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SULPHUR SUBSTITUTED ORGANOTIN COMPOUNDS

IX *. FORMATION OF [(3-CHLORO-4-*o*-NITROPHENYLTHIO)BUTYL]-TRIPHENYLTIN, $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o*, FROM REACTION OF 4-BUTENYLTRIPHENYLTIN AND *o*-NITROBENZENESULPHENYL CHLORIDE

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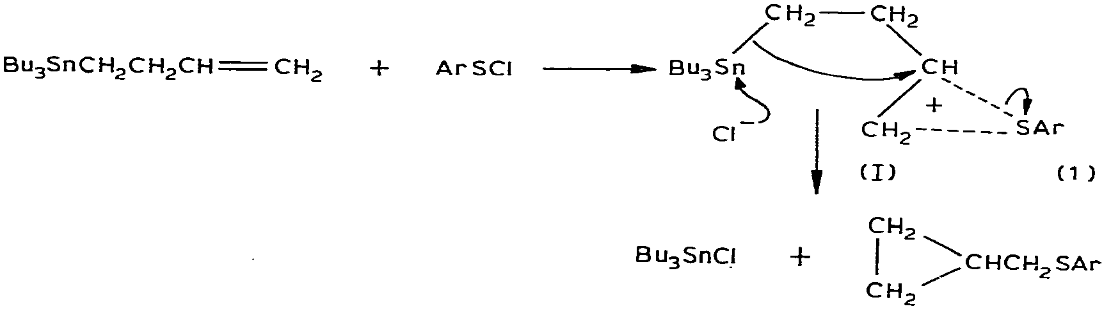
Summary

Reaction of the sulphenyl chloride, *o*-$NO_2C_6H_4SCl$, with $Ph_3SnCH_2CH_2CH{=}CH_2$ occurs to give the adduct, $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o*. In contrast, no adduct is formed with the more reactive, *p*-MeC_6H_4SCl. Instead, and as reported previously with $Bu_3SnCH_2CH_2CH{=}CH_2$, the cyclopropylmethyl aryl sulphide is obtained. The adduct is thermally stable, and reacts with I_2 and $HgCl_2$ to give phenyl—tin cleaved products, $Ph_2SnXCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o* (X = I or Cl).

Peterson et al. [2] reported reactions of various electrophiles, including sulphenyl halides, with 4-butenyltributyltin compounds, equation 1. These led to formation of cyclopropylmethyl derivatives. An intermediate cation is formed, which undergoes nucleophilic attack at the tin centre by the chloride



(1)

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[*] For part VIII see ref. 1.

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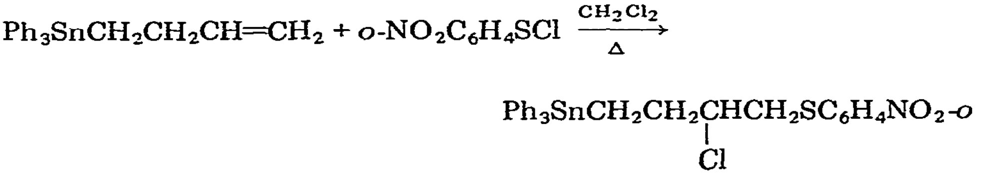
ion with the resultant formation of the cyclopropylmethyl derivative.

We have found that this type of reaction is not a general reaction of 4-butenyltin compounds and that adducts may be obtained, as we now describe.

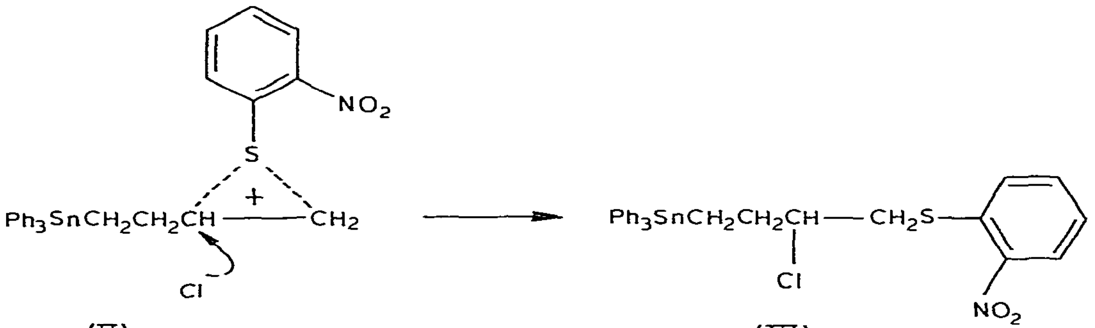
Results and discussion

Reaction of $Ph_3SnCH_2CH_2CH{=}CH_2$ with o-$NO_2C_6H_4SCl$ in methylene dichloride solution proceeded according to equation 2.



