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SULPHUR SUBSTITUTED ORGANOMETALLIC COMPOUNDS

III*. REACTIONS OF $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* WITH SOME ELECTROPHILIC REAGENTS

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Summary

Two distinct types of reactions of electrophiles, EN, with $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (I) have been established. Thus I_2 and $HgCl_2$ cleave the phenyl—tin bond:

$$I + EN \rightarrow Ph_2(N)SnCH_2CH_2SC_6H_4Me\text{-}p + PhE$$

(E = I, N = I; E = HgCl, N = Cl)

while from the reactions of Br_2 and MeI, as well as of ArSCl, as previously reported, ethylene is evolved:

$$I + EN \rightarrow Ph_3SnN + CH_2{=}CH_2 + ESC_6H_4Me\text{-}p$$

(E = Br, N = Br; E = Me, N = I)

Introduction

The preparation and some physical properties of [2-(*p*-tolylthio)ethyl]-triphenyltin, $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* [2], as well as its reaction with *o*-nitrobenzenesulphenyl chloride, *o*-$NO_2C_6H_4SCl$, [3] (eqn. 1) have been described.

$$Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p + o\text{-}NO_2C_6H_4SCl \rightarrow Ph_3SnCl + CH_2{=}CH_2 + o\text{-}NO_2C_6H_4SSC_6H_4Me\text{-}p \quad (1)$$

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* For Part II, see ref. 1.

As indicated in eqn. 1, ethylene is eliminated in the reaction of I with the sulphenyl chloride. Elimination of ethylene has been shown to occur on reaction of another β-substituted alkyltin compound, $Ph_3SnCH_2CH_2OH$, with acetic acid [4]. There are also numerous examples of ethylene elimination on reaction of β-halogenoalkylsilicon derivatives [5-7]. We have recently demonstrated [1] that reactions of sulphenyl chlorides, Ar'SCl (Ar' = p-MeC_6H_4; 2-NO_2-4-XC_6H_3, X = H, Me, NO_2) with $Ph_3SnCHClCH_2SAr$ (Ar = 2-NO_2-4-XC_6H_3, X = H, Me, NO_2) (II) also lead to elimination of an alkene unit, viz. vinyl chloride (eqn. 2*).

$$\underset{\text{(II)}}{Ph_3SnCHClCH_2SAr} + Ar'SCl \rightarrow Ph_3SnCl + ArSSAr' + CH_2{=}CHCl \qquad (2)$$

The sulphenyl chloride reactions with II are however not only in contrast to the reactions of II with halogens, proton acids and mercuric salts (eqns. 3-5) but also to the thermal decomposition of II in chloroform solution (eqn. 6). In none of these reactions is vinyl chloride evolved, although in the thermal decompositions vinyl sulphides were formed. In all the reactions with these electrophiles, the preferred sites of reaction were the phenyl—tin bonds.

$$II + X_2 \rightarrow Ph_2(X)SnCHClCH_2SAr + PhX \qquad (3)$$

(X = Br, I)

$$II + CF_3CO_2H \rightarrow Ph_2(CF_3CO_2)SnCHClCH_2SAr + PhH \qquad (4)$$

$$II + HgCl_2 \rightarrow Ph_2(Cl)SnCHClCH_2SAr + PhHgCl \qquad (5)$$

$$II \xrightarrow{CHCl_3/\Delta} Ph_3SnCl + CH_2{=}CHSAr \qquad (6)$$

Further differences between sulphenyl halides, ArSX, and other electrophiles have been found in reactions with $Ph_3SnCH{=}CH_2$. Thus, ArSX reacted with $Ph_3SnCH{=}CH_2$ within the vinyltin grouping, giving either vinyl—tin bond cleavage products or addition products (II), while other electrophiles, such as halogens and proton acids, preferentially cleaved the phenyl—tin bond [1].

In this paper, we report on reactions of Br_2, I_2, $HgCl_2$ and MeI with I and compare the products obtained with those produced in the reaction of I with ArSCl [3] and in the corresponding reactions of II.

