Fundamental Reactivity of Sulfur with Organotins: Underexploited Ar-S Bond Formation under Aqueous and Aerobic Conditions

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Received 20 September 2003; revised 19 March 2004

Abstract: This work describes a comprehensive study on the reactivity of organotins with elemental sulfur for producing organosulfur compounds and Ar-S bonds. Elemental sulfur, fluoride ions and organotins reacted under aqueous, aerobic and almost neutral conditions to selectively generate disulfides, without forming thiols or thioethers (or sometimes trisulfides). Several parameters were examined in depth: organotins, carbon ligands, fluoride sources, temperatures, solvents and equivalents of sulfur.

Key words: sulfur, organotins, fluoride ions, hypercoordination, aryl disulfides

Introduction

After nearly 150 years, since the discovery of diethyltin diiodide in 1849 by Sir Edward Frankland, a comprehensive study on the reactivity of elemental sulfur with organotins was achieved for selectively producing aryl disulfides, and most notably Ar-S bonds.[1]

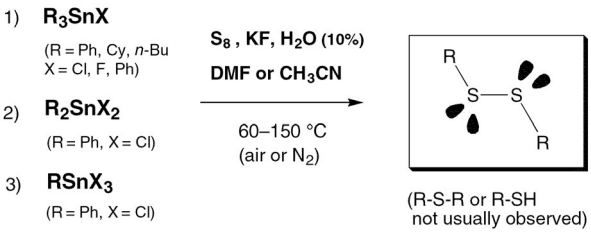
Incorporation of elemental sulfur into organic molecules is important[2] and there is a need for simple protocols for making Ar-S bond under neutral, moist and aerobic conditions. Strong bases (Grignard or organolithium reagents) used in classical methods are cumbersome because of their standardization, their pyrophoric, moisture- and air-sensitive nature, and their incompatibility with many functional groups. Moreover, arylthiols are often formed in moderate yields along with undesirable polysulfides.[3] Purification by distillation is often the only issue.

Ar-S bond formation by metal-catalyzed reactions (Pd, Cu, Ni)[4] with aryl halides or boronic acids have some limits imposed by the electron-withdrawing or donating nature of the substituents on the aromatic ring. Most high-yielding methods refer to reactions with organic iodides as substrates. Otherwise, yields over 95% from Pd catalysts are occasionally observed.[5] Moreover, several research groups can testify to the air sensitivity of most classical Pd, Ni or Cu catalysts.[5,6,7] We also experienced some limits for making poly(*p*-phenylene sulfide) oligomers.[8] Finally, the Newman-Kwart rearrangement of thionocarbonates or its variant requires high temperatures for several hours.[9]

For the above reasons, we present an innovative, but simple, sulfuration method for making Ar-S bonds and aryl disulfides. This method uses inexpensive elemental sulfur under atmospheric, aqueous and almost neutral conditions, in open vessels. Preliminary reports by Schumann and coworkers[10] opened up this field in 1962–3, but under less favorable conditions, without fluoride ions. High temperatures (200 °C), lower reactivity, lower selectivity and undesirable mixtures of products (thioethers, disulfides, organotin sulfides, aromatic compounds, etc.) resulted. Electron-rich C-Sn bonds can be activated by generating hypercoordinated nucleophilic species with fluoride ions.[11] Here, we contributed to the first comprehensive study on the reactivity of organotins with elemental sulfur in the presence of fluoride ions for selectively producing organosulfur compounds (disulfides).

Development of the Sulfuration Method

A preliminary communication[12] was limited to some electrophilic sulfur sources with our reagent (n-Bu_4N)(Ph_3SnF_2).[13] In this work, we showed that water can modify the course of the reaction. We greatly simplified and generalized the method by making hypercoordinated species in situ. We analyzed in depth several reaction parameters: a) solvents, b) amount of water, c) temperatures and reaction time, d) fluoride sources, e) sulfur/organotin molar ratio and f) classes of substrates and ligands transferred. Scheme 1 summarizes the conditions for the selective preparation of aryl disulfides, at the expense of thiols, thioethers and sometimes trisulfides.