$$Ph_3SnCH_2CH_2CH{=}CH_2 + o\text{-}NO_2C_6H_4SCl \xrightarrow[\Delta]{CH_2Cl_2} Ph_3SnCH_2CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2SC_6H_4NO_2\text{-}o \qquad (2)$$

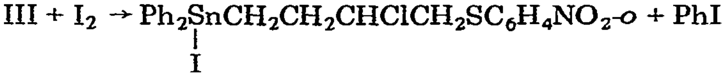
The Marknownikov adduct was obtained in an isolated yield of 53% with no indication of the other adduct. The formation of this adduct will arise from attack by Cl^- on the intermediate cation II at the positive carbon rather than at tin as in I. Phenyl substituents at the tin centre will exert different electronic and steric effects at tin compared to the butyl substituents, such that they deactivate the tin centre for nucleophilic attack by Cl^-.



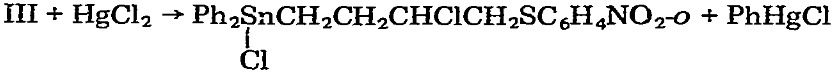
(II) (III)

Of interest, from the reaction of the more reactive sulphenyl halide, p-MeC_6H_4SCl, with $Ph_3SnCH_2CH_2CH{=}CH_2$, no adduct could be detected. The ^1H NMR spectrum of the reaction mixture indicated the presence of some cyclopropyl product.

The adduct III, had m.p. 81–83°C. The parent ion (0.9%) was weakly observed in the mass spectrum at 20 eV, with prominant tin-containing ions $[M - Cl]^+$ (0.8%), $[M - Ph]^+$ (2.5%), $[M - 2Ph]^+$ (4%), [433] (4%), $[Ph_3Sn]^+$ (100%) and [308] (35%). The Mössbauer spectrum showed the isomer shift to be 1.249(8) mm s^{-1} with no quadruple splitting. Reactions of the adduct were studied with iodine and $HgCl_2$. Both these reagents produced phenyl–tin bond cleavages, equations 3 and 4.



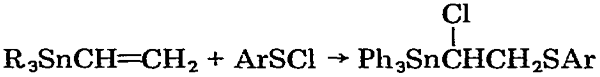
$$III + I_2 \rightarrow Ph_2\underset{\displaystyle I}{\underset{|}{S}}nCH_2CH_2CHClCH_2SC_6H_4NO_2\text{-}o + PhI \qquad (3)$$



$$III + HgCl_2 \rightarrow Ph_2\underset{\displaystyle Cl}{\underset{|}{S}}nCH_2CH_2CHClCH_2SC_6H_4NO_2\text{-}o + PhHgCl \qquad (4)$$

Similar reactions have been found with $Ph_3Sn(CH_2)_4SAr$ compounds. The adduct III is stable to heat. Thus heating a sealed solution of III in $CDCl_3$ solution at 100°C for 3 h resulted in no reaction. These sulphenyl halide reactions of 1-butenyltriphenyltin (i.e. tin—carbon bond cleavage and adduct formation) can be added to the reported reactions with vinyl—tin [3] [carbon—tin bond cleavage and adduct formation, equations 5 and 6] and to allyl—tin [carbon—tin cleavage, equation 7].

Some similarities between the 1-butenyl- and the 1-vinyl-tin reactions are apparent; for example (i) more cleavage of the carbon—tin bond occurs in each case for trialkyltin derivatives than for Ph_3Sn derivatives, (ii) much more carbon—tin bond cleavage occurred with p-MeC_6H_4SCl than with o-$NO_2C_6H_4SCl$ and (iii) Marknownikov adducts were obtained.



$$R_3SnCH{=}CH_2 + ArSCl \rightarrow Ph_3Sn\overset{\overset{Cl}{|}}{C}HCH_2SAr \qquad (5)$$

$$R_3SnCH{=}CH_2 + ArSCl \rightarrow R_3SnCl + ArSCH{=}CH_2 \qquad (6)$$

$$R_3SnCH_2CH{=}CH_2 + ArSCl \rightarrow R_3SnCl + ArSCH_2CH{=}CH_2 \qquad (7)$$

Reactions of sulphenyl halides with other organotin compounds have been studied [5—7]. Only the more reactive carbon—tin bonded compounds react, e.g. fluorenyl- [5], indenyl- [5], p-anisyl- [4], $ArSCH_2$- [6] and $ArSCH_2CH_2$-tin bonds [7] are cleaved. Phenyltin bonds have been shown to be inert [4].

