# Sulphur-substituted Organometallic Compounds. Part II.[1] Reaction of Vinyltin Compounds with Arenesulphenyl Halides and Thiocyanates and some Properties and Reactions of the (2-Arylthio-1-halogenoethyl)-triphenyltin Addition Products

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Vinyltin compounds, $[R_3Sn(CH{=}CH_2)]$ (R = Me and Ph), react with sulphenyl chlorides and thiocyanates, R'SX, in aprotic solvents to give products of addition (Markownikoff) to the vinyl bond and cleavage of the vinyl–tin bond [equation (i)]. Cleavage products are exclusively obtained from the most reactive sulphenyl chloride used, *p*-$MeC_6H_4SCl$, while both cleavage and addition occur with the less-electrophilic species, 2-$O_2N$-4-$YC_6H_3SX$ (Y = H, Me, or $NO_2$; X = Cl or SCN). Sulphenate esters do not react. The adducts, $[Ph_3Sn(CHXCH_2SR')]$, are thermally unstable in polar solvents, such as $CHCl_3$, and give $CH_2{=}CHSR'$. They react with sulphenyl halides, R''SX', to give unsymmetric disulphides, R'SSR'', $CH_2{=}CHX$, and $[Ph_3SnX']$. This type of reaction is in contrast to those with $Br_2$, $I_2$, $CF_3CO_2H$, $Hg[O_2Me]_2$, and $HgCl_2$ in which initially phenyl–tin bond cleavage occurs to give $[Ph_2ZSn(CHXCH_2SR')]$. The latter species are not stable and generally break down to $CH_2{=}CHSR'$ and $[Ph_2SnXZ]$ (Z = Cl, Br, I, $CF_3CO_2$, or $MeCO_2$).

$$[R_3Sn(CH{=}CH_2)] + R'SX \longrightarrow [R_3Sn(CHXCH_2SR')] + CH_2{=}CHSR' + [R_3SnX] \qquad \text{(i)}$$

THE electrophilic addition of *o*-nitrobenzenesulphenyl chloride, *o*-$O_2NC_6H_4SCl$, to triphenylvinyltin in carbon tetrachloride has been demonstrated.[2] Reactions of vinyltin compounds with other electrophilic species have been reported on numerous occasions. In principle, both cleavage of the vinyl–tin bond and addition to the double bond could occur. Of these two processes cleavage has been reported more often and by such electrophiles as halogens[3] (bromine and iodine), proton acids[3a,4] (inorganic and carboxylic acids, and thiols †), and mercury(II) salts.[6] The sequence of cleavage of organic groups from tin has been shown to be phenyl >

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† The report[3a] of the electrophilic cleavage by $HSCH_2CO_2Et$ contrasts with the radical additions of alkanethiols[5] to $[Bu_3Sn(CH{=}CH_2)]$ and arenethiols[1] to $[Ph_3Sn(CH{=}CH_2)]$ to give compounds of the type $[R_3Sn(CH_2CH_2SR)]$, in the presence of free-radical initiators.

[1] Part I, R. D. Taylor and J. L. Wardell, *J. Organometallic Chem.*, 1974, **77**, 311.

[2] J. L. Wardell and S. Ahmed, *J. Organometallic Chem.*, 1974, **78**, 395.

[3] See, for example, (*a*) D. Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2133; (*b*) P. Baekelmans, M. Gielen, P. Malfroid, and J. Nasielski, *Bull. Soc. chim. Belges*, 1968, **77**, 85; (*c*) S. D. Rosenberg and A. J. Gibbons, *J. Amer. Chem. Soc.*, 1957, **79**, 2138.

[4] See, for example, A. Henderson and A. K. Holliday, *J. Organometallic Chem.*, 1958, **23**, 377; A. Saitow, E. G. Rochow, and D. Seyferth, *J. Org. Chem.*, 1958, **23**, 116.

[5] M. G. Voronkov, R. G. Mirskov, and V. I. Rakhlin, *Zhur. obshchei Khim.*, 1974, **44**, 954; M. G. Voronkov, V. I. Rakhlin, and R. G. Mirskov, *Doklady Akad. Nauk. S.S.S.R.*, 1973, **209**, 261.

[6] D. Seyferth, *J. Org. Chem.*, 1957, **22**, 478; R. M. G. Roberts, *J. Organometallic Chem.*, 1969, **18**, 307.

vinyl > methyl;[3a,7] thus, in reaction of iodine with [$Ph_3Sn(CH{=}CH_2)$] in diethyl ether [$Ph_2ISn(CH{=}CH_2)$] was formed,[3a] while with [$Me_3Sn(CH{=}CH_2)$] in methanol [$Me_3SnI$] was obtained.[3b]

Electrophilic addition to the vinyl group is decidedly more limited than cleavage of the vinyl–tin bond. Two such addition reactions to [$Ph_3Sn(CH{=}CH_2)$] are epoxidation, using peracids,[8] and that by $o$-$O_2NC_6H_4SCl$.[2] Known free-radical additions to vinyltin compounds, on the other hand, are more numerous, *e.g.* by thiols,[1,5] hydrogen sulphide,[9] perfluoroalkyl iodides,[10] and polyhalogenated methanes[11] such as $CHCl_3$, $CCl_4$, and $CCl_3Br$.

TABLE 1

Isolated products from the 1 : 1 reactions of [$Ph_3Sn(CH{=}CH_2)$] with sulphenyl compounds

| Expt. no. | 2-Y-4-$ZC_6H_3SX$ Y | Z | X | Amount of R'SX/ mmol | Solvent | Reaction time, $t$/h ($\theta_c$/°C) | Product/% $CH_2{=}CHSR'$ | [$Ph_3Sn(CHXCH_2SR')$] | Recovered [$Ph_3Sn(CH{=}CH_2)$]/ % |
|---|---|---|---|---|---|---|---|---|---|
| (1) | $NO_2$ | $NO_2$ | Cl | 3.0 | $(CH_2Cl)_2$ | 3 (reflux) | 20 | 46 | 10 |
| (2) | $NO_2$ | H | Cl | 5.3 | $(CH_2Cl)_2$ | 1.5 (reflux) | 23 | 56 | 2 |
| (3) | $NO_2$ | H | Cl | 3.0 | $CCl_4$ | 8 (reflux) | 38 | 53 | 2 |
| (4) | $NO_2$ | H | Cl | 3.0 | thf | 6 (reflux) | 22 | 62 | 4 |
| (5) | $NO_2$ | H | SCN | 2.0 | PhCl | 5 (reflux) | 28 | 29 | |
| (6) | $NO_2$ | H | OMe | 3.0 | $(CH_2Cl)_2$ | 4 (reflux),<br>10 d (20) | | | 90 |
| (7) | $NO_2$ | Me | Cl | 3.0 | $(CH_2Cl)_2$ | 18 (20) | 42 | 30 | 6 |
| (8) | H | Me | Cl | 3.0 | $(CH_2Cl)_2$ | 0.25 (20) | $(p\text{-}MeC_6H_4S)_2$ = 60% | | 31 |

