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REACTIONS OF AROMATIC SULPHENYL COMPOUNDS WITH ORGANOTIN COMPOUNDS

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Summary

Aromatic sulphenyl halides and thiocyanates, RSX, cleave aryl—tin bonds, Ar—Sn≤, when the aryl groups contain strongly electron releasing substituents, to give monosulphides, RSAr. The reaction of *o*-$NO_2C_6H_4SCl$ and $Ph_3SnCH{=}CH_2$ gave both the cleavage product, $CH_2{=}CHSC_6H_4NO_2$-*o*, and the addition product, $Ph_3SnCHClCH_2SC_6H_4NO_2$-*o*. Other organotin bonds cleaved by *o*-$NO_2C_6H_4SCl$ are *p*-$MeC_6H_4SCH_2CH_2$—Sn≤ (to give *p*-$MeC_6H_4SSC_6H_4NO_2$-*o*) and allyl—tin bonds, which yield both rearranged and unrearranged allyl sulphides.

Introduction

A number of electrophilic species have been shown to react with organotin compounds. Such reactions normally lead to cleavage of the carbon—tin bond [1]. So far no report of such a reaction with electrophilic sulphenyl halides and thiocyanates, RSX, has been made. In fact it was shown earlier that tetraphenyltin was unaffected by *o*-nitrobenzenesulphenyl chloride, *o*-$NO_2C_6H_4SCl$, in refluxing carbon tetrachloride solution [2]. Subsequently it was thought that the use of more soluble and reactive compounds could possibly lead to reaction. (Tetraphenyltin is only sparingly soluble in carbon tetrachloride and it certainly is not one of the more reactive organotin compounds). We have thus attempted further reactions of aromatic sulphenyl systems with a number of organotin species, including aryl—tin, vinyl—tin, allyl—tin and β-arylthioethyl—tin compounds and we now report our results in this paper.

Results and discussion

The sulphenyl systems, RSX, used were *p*-MeC_6H_4SCl, *o*-$NO_2C_6H_4SX$

(X = Cl, Br, SCN) and 2,4-$(NO_2)_2C_6H_3SCl$. The most extensive study concerned the cleavage reactions of aryl—tin compounds and thus will be discussed first.

Cleavage of aryl—tin bonds

Reactions between various $Bu_3SnC_6H_4Y$-*p* compounds (I) and RSX were attempted in a number of aprotic solvents, mainly with 1,2-dichloroethane. With *o*-nitrobenzenesulphenyl compounds in refluxing $ClCH_2CH_2Cl$, successful reactions giving greater than 65% yields of unsymmetric sulphides (eqn. 1) were only obtained from the compounds of type I in which Y is a strongly elec-

$$Bu_3SnC_6H_4Y\text{-}p + RSX \rightarrow RSC_6H_4Y\text{-}p + Bu_3SnX' \quad (1)$$

X = X′ = Cl, Br; X = SCN, X′ = NCS

tron releasing substituent, e.g. Y = OMe, OEt, O-i-Pr, SMe. A much smaller yield (22%) of the appropriate monosulphide was obtained from I when Y was the less powerful releasing substituent Me, even with a slightly longer contact time, while for I (Y = H) and the same sulphenyl halide with an even longer reaction time, less than 2% of *o*-$NO_2C_6H_4SPh$ was produced. In the latter reaction, appreciable decomposition of *o*-$NO_2C_6H_4SCl$ to bis(*o*-nitrophenyl)disulphide occurred, while a considerable amount of Bu_3SnPh was recovered. Some decomposition of 2,4-dinitrobenzenesulphenyl chloride also occurred in its reaction with I (Y = O-i-Pr) and this had an depressing effect on the yield (only 43%) of 2,4-$(NO_2)_2C_6H_3SC_6H_4O$-i-Pr obtained.

