Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS
I. ADDITION OF THIOLS TO ALKENYLTIN COMPOUNDS

G. AYREY, R. D. BRASINGTON AND R. C. POLLER
Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH (Great Britain)

(Received August 2nd, 1971)

SUMMARY

3-(Trialkylstannyl)propyl aryl sulphides ($R_3SnCH_2CH_2CH_2SR'$; R = Me, Et, Bu; R' = Ph, *p*-tolyl) were prepared by the addition of arenethiols to allyltrialkyltin compounds. Preferential cleavage of the allyl group by the reaction $R_3SnCH_2CH{=}CH_2 + R'SH \rightarrow R_3SnSR' + CH_3CH{=}CH_2$ occurred when R = R' = Bu and R = R' = Ph. Diallyltin dibromide and benzenethiol gave stannous bromide. Mössbauer parameters of the products are recorded.

INTRODUCTION

In connection with studies on the stabilization of poly(vinyl chloride) we needed to prepare a number of functionally substituted organotin compounds. The only general method available is the hydrostannation of substituted alkenes[1] and other methods were sought for the synthesis of this class of organotin compounds. A possible route is by additions to alkenyltin compounds, for example hydrogen sulphide adds to give unstable products[2] and there are brief accounts in the patent literature of additions of thiocarboxylic acids[3] and perfluoroalkyl iodides[4] to stannylolefins. The present paper describes the preparation of stannylthioethers by the additions of thiols to alkenyltin compounds.

RESULTS AND DISCUSSION

Initial experiments with aliphatic thiols, using a wide range of conditions were unsuccessful and, for example, the predominant reaction between allyltributyltin and butanethiol is cleavage of the allyl group to give butanethiolatotributyltin. (The latter compound is readily estimated by titration with iodine[5] and can be converted to crystalline tributyltin acetate by warming with acetic acid.)

Addition of benzenethiol to allyltributyltin in hexane took place smoothly under free radical conditions using solid carbon dioxide as coolant to give 70–75% of 3-(tributylstannyl)propylphenyl sulphide. These yields were obtained with UV light irradiation of the reactants in air in a quartz flask. Less than 60% of the product was obtained when a Pyrex flask was used but yields near the optimum could be obtained in a Pyrex flask in an atmosphere of nitrogen. That the addition was anti-

Markownikoff was demonstrated by treating the product with hydrogen chloride when the only tin-free product was n-propylphenyl sulphide. It therefore seems likely that addition occurs via PhS• radicals, the higher stability of these radicals compared with those derived from alkanethiols being the reason for the difference in behaviour of butane- and benzenethiols. Under similar conditions benzenethiol gave corresponding addition products with allyltrimethyltin and allyltriethyltin, as did *p*-toluenethiol with allyltributyltin. A convenient method of showing that addition had occurred in preference to cleavage was by measuring the Mössbauer spectra of the products since the $R_3SnCH_2CH_2CH_2SR'$ compounds show a singlet whereas the R_3SnSR' structures give quadrupole split spectra. This was confirmed by preparing independently benzenethiolatotributyltin and *p*-toluenethiolatotributyltin *i.e.* typical compounds which would have been formed had cleavage occurred; the relevant Mössbauer parameters are given in Table 1. Surprisingly, benzenethiol preferentially cleaved the allyl group from allyltriphenyltin to give benzenethiolatotriphenyltin.

TABLE 1

MÖSSBAUER MEASUREMENTS MADE AT 78 K

Units are mm·sec^{-1}, isomer shifts refer to Sn^{IV} oxide.

Compound	δ	Δ
$Me_3SnCH_2CH_2CH_2SPh$	1.40	
$Et_3SnCH_2CH_2CH_2SPh$	1.51	
$Bu_3SnCH_2CH_2CH_2SPh$	1.51	
$Bu_3SnCH_2CH_2CH_2SC_6H_4Me$-*p*	1.51	
Bu_3SnSPh	1.50	2.14
$Bu_3SnSC_6H_4Me$-*p*	1.58	2.13

An interesting reaction occurred between dialkyltin dibromide and benzenethiol to give stannous bromide. The most likely possibility is that cleavage occurred to give, initially, dibenzenethiolatotin dibromide which subsequently disproportionated to stannous bromide and diphenyl disulphide:

$$(PhS)_2SnBr_2 \rightarrow SnBr_2 + PhSSPh$$

The latter compound was shown to be present though it would, in any case, be expected to occur by adventitious oxidation of the excess benzenethiol.

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere[6], the spectra were calibrated with β-tin and tin(IV) oxide, the separation being 2.70 mm·sec^{-1}. Thin layer chromatography was carried out on commercially prepared Merck silica gel G plates which were developed with either a 12/1 hexane/acetic acid mixture (alkyltin compounds) or a 12/1 benzene/acetic acid mixture (phenyltin compounds). Organotin compounds were detected by exposing the plates to an atmopsphere of bromine for 20 min followed by spraying with 0.05% pyrocatechol violet in ethanol.