TABLE 2

Ratios of trimethyltin species from the 1 : 1 reactions of [$Me_3Sn(CH{=}CH_2)$] and 2-Y-4-$ZC_6H_3SX$ in $CDCl_3$ solution at 30 °C (from $^1H$ n.m.r. spectra)

| Expt. no. | 2-Y-4-$ZC_6H_3SX$ Y | Z | X | [$Me_3Sn(CHXCH_2SC_6H_3$-2-Y-4-Z)] | [$Me_3SnX$] | [$Me_3Sn(CH{=}CH_2)$] |
|---|---|---|---|---|---|---|
| (9) | H | Me | Cl | | 1 | 1.1 |
| (10) | $NO_2$ | Me | Cl | 0.70 | 1 | |
| (11) | $NO_2$ | H | Cl | 0.62 | 1 | |
| (12) | $NO_2$ | H | SCN | 0.55 | 1 | |
| (13) | $NO_2$ | H | OMe | No reaction | | |
| (14) | $NO_2$ | $CF_3$ | Cl | 1.27 | 1 | |
| (15) | $NO_2$ | $NO_2$ | Cl | 1.20 | 1 | |

The $o$-$O_2NC_6H_4SCl$ reaction with [$Ph_3Sn(CH{=}CH_2)$] gave some cleavage product, (II), as well as the single adduct, the Markownikoff adduct,[2] (I) [equation (1)].

$$[Ph_3Sn(CH{=}CH_2)] + o\text{-}O_2NC_6H_4SCl \longrightarrow \underset{\text{(I)}}{[Ph_3Sn(CHClCH_2SC_6H_4NO_2\text{-}o)]} + \underset{\text{(II)}}{CH_2{=}CHSC_6H_4NO_2\text{-}o} \quad (1)$$

The mol ratio of (I) : (II) was 1.2 : 1. No evidence at all for phenyl–tin cleavage was obtained and thus this sulphenyl chloride showed an inverse selectivity in cleaving carbon–tin bonds (vinyl ≫ phenyl) to that of iodine (phenyl > vinyl). Furthermore, the other possible adduct, the anti-Markownikoff adduct [$Ph_3Sn$-{$CH(SC_6H_4NO_2$-$o)CH_2Cl$}], was not isolated. If it had been formed, either it had been formed to a very small extent or it had completely decomposed during the reaction and/or work-up. As there are clearly considerable differences between the reactions of halogens and $o$-$O_2NC_6H_4SCl$ with vinyltin compounds, it was thought worthwhile to investigate further such electrophilic reactions of sulphenyl systems. The results are now reported and some properties and reactions of the adducts [$Ph_3Sn(CHXCH_2SR)$] are mentioned.

## RESULTS AND DISCUSSION

The halogens are generally stronger electrophiles than $o$-$O_2NC_6H_4SCl$. Specifically, iodine has been found to cleave aryl–tin bonds more readily than does $o$-$O_2NC_6H_4SCl$ and other sulphenyl halides.[2] A range of reactivities of sulphenyl systems, R'SX (R' = aryl), can be obtained by changing the R' and X groups. The following reactivity sequences are taken from relative rates of reaction with olefins, such as cyclohexene:[12] for R'Cl, R' = $p$-$MeC_6H_4$ > 4-Me-2-$O_2NC_6H_3$ > $o$-$O_2NC_6H_4$ > 2,4-$(O_2N)_2C_6H_3$; and for $o$-$O_2NC_6H_4SX$, X = Cl > SCN > OMe.

The effect of the reactivity of R'SX on the addition–cleavage reactions with triphenyl- and trimethyl-vinyltin is shown in Tables 1 and 2 respectively. Table 1 provides the yields of isolated adducts and cleavage products from the 1 : 1 reactions of [$Ph_3Sn(CH{=}CH_2)$], mainly in 1,2-dichloroethane solution but also in other aprotic solvents. The only cleavage products were those derived from vinyl–tin bond cleavages; no

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[7] (*a*) R. C. Poller, 'Chemistry of Organotin Compounds,' Logos Press, 1970; (*b*) M. Gielen and J. Nasielski in 'Organotin Compounds,' ed. A. K. Sawyer, 1972, vol. 3, ch. 9.

[8] G. Ayrey, J. R. Parsonage, and R. C. Poller, *J. Organometallic Chem.*, 1973, **56**, 193; G. Barbieri and F. Taddei, *ibid.*, 1974, **71**, 383.

[9] W. C. Stamm, *J. Org. Chem.*, 1963, **28**, 3264.

[10] N.P. 6,509,546 (*Chem. Abs.*, 1966, **65**, 750).

[11] D. Seyferth, *J. Org. Chem.*, 1957, 1252.

[12] (*a*) C. Brown and D. R. Hogg, *J. Chem. Soc.* (*B*), 1968, 1262; (*b*) D. R. Hogg, unpublished work; (*c*) J. H. Smith, Ph.D. Thesis, University of Aberdeen, 1969.

phenyl–tin bond cleavage was detected in any reaction. The iodine–[$Ph_3Sn(CH=CH_2)$] reaction has been previously studied in diethyl ether solution.[3a] As stated in the introduction, reaction occurred at the phenyl–tin bond. This also happens in 1,2-dichloroethane solution. Thus there is a consistent difference in the sites of cleavage in [$Ph_3Sn(CH=CH_2)$] by iodine and by the whole group of R'SX, no matter how reactive the R'SX is.