Scheme 1 Simple and selective sulfuration of organotins

SYNTHESIS 2004, No. 12, pp 2052–2057
Advanced online publication: 02.08.2004
DOI: 10.1055/s-2004-829166; Art ID: Z14003SS

Solvents and Rate Enhancement with Water

The first important parameter is the choice of solvents. In Table 1, coordinating polar solvents like DMF and CH_3CN were best when combined with H_2O (entries 2–5 and 8 in Table 1). However, the amount of H_2O should not exceed 10–15% v/v, or the yield drops drastically. It is known that the coordinating ability of solvents on organotins increases the rates and the yields. Surprisingly, dried DMF (Table 1, entry 1) or CH_3CN (Table 1, entry 7), lead to unsatisfactory results. Methanol as a polar protic solvent did not lead to even a trace of product (Table 1, entry 10). Weakly or non-coordinating solvents like THF or xylene were inefficient. The exact reasons for rate and yield enhancement with H_2O is unclear. However, it has been reported that diaquo cationic triorganotin species can be formed from triorganotin halides.[14] It is also known that the dielectric constant of a solvent can increase exponentially with a small percentage of water. The debate is open on this effect; i.e. the coordinating ability of water molecules on tin or the increase of the solvent polarity (or both effects).

Biographical Sketches

from left to right: J.-M. Raimundo, Y. M. Chabre, M. Gingras

Marc Gingras was born in St-Jérôme, Québec, Canada in 1962. He studied chemistry from 1981–84 at the University of Sherbrooke, Québec, Canada where he obtained his BSc degree. From 1985–89, he completed a PhD degree at McGill University, Montréal, Canada under the co-direction of Pr. T. H. Chan and Pr. David N. Harpp. His graduate work involved the development and use of organometallic reagents of the main group elements. In 1989, he joined the team of Pr. Edwin Vedejs as an NSERC Postdoctoral Fellow at the University of Wisconsin-Madison. In 1992, he continued for another postdoctoral year at the same university with Pr. Laura L. Kiessling in the field of glycochemistry and ROMP. After obtaining a French scholarship (séjour scientifique de haut niveau), he joined the Laboratory of Supramolecular Chemistry at Strasbourg under the guidance of Pr. Jean-Marie Lehn (1993–1995). He then took up a faculty position (chargé de cours) at the Université Libre de Bruxelles. In 1999, he was appointed as professor at the University of Nice-Sophia Antipolis, France, where his interests include synthetic methodologies, advanced organic materials and supramolecular chemistry toward nanotechnology (sulfurated molecular asterisks, dendrimers, helicenes, etc.).

Yoann M. Chabre was born in Nice, France, in 1979. He received his master and DEA degrees at the University of Nice-Sophia Antipolis, Nice, France. He is currently completing his PhD work under the guidance of Pr. Marc Gingras at the same university, in the Chemical Laboratory of Organic and Organometallic Materials (CMOM). His research interests are in the field of organic synthesis, in particular sulfur chemistry and supramolecules.

Jean-Manuel Raimundo was born in Redon, France, in 1973. He obtained a BSc in biochemistry from the University of Rennes, France, and his PhD from the University of Angers (France) under the guidance of Dr. Jean Roncali on new organic materials for optoelectronic devices. In 2000, he did some postdoctoral studies in the laboratory of Pr. François Diederich at ETH, Zürich, Switzerland. He spent one year in a temporary academic position (ATER) at the University of Angers (2001). He did a second postdoctoral stay at the same university during a collaboration with TotalFina Elf (2002). He was appointed, at the University Nice Sophia-Antipolis, as Maître de Conférence in 2003. His research interests include organic synthesis, new synthetic reactions and the development of advanced organic materials.

