.,[13] b.p. 85°/0·7 mmHg, $[n]^{25}_{D}$ 1·5375).

Kinetic studies. A general spectrophotometric method, described elsewhere,[14] was used to measure the rates of cleavage of benzyl–Sn bonds. Aqueous $HClO_4$ (2 vol) of strength specified in Tables 1 and 3 was added to an ice-cold soln of the organostannane in MeOH (5 vol) and a sample of the mixture was transferred to a stoppered quartz cell contained in the sample compartment of a thermostatted block maintained at 50 ± 0·02° in a Unicam SP 500 spectrophotometer. After 5 min, optical densities (relative to MeOH as a solvent blank) were recorded at appropriate intervals up to ten half-lives and pseudo first-order rate constants were then evaluated graphically. Spectra after ten half-lives were generally found to be in fair agreement (*ca*, 80%) with solutions of the appropriately substituted toluenes in the reaction medium.

Determination of CH_4 *in the cleavage of methyl-tin bonds.* The smaller arm (*ca* 7 ml capacity of a twin-limbed reaction vessel was charged with the organostannane (*ca* 0·2 g) and the larger arm (*ca* 10 ml capacity) with MeOH (5 ml) and aqueous $HClO_4$ (2 ml) of strength given in Table 2. The vessel was connected to a gas burette, then immersed in a thermostat bath (50 ± 0·02°) and the system was allowed to attain equilibrium. (For the volatile Me_4Sn, only the acid-containing limb was immersed.) The vessel was then shaken mechanically with complete submersion of both limbs and the volume of evolved gas measured using the burette, readings being continued until no further increase in volume occurred. First-order rate constants were evaluated graphically. For comparison with the theoretical volume, the total volume of evolved gas was, of course, corrected to NTP, with allowance for the water vapour contribution.

Determination of PhMe *yield in the cleavage of* $PhCH_2SnMe_3$. A mixture of $PhCH_2SnMe_3$ (0·12 g)

Table 3. Cleavage of some $PhCH_2SnR_3$ compounds by a mixture of MeOH (5 vol) and aqueous $HClO_4$ (2 vol) at 50°

Compound	$10^3 \times [PhCH_2SnR_3]^a$/M	$[HClO_4]^b$/M	λ/nm	$10^4 k/s^{-1}$	k_{rel}
$PhCH_2SnMe_3$	1·5	12·00	275	21·9	1·00
$PhCH_2SnMe_3$	1·3	12·35		24·8	
$PhCHMeSnMe_3$	1·7	12·35		23·85	0·96
$PhCMe_2SnMe_3$	1·2	12·35		9·75	0·39
$PhCH_2SnMe_2(CH_2Cl)$	1·6	12·00	273	2·97	0·091
$PhCH_2SnEt_3$	2·8	12·35	275	4·4	0·18

[a] Concentration of initial methanol solution.
[b] Concentration of initial aqueous perchloric acid.

Table 4. $XC_6H_4CH_2SnMe_3$ compounds prepared from $XC_6H_4CH_2MgBr(Cl)$ reagents and Me_3SnBr

				Lit[13],					
X	Yield (%)	B.p.°/mmHg	$[n]_D^{25}$	B.p.°/mmHg	$(n)_D^{25}$	C_6H_4	CH_2(s)	$(CH_3)_3Sn$(s)	CH_3(s)
H	67	46/0·5	1·5408	70/30	1·5410	2·93(d)	7·71	9·98	
o-Me[a]	61	78/2·1	1·5381			3·06(m)	7·72	9·98	7·72
m-Me	67	65/1·3	1·5352	85/3·0	1·5387	3·14(m)	7·72	9·95	7·72
p-Me	63	75/1·7	1·5360	79/2·0	1·5385	3·06(q)	7·72	9·94	7·72
p-Bu^t[b]	68	88/0·7							
o-F[c]	59	52/1·0	1·5270			2·99(m)	7·70[d]	9·91	
m-F	61	58/1·1	1·5267	60/1·0	1·5272	3·23(m)	7·69	9·92	
p-F	64	47/0·45	1·5238	81/4·0	1·5260	3·14(q)	7·76	9·98	
o-Cl[e]	68	59/0·3	1·5552			2·73(m)	7·56	9·91	
m-Cl	86	60/0·15	1·5540	85/1·0	1·5558	3·01(m)	7·71	9·92	
p-Cl	88	61/0·15	1·5557	96/2·0	1·5565	3·03(q)	7·79	9·97	
o-Br[f]	62	70/0·45	1·5718			3·00(m)	7·50	9·88	
m-OMe	59	80/0·6	1·5457	80/0·6	1·5457		7·76	9·94	6·31
3,5Me$_2$[g]	64	68/0·7	1·5332			3·35(d)	7·75	9·93	7·75