Experimental

1-Butenyltriphenyltin. This was prepared by the reaction of the Grignard reagent from 4-bromobutene (10.0 g, 0.074 mol) and Ph_3SnCl (15.2 g, 0.0394 mol) in THF solution, yield 85%, m.p. 72—75°C.

p-Toluenesulphenyl chloride [8]. Dry chlorine gas was bubbled through a stirred solution of p-toluenethiol (15 g, 0.1209 mol) in carbon tetrachloride (100 ml) for 2 h, at 0°C, forming a dark red solution. The solvent was removed under reduced pressure and p-toluenesulphenyl chloride purified by vacuum distillation. Yield 67%, b.p. 62—64°C/0.1 mmHg (lit. [8] b.p. 66—68°C/0.8 mmHg).

o-Nitrobenzenesulphenyl chloride [9]. Dry chlorine gas was bubbled through a solution of bis(o-nitrophenyl)disulphide (11.084 g, 0.0361 mol) and iodine (0.5 g, 0.00196 mol) in carbon tetrachloride (150 ml) for 1.5 h. The solution was filtered and the solvent removed under reduced pressure to give o-nitrobenzenesulphenyl chloride, which was recrystallised from petroleum ether (b.p. 60—80°C) to give yellow needles, yield 72%, m.p. 74°C (lit. [9] m.p. 73—73.5°C).

Reaction of 4-butenyltriphenyltin and p-toluenesulphenyl chloride

To 4-butenyltriphenyltin (2.0 g, 0.0049 mol) in dichloromethane (15 ml) at 0°C was added dropwise with stirring, a solution of p-toluenesulphenyl chloride (0.78 g, 0.0049 mol) in dichloromethane (15 ml). After addition, the resultant mixture was heated for 30 min, cooled and the solvent removed under reduced pressure to yield a pale yellow oil. The ^1H NMR spectrum of the oil indicated some cyclopropyl protons but no adduct.

Reaction of 4-butenyltriphenyltin and o-nitrobenzenesulphenyl chloride

To a solution of 4-butenyltriphenyltin (2.0 g, 0.0049 mol) in dichloromethane (15 ml) was added *o*-nitrobenzenesulphenyl chloride (0.93 g, 0.0049 mol) in dichloromethane (15 ml), and the resultant mixture refluxed for 2 h. The solvent was removed under reduced pressure to give a yellow oily solid which was recrystallised from ethanol to give [(3-chloro-4-*o*-nitrophenylthio)-butyl]triphenyltin, yellow plates, yield 1.54 g, 53%, m.p. 81—83° C.

Analysis. Found: C, 56.6; H, 4.4; S, 5.3; Cl, 6.0; N, 2.35. $C_{28}H_{26}SClNO_2Sn$ calcd.: C, 56.6; H, 4.2; S, 5.3; Cl, 5.9; N, 2.3%.

^1H NMR. ($CDCl_3$, 30° C): δ 6.90—8.20 (m, 19H, phenyls and o-$NO_2C_6H_4$), 3.56 (m, 3H, SCH_2, $CHCl$); 1.30—2.75 (m, 4H, $SnCH_2CH_2$).

^{13}C NMR. ($CDCl_3$, 30° C): δ 125.72—138.10 (aryl C), 51.00 (C—Cl), 45.97 (CH_2S), 28.06 (CH_2CH_2CH), 7.58 (CH_2Sn).

Mössbauer spectrum. I.S. 1.249(8) mm s^{-1}; 0.85(3) mm s^{-1}.

Reaction of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-o with iodine

To a stirred solution of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o* (0.808 g, 0.00135 mol) in CCl_4 (5 ml) was added dropwise, a solution of iodine (0.342 g, 0.00135 mol) in CCl_4 (20 ml). The purple colour disappeared over 10 h to give a pale yellow solution. The solvent was removed under reduced pressure to yield a pale yellow oil, which was washed several times with petroleum ether (b.p. 60—80° C). The ^1H NMR spectrum of the resulting oil, which refused to crystallise, showed several changes ($CDCl_3$, 30° C): δ 7.00—8.40 (m, 14H, phenyls and o-$NO_2C_6H_4S$), 3.36 (m, 3H, SCH_2 and $CHCl$), 1.6—2.5 (m, 4H, CH_2CH_2Sn), which is as expected for $Ph_2Sn(I)CH_2CH_2CHClCH_2SC_6H_4NO_2$-*o*.

Reaction of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-o with mercuric chloride

To a solution of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o* (0.566 g, 0.00095 mol) in ethanol (20 ml) was added mercuric chloride (0.258 g, 0.00095 mol) in ethanol (10 ml) and the mixture refluxed for 3 h. The solvent was removed under reduced pressure to yield a yellow oily-solid to which was added $CHCl_3$. The insoluble white solid PhHgCl was filtered off and recrystallised from ethanol, m.p. 255—256° C (lit. [10] m.p. 255—257° C).

Thermolysis of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4Me$-p

A solution of $Ph_3SnCH_2CH_2CHClCH_2SC_6H_4NO_2$-*o* (0.20 g, 0.00035 mol) in $CDCl_3$ (0.3 mol) in a sealed tube was heated at 100° C for 3 h. The ^1H NMR spectrum showed that no reaction had occurred, as did TLC.

Mössbauer spectra were recorded as previously described [11].

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