Table 1 Solvent, Temperature and Water Effects on Yield, Reactivity and Selectivity in the Sulfuration of Ph_3SnCl[a,b,c]

					Yield[f,g] (%)	
Entry	Solvent[d,e]	Ratio H_2O– solvent	T (°C)	Time (h)	$(PhS)_2$	$(PhS)_2S$
1	DMF	0/100	150	0.42	23	8
2	DMF	5/95	150	0.42	69	8
3	DMF	10/90	150	0.42	83	9
4	DMF	20/80	150	0.42	55	7
5	DMF	10/90	90	19	62	12
6	DMF	10/90	60	19	30	11
7	CH_3CN	0/100	90	10	Trace	–
8	CH_3CN	10/90	90	19	75	7
9	CH_3CN	20/80	90	19	8	3
10	MeOH[h]	0/100	80	80	–	–

[a] Ph_3SnCl (1.20 mmol).
[b] Elemental sulfur (3.74 mmol).
[c] KF (3.72 mmol).
[d] DMF dried over 4 Å molecular sieves.
[e] CH_3CN dried over 3 Å molecular sieves.
[f] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[g] Isolated mixture, ratios analyzed by GC.
[h] The water content of MeOH was estimated to be 0.05%.

Sulfur/Organotin Molar Ratio

A second variable was the sulfur–organotin molar ratio. In Table 2, we show that a ratio of 3:1 (Table 2, entry 3) was the best. Higher ratios provided more trisulfide and less selectivity. However, in spite of an excess of sulfur, we were not able to produce trisulfides in good yield (Table 2, entry 1). Diminishing the ratio to 0.50 gave no trace of thioether, but traces of thiol for the first time. Selectivity for disulfide formation is astonishing despite the possibility for producing thioether, trisulfide and thiol.

Table 2 Variation of Sulfur–Organotin Molar Ratio and the Effect on Yield and Selectivity[b,c,d,e]

		Yield[f,g] (%)	
Entry	Sulfur[a] – organotin[b]	$(PhS)_2$	$(PhS)_2S$
1	8.0	71	25
2	4.5	66	16
3	3.1	83	9
4	2.9	74	4
5	2.8	75	6
6	2.7	74	2
7	2.6	67	2
8	2.5	60	–
9	1.25	25	–
10[h]	0.50	33	–

[a] Elemental sulfur (according to the molar ratio mentioned).
[b] Ph_3SnCl (1.20 mmol).
[c] KF (3.72 mmol).
[d] H_2O–DMF (10:90), 25 min, 150 °C.
[e] DMF dried over 4 Å molecular sieves.
[f] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[g] Isolated mixture, ratios analyzed by GC.
[h] 3% PhSH detected.

Fluoride Ion Sources

A third parameter was the source of fluoride ions, as shown in Table 3. They are all commercially available and inexpensive. Cryolite (Na_2SiF_6) or fluorite (CaF_2) were of special interest due to their natural abundance. Without fluoride ion, no sulfuration occurs (Table 3, entry 6). It was shown that hypercoordinated (*n*-Bu_4N)(Ph_3SnF_2) was equally reactive in this sulfuration. It was then postulated that penta- or hexacoordinated organotins might be involved as the reactive species. Fluoride ions incorporated in a complex or CaF_2 gave poor yields (Table 3, entries 3–5). In spite of the presence of protic KHF_2, no thiol was produced (Table 3, entry 2). In short, the simplest efficient fluoride source was inexpensive KF.

Table 3 Variation of Fluoride Ion Sources and the Effect on Yield and Selectivity in the Sulfuration of Triphenyltin Chloride[a,b,c]

Entry	Fluoride source	Ratio H_2O–DMF[c]	Time (h)	Yield[d,e] (%) $(PhS)_2$	$(PhS)_2S$
1	KF	10/90	0.42	83	9
2	KHF_2	10/90	22	31	7
3	Na_2SiF_6	10/90	96	29	–
4	CaF_2	10/90	0.42	–	–
5	$NaBF_4$	10/90	0.42	–	–
6	-	10/90	0.42	–	–

[a] 3.72 mmol fluoride source; 1.2 mmol Ph_3SnCl.
[b] Elemental sulfur (3.74 mmol).
[c] DMF dried over 4 Å molecular sieves. 150 °C.
[d] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[e] Isolated mixture, ratios analyzed by GC.