Reactions of two tetraaryltin compounds (II) [$(p\text{-}YC_6H_4)_4Sn$, Y = MeO, Me] with *o*-$NO_2C_6H_4SCl$ in refluxing $ClCH_2CH_2Cl$ solution were also studied. While II (Y = MeO) gave a 73% yield of *p*-$MeOC_6H_4SC_6H_4NO_2$-*o* after 4 h, 80% of II (Y = Me) was recovered after 5 h as well as bis(*o*-nitrophenyl) disulphide in an almost quantitative yield; no unsymmetric sulphide was isolated, and the *o*-$NO_2C_6H_4SCl$ had undergone decomposition.

From the results with compounds I and II (Y = Me) with *o*-$NO_2C_6H_4SCl$, the aryltributyltin series is clearly shown to be much more reactive than the tetraaryltin series. From another comparison, the reactions of *p*-MeC_6H_4SCl were appreciable faster than those of the nitrobenzenesulphenyl compounds. However, no distinction could be made between the reactivities of the series of *o*-$NO_2C_6H_4SX$ compounds (X = Cl, Br, SCN). Generally all the RSX compounds were found to be weaker electrophiles than iodine towards tin—carbon bonds; iodine, for example, has been shown to readily cleave the Ph—Sn bond in Bu_3SnPh and Ph_4Sn [3].

In none of these reactions were the organotin products isolated, but were assumed in the sulphenyl halide reactions to be the appropriate triorganotin halide; in the reaction involving *o*-$NO_2C_6H_4SSCN$ the IR spectra of the reaction mixtures indicated the presence of Bu_3SnNCS. Collection of the sulphide product from the oily solvent-freed reaction residue was most frequently achieved by precipitation after addition of a suitable medium, followed by filtration and/or chromatography (column or thin layer). Prior conversion of all organotin species in the reaction mixtures to insoluble organotin fluorides by treatment with KF/CH_3CO_2H was sometimes used in attempts to facilitate the product separation, but gave only a marginal benefit.

This method of producing unsymmetric diaryl sulphides can be compared with the more direct method using sulphenyl halides and aromatic hydrocarbons

in the presence of a Friedel—Craft catalyst [4]. Both methods are electrophilic aromatic substitutions having the same requirement that the Ar groups should

$$ArH + RSX \xrightarrow[\text{low temp.}]{AlCl_3} ArSR \leftarrow Bu_3SnAr + RSX$$

have strong electron releasing groups. A general disadvantage in the 'direct' method not applicable to the organotin route, is that more than one isomer could be produced, although one of these isomers normally dominates. A specific advantage of the organotin reaction was found in the formation of *o*-$NO_2C_6H_4SC_6H_4SMe$-*p*. The 'direct' reaction of *o*-$NO_2C_6H_4SCl$ with PhSMe at —10° in the presence of $AlCl_3$ in $ClCH_2CH_2Cl$ solutions gave a variety of products in comparable yields, whereas the $Bu_3SnC_6H_4SMe$-*p*/*o*-$NO_2C_6H_4SCl$ reaction gave a high yield of the sulphide, the separation of which was easily accomplished from the reaction mixture.

Reactions of allyl—tin compounds

As previously found for reactions with other electrophiles, cleavage of allyl—tin bonds by *o*-nitrobenzenesulphenyl chloride occurred more readily than that of aryl—tin bonds. No addition of the sulphenyl chloride to the double bond occurred. Thus reaction of $Ph_3SnCH_2CH{=}CH_2$ occurred at —10° in THF solution to give the products shown in eqn. 2.

$$Ph_3SnCH_2CH{=}CH_2 + o\text{-}NO_2C_6H_4SCl \rightarrow [Ph_3SnCl] + CH_2{=}CHCH_2SC_6H_4NO_2\text{-}o \quad (67\%) \quad (2)$$

