

REACTIONS OF SULPHENYL HALIDES AND ORGANOTIN SULPHUR COMPOUNDS

J. L. WARDELL AND D. W. GRANT

Department of Chemistry, University of Aberdeen, Old Aberdeen (Great Britain)

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SUMMARY

Organotin sulphur compounds of the type, R_3SnSAr , react under mild conditions with sulphenyl halides, $ArSX$, in aprotic solvents to give triorganotin halides and diphenyl disulphides in high yields. Tetraphenyltin is not cleaved under the same conditions.

INTRODUCTION

Sulphenyl chlorides and bromides are well known electrophilic reagents and have been extensively studied in such reactions as additions to olefins¹ and in Friedel-Crafts systems². While halogens and proton acids, all electrophiles, have been shown to cleave tin-carbon^{3,4} and tin-sulphur bonds^{5,6}, there appears to be no direct data for similar reactions with sulphenyl halides.

Some indirect evidence⁵ for a sulphenyl bromide cleavage of a tin-sulphur bond comes from the reaction of bromine with trimethyltin phenyl sulphide. The products of this reaction are trimethyltin bromide and the symmetric diphenyl disulphide. One possible route for this reaction is



In step (2) cleavage by benzenesulphenyl bromide occurs. However the pathway of the reaction could be different.

We can now confirm that cleavages of tin-sulphur bonds can be readily caused by sulphenyl halides under mild conditions.

EXPERIMENTAL

Proton magnetic resonance spectra were taken on a Varian model A60 analytical spectrometer. IR spectra were recorded on a Perkin-Elmer IR 137 spectrometer. Refractive indices were measured on a Hilger Abbe refractometer.

Materials

Triorganotin aryl sulphides. Triphenyltin 4-tert-butylphenyl sulphide was

prepared from 4-tert-butylbenzenethiol and triphenyltin chloride. Equimolar quantities (0.05 mole) were dissolved in carbon tetrachloride (50 ml) and triethylamine (0.055 mole) was added with stirring. A precipitate of triethylamine hydrochloride immediately appeared. The solution was filtered and the filtrate was evaporated to leave the crude product. The sulphide was recrystallised from ethanol (Yield 65%; m.p. 105°). The trialkyltin aryl sulphides were prepared from the appropriate bis-(organotin) oxide (*ca.* 0.01 mole) and thiol (*ca.* 0.02 mole)⁷. Gentle heating was applied for 1 h. Yields of pure distilled products were in the region of 75–80%. Some physical constants and analytical data are given in Table 1.

TABLE 1

TRIORGANOTIN ARYL SULPHIDES

Sulphide	B.p. [°C(mm)]	n_D^{20}	Analysis found (calcd.) (%)			
			C	H	S	Cl
Ph ₃ SnSC ₆ H ₄ -4-tert-Bu			65.1 (65.3)	5.4 (5.5)	6.2 (6.1)	
n-Bu ₃ SnSC ₆ H ₄ -4-Me	170–172(0.8)	1.5424	55.8 (55.2)	8.7 (8.3)	8.2 (7.8)	
n-Bu ₃ SnSC ₆ H ₄ -4-Cl	180–184(0.8)	1.5505	50.6 (49.9)	7.7 (7.2)	7.8 (7.4)	8.8 (8.2)
n-Bu ₃ SnSC ₆ H ₄ -4-tert-Bu	192–193(0.8)	1.5351	58.4 (58.0)	9.2 (8.9)	6.7 (7.0)	
n-Pr ₃ SnSC ₆ H ₄ -4-Me	162–164(1.0) ^a	1.5560 ^b	51.0 (51.8)	7.7 (7.6)	9.2 (8.6)	

^a Reported⁸: b.p. 157–158° (1 mm). ^b Reported⁸: n_D^{20} 1.5516, 1.5602.

Sulphenyl halides. 4-Toluenesulphenyl chloride was prepared by passing chlorine into a solution of 4-toluenethiol in carbon tetrachloride at room temperature in the absence of light⁹. The product was distilled under reduced pressure and had b.p. 80°/2.5 mm. (Lit.⁹ b.p. 74–76°/1.5 mm). 2-Nitro- and 2,4-dinitrobenzenesulphenyl chlorides were gifts from Dr. D. R. Hogg and had m.p. 71° and 90–92° respectively. (Lit.^{10,11} m.p. 75° and 95–96°, respectively). 2,4-Dinitrobenzenesulphenyl bromide was prepared from the sulphenyl chloride¹². The sulphenyl chloride (5.5 g) was shaken for 24 h with a suspension of potassium bromide (30 g) in carbon tetrachloride (50 ml). The solution was filtered and the solid was well washed with solvent. The solvent from the combined washings and filtrate was removed to leave the crude 2,4-dinitrobenzenesulphenyl bromide. This was recrystallised from carbon tetrachloride. (Yield 4.0 g; m.p. 103°. Lit. value¹² 105°).

