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SULPHUR SUBSTITUTED ORGANOTIN COMPOUNDS. PART 6. REACTIONS OF MERCAPTOMETHYLTIN COMPOUNDS WITH ARENESULPHENYL CHLORIDES[1]

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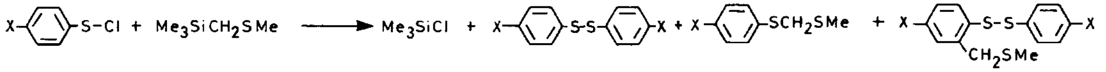
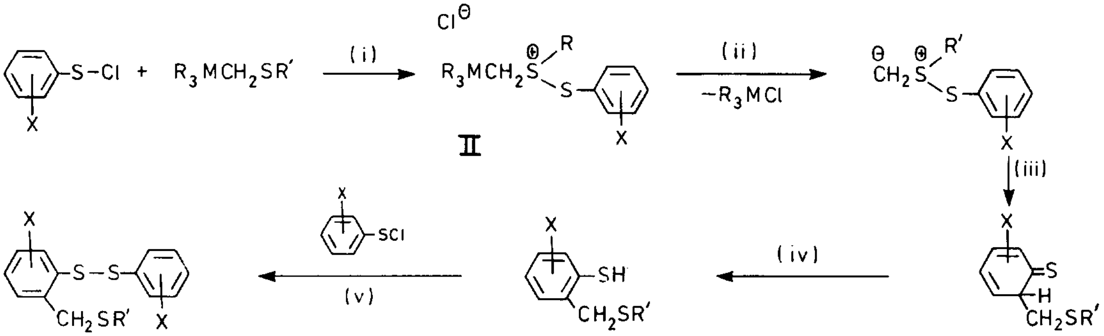
Summary: Reactions between Ph_3SnCH_2SAr and $2\text{-}NO_2C_6H_4SCl$ lead to the formation of $2\text{-}(ArSCH_2)\text{-}6\text{-}NO_2C_6H_3SSC_6H_4NO_2\text{-}2$ via the [2,3] sigmatropic rearrangement of the S-arylthiosulphonium ylides $\bar{C}H_2\text{-}\overset{+}{S}(Ar)SC_6H_4NO_2\text{-}2$.

Gassman and Miura[2] recently reported, in this Journal, reactions between arenesulphenyl chlorides and (methylthiomethyl)trimethylsilane, equation (1). Of particular interest was the compound



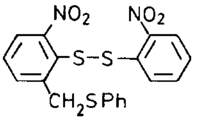
I

(I). The formation of (I) was considered to involve a spontaneous [2,3] sigmatropic rearrangement (step iii in the Scheme) of S-arylthiosulphonium ylide (II, R'=Me).

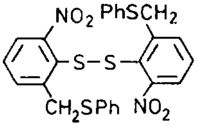


Scheme M = Si or Sn

Gassman and Muira's report has prompted us to publish similar findings with organotin compounds, Ph_3SnCH_2SAr. From Ph_3SnCH_2SPh and $2\text{-}NO_2C_6H_4SCl$, for example, compound (III) could be isolated in good yield. Clearly similar mechanisms (Scheme) must operate for the organotin system as for the organosilicon ones.



III



IV

A typical experiment was conducted with Ph_3SnCH_2SPh (8.0 g, 0.017 mole) and $2\text{-}NO_2C_6H_4SCl$ (4.4 g, 0.023 mole) in carbon tetrachloride. After refluxing 1 hour, the solvent was removed to leave an oily solid. A little cold chloroform was added and the yellow solid (III) was collected and recrystallised from chloroform/hexane; yield 2.1 g, m.p. 126-129°C. Anal. Found: C, 53.3, H, 3.6, N, 6.3, S, 22.0%. Calcd. for $C_{19}H_{14}O_4N_2S_3$: C, 53.6, H, 3.3, N, 6.5, S, 22.3%. ^1H NMR (60 MHz) in $CDCl_3$: $\delta(CH_2)$ 4.48 2H(s), δ(aryl) 7.20-8.25 12H(m). Mass spectrum: m/e 430(M^+)(0.3%), 276(90%).

Many other products were also present, including Ph_3SnCl and ($\underline{o}\text{-}NO_2C_6H_4S)_2$. We have further shown that (III) is a labile material. Thus refluxing the unsymmetric disulphide, (III), in ethanol solution for 2 hours led to the formation of symmetric disulphide, $(2\text{-}NO_2C_6H_4S)_2$ and a compound, $C_{26}H_{20}N_2O_4S_4$, m.p. 99°C, which we consider to be the other symmetric disulphide, (IV). [Anal. C, 56.5, H, 3.8, N, 4.7, S, 22.4%. Calcd. for $C_{26}H_{20}N_2O_4S_4$: C, 56.6, H, 3.6, N, 5.1, S, 22.8%. ^1H NMR (60 MHz) in $CDCl_3$: $\delta(CH_2)$ 4.22 2H(s); δ(aryl) 7.20-7.60 9H(m). Mass spectrum (70 eV): m/e 552(M)(0.5%), 276(35%)]. Of interest, a different work-up procedure of the $Ph_3SnCH_2SPh/2\text{-}NO_2C_6H_4SCl$ reaction, namely one using t.l.c. on alumina plates, gave significant amounts of (IV) and ($\underline{o}\text{-}NO_2C_6H_4S)_2$. It would appear that the unsymmetrical disulphide, (III), disproportionates on alumina.

Other organotin substituted sulphonium salts have been shown by Peterson to give rise to ylides, e.g. $Bu_3SnCH_2\overset{+}{S}Me_2,I^-$ (from Bu_3SnSMe and MeI) spontaneously provides $\overset{-}{C}H_2\overset{+}{S}Me_2$ and Bu_3SnI. Thus halides, Cl^- and I^-, are sufficiently nucleophilic to cleave the carbon-tin bonds in sulphonium salts. In contrast, the sulphonium salt, $Bu_3SnCH_2\overset{+}{S}Me_2,MeSO_4^-$ is stable; this is a consequence of $MeSO_4^-$ being insufficiently nucleophilic.

Reactions of sulphenyl halides, RSCl, with organotin compounds have been previously reported.[5,6] Only the more reactive tin-carbon bonds such as allylic tin bonds are readily cleaved by RSCl. Tin bonds to phenyl and simple alkyl groups are normally unaffected by such reagents in the absence of a catalyst.

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[2] P.G. Gassman and T. Muira, *Tetrahedron Lett.*, 1981, 4787.

[3] The chemical shifts of the protons *ortho* to the two NO_2 groups in (IV) are not too low field of (and hence separated from) the remainder of the aryl protons as is the case with (III) and also with $PhSCH_2SC_6H_4NO_2\text{-}2$. We assume that in (IV) the favoured conformation has the nitroaryl ring close to the $PhSCH_2$ group and that an interaction between these groups occurs.

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