(*trans*-3-Phenylallyl)triphenyltin, *trans*-Ph_3SnCH_2—CH=CHPh, was also treated with *o*-nitrobenzenesulphenyl chloride in 1,2-dichloroethane solution and (assuming a bimolecular mechanism) the product of an S_E2 reaction, $PhCH{=}CHCH_2SC_6H_4NO_2$-*o* (III), and that of an S_E2' reaction, $CH_2{=}CHCHPhSC_6H_4NO_2$-*o* (IV), were both obtained, in a mole ratio of 2/5 and a total yield of 65%. The PMR spectrum of III, also produced directly from *o*-$NO_2C_6H_4SH$ and *trans*-$PhCH{=}CHCH_2Br$, indicated a *trans* configuration of the olefinic protons (see Experimental). It thus appears that the following sequence of transformations proceeds with retention of configuration of the double bond. The isomers,

$$PhCH{=}CHCH_2Br \rightarrow PhCH{=}CHCH_2MgBr \rightarrow PhCH{=}CHCH_2SnPh_3 \rightarrow PhCH{=}CHCH_2SC_6H_4NO_2\text{-}o$$

III and IV, were separated by preparative TLC; each was shown not to isomerise on the silica gel TLC plates nor in 1,2-dichloroethane solution and thus the ratio of products was thought not to reflect an equilibrium ratio but rather the ratio in which the isomers were formed.

From other studies, S_E2' products as well as S_E2 products have also been found in allyl—tin cleavages, e.g. in the HCl cleavage of $MeCH{=}CHCH_2SnMe_3$ [5] and in the I_2 cleavage of $MeCH{=}CHCH_2SnPh_3$ [6], although in the I_2/$PhCH{=}CHCH_2SnPh_3$ reaction, only the S_E2 product could be isolated [6].

Reaction with triphenylvinyltin

The reaction of *o*-nitrobenzenesulphenyl chloride with $Ph_3SnCH{=}CH_2$, un-

like those with aryl—tin and allyl—tin compounds, did not lead exclusively to carbon—tin bond cleavage. Some addition of the sulphenyl halide to the vinyl group occurred along with the vinyl—tin bond cleavage (the mole ratio of the

$$Ph_3SnCH{=}CH_2 + o\text{-}NO_2C_6H_4SCl \rightarrow Ph_3SnCHClCH_2SC_6H_4NO_2\text{-}o +$$

$$+ CH_2{=}CHSC_6H_4NO_2\text{-}o + [Ph_3SnCl] \quad (3)$$

products being 1/1.2) (eqn. 3). Only the Markownikoff-adduct was obtained. The other possible adduct $Ph_3SnCH(SC_6H_4NO_2\text{-}o)CH_2Cl$ was not isolated and if it had been formed it must have either decomposed under the reaction conditions (several hours of reflux in CCl_4) or have been formed to a very small extent. Sulphenyl halide additions to unsymmetric olefins more often than not lea to both products [7].

The sulphenyl halide addition to $Ph_3SnCH{=}CH_2$ is the first reported additi of an electrophile to a vinyl—tin species; previously only cleavage has been repo ed to occur, even with iodine [8]. Homolytic additions to vinyltin species have, however, been reported [1], including the addition of several sulphur containing compounds, including *p*-MeC_6H_4SH [9], H_2S and CH_3COSH [10].