The diphenyl disulphides and triorganotin halides produced in the cleavage reactions were also unambiguously obtained from other sources and were used as reference compounds.

Diphenyl disulphides. Bis(2-nitrophenyl) and bis(2,4-dinitrophenyl) disulphides were generously given by Dr. D. R. Hogg. All other symmetric disulphides¹³ were prepared from the reactions of thiols (*ca.* 0.05 mole) and iodine (95% equivalent of the thiol) in 10% sodium hydroxide solution (25 ml). The products precipitated from the aqueous solution. Unsymmetric diphenyl disulphides¹⁴ were obtained from

the reaction of thiols and sulphenyl chlorides (equimolar, *ca.* 0.05 mole) in acetic acid (30 ml). The disulphide products were precipitated on addition of water. All the prepared disulphides were recrystallised.

TABLE 2

DIPHENYL DISULPHIDES

RC ₆ H ₄ -SS-C ₆ H ₃ R'R''			M.p. (°C)	S (%)	
R	R'	R''		Calcd.	Found
4-Me	4-Me	H	39	26.0	26.5
4-Cl	4-Cl	H	69	22.3	22.3
4-tert-Bu	4-tert-Bu	H	85	19.4	18.9
4-tert-Bu	2-NO ₂	H	61	20.1	20.9
4-Cl	2-NO ₂	H	103-104	21.6	21.8
4-Me	2-NO ₂	4-NO ₂	106-107	20.4	19.9

Triorganotin halides. Triphenyltin and tributyltin chlorides were purified commercial samples. Tributyltin and tripropyltin bromides were obtained from the tetraalkyltins, commercial samples, and stannic bromide¹⁵. Tripropyltin iodide was obtained from tetrapropyltin and iodine¹⁵. All the halides had m.p. or b.p. in close agreement with the literature values.

Reactions of the triorganotin aryl sulphides with sulphenyl halides

An exothermic reaction occurred on mixing solutions of an organotin aryl sulphide and a sulphenyl halide. Equimolar quantities of the reagents were taken and the usual scale was 0.01–0.02 mole in a total volume of 20–25 ml. To ensure a completed reaction, the solution was heated under reflux for a short time, usually between 20 and 30 min. Thin layer chromatography [with silica gel as the stationary phase and benzene/hexane (1/1 by volume) as irrigant] showed the presence in the reaction mixture of three disulphide products, except of course in reaction (5) (see below) where only one disulphide is possible. The organotin halide always followed the solvent front. It was detected (as a red spot) on spraying with a 0.1% solution of thiozone in chloroform. One of the three diphenyl disulphides was by far the major product and this was the one predicted from eqn. (3). The remaining two diphenyl disulphide products appeared as traces and were estimated to be only 0.5–1.0% of the total diphenyl disulphide fraction. These were the symmetric diphenyl disulphides. For these two minor products, only retention times were used in the main to establish their identity. The number of product possibilities in each experiment was limited and the differences in retention times was sufficiently large to guarantee satisfactory identification. In reaction (2), much more of the reaction mixture was chromatographed and enough of the separated minor diphenyl disulphides products were obtained for IR spectra to be obtained. The spectral data were used to augment the retention time data.

On cooling the reaction mixture, the major diphenyl disulphide product crystallised out. This was collected and well washed with very small volumes of hexane. On partial evaporation the combined filtrate and washings yielded more

diphenyl disulphides; complete removal of the solvents left a mixture of the triorganotin halide and a small quantity of the diphenyl disulphides. The organotin halides in all but one case were obtained from this mixture by distillation under reduced pressure. An alumina column was used to separate triphenyltin chloride from the residue of reaction (1). IR spectra were used to identify the tin halides.

The combined diphenyl disulphide crystals from each reaction were recrystallised and infrared and ^1H NMR spectra and m.p. were compared with those of the reference diphenyl disulphides.

The following reactions were performed.

