

REACTIONS OF ORGANOTIN SULPHIDES II. CLEAVAGE OF ORGANOTIN SULPHIDES BY AROMATIC SULPHENYL COMPOUNDS AND DIVALENT SULPHUR CHLORIDES

J. L. WARDELL AND P. L. CLARKE

Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE (Great Britain)

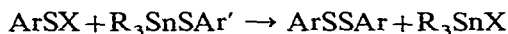
(Received August 27th, 1970)

SUMMARY

Reactions of sulphenyl compounds and sulphur chlorides with organotin sulphides have been studied. Both sulphur dichloride and disulphur dichloride reacted with the organotin sulphides as did sulphenyl bromides ArSBr, chlorides ArSCl, and thiocyanates ArSSCN, but not sulphenyl cyanides ArSCN, sulphenamides ArSNR₂, sulphenyl esters ArSOR, and disulphides ArSSAr. Disulphide products were obtained from sulphenyl halides and thiocyanates with organotin alkyl and aryl sulphides, R₃SnSR and R₂Sn(SR)₂; trisulphides were produced from bis(trialkyltin) sulphides, (R₃Sn)₂S, or dialkyltin sulphides, R₂SnS, and sulphenyl halides and thiocyanates, as well as from sulphur dichloride and organotin aryl sulphides; tetrasulphides were formed from disulphur dichloride and organotin aryl sulphides.

INTRODUCTION

Tin sulphides R₃SnSAr' have been shown to react readily with sulphenyl halides ArSCl and ArSBr in aprotic solvents to give triorganotin halides and diaryl disulphides in good yield¹.



Sulphenyl bromides and chlorides are only two of the members of an extensive series of electrophilic sulphenyl compounds, ArSX (with X = Br, Cl, SCN, OR, SR, NR₂ etc.)². Although the sulphenyl halides have been most widely used, several studies of the other members have been made and reactivity sequences obtained^{3,4}. One aim of the present work was to compare qualitatively the reactivities of sulphenyl compounds in tin-sulphur bond cleavage reactions and to contrast the sequence so obtained with those derived from hydrolyses reactions and additions to olefins. As well as the sulphenyl halides ArSX, two divalent sulphur chlorides were used. Both sulphur dichloride and disulphur dichloride have been used previously to cleave organosilicon alkyl sulphides⁵ to give dialkyl trisulphides. Other sulphide products were also obtained from the S₂Cl₂ reactions.

A further object of this work was to use a number of tin-sulphur bonded com-

pounds and to extend the type of polysulphide products obtainable by this route.

RESULTS AND DISCUSSION

Effect of the sulphenyl compounds on tin-sulphur bond cleavage

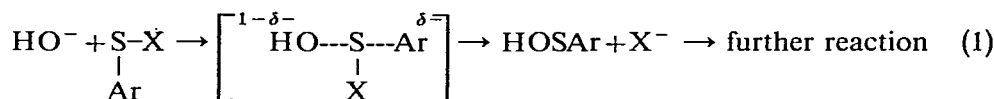
The types of sulphenyl compounds generally used in the cleavage reactions of tin-sulphur bonded compounds were sulphenamides ArSNR_2 , sulphenyl esters ArSOR , sulphenyl thiocyanates ArSSCN , disulphides ArSSAr , and sulphenyl cyanides ArSCN , as well as the sulphenyl halides, which were also used previously¹. The only compounds which successfully reacted with the organotin compounds to give good yields of pure isolatable sulphide products were the halides and the thiocyanate. These gave, for example, diaryl disulphide products with triorganotin aryl sulphides and diaryl trisulphides with bis(tri-*n*-butyltin) sulphide (see later). The organotin product in the thiocyanate reactions was assumed to be the appropriate isothiocyanate rather than the thiocyanate⁶; the IR of the reaction solution showed bands in the 2050 cm^{-1} region.

None of the other types of sulphenyl compounds reacted with any of the tin sulphides even after prolonged periods of heating under reflux. A list of these unsuccessful reactions is given in the experimental section. In each of these reactions, both the reagents could be recovered in good yield.