Reaction Time, Temperatures and Yields

We next turned our attention to reaction time and temperatures in DMF and in CH_3CN (Tables 1 and 4). The temperature was lowered to 90 °C in CH_3CN or DMF, but at the expense of a longer reaction time (Table 1, entries 5, 8). The reaction progressed even at 60 °C, but provided only 30% yield of disulfide (Table 1, entry 6). The optimized time in 10% water–DMF and a sulfur–organotin ratio of 3.1 was about 25 minutes at 150 °C. A distinct brown color was indicative of a quick and successful reaction.

Table 4 Variation of Reaction Time and Yields for the Reaction of Triphenyltin Chloride in the Presence of Sulfur and Fluoride Ions[a]

Entry	Time (min)	Yield[b,c] (%) $(PhS)_2$	$(PhS)_2S$
1	15	42	–
2	25	60	–
3	60	78	–
4	120	66	–

[a] Ph_3SnCl (1.2 mmol), elemental sulfur (3.00 mmol), KF (3.72 mmol), H_2O–DMF (10:90, DMF dried over 4Å molecular sieves), 150 °C.
[b] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[c] Isolated mixture, ratios analyzed by GC.

Organotins and the Number of Carbon Ligands Delivered

The next variable was the number of carbon ligands liberated from tin, as shown in Table 5. The best substrates were triphenyltin chloride and tetraphenyltin (Table 5, entries 3, 4). Under fluorinating conditions, one may speculate that the increase of fluorine ligands on the organotin complex decreases its carbon nucleophilicity. A good compromise could be achieved with hypercoordinated triphenyltin and tetraphenyltin species. It was only under forcing conditions, after 44 hours at 150 °C, that diphenyltin dichloride (Table 5, entry 2) could possibly deliver a phenyl group in a 88% yield. A higher lack of reactivity was found for phenyltin trichloride (Table 5, entry 1). Those observations were necessary for ruling out any significant organotin disproportionation within 25 minutes at 150 °C for an in situ generation of triphenyltin or tetraphenyltin species. An important dynamic exchange of phenyl ligands on tin seems unlikely here. A second important point is the number of carbon ligands reacting with sulfur under those conditions. Due to the kinetics, it is probable that diphenyltin species mainly delivered one ligand, from comparison with phenyltin species (entry 1). However, the delivery of two ligands from triphenyltin species is apparently favorable, otherwise a yield of 166% would be reached when assuming a stoichiometry with one carbon ligand transferred. In the case of tetraphenyltin, a combination of one or two ligands transferred cannot be excluded.

Table 5 Reactivity of Mono-, Di-, Tri- and Tetraorganotins toward Sulfur and Fluoride Ions: Determination of the Number of Carbon Ligands Delivered from the Organotin Substrate [a]

Entry	Organotin	Time (h)	Yield[b,c,d] (%) $(PhS)_2$	$(PhS)_2S$
1	$PhSnCl_3$	44	– (18)	– (10)
2	Ph_2SnCl_2	44	44 (88)	1 (2)
3	Ph_3SnCl	0.42	83 (166)	9 (18)
4	Ph_4Sn	5	50 (100)	–

[a] Organotin (1.2 mmol), elemental sulfur (3.74 mmol), KF (3.72 mmol), H_2O–DMF (10:90, DMF dried over 4 Å molecular sieves), 150 °C.
[b] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[c] Isolated mixture, ratios analyzed by GC.
[d] Yields in parentheses are calculated from the stoichiometric release of one phenyl ligand. Other yields are based on the transfer of two phenyl ligands.

Substrate Studies, Substituent Effects and Relative Rates of Carbon Ligand Delivery

Another important parameter was the electronic significance of the para-substitution on the aromatic ring of tetraphenyltin compounds, as shown in Table 6. In short, it was found that electron-withdrawing substituents were the most reactive,[15] leading to a quick reaction for Cl substitution (entry 2). There was almost no reactivity for a donor MeO group (entry 4).

At last, aryl, primary and secondary alkyl ligands reacted selectively with sulfur, as shown in Table 7. Relative rates of carbon ligand transfer are: Ph >> cyclohexyl > butyl.