The $^1H$ n.m.r. spectra of the isolated adducts confirmed the Markownikoff structure in all cases. The anti-Markownikoff adduct was never isolated. Attempts to optimise the yields were not made and the method of separating the products is given in the Experimental section. From the $^1H$ n.m.r. spectrum of the [$Ph_3Sn(CH=CH_2)$]–$o$-$O_2NC_6H_4SCl$ reaction in $CCl_4$ solution, a slightly larger [adduct] : [cleavage] ratio (*ca.* 2) was estimated, from integration of the adduct's $CHCH_2$ protons and the vinyl protons of the cleavage product, than was calculated from the isolated yields. Unfortunately such a direct estimation could not be made for reactions in 1,2-dichloroethane, since the solvent absorption appeared in the same region as the adduct's $CHCH_2$ protons. The adduct, [(4-Me-2-$O_2NC_6H_3SCH_2CHCl)SnPh_3$], is stable in refluxing $CCl_4$ solution for at least 48 h but decomposes in deuteriochloroform solution on heating (for example, to an extent of 50% at 100 °C for 6 h). The sulphur-containing product was 4-Me-2-$O_2NC_6H_3SCH=CH_2$ [equation (2)]

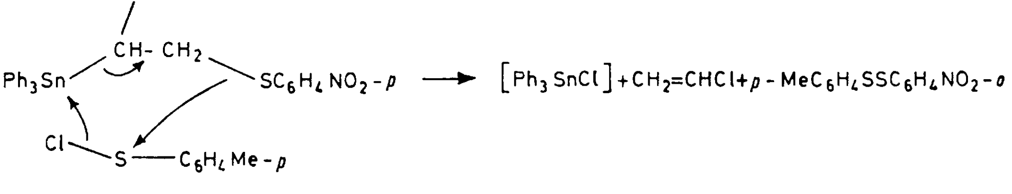
$$[Ph_3Sn(CHXCH_2SR')] \longrightarrow [Ph_3SnX] + CH_2{=}CHSR' \quad (2)$$

($X = Cl$, $R' = $ 4-Me-2-$O_2NC_6H_3$). While the yields in Table 1 are of practical significance, they may not accurately reflect the ratios of cleavage : addition produced for each [$Ph_3Sn(CH=CH_2)$]–R'SX reaction since some decomposition of the adducts could occur, particularly in the more polar solvents and on work-up. Furthermore the amount of vinyl material accounted for was always less than 100% (between 76 and 90%).

To gain more reliable information about the changes in cleavage to addition on changing R'SX, [$Me_3Sn(CH=CH_2)$] reactions in $CDCl_3$ were studied. The ratios (Table 2) are based on the integration of the methyl signals of the $Me_3Sn$ moieties, with due account taken of the $^{117,119}Sn$–$^1H$ couplings, in the $^1H$ n.m.r. spectra of the total reaction media. All the $Me_3Sn$ species in solution had distinct resonances at τ 9.34 ([$Me_3SnCl$]), 9.87 {[$Me_3Sn(CH=CH_2)$]}, and 9.67—9.74 ($Me_3Sn$ adducts). Only one sharp Me resonance, attributable to adduct(s), was found in each of the experiments, (10)—(15), in Table 2. The sharpness suggested only one species, that is one adduct, in these reactions and these were considered to be the Markownikoff adducts, [$Me_3Sn(CHXCH_2SR')$]. Resonances due to $Me_2Sn$ species were not seen and hence no Me–Sn bond cleavage occurred.

Comparing the [$Me_3Sn(CH=CH_2)$] and [$Ph_3Sn(CH=CH_2)$] reactions, more addition occurred to [$Ph_3Sn(CH=CH_2)$]. The same basic trends were, however, found in each series of reactions. The most reactive sulphenyl halide, toluene-*p*-sulphenyl chloride, gave no adducts and appreciable amounts of the vinyltin compounds were unused, although all the toluenesulphenyl chloride had reacted in both cases. The major sulphur-containing product was di-*p*-tolyl disulphide; there was only a little *p*-tolyl vinyl sulphide. The least electrophilic sulphenyl compound used was $o$-$O_2NC_6H_4SOMe$ and this did not react with [$R_3Sn(CH=CH_2)$]. All the other sulphenyl halides and thiocyanates of intermediate reactivity gave both cleavage and addition products. As a general trend, relatively more addition occurred as the reactivity of R'SX decreased.[*] Some [$Ph_3Sn(CH=CH_2)$] was recovered in its reactions with R'SX of intermediate reactivity. Normally the amount recovered was in the region of 2—6%. However, in the 2,4-$(O_2N)_2C_6H_3SCl$ reaction, 10% [$Ph_3Sn(CH=CH_2)$] was unused as a result of some decomposition of 2,4-$(O_2N)_2C_6H_3SCl$ to disulphide.

Some other comments can be made regarding Tables 1 and 2. First, only slight solvent effects on the products and rates were observed with the [$Ph_3Sn(CH=CH_2)$]–$o$-$O_2NC_6H_4SCl$ reactions. Secondly, the reactions of $o$-$O_2NC_6H_4SSCN$ were considerably slower than those of $o$-$O_2NC_6H_4SCl$. Thus, considering the lack of reactivity of $o$-$O_2NC_6H_4SOMe$, a reactivity sequence for $o$-$O_2NC_6H_4SX$ of $X = Cl > SCN \gg OMe$ was obtained, *i.e.* the same as obtained previously.[12] Quantitative data on reactivities awaits the completion of a kinetic study.



(3)

Returning to the *p*-$MeC_6H_4SCl$ reactions, the fact that all the *p*-$MeC_6H_4SCl$ was used and appreciable amounts of [$R_3Sn(CH=CH_2)$] were recovered suggests that this sulphenyl halide has reacted with some primary product(s) in preference to reaction with [$R_3Sn(CH=CH_2)$]. Confirmation of a secondary reaction was indeed obtained; the adduct [$Ph_3Sn(CHClCH_2SC_6H_4NO_2$-$o$)] was treated with *p*-$MeC_6H_4SCl$ in 1,2-dichloroethane and the products identified were [$Ph_3SnCl$] and *p*-$MeC_6H_4SSC_6H_4NO_2$-$o$. In a sealed vessel in $CDCl_3$, vinyl chloride was also detected from the $^1H$ n.m.r. spectrum. Thus

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[*] The [$Me_3SnCl$] obtained in each reaction (Table 2) need not exclusively come from cleavage of the vinyl–tin bond, some could also arise from cleavage of the adduct (see later).

reaction (3) occurred, probably in a concerted process. A similar mechanism [2] was proposed for the reaction of $[Ph_3Sn(CH_2CH_2SC_6H_4Me\text{-}p)]$ and $o\text{-}O_2NC_6H_4SCl$, which also gave $p\text{-}MeC_6H_4SSC_6H_4NO_2\text{-}o$. Isolation of an adduct from the reaction of $[R_3Sn(CH{=}CH_2)]$ with R'SX implies that R'SX must preferentially react with $[R_3Sn(CH{=}CH_2)]$ than with the adduct.