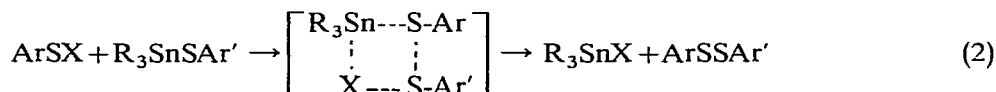
Thiocyanates are considered as reactive as the corresponding chlorides. This assessment is based on 2-nitrobenzenesulphenyl chloride and thiocyanate reacting in similarly short time intervals with bis(tri-*n*-butyltin) sulphide. From earlier work¹, it was concluded that sulphenyl bromides and chlorides were equally as effective in cleaving tin-sulphur bonds. From these qualitative data, the sulphenyl thiocyanates, bromides and chlorides could be grouped together as being comparably reactive and could be contrasted with the other sulphenyl compounds, ArSX with $\text{X} = \text{SAr}$, OEt , NR_2 and CN , which did not react at all. Two distinct groupings were thus obtained without any distinction possible within each group.

Reactivity sequences from previous studies were obtained essentially from kinetic data by Hogg *et al.*^{3,4}. Electrophilic additions of a series of 2-nitrobenzenesulphenyl compounds ArSX , to olefins in methanol and acetic acid solutions gave rise to the order $\text{X} = \text{Br} > \text{Cl} > \text{SCN} \approx \text{OAc} > \text{OMe}^3$ with the latter compound requiring much more forcing conditions than the others before reacting. Hydrolyses of the same series of compounds either in neutral or basic aqueous organic solvents produced the sequence $\text{X} = \text{Br} > \text{Cl} > 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{S} > \text{SCN} > 2\text{-NO}_2\text{C}_6\text{H}_4\text{S} > \text{OEt} > \text{NR}_2 > \text{CN}^{4b}$. The latter compound did not react at all as a sulphenyl compound, some other reaction occurred instead at the cyanide group. Some significant differences between the sequences obtained from the kinetic data and our qualitative assessments are apparent.

A particularly striking difference is that disulphides and sulphenyl esters are hydrolysed within an order or two of the rate for sulphenyl thiocyanates, but the disulphides and sulphenyl esters are clearly very much less reactive than the thiocyanates in tin-sulphur bond cleavage reactions. Different mechanisms are possible for each reaction. The hydrolysis mechanism is considered to be $\text{S}_{\text{N}}2$ -like with a two centred transition state⁷.



A four centred transition state could occur in the tin sulphide reactions in the non-aqueous and essentially poor solvating media used. If so, the relative strengths of



[Similarly for $\text{R}_2\text{Sn}(\text{SAr}')_2$ and $\text{R}_3\text{SnSR}'$]

the tin-sulphur and the tin-X bonds are as important as the polarisation and strength of the S-X bond, in contrast to a hydrolysis reaction in which, as well as the latter, the stability of the leaving group X^- is significant. A detailed kinetic study of these tin sulphide cleavage reactions should be of value.

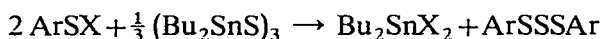
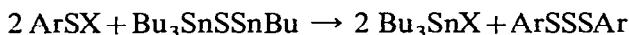
Reactions giving disulphide products

In the previous report, only triorganotin aryl sulphides were used with sulphenyl halides. Diorganotin bis(aryl sulphides), $\text{R}'_2\text{Sn}(\text{SAr})_2$, and triorganotin alkyl sulphides, $\text{R}'_3\text{SnSR}$, have now been found to react as readily to give the appropriate disulphide products under equally mild conditions. Since both simple and functionally substituted alkyl sulphide groups, *e.g.* $\text{RS}^- = \text{C}_{12}\text{H}_{25}\text{S}^-$ and $\text{MeOCOCH}_2\text{S}^-$, as well as aryl sulphides are cleaved, this reaction is a useful general one for production of unsymmetric (as well as symmetric) disulphides. Apart from small percentages of symmetric disulphide impurities, obtained when Ar and Ar' are different (equation 2) as indicated earlier¹, no mono- or other polysulphide products are obtained. This contrasts, for example, with the reaction of sulphur with tetraphenyltin which produced a variety of products⁸.