(1). *Ph₃SnSC₆H₄-4-tert-Bu and 2-nitrobenzenesulphenyl chloride in benzene solution.* Products: Ph₃SnCl (m.p. 106–107°, yield 65%); 4-tert-butylphenyl 2-nitrophenyl disulphide (m.p. 61–62°, yield 67%); trace amounts of bis(4-tert-butylphenyl) disulphide and bis(2-nitrophenyl) disulphide.

(2). *n-Bu₃SnSC₆H₄-4-Cl and 2-nitrobenzenesulphenyl chloride in carbon tetrachloride solution.* Products: n-Bu₃SnCl (b.p. 106°/0.8 mm, yield 75%); 4-chlorophenyl 2-nitrophenyl disulphide (m.p. 102°, yield 67%); small amount of bis(4-chlorophenyl) disulphide and bis(2-nitrophenyl) disulphide.

(3). *n-Bu₃SnSC₆H₄-4-tert-Bu and 2-nitrobenzenesulphenyl chloride in carbon tetrachloride solution.* Products: n-Bu₃SnCl (b.p. 106°/0.8 mm, yield 72%); 4-tert-butylphenyl 2-nitrophenyl disulphide (m.p. 62°, yield 74%); small amounts of bis(4-tert-butylphenyl) disulphide and bis(2-nitrophenyl) disulphide.

(4). *n-Bu₃SnSC₆H₄-4-Me and 2,4-dinitrobenzenesulphenyl chloride in benzene solution.* Products: n-Bu₃SnCl (b.p. 107°/0.8 mm, yield 70%); 4-tolyl 2,4-dinitrophenyl disulphide (m.p. 106°, yield 80%); small amounts of di-4-tolyl disulphide and bis(2,4-dinitrophenyl) disulphide.

(5). *n-Bu₃SnSC₆H₄-4-Me and 4-toluenesulphenyl chloride in hexane solution.* Products: n-Bu₃SnCl (b.p. 107°/0.8 mm, yield 74%); di-4-tolyl disulphide (m.p. 40°, yield 78%).

(6). *n-Pr₃SnSC₆H₄-4-Me and 2,4-dinitrobenzenesulphenyl bromide in carbon tetrachloride solution.* Products: n-Pr₃SnBr (b.p. 94°/0.8 mm, yield 60%); 4-tolyl 2,4-dinitrophenyl disulphide (m.p. 105–106°, yield 74%); small amounts of di-4-tolyl disulphide and bis(2,4-dinitrophenyl) disulphide.

(7). *n-Bu₃SnSC₆H₄-4-Me and 2,4-dinitrobenzene sulphenyl bromide in carbon tetrachloride solution.* Products: n-Bu₃SnBr (b.p. 110°/0.8 mm, yield 62%); 4-tolyl 2,4-dinitrophenyl disulphide (m.p. 106°, yield 71%); small amounts of di-4-tolyl disulphide and bis(2,4-dinitrophenyl) disulphide.

Tri-n-propyltin 4-tolyl sulphide and iodine

n-Pr₃SnSC₆H₄-4-Me (0.05 mole) and iodine (0.025 mole) were dissolved in hexane. The solution was stirred until the colour of iodine disappeared. Di-4-tolyl disulphide was frozen out in an acetone/solid carbon dioxide bath and was recrystallised from aqueous acetone (m.p. 39°, yield 84%; ^1H NMR and IR spectra were identical with those of an authentic sample). Tripropyltin iodide was obtained from the filtrate by distillation (b.p. 86°/0.6 mm, yield 75%).

Tetraphenyltin and 2,4-dinitrobenzenesulphenyl chloride

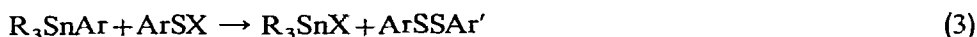
Equimolar quantities (0.025 mole) were heated under reflux in carbon tetra-

chloride solution (30 ml) for 12 h. Not all the tetraphenyltin dissolved even after heating for this period. On cooling, more tetraphenyltin crystallised from the solution. The crystals were filtered and washed well with carbon tetrachloride (m.p. 106°, 95% of the starting material). The washings and filtrate gave a pale yellow solid on evaporation. The solid was recrystallised from acetic acid and had an identical IR spectrum with the sulphenyl chloride starting material (m.p. 91°, 85% of starting material). A sparingly soluble yellow residue was also obtained and this had an identical IR spectrum with bis(2,4-dinitrophenyl) disulphide. No triphenyltin chloride nor 2,4-dinitrophenyl phenyl sulphide was detected.