Results and discussion

The reactions of I with electrophiles are listed in eqns. 7-10 and they clearly fall into two distinct groupings; ethylene elimination occurring on reaction with MeI and Br_2 (as well as on reaction with ArSCl) and phenyl—tin

$$I + MeI \rightarrow Ph_3SnI + MeSC_6H_4Me\text{-}p + CH_2{=}CH_2 \qquad (7)$$

$$I + Br_2 \rightarrow Ph_3SnBr + BrSC_6H_4Me\text{-}p + CH_2{=}CH_2 \qquad (8)$$

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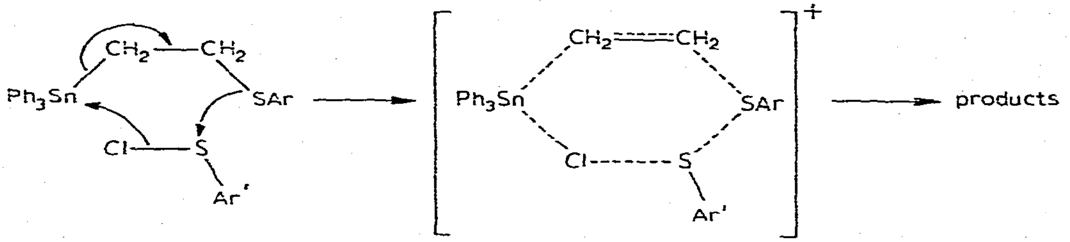
* In the mass spectra of both $Ph_3SnCH_2CH_2SAr$ [2] and $Ph_3SnCHClCH_2SAr$ [1], the largest M^+ were $[Ph_3SnSAr]^+$, i.e. loss of $CH_2{=}CH_2$ and $CHCl{=}CH_2$ respectively.

$$I + I_2 \rightarrow Ph_2(I)SnCH_2CH_2SC_6H_4Me\text{-}p + PhI \qquad (9)$$

$$I + HgCl_2 \rightarrow Ph_2(Cl)SnCH_2CH_2SC_6H_4\text{-}p + PhHgCl \qquad (10)$$

bond cleavage on reaction with I_2 and $HgCl_2$. Such a division in the type of reaction is clearly not based on the reactivities of the electrophiles*. A case could be made out for the division to be based on steric reasons, since the three smallest electrophiles, ArSCl, MeI and Br_2, all gave ethylene elimination, while the two largest, I_2 and $HgCl_2$, gave the other reaction type. However this is thought to be simply coincidental and that the basic reason for the difference lies elsewhere. Whatever the reason, ArSCl, among the electrophiles studied, did not lead to a unique reaction with I as it did with both II and $Ph_3SnCH{=}CH_2$.

The mechanism for the ethylene elimination reaction of $o\text{-}NO_2C_6H_4SCl/I$ could either be considered as a concerted process involving a cyclic transition state (III; Ar′ = $o\text{-}NO_2C_6H_4$; Ar = $p\text{-}MeC_6H_4$) or a process involving an initial interaction of the two sulphur atoms leading to the sulphonium ion (IV) or a related ion-pair, followed by a nucleophilic attack of chloride ion on IV to give an overall consecutive rather than concerted reaction. Some basis for the sulphonium ion mechanism comes from reactions of sulphenyl chlorides, RSX, with totally organic sulphides, $R'SR^2$, in which the products were R′SSR and others derived from the carbonium ion, $[R^2]^+$ [8-11]. In particular from a kinetic study of the reaction of PhMeCHSMe with $PhSCl$, the rate limiting step was the formation of the sulphonium ion, $[(PhMeCH)MeSSPh]Cl^-$ [9b]. However, a concerted mechanism cannot be totally discarded for the reaction of $Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p$, since the tin atom is ideally placed for such a reaction as well as being sufficiently reactive towards nucleophiles. Of course, a spectrum



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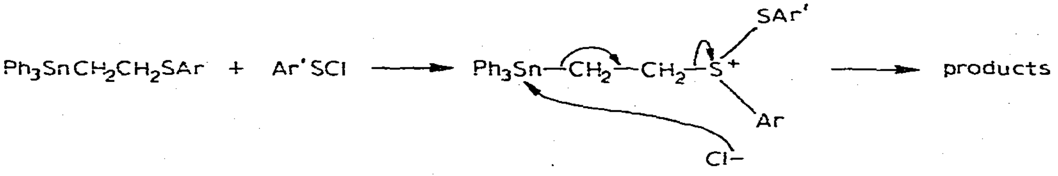