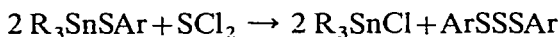
Reactions giving trisulphide products

Symmetric diaryl trisulphides were produced by two routes from tin sulphides and divalent sulphur chlorides. These were:

(a). Reaction of a compound containing a Sn-S-Sn unit, such as $\text{Bu}_3\text{SnSSnBu}_3$ and $(\text{Bu}_2\text{SnS})_3$, with a sulphenyl halide or thiocyanate



(b). Reaction of an organotin aryl (or alkyl) sulphide with sulphur dichloride



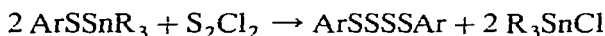
Each method was equally effective and easy to use with the yields being equally good. Although a number of methods of trisulphide formation have been reported, many of these give rise to a mixture of di-, tri- and tetrasulphide products⁹. These methods using the organotin materials compare favourably with the best of the published methods especially as only trisulphides were obtained—there being no other sulphide products—thus eliminating laborious purifications.

Some methods of preparation of trisulphides using Group IVB sulphides have

been published. The most related method is that using sulphur dichloride and silicon sulphides such as chlorodimethylsilicon ethyl sulphide⁵. Other methods involve sulphenyl halides with lead sulphide PbS^{10} and lead mercaptides $Pb(SAr)_2$ with sulphur dichloride¹¹.

Reactions giving tetrasulphide products

Symmetric tetrasulphides were conveniently obtained from disulphur dichloride and organotin aryl sulphides



As with the methods of trisulphide formation, no complications from other polysulphide products were accounted. This again makes this method of formation an attractive one when compared to some existing procedures⁹. The reaction of organosilicon alkyl sulphides with S_2Cl_2 is in contrast to the tin reaction, since a mixture of tri- and tetrasulphide products was produced and the only material isolated was the dialkyl trisulphide⁵. The silicon reaction appeared to be more vigorous than the tin reaction since the former readily occurred at -78° .

EXPERIMENTAL

Materials

Organotin compounds. Bis(tri-*n*-butyltin) sulphide and tri-*n*-butyltin lauryl sulphide were gifts from Albright & Wilson Mfg. Co. Di-*n*-butyltin sulphide was a commercial sample. Tri-*n*-butyltin and tri-*n*-propyltin 4-tolyl sulphides were prepared previously¹. Tri-*n*-butyltin methyl glycollate, tri-*n*-propyltin 4-chlorophenyl sulphide and di-*n*-butyltin bis(*p*-chlorophenyl sulphide) were obtained from the appropriate organotin chloride or oxide and the thiophenol as described earlier¹. They had b.p. $117^\circ/0.02 \text{ mm}$; $158^\circ/0.7 \text{ mm}$ and $220^\circ/1 \text{ mm}$, respectively.

Sulphenyl compounds and sulphur chlorides. Ethyl 2,4-dinitrobenzenesulphate and 2-nitrophenyl thiocyanate were generously given by Dr. P. W. Vipond. They had m.p. 123° and 126° respectively (lit.^{12,13} m.p. 125° and 136° , respectively). 2-Nitrobenzenesulphenyl thiocyanate was obtained by shaking the sulphenyl chloride and a 5 fold excess of anhydrous potassium thiocyanate in benzene for 24 h in the dark. Removal of the solvent after filtering gave a yellow solid, which was crystallised repeatedly from carbon tetrachloride m.p. 90° (lit.¹⁴ m.p. $91-92^\circ$). *N,N*-Dimethyl 2,4-dinitrobenzenesulphenamide was prepared according to the method of Billman *et al.*¹⁵, from the sulphenyl chloride and dimethylamine (1/2 mole ratio) in dry ether. Removal of the solvent after filtration gave a red solid, which was recrystallised from ethanol. Both red and yellow crystals were obtained, each with the same m.p. ($109-111^\circ$) and identical ¹H-NMR [singlet at τ 7.05 (NMe₂), quartet at τ 1.75 and doublet at τ 1.05 (aromatic protons)] and IR spectra.