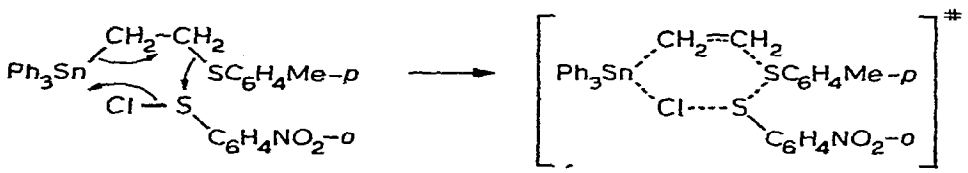
The adduct, $Ph_3SnCHClCH_2SC_6H_4NO_2$-*o*, has Mössbauer parameters, isome shift 1.32 (relative to $BaSnO_3$) and quadrupole splitting 0.51 mm/sec. Analysis of the Mössbauer spectra indicated that the small quadrupole splitting gave a better fit (χ^2 test) than did a single line. This small quadrupole splitting implies that there must be a slight distortion of the electron distribution away from cubic symmetry about the Sn atom in the solid state. Whether this is due to coordination or steric effects of the chlorine and sulphur groups (of either intra- or inter-molecular natures) cannot be readily decided. As no quadrupole splittin were detected for Ph_3SnCH_2I, Ph_3SnCH_2SAr and $Ph_3SnCH_2CH_2SAr$ [9], both an *α*-halogen and a *β*-mercapto group to the tin atom appear necessary before a small quadrupole splitting is observed. Intramolecular coordination has been assumed to cause quadrupole splittings in the Mössbauer spectra of the tetraorgan tin compounds, R_3SnCH_2COMe (R = Me and Et) [11]. Much more frequently however, for tetraorganotin species, no quadrupole splittings are observed [12]. No molecular ion was observed in the mass spectrum at 70 eV; the highest *m/e* clusters were due to $[Ph_3SnSC_6H_4NO_2\text{-}o]^+$, i.e. loss of CH_2CHCl.

Reaction of [β-(p-tolylthio)ethyl]triphenyltin (III)

The reaction of III with *o*-nitrobenzenesulphenyl chloride is shown in eqn. 4. The loss of the central ethylene unit during the reaction had not been expect

$$Ph_3SnCH_2CH_2SC_6H_4CH_3\text{-}p + o\text{-}NO_2C_6H_4SCl \rightarrow$$

$$o\text{-}NO_2C_6H_4SSC_6H_4Me\text{-}p + Ph_3SnCl + [CH_2{=}CH_2] \quad (4)$$



(IV)

It most probably occurred in the concerted process represented by IV. The same disulphide product would be the expected product of the reaction between $Ph_3SnSC_6H_4Me$-*p* and *o*-$NO_2C_6H_4SCl$ [2, 13]. While simple alkyl groups, such as butyl and methyl, are not cleaved from tin by sulphenyl halides, initial findings indicate that the Sn—CH_2 bonds are cleaved in Ph_3SnCH_2SAr as in Ph_3SnCH_2-SC_6H_4Me-*p*. However the products have not yet been completely established [14].

Experimental

Materials

The solvents used were the purest commercial grades available, and were dried over calcium hydride. Sulphenyl halides and thiocyanates were prepared according to established procedures, *p*-MeC_6H_4SCl [18], *o*-$NO_2C_6H_4SCl$ [19], *o*-$NO_2C_6H_4SBr$ [20], *o*-$NO_2C_6H_4SSCN$ [21], 2,4-$(NO_2)_2C_6H_3SCl$ [22]. Their physical properties were in agreement with those published.

Aryltributyltin compounds

$Bu_3SnC_6H_4Y$-*p* compounds were obtained from the reactions of Bu_3SnCl and the Grignard reagents from *p*-YC_6H_4Br. The products were obtained in the usual manner and were purified by distillation and by column chromatography.

$Bu_3SnC_6H_4SCH_3$-p. B.p. 166-168°/0.05 mm; n_D^{23} 1.5508. (Found: C, 54.9; H, 8.4; S, 7.8. $C_{19}H_{34}SSn$ calcd.: C, 55.2; H, 8.2; S, 7.7%.) ^{1}H NMR (60 MHz): τ 2.54-2.87q (4H), 7.54s (3H), and 8.4-9.3m (27H) ppm.

$Bu_3SnC_6H_5$. B.p. 128°/0.2 mm (lit. [23], 139°/0.6 mm), n_D^{20} 1.5168 (lit. [23], n_D^{20} 1.5155). (Found: C, 58.9; H, 8.4. $C_{18}H_{32}Sn$ calcd.: C, 58.9; H, 8.7%.) ^{1}H NMR (60 MHz): τ 2.60-2.85m (5H) and 8.35-9.17m (27H) ppm.