From the reaction of $o\text{-}O_2NC_6H_4SCl$ with $[Ph_3Sn(CH{=}CH_2)]$ (2 : 1 mol ratio) in refluxing 1,2-dichloroethane, no adduct was recovered, the products being di(*o*-nitrophenyl) disulphide and $[Ph_3SnCl]$. This reaction took a much longer time to go to completion than did the 1 : 1 reaction. When the 2 : 1 reaction (in $CDCl_3$ solution) was conducted in a sealed vessel and followed by $^1H$ n.m.r. spectroscopy over a period of 5 d at 30 ± 1 °C the initial formation of the adduct, $[Ph_3Sn(CHClCH_2SC_6H_4NO_2\text{-}o)]$, its subsequent reaction, and consequent formation of vinyl chloride were apparent. After 19 d some precipitation of di(*o*-nitrophenyl) disulphide had occurred while no vinyl compound was present in the solution. Thus, as well as the

$$[R_3Sn(CH{=}CH_2)] + R'SX \longrightarrow [R_3SnX] + CH_2{=}CHSR' \quad (4)$$

$$[R_3Sn(CH{=}CH_2)] + R'SX \longrightarrow [R_3Sn(CHXCH_2SR')] \quad (5)$$

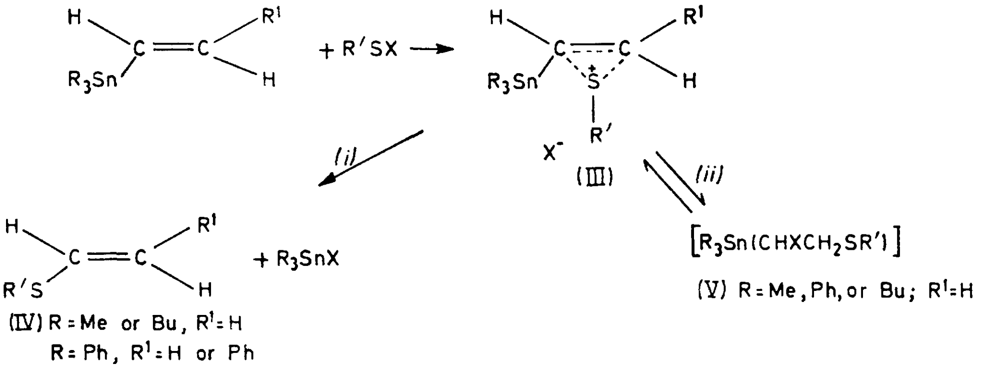
$$[R_3Sn(CHXCH_2SR')] + R'SX \longrightarrow [R_3SnX] + CH_2{=}CHX + R'SSR' \quad (6)$$

secondary reaction of the adduct with $o\text{-}O_2NC_6H_4SCl$, there were other secondary reactions including one with $CH_2{=}CHSC_6H_4NO_2\text{-}o$. No secondary product from $CH_2{=}CHSC_6H_4NO_2\text{-}o$ was collected or even identified from the reaction in 1,2-dichloroethane solution. However, the major product of the $CH_2{=}CHSC_6H_4NO_2\text{-}o$–$p\text{-}MeC_6H_4SCl$ reaction in carbon tetrachloride solution was $p\text{-}MeC_6H_4SCH_2CHClC_6H_4NO_2\text{-}o$ [$\tau$ 4.65 (t) (1 H) and 6.48 (2 H), $J$ 7 Hz]. Attempts to collect and purify this compound by thin-layer or column chromatography on silica or alumina stationary phases failed as decomposition always occurred.

In general, therefore, reactions (4)—(6) involving organotin species occur in the $[R_3Sn(CH{=}CH_2)]$–R'SX systems. Each pair of reactants will show a different selectivity in these reactions and different yields will be obtained. Of the pair of reagents, R'SX is clearly the more important in determining the major products. For example, $[Bu_3Sn(CH{=}CH_2)]$ behaved similarly to $[Me_3Sn(CH{=}CH_2)]$ and $[Ph_3Sn(CH{=}CH_2)]$ in reactions with $p\text{-}MeC_6H_4SCl$ (no adduct formed) and with $o\text{-}O_2NC_6H_4SCl$ (both cleavage and addition in a ratio of 3 : 2).

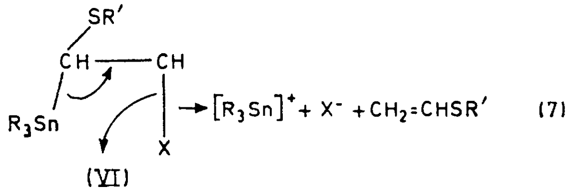
Only one reaction of a substituted vinyltin compound, *trans*-$[Ph_3Sn(CH{=}CHPh)]$, was studied. From its reaction with $o\text{-}O_2NC_6H_4SCl$ only the cleavage product, *trans*-$o\text{-}O_2NC_6H_4SCH{=}CHPh$, was isolated (82% yield). Cleavage of vinyl–tin bonds normally occurs with retention [3a,13] and so the sulphenyl chloride reaction follows this general trend.

*Mechanism of the Primary Reaction between Vinyltin and Sulphenyl Compounds.*—The mechanism is considered to involve formation of episulphonium ions, (III), or ion-pairs analogous to those formed in the reactions of totally organic alkenes.[14] Subsequent reactions of (III) will lead to cleavage or addition products. The more electron withdrawing the R' group, the more will be the positive character of the three-membered ring and hence the greater attraction to the counter-ion, X⁻. It is clear, however, from Tables 1 and 2 that the ratio of addition : cleavage did not increase regularly with electron-withdrawing ability of the R' group.



(*i*), Cleavage, X⁻ attack on the Sn atom; (*ii*), addition, X⁻ attack on the α-carbon atom.

Products from attack on the β-carbon atom were not isolated; it is probable that the product (VI) more readily reacts or decomposes than do the adducts (V).



A reaction, such as (7), is suggested from reactions in silicon chemistry. β-Halogenoalkylsilicon derivatives

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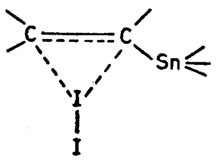
[13] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, 1957, **1**, 158.