(IV)

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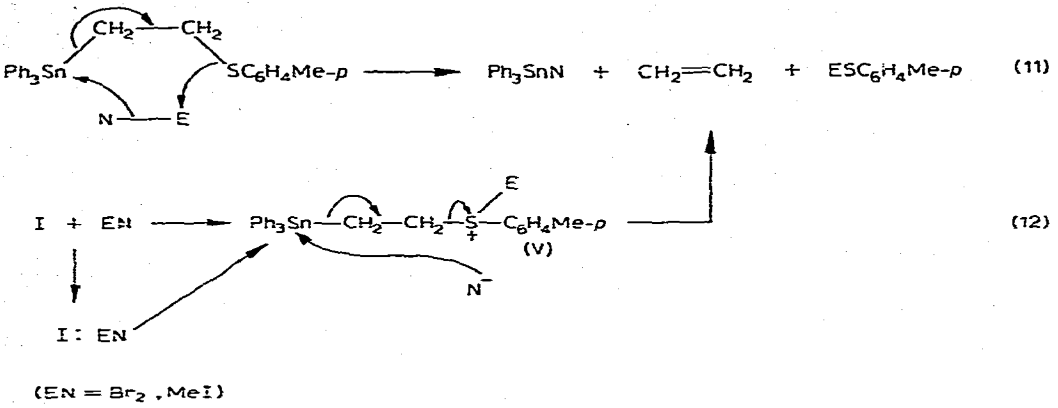
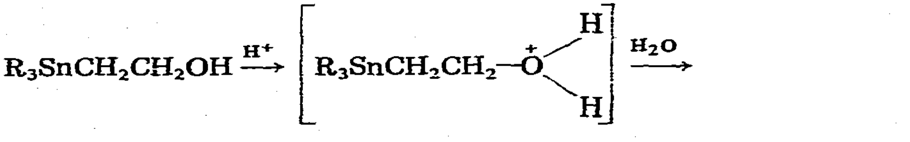
* However the rates of reaction of Br_2, I_2 and MeI, for example, do follow the generally considered order of reactivity, viz. $Br_2 > I_2 >$ MeI.

of mechanisms between fully consecutive and concerted extremes could be envisaged.

Related mechanisms can be considered for the other reactions of I which lead to ethylene elimination:



There is some evidence that a positive (as in V) or even a partial positive charged substituent on the β-carbon of an alkyltin compound results in that alkyl—tin bond becoming labile; for example, Petersen et al. have described reactions of $Ph_3SnCH_2CH{=}CH_2$ with electrophiles, E^+, which give products derived from Sn—CH_2 bond cleavage. In these reactions potential or actual carbonium ions, $R_3SnCH_2CH_2\overset{+}{C}HCH_2E$, were produced and these led to fragmentation of the tin—carbon bonds and formation of cyclopropylcarbinyl compounds [12]. Another example is the acid promoted 1,2-elimination from $R_3SnCH_2CH_2OH$, in which another positively charged substituent on a β-carbon is a possiblity [4].

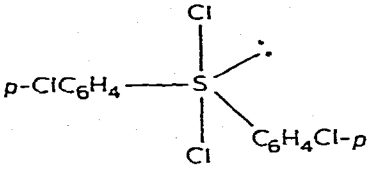


$$R_3SnCH_2CH_2OH \xrightarrow{H^+} \left[R_3SnCH_2CH_2{-}\overset{+}{O}\begin{matrix} \diagup H \\ \diagdown H \end{matrix} \right] \xrightarrow{H_2O} R_3SnOH + CH_2{=}CH_2 + H_2O + H^+ \qquad (13)$$

To these reactions, we can now add those of ArSCl, MeI and Br_2 with I.