Sulphur dichloride and disulphur dichloride were redistilled commercial samples.

Reactions

The various reactions are given below. Two basic methods of working up the reaction mixture were used. In a number of cases, conversion of the organotin chloride

or isothiocyanate to the insoluble organotin fluoride was found to be a convenient way of separating this product from the polysulphide. Alternatively, simply cooling the reaction mixture was employed to crystallise out the polysulphide. This latter approach was more useful with the less soluble sulphide products, especially as any absorbed organotin material could be removed by recrystallisation. In all reactions, either method could be used. It was noted that the organotin fluorides dissolved in solvents, such as carbon tetrachloride to give highly viscous solutions. However addition of acetone or diethyl ether, for example, would precipitate the tin fluorides.

Preparation of unsymmetric disulphides

1. *Reaction between tri-*n*-butyltin lauryl sulphide and 2,4-dinitrobenzenesulphenyl chloride.* $n\text{-Bu}_3\text{SnSC}_{12}\text{H}_{25}$ (1 g, 2.04×10^{-3} M) and $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SCl}$ (0.48 g, 2.04×10^{-3} M) in carbon tetrachloride were refluxed for 10 min. KF (1 g) was added and heating continued for a further 10 min. The solvent was removed and diethyl ether added. The solid fluoride residue was collected and the filtrate on evaporation gave the disulphide, $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SSC}_{12}\text{H}_{25}$, which was recrystallised from acetone, using an acetone/ CO_2 bath for cooling. It was a pale yellow solid, m.p. $66\text{--}66.5^\circ$, yield 0.65 g, 80%. (Found: C, 53.8; H, 6.9; S, 15.9. $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$ calcd.: C, 54.0; H, 7.0; S, 16.0%.)

2. *Reaction between tri-*n*-butyltin methyl thioglycollate and 2,4-dinitrobenzenesulphenyl chloride.* $n\text{-Bu}_3\text{SnSCH}_2\text{CO}_2\text{Me}$ (0.59 g, 1.5×10^{-3} M) and $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{-SCl}$ (0.35 g, 1.5×10^{-3} M) were dissolved in diethyl ether (20 ml). The solution was heated for 10 min and then cooled in an ice-salt bath. $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SSCH}_2\text{CO}_2\text{-Me}$, a yellow solid, precipitated and was recrystallised from diethyl ether, m.p. $99\text{--}100^\circ$ (0.31 g, 69%). (Found: S, 21.2. $\text{C}_9\text{H}_8\text{N}_2\text{O}_6\text{S}_2$ calcd.: S, 21.1%.)

3. *Reaction between di-*n*-butyltin (bis 4-chlorophenyl sulphide) and 2-nitrobenzenesulphenyl chloride.* $n\text{-Bu}_2\text{Sn(4-ClC}_6\text{H}_4\text{S)}_2$ (1.5 g, 2.9×10^{-3} M) and $2\text{-NO}_2\text{C}_6\text{H}_4\text{-SCl}$ (1.1 g, 5.8×10^{-3} M) were dissolved in benzene (20 ml). The solution was left overnight. The solvent was removed and the residue partially crystallised on cooling. The yellow crystals were well washed with small volumes of petroleum ether $60\text{--}80$ and recrystallised from acetone, m.p. 103° (1.1 g, 64%). $^1\text{H-NMR}$ and IR spectra were identical to those of an authentic sample of 4-chlorophenyl 2-nitrophenyl disulphide¹.