[14] D. R. Hogg, 'Mechanisms of Reactions of Sulphur Compounds,' 1970, vol. 5, p. 87.

readily eliminate alkenes and are much less stable than the isomeric α-halogenoalkylsilanes.[15-17] This, plus the fact that β-sulphur-substituted alkylsilanes appear, from the methods of preparation,[18] to be more resistant than are β-halogenoalkylsilanes towards nucleophiles, points to [$R_3M(CHXCH_2SR')$] being less reactive than [$R_3M(CHSR'CH_2)$], certainly for M = Si and probably too for M = Sn. Even the isolated adducts, [$Ph_3Sn(CHXCH_2SR')$], were shown to be somewhat thermally unstable giving [$Ph_3SnX$] + $R'SCH{=}CH_2$ in chloroform solution but not in the less polar carbon tetrachloride solvent. The solvent effects suggest some ionic process, such as the reformation of the episulphonium ion, (III), which then gives the aryl vinyl sulphide. The reaction of [$Ph_3Sn(CH_2CH_2OH)$] with acetic acid also leads to elimination of an alkene (ethylene).[19]

The episulphonium ion, (III), will not allow rotation of the central carbon–carbon bond and hence retention of configuration in the cleaved vinyl fragment will be maintained, as occurs in the *trans*-[$Ph_3Sn(CH{=}CHPh)$] reaction. To account for this compound giving only cleavage products on reaction with *o*-$O_2NC_6H_4SCl$ while [$Ph_3Sn(CH{=}CH_2)$] also gave some addition product, either the steric or the electron-withdrawing effect of the phenyl group could be involved. Previous studies have shown phenyl–tin bonds[2,20] to be unreactive towards R'SX and hence it is not too surprising that any reaction of [$Ph_3Sn(CH{=}CH_2)$] occurs within the vinyltin grouping and not at the phenyl–tin bond. Iodine and bromine react much more readily than do R'SX with aryl–tin bonds; for example iodine reacts with tetraphenyltin.[21] To account for the cleavage sequences for $I_2$ (phenyltin > vinyltin) and the reverse for R'SX, either $I_2$ has a relatively depressed or R'SX a relatively enhanced reactivity towards vinyl–tin bonds. The mechanism for the iodine–vinyltin reaction[3b] is also considered to involve a cyclic structure (VII).



(VII)

*Adducts*.—M.p. and Mössbauer data at 77 K for the adducts are shown in Table 3. The isomer shifts were similar in value and are typical for triphenyltin derivatives; the quadrupole splittings for all adducts were small and are unusual for tetraorganotin compounds. Compounds with four carbon–tin bonds normally have zero quadrupole splittings[22] except where intramolecular co-ordination as in [$R_3Sn(CH_2COMe)$] can occur[23] and so change the geometry around tin from tetrahedral. It is possible that intramolecular co-ordination occurs in the adducts. However, it is also possible that considerable steric effects might arise as a result of the two substituents in the alkyl group. In either case, the geometry would be changed from a tetrahedral arrangement and an electric-field gradient created. It is of interest to note that such effects are absent in [$Ph_3Sn(CH_2I)$], [$Ph_3Sn(CH_2SR')$], and [$Ph_3Sn(CH_2CH_2SR')$].[2]

TABLE 3

Analytical and other data of [$(4\text{-Y-}2\text{-}O_2NC_6H_3SCH_2CHX)SnPh_3$]

| | | | Mössbauer (mm s$^{-1}$) [a] at 77 K | | Analyses [b] (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Y | X | M.p. ($\theta_c$/°C) | δ | $\Delta E_q$ | C | H | Cl | N | S |
| H | Cl | 115—116 | 1.32 | 0.51 | 55.9 (55.6) | 4.0 (3.9) | 6.1 (6.3) | | 5.8 (5.6) |
| H | SCN | 123—125 | 1.32 | 0.76 | 55.3 (55.1) | 4.2 (3.9) | | 4.9 (4.7) | 11.1 (10.7) |
| Me | Cl | 139—141 | 1.29 | 0.46 | 56.0 (55.8) | 4.4 (4.2) | 6.2 (6.1) | 2.4 (2.4) | 5.4 (5.5) |
| $NO_2$ | Cl | 141—142 | 1.30 | 0.55 | 50.9 (51.1) | 3.7 (3.4) | 6.1 (5.8) | | 5.7 (5.6) |

[a] Relative to $SnO_2$. [b] Calculated values are given in parentheses.

No parent ions were seen in the mass spectra of any of the adducts at 70 eV.* In all the mass spectra, the highest tin-containing ions were [$Ph_3SnSR'$]$^+$, indicating that one fragmentation involved loss of the central $CH_2CHX$ units. One other general breakdown gave [$Ph_3SnX$] and $CH_2{=}CHSR'$. All the ions present in the mass spectra of [$Ph_3Sn(SR')$], [$Ph_3SnX$], and $CH_2{=}CHSR'$ were apparent in the mass spectra of [$Ph_3Sn(CHXCH_2SR')$].

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* 1 eV ≈ $1.60 \times 10^{-19}$ J.

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The $^1$H n.m.r. spectra of the adduct [Ph$_3$Sn(CHXCH$_2$SR′)] were complex in the region τ 5.5—6.7, that is where the central CHCH$_2$ unit resonates. Basically, however, the 60 MHz spectra at 30 °C of the adducts where X = Cl consisted of triplets centred at 5.66—5.67 [*J* 8 Hz (1 H)] and doublets centred at 6.25—6.35 p.p.m. (1 H); each of the latter doublets could be just resolved into further doublets. For X = SCN, the CHCH$_2$ resonances were more compact and in the region τ 6.1—6.7. Solvent and temperature effects were noted particularly for the CH$_2$ resonances of [(4-Me-2-O$_2$NC$_6$H$_3$SCH$_2$CHCl)SnPh$_3$].

*Adduct Reactions.*—Most reactions of electrophiles were studied with the adduct [(4-Me-2-O$_2$NC$_6$H$_3$SCH$_2$CHCl)SnPh$_3$]. Two different types of reaction were observed: by sulphenyl halides, as already has been described, to produce disulphides and vinyl halides [equation (3)], and by the other electrophiles, iodine, bromine, trifluoroacetic acid, and mercury(II) salts, which all initially cleaved a phenyl–tin bond [equations (8)—(10)] (R′ = 4-Me-2-O$_2$NC$_6$H$_3$). No phenyl–tin bond cleavage occurred in the sulphenyl halide reactions. Thus, again a difference is seen in the reactions of sulphenyl halides and other electrophiles with organometallic compounds. The volatile products, PhBr, PhI, and PhH, from equations (8) and (9) were confirmed by g.l.c. and formed in 74, 78, and 102% yield respectively. Phenylmercury chloride was precipitated from the mercury(II) chloride reaction in 90% yield; this was also produced in the mercury(II) acetate reaction (50%).

$$[\mathrm{Ph_3Sn(CHClCH_2SR')}] + \mathrm{X_2} \longrightarrow [\mathrm{Ph_2XSn(CHClCH_2SR')}] + \mathrm{PhX}\ (\mathrm{X = Br\ or\ I}) \tag{8}$$

$$[\mathrm{Ph_3Sn(CHClCH_2SR')}] + \mathrm{CF_3CO_2H} \longrightarrow [\mathrm{Ph_2(CF_3CO_2)Sn(CHClCH_2SR')}] + \mathrm{PhH} \tag{9}$$

$$[\mathrm{Ph_3Sn(CHClCH_2SR')}] + \mathrm{HgCl_2} \longrightarrow [\mathrm{Ph_2ClSn(CHClCH_2SR')}] + \mathrm{PhHgCl} \tag{10}$$

$$[\mathrm{Ph_3Sn(CHClCH_2SR')}] + \mathrm{Hg[O_2CMe]_2} \longrightarrow \mathrm{PhHgCl} \tag{11}$$

The bromine reaction was very much faster than that of iodine.