From previous work, both MeI and *o*-$NO_2C_6H_4SCl$ are insufficiently electrophilic to react directly with phenyl—tin bonds and thus any reaction of these species would have to occur elsewhere in the organotin molecule. As simple alkyl groups are even less reactive than are aryl groups towards electrophiles, involvement of MeI or *o*-$NO_2C_6H_4SCl$ with the sulphur atom of I must be a requisite for reaction. It is of interest to note that MeI did not react with II within the same time used for reaction with I. The sulphur atom in II must be less basic than in I and so would less readily act as a donor towards MeI and hence the sulphonium ion would not be so easily formed.

Unlike MeI and ArSCl, Br_2 (and also I_2 and $HgCl_2$) has been shown to cleave phenyl—tin bonds [13]. However, the predominant bromine reaction with I is at the functionally substituted alkyl group. The interaction of the sulphur and bromine must be sufficiently strong and of a type to limit the reaction to the alkyl group and to eliminate reaction at the phenyl—tin bond. Complexes of halogens, particularly Cl_2 and Br_2, with sulphides are well established [14] and, in fact, a crystal structure of one complex, $(p\text{-}C_6H_4)_2SCl_2$ (VI) has been determined [15].



(VI)

Sulphide-bromide complexes, $R'R^2SBr_2$, most probably have related structures. Their ionisation to $[R'R^2SBr]^+Br^-$ has been considered in the mechanism for solvolysis [16] and in bromination of alkyl phenyl sulphides [17]. Thus, there is some basis for the mechanism shown in eqn. 12 (E = N = Br).

The difference in the sites of reaction of I and of II with Br_2 (eqns. 3 and 8) is again accounted for by the reduced basicity or donor ability of the sulphur atom in II, which reduces, if not totally suppresses the interaction between Br_2 and the sulphur atom with the result that reaction occurs at the phenyl—tin bond in II.

Iodine forms much weaker complexes with sulphides than does bromine. This would severely limit the reaction in the substituted alkyl group of I and as iodine is sufficiently reactive to cleave phenyl—tin bonds, such cleavage is more probable than in the bromine reaction. This is borne out and in fact no ethylene elimination occurred.

Reaction with $HgCl_2$ also led exclusively to phenyl—tin bond cleavage. There are numerous examples of mercuric chloride complexes with sulphides [18-20]. In general, complexes of alkyl aryl sulphides are less stable than those of dialkyl sulphides [20]. In ethanol solution, even the dialkyl sulphide complexes are appreciably dissociated [18]. Thus for the $Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p/HgCl_2/EtOH$ system, there must be, at the very most, only a little complex in solution with most of the $HgCl_2$ free. Furthermore, such complexes are best viewed [18] as adducts, $R'R^2SHgCl_2$, rather than sulphonium salts $[R'R^2SHgCl]^+Cl^-$. All this suggests that reaction 12, EN=$HgCl_2$ will play a subordinate role to that of phenyl—tin bond cleavage arising from reaction of uncomplexed I with free $HgCl_2$.

Both iodine and $HgCl_2$ also reacted with $Ph_3SnCHClCH_2SAr$ at the phenyl—tin bond.

No products were isolated from the simple and direct cleavage of the tin—alkyl bond. In contrast, some products of cleavages of the tin—alkyl bond in $Ph_3SnCH_2SC_6H_4Me\text{-}p$ on reaction with bromine and iodine were detected [21]. Such a difference in behaviour can be accounted for from the stabilities of carbanions, $^-CH_2SC_6H_4Me\text{-}p$ and $^-CH_2CH_2SC_6H_4Me\text{-}p$: the former is the more stable. Thus it is argued that reaction leading to some charge separation or development in the Sn—CH_2 bond would be much more favoured in $Ph_3SnCH_2SC_6H_4Me$-*p* than in $Ph_3SnCH_2CH_2SC_6H_4Me$-*p*.

Experimental

$Ph_3SnCH_2CH_2SC_6H_4Me$-*p* was prepared as described previously [2].

Reaction of bromine and $Ph_3SnCH_2CH_2SC_6H_4Me$-p

Solutions of bromine (0.16 g, 1 mmol) and $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (0.5 g, 1 mmol), each in carbon tetrachloride (10 ml) were mixed at 0°C. The red colour of the bromine was immediately replaced by an orange colour (due to *p*-MeC_6H_4SBr), which disappeared on evaporation of the solution under reduced pressure. The compounds in the residue were separated by TLC (petroleum ether/chloroform 75/25 as eluant). There were three bands, *A*, *B*, *C* in order of increasing R_f value.