4. *Reaction between tri-*n*-butyltin 4-tolyl sulphide and 2-nitrobenzenesulphenyl thiocyanate.* A solution of $n\text{-Bu}_3\text{SnS(4-MeC}_6\text{H}_4)$ (0.4 g, 9.8×10^{-4} M) and $2\text{-NO}_2\text{-C}_6\text{H}_4\text{SSCN}$ (0.2 g, 9.5×10^{-4} M) in benzene was refluxed for 30 min. On removing the solvent, a yellow oily residue was obtained and this partially solidified on standing. The solid was recrystallised from petroleum ether $60\text{--}80$, m.p. 107° (0.21 g, 71%). $^1\text{H-NMR}$ and IR spectra were identical with those of an authentic sample of 4-tolyl 2-nitrophenyl disulphide prepared previously¹.

Preparation of di-(2-nitrophenyl) trisulphide

5. *Reaction of bis(tri-*n*-butyltin) sulphide and 2-nitrobenzenesulphenyl chloride.* $(n\text{-Bu}_3\text{Sn})_2\text{S}$ (0.48 g, 7.8×10^{-4} M) and $2\text{-NO}_2\text{C}_6\text{H}_4\text{SCl}$ (0.30 g, 1.56×10^{-3} M) in carbon tetrachloride (10 ml) were refluxed for 10 min. On cooling, a yellow solid precipitated. Bis(2-nitrophenyl)trisulphide was crystallised from carbon tetrachloride, m.p. 176° (lit.¹⁶ m.p. 176°). (Found: C, 42.4; H, 2.1; S, 28.2. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{S}_3$ calcd.:

C, 42.4; H, 2.4; S, 28.3%.)

6. *Reaction of di-n-butyltin sulphide and 2-nitrobenzenesulphenyl chloride.* $n\text{-Bu}_2\text{SnS}$ (1.06 g, 4.00×10^{-3} M) and $2\text{-NO}_2\text{C}_6\text{H}_4\text{SCl}$ (1.49 g, 7.9×10^{-3} M) (in carbon tetrachloride (10 ml) gave, as in reaction (5), bis(2-nitrophenyl) trisulphide, m.p. 176° (1.10 g, 82%). (Found: C, 42.4; H, 2.2; S, 27.9. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{S}_3$ calcd.: C, 42.4; H, 2.4; S, 28.3%.)

7. *Reaction of bis(tri-n-butyltin) sulphide and 2-nitrobenzenesulphenyl thiocyanate.* $(n\text{-Bu}_3\text{Sn})_2\text{S}$ (0.96 g, 1.56×10^{-3} M) and $2\text{-NO}_2\text{C}_6\text{H}_4\text{SSCN}$ (0.66 g, 3.11×10^{-3} M) were dissolved in ether. After leaving at room temperature for 30 min, the solution was cooled in an ice/salt bath. Bis(2-nitrophenyl) trisulphide precipitated and was recrystallised from acetone, m.p. $177\text{--}180^\circ$ (0.43 g, 81%). (Found: S, 28.1. $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{S}_3$ calcd.: S, 28.3%.)

Preparation of di(4-tolyl) trisulphide

8. *Reaction of di-n-butyltin sulphide and 4-toluenesulphenyl chloride.* $4\text{-MeC}_6\text{H}_4\text{-SCl}$ (1.0 g, 6.31×10^{-3} M) in carbon tetrachloride (10 ml) was added to $n\text{-Bu}_2\text{SnS}$ (0.84 g, 3.16×10^{-3} M). Immediate decolouration of the red sulphenyl halide occurred. Excess potassium fluoride was added and the mixture heated for 10 min. The solvent was removed and diethyl ether added to the residue. The insoluble fluoride residues were filtered off and the filtrate evaporated to dryness to give a pale yellow solid. Di(4-tolyl) trisulphide was recrystallised from petroleum ether 60–80, m.p. 83° (lit.¹⁷ 82°). (Found: C, 60.7; H, 5.3; S, 34.6. $\text{C}_{14}\text{H}_{14}\text{S}_3$ calcd.: C, 60.4; H, 5.0; S, 34.6%.)