The initial products [Ph$_2$ZSn(CHClCH$_2$SR′)] (Z = Cl, Br, I, or CF$_3$CO$_2$) are not stable and could not be isolated in a pure state. Decomposition occurred on leaving in solution and particularly on silica columns or plates and led to diphenyltin dihalides and aryl vinyl sulphides, CH$_2$=CHSR′. The decomposition of all [Ph$_2$ZSn(CHClCH$_2$SR′)] clearly paralleled that of [Ph$_3$Sn(CHClCH$_2$SR′)]. Details of the decompositions are given in the Experimental section. The rates of decomposition of [Ph$_2$BrSn(CHClCH$_2$SC$_6$H$_3$NO$_2$-2-X-4)] were in the sequence X = Me > H > NO$_2$.

In contrast to the reaction with electrophiles, there were no reactions of the adducts with such nucleophiles as Na[OEt] and Na[SC$_6$H$_4$Me-*p*].

## EXPERIMENTAL

$^1$H N.m.r. spectra were recorded on Varian HA 100D and Perkin-Elmer R12A instruments; g.l.c. was run on a Perkin-Elmer F11 instrument, Mössbauer spectra being recorded as described [24] previously and obtained by Dr. R. A. Howie; mass spectra were determined using an A.E.I. H30 instrument. Solvents were dried and stored over calcium hydride. They were distilled prior to use.

The following compounds were prepared by published procedures: toluene-*p*-sulphenyl chloride,[25] *o*-nitrobenzenesulphenyl chloride,[26] methyl *o*-nitrobenzenesulphenate,[26] *o*-nitrobenzenesulphenyl thiocyanate,[27] 4-methyl-2-nitrobenzenesulphenyl chloride,[12a,28] 2,4-dinitrobenzenesulphenyl chloride,[29] and tributyl-, trimethyl-, and triphenyl-vinyltin.[30] 2-Nitro-4-trifluoromethylbenzenesulphenyl chloride was a gift from Dr. D. R. Hogg and Mr. A. Robertson. All compounds had physical constants in agreement with published values.

trans-1-*Phenyl-2-triphenylstannylethylene*, trans-[Ph$_3$Sn(CH=CHPh)].—This compound was prepared by careful addition of [Ph$_3$SnCl] to the Grignard reagent from PhCH=CHBr in tetrahydrofuran (thf). The reaction mixture was heated under reflux for 2 h. The solvent was removed by evaporation and diethyl ether and an aqueous ammonium chloride solution added. The ether layer was collected, dried, and the solvent removed. The residue was recrystallised from light petroleum (b.p. 60—80 °C); it had m.p. 118—120 °C (lit.,[31] 119—120 °C).

*Reactions of Triphenylvinyltin and Sulphenyl Halides and Thiocyanates.*—(a) 1 : 1 *Mol ratio, product isolation.* Triphenylvinyltin and the sulphenyl compound were dissolved in an aprotic solvent and heating was applied, if necessary, to bring the reaction to completion, that is total consumption of the sulphenyl compound, as shown by t.l.c. After any cooling, the solvent was removed to leave yellow oils or oily solids. For all systems, except the toluene-*p*-sulphenyl chloride ones, these residues were crystallised from ethanol. The yellow solid crystalline materials were the adducts and some of their physical data are given in Table 3. The toluene-*p*-sulphenyl chloride residues and all the filtrates from the crystallisation were chromatographed on alumina columns using light petroleum (b.p. 60—80 °C)–CHCl$_3$ (1 : 4) as eluant. Unchanged triphenylvinyltin, diaryl disulphide, and/or aryl vinyl sulphide were thereby separated. Yields are given in Table 1. 2-Nitrophenyl vinyl sulphides were purified by chromatography (t.l.c. and columns). There was insufficient material to obtain the b.p. of the liquid sulphide. Mass-spectral, analytical, and $^1$H n.m.r. data confirmed their structure (Table 4).

(b) *Triphenylvinyltin and* o-*nitrobenzenesulphenyl chloride* (1 : 2 *mol ratio*). Triphenylvinyltin (1.131 g, 3 mmol) and *o*-O$_2$NC$_6$H$_4$SCl (1.134 g, 6 mmol) were dissolved in 1,2-dichloroethane (40 cm$^3$) and the solution heated under reflux until all the sulphenyl halide was consumed. After evaporation of the solvent, the residue, which contained no

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vinyl components, was washed with a little $CHCl_3$. The insoluble portion, di(*o*-nitrophenyl) disulphide (0.39 g), was collected. The filtrate on evaporation gave a residue which was washed with light petroleum. The insoluble portion, [$Ph_3SnCl$], was recrystallised from light petroleum, 0.62 g (55%), m.p. 105 °C (lit.,[32] 106 °C). More disulphide (0.48 g) was obtained from the combined filtrates and washings by column chromatography. Total di(*o*-nitrophenyl) disulphide collected was 0.87 g (94%), m.p. 191 °C (lit.,[33] 192—195 °C).

(c) *Triphenylvinyltin and* o-*nitrobenzenesulphenyl chloride* (1 : 2 *mol ratio in a sealed vessel*). Triphenylvinyltin (57 mg, 0.15 mmol) and *o*-$O_2NC_6H_4SCl$ (57 mg, 0.30 mmol) were added to cold $CDCl_3$ (1 $cm^3$) in a n.m.r. tube and the tube sealed. The solution was maintained at 30 °C and the reaction followed by n.m.r. spectroscopy for 19 d. The initial formation of *o*-nitrophenyl vinyl sulphide and the adduct, their reaction, and consequent formation of vinyl chloride were evident within the first few days. Later, even these vinyl products had further reacted and after 19 d no vinyl protons were present in the n.m.r. spectrum.