$Bu_3SnC_6H_4Me$-p. B.p. 155-60°/0.2 mm; n_D^{20} 1.5161. (Found: C, 60.0; H, 9.0; $C_{19}H_{34}Sn$ calcd.: C, 60.0; H, 8.9%.) ^{1}H NMR (100 MHz): τ 2.73-3.01d (4H), 7.70s (3H) and 8.42-9.17m (27H) ppm.

$Bu_3SnC_6H_4OMe$-p. B.p. 158-160°/0.5 mm; n_D^{22} 1.5131. (Found: C, 57.3; H, 8.5. $C_{19}H_{34}OSn$ calcd.: C, 57.4; H, 8.6%.) ^{1}H NMR (60 MHz): τ 2.70-3.30m (4H), 6.25s (3H) and 8.30-9.30m (27H) ppm.

$Bu_3SnC_6H_4OEt$-p. B.p. 168-170°/0.5 mm: n_D^{22} 1.5189. (Found: C, 58.5; H, 8.6. $C_{20}H_{36}OSn$ calcd.: C, 58.4; H, 8.7%.) ^{1}H NMR (100 MHz): τ 2.75-3.32m (4H), 5.91-6.15m (2H) and 8.34-9.10m (30H) ppm.

$Bu_3SnC_6H_4O$-i-Pr-p. B.p. 198°/0.7 mm: n_D^{22} 1.5200. (Found: C, 59.5; H, 8.9. $C_{21}H_{38}OSn$ calcd.: C, 59.3; H, 8.9%.) ^{1}H NMR (60 MHz): τ 2.75-3.45m (4H), 5.35-5.75m (1H) and 8.40-9.30m (33H) ppm.

Tetrakis(p-tolyl)tin, m.p. 236° (lit. [24] 238°) and *tetrakis(p-anisyl)tin*, m.p. 133° (lit. [24] 134.8°) were prepared from $SnCl_4$ and the appropriate Grignard reagent.

The *p*-YC_6H_4Br (Y = MeO, EtO, i-PrO) required for the Grignard reactions were prepared from *p*-HOC_6H_4Br and the appropriate alkyl iodide while *p*-$MeSC_6H_4Br$ was obtained by bromination of thioanisole in 95% (v/v) aqueous acid. All were distilled using a spinning band column.

Allyltriphenyltin was prepared according to a published procedure [25], m.p. 73-75° (lit. [25] 74°); *triphenylvinyltin* and *[β-(p-tolylthio)ethyl]triphenyltin* were from a previous study [9].

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TABLE 1

REACTIONS OF RSX WITH ARYLTIN COMPOUNDS, p-$YC_6H_4SnR'_3$

Reagents	(mmol)	Reaction conditions Solvent/time/temp.	Product (RSC_6H_4Y-p)					
			M.p.	Yield	Analysis Found (calcd.) (%)			
			(°C)	(%)	C	H	N	S
p-MeC_6H_4SCl $Bu_3SnC_6H_4Me$-p	(7.6)	PhCl/1h Reflux	58[a]	70	78.4 (78.5)	6.4 (6.5)		15.2 (15.0)
o-$NO_2C_6H_4SCl$ $Bu_3SnC_6H_4OMe$-p	(4.0)	PhCl/3h Reflux	94-95[b, c]	67	60.0 (59.8)	4.4 (4.3)	5.1 (5.4)	12.3 (12.3)
	(8.2)	$(CH_2Cl)_2/2\frac{1}{2}$h Reflux	94[b, c]	86	59.7 (59.8)	4.3 (4.3)	5.4 (5.4)	12.5 (12.3)
o-$NO_2C_6H_4SBr$ $Bu_3SnC_6H_4OMe$-p	(2.0)	$(CH_2Cl)_2/1\frac{1}{2}$h Reflux	95[b, c]	75				
o-$NO_2C_6H_4SSCN$ $Bu_3SnC_6H_4OMe$-p	(1.3)	(CH_2Cl_2)/3h Reflux	94[b, c]	85				