9. *Reaction of bis(tri-n-butyltin) sulphide and 4-toluenesulphenyl chloride.* $(n\text{-Bu}_3\text{Sn})_2\text{S}$ (0.96 g, 1.56×10^{-3} M) and $4\text{-CH}_3\text{C}_6\text{H}_4\text{SCl}$ (0.50 g, 3.16×10^{-3} M) in carbon tetrachloride gave as in reaction (8), di(4-tolyl) trisulphide, m.p. 80° (0.20 g, 45%).

10. *Reaction of tri-n-butyltin 4-tolyl sulphide and sulphur dichloride.* $n\text{-Bu}_3\text{SnS-}(4\text{-MeC}_6\text{H}_4)$ (4.0 g, 9.7×10^{-3} M) and SCl_2 (0.5 g, 4.85×10^{-3} M) in chloroform (30 ml) were refluxed for 30 min. The solvent was removed and diethyl ether was added to the residue. Crude di(4-tolyl) trisulphide (1.16 g) precipitated on cooling in an acetone/ CO_2 bath. It was recrystallised from petroleum ether 60–80, m.p. $80\text{--}82^\circ$ (0.33 g, 25%). (Found: C, 60.5; H, 5.2; S, 34.8. $\text{C}_{14}\text{H}_{14}\text{S}_3$ calcd.: C, 60.4; H, 5.0; S, 34.6%.)

Preparation of bis(2,4-dinitrophenyl) trisulphide

11. *Reaction of bis(tri-n-butyltin) sulphide and 2,4-dinitrobenzenesulphenyl bromide.* $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SBr}$ (0.35 g, 1.25×10^{-3} M) in ether (10 ml) was added to $(n\text{-Bu}_3\text{Sn})_2\text{S}$ (0.39 g, 0.63×10^{-3} M). A pale yellow solid precipitated. This was bis(2,4-dinitrophenyl) trisulphide (0.25 g, 90%), m.p. 214° (lit.¹⁰ 218°).

12. *Reaction of bis(tri-n-butyltin) sulphide and 2,4-dinitrobenzenesulphenyl chloride.* $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SCl}$ (1.03 g, 4.4×10^{-3} M) and $(n\text{-Bu}_3\text{Sn})_2\text{S}$ (1.39 g, 2.2×10^{-3} M) similarly gave bis(2,4-dinitrophenyl) trisulphide, m.p. 214° , (0.83 g, 85%). (Found: C, 33.3; H, 1.4; S, 22.5. $\text{C}_{12}\text{H}_6\text{N}_4\text{O}_8\text{S}_3$ calcd.: C, 33.5; H, 1.4; S, 22.4%.)

Preparation of tetrasulphides

13. *Reaction of tri-n-propyltin 4-tolyl sulphide and disulphur dichloride.* $n\text{-PrSnS-C}_6\text{H}_4\text{Me}$ (1.16 g, 3.13×10^{-3} M) and S_2Cl_2 (0.21 g, 1.56×10^{-3} M) in chloroform (50 ml) were refluxed for 30 min. The solvent was removed and diethyl ether was added.

On cooling in an acetone/CO₂ bath, yellow di(4-tolyl) tetrasulphide precipitated. It was recrystallised from petroleum ether 60–80, m.p. 70–71° (lit.¹⁷ 75°) (0.37 g, 79%). (Found: S, 41.2. C₁₄H₁₄S₄ calcd.: S, 41.3%.)

14. Reaction of tri-*n*-propyltin 4-chlorophenyl sulphide and disulphur dichloride. n-Pr₃SnS(4-ClC₆H₄) (3.00 g, 7.7 × 10⁻³ M) and S₂Cl₂ (0.52 g, 3.8 × 10⁻³ M) similarly gave bis(4-chlorophenyl) tetrasulphide, m.p. 56° (lit.¹⁸ 57°) (0.85 g, 66%). (Found: S, 35.9. C₁₂H₈Cl₂S₄ calcd.: S, 36.5%.)