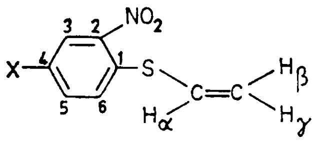
*Reaction of* trans-1-*Phenyl*-2-*triphenylstannylethylene and* 4-*Methyl*-2-*nitrobenzenesulphenyl Chloride*.—A solution of *trans*-[$Ph_3Sn(CH{=}CHPh)$] (1.36 g, 3 mmol) and 4-Me-2-$O_2NC_6H_3SCl$ (0.61 g, 3 mmol) in 1,2-dichloroethane (25 $cm^3$) was heated under reflux for 1.5 h, after which time t.l.c. showed all the sulphenyl chloride had reacted. The solvent was removed to leave a residue which was crystallised from ethanol as *trans*-$PhCH{=}CHSC_6H_3Me$-4-$NO_2$-2, m.p. 130—132 °C, 0.59 g (82%); $^1H$ n.m.r. spectrum (60 MHz) of $PhCH_\beta{=}CH_\alpha SC_6H_3Me$-4-$NO_3$-2 $\tau$ 1.97 (1 H), 2.62 (8 H, 2.91 ($H_\alpha$), 3.19 ($H_\beta$) ($J$ 15 Hz), and 7.60 (3 H). The filtrate was evaporated and the residue was crystallised from ethanol as [$Ph_3SnCl$], m.p. 104 °C (lit.,[32] 106 °C), 0.65 g (56%).

*Reactions of Trimethylvinyltin and Sulphenyl Compounds.*—(*a*) Equimolar amounts of [$Me_3Sn(CH{=}CH_2)$] and R′SX (0.3—0.4 mmol) were dissolved in $CDCl_3$ (1 $cm^3$). The solutions were left until all the R′SX had reacted (immediately for *p*-$MeC_6H_4SCl$, within a few hours for all the other R′SCl, and overnight for *o*-$O_2NC_6H_4SSCN$) and then the $^1H$ n.m.r. spectra were obtained. The distinct resonances for [$Me_3Sn(CH{=}CH_2)$] ($\tau$ 9.87), [$Me_3SnCl$] (9.34), [$Me_3SnNCS$] (9.37), and the adducts (9.67—9.74) enabled the relative amounts of the trimethyltin species in each solution to be calculated (Table 2). Allowances for the Sn–H couplings were made, since there were some overlap of a main $Me_3Sn$ resonance with such couplings of another $Me_3Sn$ moiety. All the adducts had $^{117}Sn$–$^1H$ and $^{119}Sn$–$^1H$ coupling constants of 53 and 55 Hz; the chemical shifts of [$Me_3Sn(CHXCH_2SC_6H_3NO_2$-2-Y-4)] were $\tau$ 9.67 (Y = H, X = SCN) and 9.74, 9.74, 9.71, and 9.70 for X = Cl, Y = Me, H, $CF_3$, and $NO_2$ respectively.

(*b*) A solution containing [$Me_3Sn(CH{=}CH_2)$] (38 mg, 0.2 mmol) and *o*-$O_2NC_6H_4SCl$ (76 mg, 0.4 mmol) in $CDCl_3$ (1 $cm^3$) was made up. The $^1H$ n.m.r. spectra, after the reaction was completed, indicated that the only tin species present was [$Me_3SnCl$].

TABLE 4

Analytical and $^1H$ n.m.r. data for 2-nitrophenyl vinyl sulphides



| | Analysis [a](%) | | | | $^1H$ N.m.r. data [b] | | | | | | | J(cis) | J(trans) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | C | H | N | S | $H^3$ | $H^4$ | $H^5$ | $H^6$ | $H_\alpha$ | $H_\beta$ | $H_\gamma$ | Hz | |
| H | 52.8<br>(53.0) | 4.1<br>(3.9) | 7.8<br>(7.7) | 17.8<br>(17.7) | 1.84<br>($J_o$ 8)<br>($J_m$ 2) | 2.35—2.80 | | | 3.44 | 4.16 | 4.25 | 9 | 17 |
| Me [d] | 55.7<br>(55.4) | 4.9<br>(4.7) | 7.6<br>(7.2) | 16.5<br>(16.4) | 2.04<br>($J_m$ 2) | | 2.66 | | 3.46 | 4.20 | 4.29 | 9 | 17 |
| $NO_2$ [e] | 42.7<br>(42.5) | 3.0<br>(2.7) | 12.2<br>(12.4) | 14.1<br>(14.2) | 0.97<br>($J_m$ 2) | | 1.66<br>($J_o$ 9)<br>($J_m$ 2) | 2.36<br>($J_o$ 9) | 3.29 | 3.99 | 4.01 | 9 | 17 |

[a] Calculated values are given in parentheses. [b] In $CDCl_3$ solution, $\tau$ values relative to $SiMe_4$. [c] $J(gem)$ 0. [d] M.p. 32—32.5 °C, $\tau(CH_3)$ 7.62. [e] M.p. 75—76 °C.

*Reaction of* o-*Nitrophenyl Vinyl Sulphides and Toluene*-p-*sulphenyl Chloride*.—Equimolar amounts of *o*-$O_2NC_6H_4$-$SCH{=}CH_2$ and *p*-$MeC_6H_4SCl$ (2.1 mmol) were dissolved in methylene chloride (10 $cm^3$). The solution was left overnight at room temperature. The solvent was removed to leave a residue. $^1H$ N.m.r. spectrum (60 MHz): $\tau$ 7.71 (s) (3 H); 6.48 (d) (2 H); 4.63 (t) (1 H) ($J$ 7 Hz); 2.4—3.0 (m) (7 H); and 1.93 (d of d) (1 H). This suggested the residue was 2-$O_2NC_6H_4SCHClCH_2SC_6H_4Me$-*p*. The product slowly darkened on standing and decomposed on silica.

*Reactions of the Adducts.*—(a) *Action of heat on* [(4-Me-2-$NO_2C_6H_3SCH_2CHCl)SnPh_3$] *in* $CDCl_3$. A solution of [(4-Me-2-$NO_2C_6H_3SCH_2CHCl)SnPh_3$] (5 mg) in $CDCl_3$ (0.3 $cm^3$) in a sealed tube was heated at 100 °C. $^1H$ N.m.r. spectra taken at various times showed a gradual decrease in the adduct absorption at $\tau$ 6.35 (d) and 5.70 (t), and an increase in the vinyl absorption of 4-Me-2-$NO_2C_6H_3SCH{=}CH_2$ in the region $\tau$ 3.25—4.4; decompositions at 3.5, 5.5, and 23 h were 30, 50, and 90% complete respectively. A similar concentration in carbon tetrachloride was unaffected on heating at 100 °C for 48 h.

(b) *With sulphenyl halides.* (i) The compound [(*o*-$O_2NC_6H_4SCH_2CHCl)SnPh_3$] (0.566 g, 1 mmol) and *p*-$MeC_6H_4SCl$ (0.158 g, 1 mmol) were dissolved in 1,2-dichloroethane (30 $cm^3$) and left overnight at room temperature. Only two products were shown to be present by t.l.c., [$Ph_3SnCl$] and *o*-$O_2NC_6H_4SSC_6H_4Me$-*p*. The latter was

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[32] Ref. 7*a*, p. 59.