Table 6 Variation of Substituents on Tetraaryltins and Their Relative Reactivity with Elemental Sulfur in the Presence of Fluoride Ions

			Yield[c,d] (%)	
Entry	Tetraorganotin	Time (h)	$(PhS)_2$	$(PhS)_2S$
1[a]	Ph_4Sn	5.0	50	–
2[b]	$(p\text{-ClPh})_4Sn$	0.42	58	–
3[b]	$(p\text{-}CH_3Ph)_4Sn$	5.0	33	Trace
4[b]	$(p\text{-}CH_3OPh)_4Sn$	5.0	–	–

[a] Organotin (1.20 mmol), elemental sulfur (3.74 mmol), KF (3.72 mmol), H_2O–DMF (10:90, DMF dried over 4 Å molecular sieves), 150 °C.
[b] Organotin (0.60 mmol), elemental sulfur (1.87 mmol), KF (1.86 mmol), H_2O–DMF (10:90, DMF dried over 4 Å molecular sieves), 150 °C.
[c] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS. Isolated yields, purity >95% as checked by GC.
[d] Yield are based on the transfer of two ligands.

The reactivity difference between aromatic and alkyl groups is noteworthy. Only under forcing conditions (22 h at 150 °C) could cyclohexyl ligands be transferred to provide disulfide in 50% yield (Table 7, entry 2). With mixed organotin derivatives such as *n*-Bu_3SnPh or *n*-Bu_3SnCl, there was a significant lack of reactivity.

In this paper, we have delineated, for the first time, important parameters for the reactivity of organotins with elemental sulfur, although an exact mechanism is still unknown. Those studies are fundamental in organotin chemistry. However, a surprising fact is that fluorodestannylation-protonation under aqueous (and even protic) conditions at 150 °C is not a major reaction pathway in DMF; neither is the formation of thiols from trapping an intermediate complex. Selectivity for disulfide formation, even in the presence of excess sulfur or under a nitrogen atmosphere, might come from the dimerization of PhS moieties. This postulate is consistent with the common intermediate and the independence of the electrophilic sulfur source described in a previous communication.[12] A mechanism involving the insertion of a sulfur atom between a tin-carbon bond has been documented with SO_2[16] and SO_3,[17] and some organotin sulfide by-products were found by Schumann et al.[10] in their sulfuration method (which was carried out in the absence of fluoride ions). A similar mechanism could be evoked here with elemental sulfur, with a dimerization following. One should also note that a thermodynamic disproportionation of trisulfide into disulfide is possible at high temperature, often above 200 °C. However, our results in CH_3CN at 90 °C do not suggest this as a logical possibility. Moreover, after only 15 minutes in DMF at 150 °C, there was no trisulfide observed (Table 4, entry 1). The polymeric nature and the insolubility of the organotin fluoride by-products complicate the characterization of intermediates and the elucidation of the reaction mechanism. However, these by-products could be removed by a simple filtration on a silica gel column, using only EtOAc as solvent. This solvent helps in the precipitation of the organotin fluoride polymer.

Table 7 Variation of Carbon Ligands on Tetra- and Triorganotins and Their Reactivity with Elemental Sulfur in the Presence of Fluoride Ions[a]

			Yield[b,c] (%)	
Entry	Organotin	Time (h)	$(RS)_2$	$(RS)_2S$
1	Ph_3SnCl	0.42	83 (166)[d]	9 (18)[d]
2	Cy_3SnCl	22	50 (99)[d]	Traces
3	*n*-Bu_3SnCl	48	Traces	Traces
4	*n*-Bu_3SnPh	48	Traces	Traces

[a] Organotin (1.20 mmol), elemental sulfur (3.74 mmol), KF (3.72 mmol), H_2O–DMF (10:90, DMF dried over 4 Å molecular sieves), 150 °C.
[b] Products were characterized by ^1H NMR, ^{13}C NMR and GC/MS.
[c] Isolated mixture, ratios analyzed by GC.
[d] Hypothetical yields in parentheses are calculated from the stoichiometric release of one phenyl ligand.