Unsuccessful reactions

15. Reactants: bis(tri-*n*-butyltin) sulphide and 2,4-dinitrophenyl 4-tolyl disulphide. Solvent: benzene. Reflux time: 24 h.

16. Reactants: bis(tri-*n*-butyltin) sulphide and 2,4-dinitrobenzene dimethylsulphenamide. Solvent: benzene. Reflux time: 16 h

17. Reactants: tri-*n*-butyltin 4-tolyl sulphide and 2,4-dinitrobenzene dimethylsulphenamide. Solvent: benzene. Reflux time: 2 h.

18. Reactants: bis(tri-*n*-butyltin) sulphide and ethyl 2,4-dinitrobenzenesulphenate. Solvent: ether. Reflux time: 30 h.

19. Reactants: bis(tri-*n*-butyltin) sulphide and 2-nitrophenyl thiocyanate. Solvent: ether. Reflux time: 10 h.

20. Reactants: tri-*n*-propyltin 4-tolyl sulphide and 2-nitrophenyl thiocyanate. Solvent: toluene. Reflux time: 46 h.

21. Reactants: tri-*n*-propyltin 4-chlorophenyl sulphide and di-4-tolyl disulphide. Solvent: benzene. Reflux time: 15 h.

ACKNOWLEDGEMENT

The authors wish to thank Mr. D. W. Grant who initially investigated some of the reactions.

REFERENCES

- 1 J. L. WARDELL AND D. W. GRANT, *J. Organometal. Chem.*, 20 (1969) 91.
- 2 e.g. N. KHARASCH, in N. KHARASCH (Ed.), *Organic Sulphur Compounds*, Vol. 1, Pergamon, 1961 ch. 32.
- 3 e.g. C. BROWN AND D. R. HOGG, *J. Chem. Soc. B*, (1969) 1054; D. R. HOGG, J. A. SMITH AND P. W. VIPOND, *J. Chem. Soc. C*, (1968) 2713; D. R. HOGG AND coworkers, unpublished observations, quoted in ref. 4b.
- 4 e.g. (a) C. BROWN AND D. R. HOGG, *Chem. Commun.*, (1967) 38.
(b) P. W. VIPOND, Ph. D. Thesis, University of Aberdeen (1969)
- 5 E. W. ABEL AND D. A. ARMITAGE, *J. Chem. Soc.*, (1964) 5975.
- 6 M. WADA AND R. OKAWARA, *J. Organometal. Chem.*, 8 (1967) 261.
- 7 E. CUIFFARIN AND A. FAVA, *Progr. Phys. Org. Chem.*, 6 (1968) 81.
- 8 R. W. BOST AND P. BORGSTRON, *J. Amer. Chem. Soc.*, 51 (1929) 1922.
- 9 E. E. REID, in *Organic Chemistry of Bivalent Sulphur*, Vol. III, Chemical Publishing Co., New York, 1960 p. 387.
- 10 L. R. M. PITOMBO, *Chem. Ber.*, 95 (1962) 2960.
- 11 S. BEZZI AND P. LANZA, *Gazz. Chim. Ital.*, 80 (1950) 180.
- 12 N. KHARASCH, D. P. MCQUARRIE AND C. M. BUSS, *J. Amer. Chem. Soc.*, 75 (1953) 2658.
- 13 T. WAGNER-JAUREGG AND E. HELMERT, *Ber.*, 75 (1942) 935.
- 14 N. KHARASCH, H. L. WEHRMEISTER AND H. TIGERMAN, *J. Amer. Chem. Soc.*, 69 (1947) 1612.

- 15 J. H. BILLMAN, J. GARRISON, R. ANDERSON AND B. WOLNAK, *J. Amer. Chem. Soc.*, 63 (1941) 1920.
- 16 H. LECHER AND K. SIMON, *Ber.*, 55 (1922) 2433.
- 17 B. HOLMBERG, *Ber.*, 43 (1910) 226.
- 18 G. F. BLOOMFIELD, *J. Chem. Soc.*, (1947) 1547.

J. Organometal. Chem., 26 (1971) 345-352