Column chromatography was carried out on silica gel with a 1/10 benzene/carbon tetrachloride mixture used for elution. All the compounds prepared had IR and NMR spectra which were consistent with the structures assigned.

Allyltrimethyltin[7], allyltriethyltin[8], allyltributyltin[8], allyltriphenyltin[9], diallyltin dibromide[10] and benzenethiolatotributyltin[11] were made by published procedures and had physical constants which were in accord with the literature values.

3-(Tributylstannyl)propyl phenyl sulphide

A solution of allyltributyltin (1.00 g, 3.0 mmole), benzoyl peroxide (0.01 g, 0.4 mmole), benzenethiol (0.50 g, 4.5 mmole) in hexane (15 ml) was placed in a quartz flask, stirred magnetically, cooled with solid carbon dioxide, and irradiated with a Mazda "Black Light", high pressure mercury lamp, type MBW/U from which the glass envelope had been removed (maximum emission at 365 nm). After 1 h the IR spectrum indicated that the allyl group was absent and thin layer chromatography showed the presence of two tin compounds (*Rf* 0.5 and 0.7). The solvent was removed under reduced pressure and the residue heated at 100°/0.1 mm for 2.5 h to remove unreacted benzenethiol giving the crude product (1.5 g). Purification by column chromatography gave pure colourless 3-(tributylstannyl)propyl phenyl sulphide with a 64% recovery from the column equivalent to an overall yield of 71%. This material showed a single spot on a thin layer chromatogram (*Rf* 0.7). (Found: C, 57.1, H, 8.8; S, 7.3. $C_{21}H_{38}SSn$ calcd.: C, 57.2; H, 8.7; S, 7.3%.) The product from a larger scale preparation was distilled when it had b.p. 160–164°/0.02 mm, n_D^{25} 1.5304.

3-(Triethylstannyl)propyl phenyl sulphide

This was prepared in a similar manner by the addition of benzenethiol to allyltriethyltin to give the product in 63% yield as a colourless liquid b.p. 118–120°/0.05 mm, n_D^{25} 1.5528 (Found: C, 50.4; H, 7.3; S, 9.0. $C_{15}H_{26}SSn$ calcd.: C, 50.4; H, 7.3; S, 9.0%.)

3-(Trimethylstannyl)propyl phenyl sulphide

Prepared similarly from benzenethiol and allyltrimethyltin, 26% yield b.p. 95–96°/0.05 mm n_D^{25} 1.5611. (Found: C, 46.75; H, 6.6; S, 9.5. $C_{12}H_{20}SSn$ calcd.: C, 45.75; H, 6.4; S, 10.2%.)

3-(Tributylstannyl)propyl p-tolyl sulphide

Prepared similarly from *p*-toluenethiol and allyltributyltin, 15% yield, n_D^{25} 1.5350. (Found: C, 58.0; H, 8.6; S, 7.6. $C_{22}H_{40}SSn$ calcd.: C, 58.0; H, 8.9; S, 7.0%.)

p-Toluenethiolatotributyltin

A solution of tributyltin oxide (10.0 g, 16.7 mmole) and *p*-toluenethiol (4.5 g, 36.3 mmole) in benzene (50 ml) was boiled under reflux overnight. The solution was cooled, dried over a molecular sieve and the benzene evaporated under reduced pressure. Distillation of the residue gave pure *p*-toluenethiolatotributyltin (11.2 g, 81%); b.p. 145°/0.05 mm. (Found: C, 55.4; H, 8.6. $C_{19}H_{34}SSn$ calcd.: C, 55.2; H, 8.3%.)

Reaction between allyltriphenyltin and benzenethiol

A Pyrex flask containing allyltriphenyltin (1.0 g, 2.6 mmole), benzenethiol (0.3 g, 2.7 mmole) and hexane (20 ml) was stirred magnetically, cooled in solid carbon dioxide and irradiated with the UV lamp for 1.5 h and left overnight. The colourless crystals which had formed were filtered off and the filtrate irradiated for a further 2.5 h to give a second crop of crystals. The crystals were combined, washed with methanol and shown to be benzenethiolatotriphenyltin (0.50 g, 43%) m.p. 103–104° (lit.[12] m.p. 103°). (Found: C, 63.0; H, 4.3; S, 7.0. $C_{24}H_{20}SSn$ calcd.: C, 62.8; H, 4.4; S, 7.0%.)

Reaction between allyltributyltin and butanethiol.

