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**Preliminary communication**

# NEIGHBOURING GROUP PARTICIPATION IN REACTIONS BETWEEN IODINE AND $Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me$-*p*

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## Summary

Reactions of $Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me$-*p* ($n$ = 2, 3 or 4; $m$ = 0, 1 or 2) with iodine in $CCl_4$ result in phenyl—tin bond cleavage. The relative reactivities indicate intramolecular nucleophilic catalysis by the sulphur-containing substituents.

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There have been few indications in carbon—tin bond cleavage reactions for enhancement of reactivity arising from assistance by a group not directly bonded to tin. One such report came from Kuivila's group [1], who showed that the rate of the forward reaction ($k_1$) in equilibrium 1 is considerably larger than that for the analogous reaction involving $Me_3SnBu$ and $Me_3SnCl$.

$$Me_3SnCl + Me_3Sn(CH_2)_nCOR \overset{k_1}{\rightleftharpoons} Me_2Sn(Cl)(CH_2)_nCOR + Me_4Sn \qquad (1)$$

R = Me or Ph; $n$ = 2 or 3.

The rate enhancement was attributed to the carbonyl group providing intramolecular nucleophilic catalysis or neighbouring group participation.

We have observed appreciable rate differences in the reactions of iodine with $Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me$-*p* (I; $n$ = 2, 3 or 4; $m$ = 0, 1 or 2) in $CCl_4$ solution at 30°C (eq. 2). All the reactions lead to phenyl—tin cleavage.

$$I_2 + Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me\text{-}p \rightarrow PhI + Ph_2(I)Sn(CH_2)_nS(O)_mC_6H_4Me\text{-}p \qquad (2)$$

The relative reactivities were obtained from competitive reactions of compound I and $(p\text{-}MeC_6H_4)_4Sn$ for a deficiency of iodine; typical concentrations were ca. $10^{-2}$ *M* each for the organotins and $[I_2]$ = ca. $2 \times 10^{-3}$ *M*. The

TABLE 1

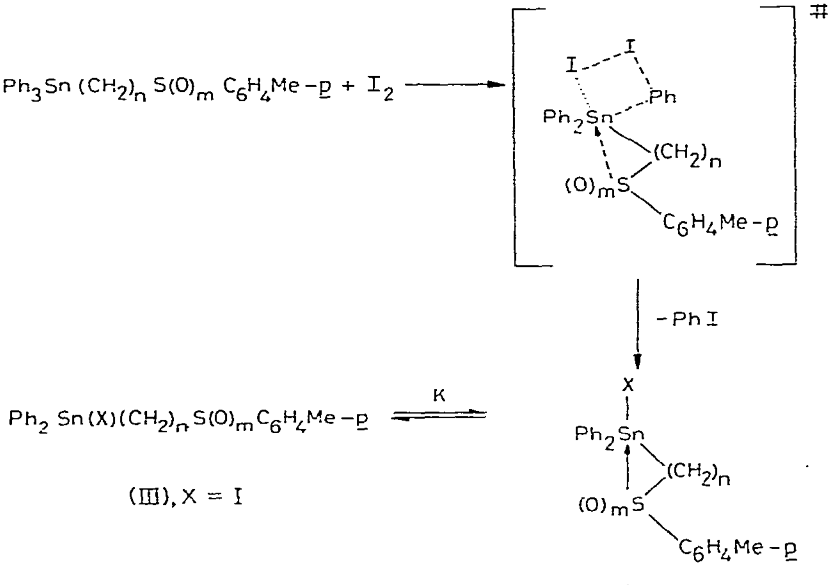
RELATIVE REACTIVITIES[a] OF $Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me$-*p* TOWARDS IODINE AT 30 ± 0.2°C IN $CCl_4$ SOLUTION

| *n* | *m* = | | |
|---|---|---|---|
| | 0 | 1 | 2 |
| 2 | 0.25 ± 0.04 | — | 3.6 ± 0.1 |
| 3 | 1.20 ± 0.06 | 2300 ± 100 | 2.6 ± 0.1 |
| 4 | 0.23 ± 0.03 | 2.15 ± 0.10 | 0.49 ± 0.04 |

[a] Values are averages from 4 experiments. Reactivity of $(p\text{-}MeC_6H_4)_4Sn$ = 1; relative reactivity of $Ph_3SnBu$ = 0.16 ± 0.02.

ratios [PhI] :[*p*-$MeC_6H_4I$] were determined by GLC. The quoted reactivities (Table 1) are each averages of four experiments and are calculated from $[(p\text{-}MeC_6H_4)_4Sn][PhI]/[\text{compound I}][p\text{-}MeC_6H_4I]$.

The rate differences reflect differences in participation by the functional substituent. As shown by the substituent effects on cleavage by $I_2$ of aryl—tin bonds [2], a substantial degree of positive charge is developed on the aromatic ring in the transition state. Additional electron release from the tin centre to the phenyl ring, such as would result from coordination of the substituent, $S(O)_m$ to the tin, will increase the rate. As it is unlikely that free ions, $I^-$ and $Ph_2Sn^+(CH_2)_nS(O)_mC_6H_4Me$-*p*, will be formed in $CCl_4$, some interaction between the tin centre and the developing iodide ion is envisaged. A simplified scheme is shown in Scheme 1*.



SCHEME 1

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*Cleavage of carbon—tin bonds, including aryl—tin [2], alkenyl—tin, alkynyl—tin and benzyl—tin bonds [3] by iodine in $CCl_4$ are third order processes (first order in organotin and second order in iodine). Scheme 1 ignores the extra molecule of iodine, which is considered to be involved either in a π-complex with the organotin or in formation of $I_4$ [2, 3].

As expected from other findings on donor abilities, the greatest effect is found with the sulphoxide substituent. As well as the type of the particular functional group, another important factor is the size of the potential chelate ring formed during the reaction. It is worth remembering that for the sulphoxides and sulphones, any coordination will be via oxygen and thus the potential chelate ring size is $(n + 3)$ from compound I $(m = 1$ or $2)$ in contrast to a $(n + 2)$ membered ring from sulphide I $(m = 0)$.

Evidence was obtained to support the basis of intramolecular complexation for halodiphenyl derivatives, such as II. The $\lambda_{max.}$ value for charge-transfer adducts of $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* $(n = 2, 3$ and $4)$ and $(CN)_2C{=}C(CN)_2$ in $CH_2Cl_2$ solution were at 610 ± 1 nm (an indication of similar donor abilities for all these sulphides) while $\lambda_{max.}$ for the $Ph_2Sn(X)(CH_2)_3SC_6H_4Me$-*p* adducts were at 598 ± 1 $(X = Cl)$ and 602 ± 1 $(X = I)$ nm; these are small but significant differences. The $\nu(SO)$ frequencies for $Ph_2Sn(Cl)(CH_2)_nSOC_6H_4Me$-*p* in $CH_2Cl_2$ solution appear at ca. 1040 (free SO) and 980 $cm^{-1}$ (complexed SO). Equilibrium constants $(K = [II, X = Cl]/[III, X = Cl])$ were calculated (at 25°C) to be 10 ± 1 and 0.9 ± 1 for $n = 3$ and 4, respectively. Thus the greater intramolecular complexation is found for the compound, $n = 3$, which compliments the reactivity finding.

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