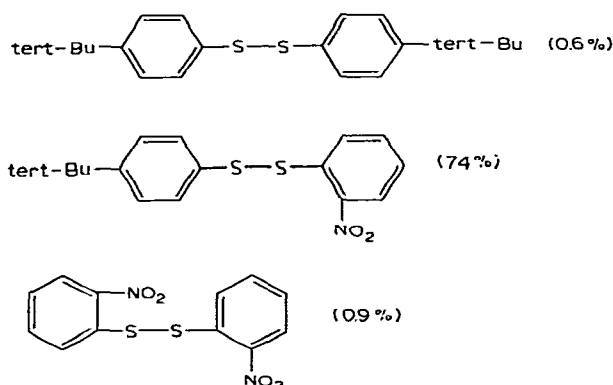
DISCUSSION

Five different triorganotin aryl sulphides and four aromatic sulphenyl halides were used in a total of seven reactions. All the reactions proceeded readily to give high yields of diphenyl disulphides and organotin halides.

According to the equation,



an unsymmetric diphenyl disulphide should be produced if the two Ar groupings are different. In each of the reactions studied in which these groups were different, the unsymmetric diphenyl disulphide was indeed formed as one of the major products (65–80%) with the organotin halide (also *ca.* 70%), but also present were very small amounts of the symmetric diphenyl disulphides (up to 1%); *i.e.* the disulphide products of the reaction of triphenyltin 4-*tert*-butylphenyl sulphide and 2-nitrobenzenesulphenyl chloride were



These symmetric products could have been formed from the disproportionation of the initially formed unsymmetric diphenyl disulphides. The fact that slightly more of the symmetric disulphides were obtained the longer the reaction time, suggested that this could be so. Hydrolysis of the sulphenyl halides by residual water in the systems could also lead to the appropriate symmetric diphenyl disulphides.

Of all the systems studied, the interaction between 4-toluenesulphenyl chloride and tri-*n*-butyltin 4-tolyl sulphide was by far the most exothermic. All the reactions in this product study were rapid and a crude qualitative assessment of the heat evolved

was the only method used to attempt to differentiate reactivities. There were no significant differences in heat evolved in any of the other reactions, *i.e.* there appeared to be no large differences in the reactivities of 2,4-dinitrobenzenesulphenyl chloride and bromide, of tri-*n*-propyltin and tri-*n*-butyltin 4-tolyl sulphides and of reactions in carbon tetrachloride, hexane and benzene solutions. (A series of preliminary kinetic measurements failed to show any major differences in the reaction rates of some $\text{Ph}_3\text{SnSC}_6\text{H}_4\text{-4-Y}$; $\text{Y} = \text{Me, H, Cl or NO}_2$, with 2-nitrobenzenesulphenyl chloride).

The attempted cleavage of tetraphenyltin by 2,4-dinitrobenzenesulphenyl chloride in carbon tetrachloride clearly showed the large differences in reactivity of a tin-carbon and a tin-sulphur bond. The reaction mixture was refluxed for a period of 12 h without any major chemical reaction occurring. Greater than 95% of the tetraphenyltin was recovered along with 85% of the sulphenyl chloride and some disulphide. This bis(2,4-dinitrophenyl) disulphide was most probably produced by the hydrolysis of the sulphenyl chloride. In comparison, all the reactions with the tin sulphur compounds were exothermic and occurred at room temperature.

Cleavages of tin-carbon bonds did not occur in the triorganotin aryl sulphide-sulphenyl halide reactions. Such cleavages would have produced diorganotin compounds. Using as irrigant a 1% acetic acid solution in ethyl acetate, TLC showed the presence only of triorganotin materials on spraying with the dithiozone solution. The typical yellow colouration of diorganotin species were always absent.

The reaction of bromine with a tin sulphide as already indicated⁵ led to the symmetric disulphide and the tin bromide. Similarly iodine has been shown to readily cleave such compounds to give analogous products. *n*- $\text{Pr}_3\text{SnSC}_6\text{H}_4\text{-4-Me}$ and iodine at room temperature gave Pr_3SnI and di-4-tolyl disulphide in 75% and 84% yields respectively. Iodine was obviously a much more effective reagent than 2,4-dinitro- and 2-nitrobenzenesulphenyl chlorides in cleaving tin-sulphur and tin-carbon bonds.

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