Under a variety of conditions preferential cleavage occurred; the following is typical. A solution of allyltributyltin (5.0 g, 15 mmole) cumene hydroperoxide (0.05 g, 0.3 mmole) and butanethiol (1.8 g, 20 mmole) in acetone (30 ml) in a Pyrex flask was irradiated for 17 h. The heat of the lamp caused the solution to boil under reflux. Removal of the solvent under reduced pressure gave an oily residue (3.4 g) which was shown by titration with a solution of iodine in carbon tetrachloride to consist essentially of pure butanethiolatotributyltin (0.1265 g required 3.40 ml of 0.100 *N* iodine solution = 102% butanethiolatotributyltin). To obtain a solid derivative the remaining product (3.3 g) was treated with excess glacial acetic acid at 60° for 2 h to give colourless crystals of tributyltin acetate (3.2 g, 92%) m.p. 81–84.5 (lit.[13] m.p. 84.5-85°) IR spectrum identical with that of an authentic spectrum.

Reaction between diallyltin dibromide and benzenethiol

A stirred solution of diallyltin dibromide (10.0 g, 26 mmole) and benzenethiol (15.0 g, 140 mmole) in hexane (50 ml) under nitrogen in a Pyrex flask was cooled in solid carbon dioxide and irradiated for 3 h, filtration gave a white solid (2.0 g). This product had m.p. 225°, contained no carbon, hydrogen or sulphur and appeared to be an impure specimen of stannous bromide (lit.[14] m.p. 215.5°). (Found: Br, 54.7. Br_2Sn calcd.: Br, 57.4%.)

The principal absorption in the Mössbauer spectrum of this material occurred at δ 4.17 mm·sec^{-1}, the isomer shift for pure stannous bromide is 4.3 mm·sec^{-1} [15]. Although diphenyl disulphide was shown to be present in the filtrate, no pure compound could be isolated.

Reaction between 3-*(tributylstannyl)propyl phenyl sulphide and hydrogen chloride*

Gaseous hydrogen chloride was passed into 3-(tributylstannyl)propyl phenyl sulphide (3.0 g) at room temperature for 8 h. Thin layer chromatography of the resulting mixture showed that no starting material remained and that the 2 principal components had *Rf* values of 0.4 and 0.2 identical with those of tributyltin chloride and dibutyltin dichloride. The residue was heated in a micro distillation apparatus and the distillate b.p. 25–60°/0.1 mm had an IR spectrum which indicated that it was n-propyl phenyl sulphide. Confirmation was obtained by gas chromatography using a Perkin–Elmer F11 instrument at 158° with silicone fluid 550 as the liquid phase when authentic n-propyl phenyl sulphide had retention time 19.6 min. while authentic *iso*-propyl phenyl sulphide had retention time 13.2 min. The distillate showed a single peak with retention time 19.6 min.

ACKNOWLEDGEMENT

We thank the Science Research Council for a CAPS award (to RDB) and Messrs. Albright and Wilson for generous support.

REFERENCES

1 R. C. POLLER, *The Chemistry of Organotin Compounds*, Logos Press, London and Academic Press, New York, 1970, p. 107.
2 W. T. SCHWARTZ AND H. W. POST, *J. Organometal. Chem.*, 2 (1964) 425.
3 *U.S.Pat.* 3206489, Sept. 14, 1965 [*Chem. Abstr.*, 63 (1965) 18152f].
4 *Neth. Pat.* 6509546, Jan. 31, 1966 [*Chem. Abstr.*, 65 (1966) 750c].
5 E. W. ABEL AND D. B. BRADY, *J. Chem. Soc.*, (1965) 1192.
6 R. C. POLLER AND J. N. R. RUDDICK, *J. Chem. Soc. A*, (1969) 2273.
7 D. SEYFERTH AND F. G. A. STONE, *J. Amer. Chem. Soc.*, 79 (1957) 515.
8 W. J. JONES *et al.*, *J. Chem. Soc.*, (1947) 1446.
9 H. C. CLARK AND R. C. POLLER, *Can. J. Chem.*, 48 (1970) 2670.
10 K. SISIDO AND Y. TAKEDA, *J. Org. Chem.*, 26 (1961) 2301.
11 M. E. PEACH, *Can. J. Chem.*, 46 (1968) 211.
12 D. BLAKE, G. E. COATES AND J. M. TATE, *J. Chem. Soc.*, (1961) 618.
13 G. J. M. VAN DER KERK AND J. G. A. LUIJTEN, *J. Appl. Chem.*, 6 (1956) 49.
14 R. C. WEAST (Ed.), *Handbook of Chemistry and Physics*, 49th ed., Chemical Rubber Co., Cleveland, 1968/1969, p. B-257.
15 M. CORDEY-HAYES, *J. Inorg. Nucl. Chem.*, 26 (1964) 915.