o-$NO_2C_6H_4SCl$ $Bu_3SnC_6H_4SMe$-*p*	(1.8)	$(CH_2Cl)_2$/1 day 20	107-108	76	56.1 (56.3)	4.0 (4.0)	5.1 (5.1)	23.0 (23.1)
	(1.2)	$(CH_2Cl)_2$/2h Reflux	107	86	56.2 (56.3)	4.2 (4.0)	5.1 (5.1)	23.1 (23.1)
o-$NO_2C_6H_4SSCN$ $Bu_3SnC_6H_4OEt$	(1.5)	$(CH_2Cl)_2$/1h Reflux	112	70	60.7 (61.1)	4.4 (4.8)	5.0 (5.1)	12.1 (11.7)
2,4-$(NO_2)_2C_6H_3SCl$ $Bu_3SnC_6H_4O$-*i*-Pr-*p*	(5.0)	$(CH_2Cl)_2/\frac{1}{2}$h Reflux	100-101	43	53.9 (53.9)	4.3 (4.2)	7.7 (8.4)	10.2 (9.6)
o-$NO_2C_6H_4SCl$ $Bu_3SnC_6H_4Me$-*p*	(5.2)	$(CH_2Cl)_2$/4h Reflux	88- 89[d]	22	63.7 (63.6)	5.1 (4.5)	5.8 (5.7)	13.0 (13.1)
o-$NO_2C_6H_4SCl$ Bu_3SnPh	(3.5)	$(CH_2Cl)_2$/6h Reflux		2[e]				
o-$NO_2C_6H_4SCl$ (*p*-$MeC_6H_4)_4Sn$	(1.3)	$(CH_2Cl)_2$/5h Reflux		0				
o-$NO_2C_6H_4SCl$ (*p*-$MeOC_6H_4)_4Sn$	(0.26)	$(CH_2Cl)_2$/4h Reflux	94-95[b, c]	75				

[a] Lit. [15] m.p. 57°. [b] Lit. [16] m.p. 95°. [c] Identical samples. [d] Lit. [17] m.p. 90°. [e] Identified from mass spectrum.

(trans-3-Phenylallyl)triphenyltin, $PhCH{=}CHCH_2SnPh_3$

A solution of *trans*-3-phenylallyl bromide (14.9 g, 0.075 mol) and triphenyl tin chloride (28.8 g, 0.075 mole) in THF (200 ml) was added to magnesium (7.5 g, 0.31 mol) and THF (100 ml). The mixture was refluxed for 6 h, cooled, hydrolysed with saturated ammonium chloride solution and extracted with ether The organic extracts were dried and the solvent removed to leave a viscous oil, which was chromatographed on alumina using petr. ether/$CHCl_3$ as eluant. $Ph_3SnCH_2CH{=}CHPh$ was collected and recrystallised from hexane, m.p. 73° (lit. [6] m.p. 73°). (Found: C, 69.2; H, 5.4. $C_{27}H_{24}Sn$ calcd.: C, 69.4; H, 5.2%.) ^1H NMR (100 MHz) of $PhC^3H{=}C^2H{-}C^1H_2Br$; τ 2.70-3.97m (5H), 3.11-3.82m (2H and 5.86-5.94d (2H) ppm: δ_1 4.10; δ_2 6.36 and δ_3 6.65; $J_{2,3} = 15.6$ and $J_{1,2} = 7$ Hz. ^1H NMR (100 MHz) of $PhC^3H{=}C^2H{-}C^1H_2SnPh_3$: τ 2.20-2.85m (20H), 3.36-3.80m (2H) and 7.38-7.45d (2H) ppm: $J_{1,2} = 7$ and $J(^{119}Sn{-}^1H) = 72$ Hz.

Reactions

Aryltin compounds and sulphenyl halides and thiocyanates

Three procedures will be given as representative examples. All reactions are listed in Table 1.