A. ^1H NMR (60 MHz) ($CDCl_3$ solution) τ 1.60-2.80(m). Recrystallisation from petroleum ether yielded Ph_3SnBr, m.p. 119-121°C (lit. [22] m.p. 121-122°C). It was identical to an authentic sample.

B. ^1H NMR (60 MHz; $CDCl_3$ solution) τ 1.80-2.90 (19H, m); 6.60-6.90 (2H; m); 7.70 (3H, s); 8.05-8.35 (2H, m). This is identical to that of the starting material, $Ph_3SnCH_2CH_2SC_6H_4Me$-*p*. Yield 50 mg, m.p. 70-73°C.

C. ^1H NMR (60 MHz; $CDCl_3$ solution) τ 2.50-3.05 (4H, m); 7.70 (3H, s). The spectra and other physical data were identical to those of an authentic sample of di-*p*-tolyl disulphide. Yield 90 mg, 78%; m.p. 42-45°C (lit. [23] m.p. 46°C).

Reaction of iodine with $Ph_3SnCH_2CH_2SC_6H_4Me$-p

A solution of iodine (0.25 g, 1 mmol) in carbon tetrachloride was added dropwise to a stirred, boiling solution of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (0.5 g, 1 mmol) in carbon tetrachloride and the mixture heated under reflux for 1½ h, after which the purple colour of the iodine had almost disappeared. The solvent was removed under reduced pressure to leave a residue, which contained only two products, PhI and $Ph_2(I)SnCH_2CH_2SC_6H_4Me$-*p* [TLC with petroleum ether/chloroform (70/30) as eluant].

$Ph_2(I)SnCH_2CH_2SC_6H_4Me$-p. ^1H NMR (60 MHz in $CDCl_3$): τ 1.80-2.95 (14H, m); 6.55-6.84 (2H, m); 7.71-7.98 (5H, m). Mass spectrum: molecular ion (0.3); $[Ph_2Sn(I)SC_6H_4Me\text{-}p]^+$ 16; $[Ph_2SnI]^+$ 100%. $Ph_2(I)SnCH_2CH_2SC_6H_4Me$-*p* decomposed in the residue on standing.

Reaction of methyl iodide and $Ph_3SnCH_2CH_2SC_6H_4Me$-p

$Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (0.2 g, 0.4 mmol) was refluxed in purified methyl iodide (5 ml) for 2 days. The solvent was evaporated under reduced pressure to leave an oily residue, which had the characteristic unpleasant odour of methyl *p*-tolyl sulphide. The presence of this compound as a major reaction product in the residue was confirmed from the ^1H NMR spectrum in $CDCl_3$ solution (τ 7.60 and 7.72 for the two Me groups in $MeSC_6H_4Me$-*p*). Methyl *p*-tolyl sulphide was removed under vacuum at 90°C to leave triphenyltin iodide, which was recrystallised from petroleum ether, m.p. 119-122°C (lit. [24] m.p. 120-121°C).

Reaction of mercuric chloride and $Ph_3SnCH_2CH_2SC_6H_4Me$-p

A solution of mercuric chloride (0.107 g, 4 mmol) in ethanol was added to a boiling ethanolic solution of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (0.2 g, 4 mmol) and the mixture was heated under reflux for 5 min, after which time TLC showed that all the $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* had reacted. The solvent was removed under reduced pressure and to the residue was added ethanol (5 ml). The solid PhHgCl was collected, on filtration, m.p. 249-255°C (lit. [25] m.p. 250°C), yield 0.84 g, 71%. The solvent was evaporated from the filtrate under reduced pressure and the ^1H NMR spectrum of the residue obtained. The pattern of peaks due to the four protons in the *p*-disubstituted aryl ring of each of the pairs of methylene protons were similar to those in the ^1H NMR spectrum of $Ph_2(I)SnCH_2CH_2SC_6H_4Me$-*p* suggested the residue was $Ph_2(Cl)SnCH_2CH_2SC_6H_4Me$-*p*.

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