[a] Found: C, 49·1; H, 6·9. $C_{11}H_{18}Sn$ requires: C, 49·1, H, 6·7%. [b] Found: C, 54·0; H, 7·8. $C_{14}H_{24}Sn$ requires: C, 53·7; H, 7·7%. [c] Found: C, 44·4; H, 5·5. $C_{10}H_{15}FSn$ requires: C, 44·0; H, 5·5%. [d] Centre of doublet (singlet resonance split by *o*-F substituent). [e] Found: C, 41·4; H, 5·2. $C_{10}H_{15}ClSn$ requires: C, 41·5; H, 5·2%. [f] Found: C, 36·3; H, 4·6. $C_{10}H_{15}BrSn$ requires: C, 36·0; H, 4·5%. [g] Found: C, 50·9; H, 7·0%. $C_{12}H_{20}Sn$ requires: C, 50·7; H, 7·0%.

MeOH (10 ml) and 12 M $HClO_4$ (4 ml) was thermostatted at 50° for 1 h, then cooled and carefully neutralised with aqueous NaOH. Organic products were extracted with ether and the ether layer was dried (Na_2SO_4) and concentrated. n-C_8H_{18} (0·5 ml) was added to this concentrate and the mixture analysed quantitively by GLPC using a 2·8 metre SE30 column operating at 80° with N_2 (50 ml min^{-1}) as carrier gas. The yield of PhMe (60%) was estimated by comparison of peak area ratios with similar ratios produced by an authentic specimen mixture.

Deuterium labelling studies

(a) $PhCH_2SnMe_3$ (0·5 g) was dissolved in an ice-cold mixture of MeOD (5 ml, > 99% MeOD), aqueous 60% $HClO_4$ (1 ml) and D_2O (1 ml, > 99% D_2O). The mixture was kept at 50° for 48 h then a sample was injected through a column of 4A molecular sieves (to remove H_2O, MeOD and $HClO_4$) into Pye 104 Model 64 gas chromatograph linked to an Edwards E 606 fast scan mass spectrometer. The mass spectrum of the $PhCH_3$ showed that < 5% of $PhCH_3$-d_2 was present.

(b) *p*-DC_6H_4Me was made by treatment of *p*-MeC_6H_4-MgBr in ether with D_2O and found to give rise to an m/(m + 1) ratio of 1·55 ± 0·03 on examination in the linked GLPC-mass spectrometer system mentioned above. A sample was converted into *p*-$DC_6H_4CH_2Br$ by treatment with N-bromosuccinimide, and the Grignard reagent from this bromide was treated with Me_3SnCl to give *p*-$DC_6H_4CH_2SnMe_3$. A sample (0·5 g) was dissolved in a mixture of MeOH (5 ml) and aqueous 60% $HClO_4$ (2 ml) and the solution was kept in a sealed ampoule at 50° for 7 h. The mixture was then added to ice-cold aqueous Na_2CO_3 (5 ml) and organic material was extracted with n-C_5H_{12} (2 × 2·5 ml). The n-C_5H_{12} extract was introduced into the GLPC-mass spectrometer system and gave an m/(m + 1) peak ratio of 1·52 ± 0·03 for the toluene.

A sample of *p*-$DC_6H_4CH_2SnMe_3$ was cleaved with a mixture of MeOH (5 vol) and aqueous *ca* 2 M NaOH (2 vol) and the resulting toluene gave an m/(m + 1) peak ratio of 1·59 ± 0·03.

(c) Analogous results were obtained starting from *o*-BrC_6H_4Me.

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