Conclusion: A Simple Sulfuration of Organotins that Provides a High Selectivity for Aryl Disulfide Formation under Aqueous and Atmospheric Conditions

In summary, we report herein a comprehensive study on the sulfuration of organotins with inexpensive elemental sulfur, under almost neutral, aqueous and aerobic conditions, to make Ar-S bonds. Fluoride ions and water enhanced the reactivity and the efficiency of the method. It avoids strong bases and the associated disadvantages. Eventually, disufides could be easily reduced to thiols, if needed. Hypercoordinated tin species might be involved in this reaction, as we have already shown similar reactivity to occur with Gingras' reagent $(nBu_4N)(Ph_3SnF_2)$.[13]

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument at 200 MHz and 50 MHz, respectively, in $CDCl_3$. Chemical shifts (δ) are reported in part per million (ppm) downfield from TMS. GC analyses were achieved on a Hewlett Packard 5890 Series II, a FID detector and an apolar HP5 column (0.25 mm ID, 25 m). GC/MS spectra were recorded on a Thermoquest Finnigan Trace GC/Automass III Multi equipped with a DB5MS column [(5% phenyl)-methylpolysiloxane; 0.25 mm ID, 25 m], an EI source and a quadrupole analyzer. Characterization and analysis of the mixture of products was achieved by comparison to authentic samples and/or from GC/MS, ^1H and ^{13}C NMR spectroscopy. Characterization of the isolated mixture of PhSSPh and PhSSSPh was achieved by ^1H, ^{13}C NMR and GC/MS. GC analyses of PhSPh, PhSSPh and PhSH were done with reference to authentic samples. Anhydrous reactions were run in an inert atmosphere with oven-dried glassware, a Teflon stirring bar and a condenser equipped with a rubber septum. Reactions were monitored with analytical TLC using precoated aluminium sheets (SiO_2 60F254, SDS; thickness 0.2 mm, 15–60 microns). TLC visualization was achieved by UV (254, 312 nm) and/or development with a molybdenum–cerium acidic so-

lution (10 mL H_2SO_4, 900 mL H_2O, 25 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 10 g $NH_4Ce(SO_4)_2$). Purification by flash chromatography was performed using Merck silica gel (230–400 mesh, 60 Å). Molecular sieves were activated (250 °C, 3 h). DMF and CH_3CN (99%, Acros Organics) were distilled under reduced pressure over CaH_2 and kept over 4 Å and 3 Å MS, respectively. MeOH (Prolabo) was used as received (estimated water content <0.05%). Most organotins (Sigma-Aldrich) and elemental sulfur were used as received. Fluoride sources: KF, $NaBF_4$ (Acros Organics), CaF_2, Na_2SiF_6, KHF_2 (Sigma-Aldrich), were used as supplied or vacuum-dried.

Typical Procedure: Into a 10 mL oven-dried round-bottom flask was weighed the organotin (1.20 mmol). A fluoride ion source (3.72 mmol) and elemental sulfur (0.60 to 9.60 mmol) were added. Dry DMF and a controlled amount of distilled water (0% to 20% relative to DMF) were injected for a total volume of 3.0 mL. After installing a water condenser, the mixture was immersed in an oil bath at 150 °C under atmospheric conditions, while vigorously stirring for the required time. Appearance of a brown color was often indicative of a successful sulfuration. After cooling down to r.t., the mixture was filtered while rinsing with EtOAc (10 mL). Into the filtrate was poured H_2O (100 mL) and the aqueous phase was extracted with EtOAc (80 mL or less). The organic phase was washed with H_2O (3×30 mL). The organic phase was dried over $MgSO_4$ then filtered, and the solvent was removed under reduced pressure. The crude product was purified on a short chromatography column (SiO_2; hexane) to provide the corresponding disulfide as a major component, as shown by GC, GC/MS, ^{1}H NMR and ^{13}C NMR analyses and comparisons to authentic samples of thioethers, disulfides or thiols. Trisulfides were characterized by GC/MS, ^{1}H NMR and ^{13}C NMR.

Acknowledgment

We (I or the authors) thank the Ministère de la Jeunesse, de l'Education Nationale et de la Recherche de France and Mrs. Claire Gratay for a specific reaction. Dr. André Loupy from the Université of Paris-Sud, Orsay is thanked for helping us at the initial stage of this study.

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