(a). Tributyl(p-thioanisyl)tin and o-nitrobenzenesulphenyl chloride. A solution of $Bu_3SnC_6H_4SMe$-*p* (0.50 g, 1.2 mmol) and *o*-$NO_2C_6H_4SCl$ (0.23 g, 1.2 mmol) in 1,2-dichloroethane (10 ml) was refluxed for 2 h. The solvent was removed and on addition of petr. ether to the oily residue, some solid (*o*-$NO_2C_6H_4SC_6H_4SMe$-*p*) separated out. This was collected and well washed with small portions of petr. ether. The combined washings and filtrate were chromatographed on an alumina column to give more unsymmetric sulphide. The combined sulphide fractions were recrystallised from ethanol, m.p. 107-108°, 0.29 g (86%).

(b). Tributyl(p-anisyl)tin and o-nitrobenzenesulphenyl bromide. A solution of $Bu_3SnC_6H_4OMe$-*p* (0.79 g, 2.0 mmol) and *o*-$NO_2C_6H_4SBr$ (0.47 g, 2.0 mmol) in 1,2-dichloroethane (12 ml) was refluxed for 1½ h. TLC indicated the reaction was then complete. The solvent was removed to leave an oily solid (1.26 g) which was all chromatographed on an alumina column using $CHCl_3$/petr. ether (4/1). A yellow solid, (0.50 g) slightly contaminated with Bu_3SnCl was collected and recrystallised from petr. ether/CH_2Cl_2; m.p. 94°, 0.393 g (75%).

(c). Tributyl(p-anisyl)tin and o-nitrobenzenesulphenyl chloride. A solution of $Bu_3SnC_6H_4OMe$-*p* (1.59 g, 4.0 mmol) and *o*-$NO_2C_6H_4SCl$ (0.76 g, 4.0 mmol) in PhCl (10 ml) was refluxed for 3 h. To the cooled solution was added H_2O/CH_3CO_2H/KF. The mixture was gently heated for 1 h, cooled and extracted with Et_2O. The combined ether extracts after removal of the solvent were chromatographed on alumina. The yellow solid unsymmetric sulphide was collected and recrystallised from petr. ether: m.p. 94-95°, 0.69 g (67%).

Allyltriphenyltin and o-nitrobenzenesulphenyl chloride

A solution of *o*-$NO_2C_6H_4SCl$ (0.67 g, 3.5 mmol) in THF (5 ml) was added dropwise to a solution of $Ph_3SnCH_2CH{=}CH_2$ (1.37 g, 3.5 mmol) in THF (10 ml) at −10°. After the addition was complete, the reaction solution was maintained at −10° for 1 h, then the solvent was removed and the residue chromatographed on alumina (petr. ether/benzene (1/1) eluant). Allyl *o*-nitrophenyl sulphide,

0.46 g, 67%, was collected, m.p. 52° (lit. [26] 54°) (Found: C, 55.1; H, 4.5; N, 6.9; S, 16.1. $C_9H_9NO_2S$ calcd.: C, 55.4; H, 4.6; N, 7.2; S, 16.4%.)