[33] M. T. Bogert and A. Stull, *Org. Synth.*, 1964, **1**, 220.

collected and shown to be identical with an authentic sample.[34] (ii) The compound [($o$-$O_2NC_6H_4SCH_2CHCl$)$SnPh_3$] (57 mg, 0.1 mmol) and $p$-$MeC_6H_4SCl$ (16 mg, 0.1 mmol) were each dissolved in $CDCl_3$ (0.2 $cm^3$). The two solutions were mixed in an n.m.r. tube immersed in liquid nitrogen. The tube was immediately sealed. After 30 min, in which time reaction was completed, the $^1H$ n.m.r. spectra showed the presence of vinyl protons corresponding to those of an authentic sample of vinyl chloride. An approximately equimolar amount of vinyl chloride was obtained from the adduct.

(c) *With bromine, reaction of* $Br_2$ *and* [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$]. (i) To a solution of $Br_2$ (61.5 mg, 0.38 mmol) in $CHCl_3$ (4 $cm^3$) was added [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (223 mg, 0.38 mmol). The colour change was immediate. After 2 h, toluene (14 mg) was added to the solution as a reference and a g.l.c. analysis was obtained [column 2 m × 0.5 in o.d., silicon gum rubber E 301 on chromosorb G AW-DMCS (2.5 : 97.5) 80—100 mesh]. From the peak areas for PhBr and PhMe, and taking into account the response factors, the yield of PhBr was calculated to be 74%. (ii) 0.25 $cm^3$ Of a bromine solution (84.8 mg) in $CDCl_3$ (1 $cm^3$) was added to [(4-Me-2-$O_2NC_6H_3CH_2CHCl$)$SnPh_3$] (76 mg, 0.13 mmol) in $CDCl_3$ (0.25 $cm^3$) solution and the vessel sealed. $^1H$ N.m.r. spectra at 30 °C were recorded at various times. The bromine reacted immediately. The $^1H$ n.m.r. spectrum taken as quickly as possible after sealing the tube showed a small absorption in the vinyl region (vinyl bromide) with only minor changes in the $\tau$ 5.5—6.5 region. Over a period of time, subsequent and substantial changes occurred, namely loss of intensity of absorption at $\tau$ 5.5—6.5 and the consequent appearance of vinyl absorption (of 4-Me-2-$O_2NC_6H_3SCH{=}CH_2$). There was also a more subtle change in the chemical shift of the Me group from $\tau$ 7.69 of the reactant adduct to 7.60 of the product vinyl sulphide. After 3 d at 30 °C, *ca.* 50% conversion had occurred. The completion of the reaction was hastened by heating the sealed vessel at 100 °C. On opening the vessel the vinyl bromide was lost while the aryl vinyl sulphide remained and was collected by t.l.c. The n.m.r. spectra of the final reaction showed some residual absorption at $\tau$ 6.30.

(d) *Iodine and* [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$]. (i) Iodine (25 mg, 0.1 mmol) and [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (58 mg, 0.1 mmol) were dissolved in 1,2-dichloroethane. After the iodine had reacted (20 min at room temperature), toluene (20 mg) was added to the reaction solution and the g.l.c. analysis obtained (using the same column as used for the $Br_2$ reaction). From the peak areas for PhI and PhMe, and taking into account the response factors, a yield for PhI of 78% was calculated. The solvent was removed from the reaction solution, and the residue was chromatographed, first using silica columns and secondly on silica thin-layer plates [light petroleum (b.p. 60—80 °C)–$CHCl_3$ (4 : 1) as eluant]. The compound 4-Me-2-$O_2NC_6H_3CH{=}CH_2$ was obtained, 13 mg (70%). (ii) Iodine (63 mg, 0.25 mmol) and [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (145 mg, 0.25 mmol) were dissolved in $CDCl_3$ and immediately after the iodine had been decolourised the $^1H$ n.m.r. spectrum was obtained. No vinyl protons were observed.

(e) *Trifluoroacetic acid and* [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$]. (i) Trifluoroacetic acid (12.7 mg, 0.11 mmol) was dissolved in $CDCl_3$ (1 $cm^3$) and added to a solution of [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (63.4 mg, 0.11 mmol) in $CDCl_3$ (1 $cm^3$). The mixture was left for 1.5 d. The $^1H$ n.m.r. spectra indicated the presence of 4-Me-2-$O_2NC_6H_3SCH{=}CH_2$ and the absence of any adduct absorption. To the solution was added toluene (6.2 mg) and the g.l.c. analysis obtained. The yield of PhH was calculated to be 102%. (ii) The reaction between $CF_3CO_2D$ (25 mg, 0.22 mmol) and [(4-Me-2-$NO_2C_6H_3SCH_2CHCl$)$SnPh_3$] (127 mg, 0.22 mmol) in $CDCl_3$ (2 $cm^3$) was followed by $^1H$ n.m.r. spectroscopy. Within minutes of mixing, vinyl and PhD absorption was observed as were changes in the alkyl absorption of the adduct. The formation of PhD appeared not to be completed immediately but continued to occur for some time after the start of the reaction.

(f) *Mercury*(II) *Salts.* (i) *Mercury*(II) *chloride and* [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$]. Solutions of [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (0.870 g, 1.5 mmol) in boiling ethanol (100 $cm^3$) and $HgCl_2$ (0.406 g, 1.5 mmol) in ethanol (30 $cm^3$) were mixed. The resulting solution was heated under reflux for 1 h, cooled, and the solution concentrated. On leaving overnight, PhHgCl crystallised out, 0.415 g, m.p. 249—253 °C (lit.,[35] 252 °C). The filtrate was shown to contain 4-Me-2-$NO_2C_6H_3SCH{=}CH_2$.

(ii) *Mercury*(II) *acetate and* [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$]. A solution of [(4-Me-2-$O_2NC_6H_3SCH_2CHCl$)$SnPh_3$] (58 mg, 0.1 mmol) and $Hg[O_2CMe]_2$ (32 mg, 0.1 mmol) in $CDCl_3$ was made up and the progress of the reaction followed by $^1H$ n.m.r. spectroscopy over a period of 13 d at 30 °C. Changes in the $\tau$ 5.5—6.5 region occurred first; the vinyl absorption increased much more slowly with concurrent loss of intensity of the adduct's alkyl absorption at $\tau$ 5.5—6.5 (30—35% formation of 4-Me-2-$O_2NC_6H_3SCH{=}CH_2$ after 7 d). Some PhHgCl was precipitated and collected (0.15 g after 13 d).

I thank D. W. Grant for aid with the experiments.

[4/2657 *Received, 20th December,* 1974]

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