trans-3-Phenylallyltriphenyltin and o-nitrobenzenesulphenyl chloride

Solutions of *trans*-$Ph_3SnCH_2CH{=}CHPh$ (0.466 g, 1 mmol) and 2-$NO_2C_6H_4SCl$ (0.189 g, 1 mmol) in $(CH_2Cl)_2$ were mixed at room temperature and left for 5 h. TLC indicated several compounds present in the reaction mixture, including two yellow products with similar R_f values. Separation of these two components was achieved by preparative TLC [Silica gel GF 254 stationary phase and light petroleum/$CHCl_3$ (3/1) eluant] using multiple developments. *o*-$NO_2C_6H_4$-$SCHPhCH{=}CH_2$ (125 mg), m.p. 54-55°. (Found: C, 66.6; H, 5.0; N, 5.3; S, 12.2%. Mol. wt. 271.0667. $C_{15}H_{13}NO_2S$ calcd. C, 66.4; H, 4.8; N, 5.2; S, 11.8%. Mol. wt. 271.0666.) ^{1}H NMR (100 MHz) of *o*-$NO_2C_6H_4SCHPhCH{=}CH_2$ showed a conformational equilibrium; in $CDCl_3$ solution at 30°: τ 1.91-2.00d (1H), 2.54-2.74m (3H), 3.70-4.04m (1H) and 4.66-4.98m (2H) ppm, and *o*-$NO_2C_6H_4SCH_2CH{=}CHPh$ (50 mg), m.p. 90-91° (Found: C, 66.2; H, 4.9; N, 5.4; S, 12.2%. Mol. wt. 271.0667.) ^{1}H NMR (100 MHz): τ 1.81-1.89d (1H), 2.54-2.80m (3H), 3.26-3.93m (2H) and 6.18-6.24d (2H); δ_1 6.65, δ_2 6.25 and δ_3 3.85 ppm: $J_{1,2}$ = 16 and $J_{2,3}$ = 6.6 Hz. These two products were purified by repeated TLC until there was only one spot for each.

Preparation of o-$NO_2C_6H_4SCH_2$—CH=CHPh

trans-$PhCH{=}CHCH_2Br$ (19.7 mg, 0.1 mmol) and *o*-$NO_2C_6H_4SH$ (15.5 g, 0.1 mmol) were dissolved in CCl_4 (5 ml). On addition of a few drops of Et_3N a deep red coloured solution was formed, which on warming on a steam bath decolourised and a precipitate formed. After filtration, 3-phenylallyl-*o*-nitrophenyl sulphide was obtained on TLC. (Found: C, 66.1; H, 4.7; N, 5.0; S, 12.2%.)

Triphenylvinyltin and o-nitrobenzenesulphenyl chloride

A solution of $Ph_3SnCH{=}CH_2$ (1.131 g, 3.0 mmol) and *o*-$NO_2C_6H_4SCl$ (0.567 g, 3.0 mmol) in CCl_4 (25 ml) was refluxed for 8 h. The solvent was removed and the residue was dissolved in hot ethanol. On cooling, yellow $Ph_3SnCHClCH_2SC_6H_4NO_2$-*o* crystallised out and was collected, m.p. 115-117°, 0.893 g, 1.34 mmol (Found: C, 55.6; H, 4.1; Cl, 6.1; S, 5.8. $C_{26}H_{22}ClNO_2SSn$ calcd.: C, 55.1; H, 3.9; Cl, 6.3; S, 5.7%.) ^{1}H NMR (100 MHz) spectrum: τ 1.82d (1H), 2.10-2.90m (8H), 5.56-5.77t (1H) and 6.15-6.60m (2H) ppm. The filtrate, after evaporation of the solvent, was chromatographed on alumina [petr. ether/$CHCl_3$ (4/1) as eluant]. *o*-Nitrophenylvinyl sulphide was collected and further purified by TLC: yellow oil, 0.204 g (1.13 mmol) (Found: C, 53.0; H, 4.1; N, 7.8; S, 17.6. $C_8H_7NO_2S$ calcd.: C, 53.1; H, 3.9; N, 7.7; S, 17.7%.)

[β-(p-Tolylthio)ethyl]triphenyltin and o-nitrobenzenesulphenyl chloride

A solution of *o*-$NO_2C_6H_4SCl$ (0.15 g, 0.8 mmol) and $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (0.4 g, 0.8 mmol) in CCl_4 was refluxed for 75 min. The solvent was removed and the products were separated using TLC [petr. ether/$CHCl_3$ (1/1) as eluant]. Yellow *o*-$NO_2C_6H_4SSC_6H_4Me$-*p* was obtained and recrystallised from ethanol, 0.173 g (79%); m.p. 74-75° (lit. [27] 74°). ^{1}H NMR (60 MHz): τ 1.63-3.00m (8H) and 7.70s (3H) ppm.

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