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Reactivity of hypervalent silicon and tin compounds toward electrophilic sulfur

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Abstract

Sulfuration of hypervalent complexes of silicon and tin was attempted with several electrophilic sulfur reagents for making carbon–sulfur bonds under almost neutral conditions. We provided a qualitative scale of reactivity between various hypervalent salts. Simple and practical methodologies involving non-odorous elemental sulfur were developed. It avoided the use of H_2S or standardized organolithium and Grignard solutions with sulfur, under highly basic conditions. © 2000 Elsevier Science Ltd. All rights reserved.

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Although several methods have been created for introducing sulfur into organic molecules, there is a general lack of studies involving hypervalent complexes.[1] Sulfuration of these species is the purpose of this study. Hypervalent compounds have lead to a great interest in recent organic methodologies, due to a larger electronic density and particularly, to the weakening of some carbon–heteroatom bonds; it was exploited in Pd-catalyzed procedures involving boron,[2] silicon[3] and tin compounds.[4] Furthermore, hypervalent species are thought to be the reactive intermediates in the sequence hydroboration–oxidation, or the Tamao's oxidation with organosilicons. Because commercial hypervalent fluorinating agent **1** was originally produced by one of us, as an anhydrous synthetic equivalent to TBAF, it served as a starting point in this study.[5,6]

The question raised here concerns electron-rich hypervalent species and a scale of reactivity towards some electrophilic sulfur reagents. Another curiosity is the relative reactivity of hypervalent silicon and tin compounds. A goal pursued is the creation of simple sulfuration procedures. The abundance of sulfur, its low cost and its almost non-odorous nature, is highly desirable in industrial or academic processes. It sharply contrasts to the regulated use of poisonous, smelly and gaseous H_2S.

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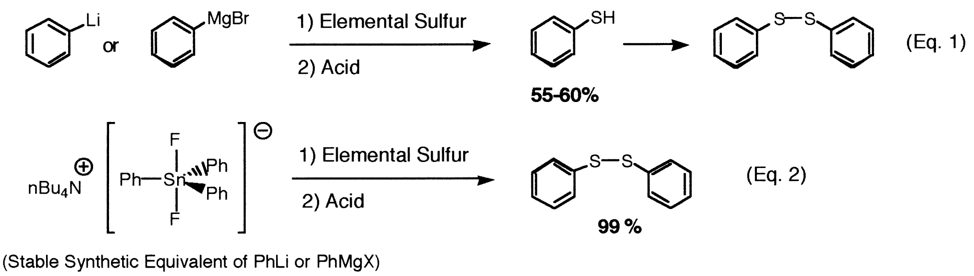
Equation 1 (in Scheme 1) shows classic methods for making Ar–S bonds, when using strong bases. Our procedures avoid the use of pyrophoric materials, highly basic organolithiums, or Grignard reagents.^{7}



Scheme 1. Reaction of nucleophiles with elemental sulfur

Manipulation of a large amount of highly reactive, air- and moisture-sensitive carbanions is undesirable. Some synthetic equivalents to these carbanions are commercial, crystalline and non-hygroscopic salts, which are operating under almost neutral conditions. Importantly, they can be weighed in open air and do not need a standardization with some anhydrous and cumbersome titrations. Alternatively, they can be prepared in situ (Fig. 1). The most stable structures proposed for **3** and **4** agree with the 'electronegativity rules' for the stereochemistry of TBP complexes (the most electronegative groups are in the apical positions).

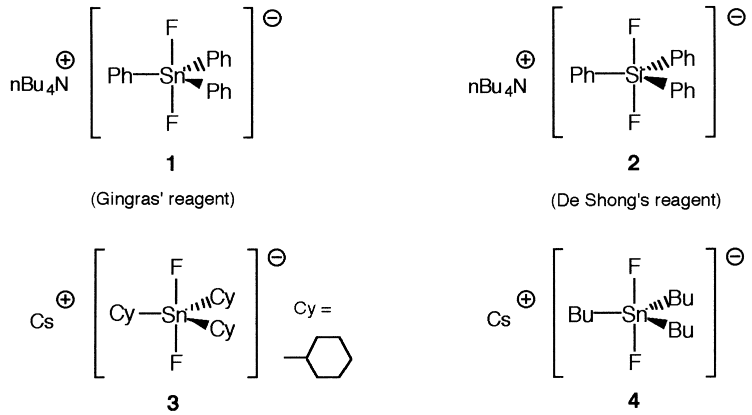


Figure 1. List of hypervalent complexes used or generated

We then investigated their reactivities under various experimental conditions: sulfurating agents, variation of the elements (Si, Sn), solvent, temperatures, time, molar ratios and ligand transferred (Table 1). A constant observation is the delivery of only one ligand and the highly selective formation of alkyl or aryl disulfides.

The electrophilic sulfur species utilized are presented in Fig. 2. From this list, only sulfur dichloride (SCl_2) is less convenient, because of its easy decomposition to sulfur monochloride (S_2Cl_2). Powdered sulfur and **8** are convenient stable solids, and S_2Cl_2 is cheap and produced in bulk amount.

Table 1
Sulfuration of hypervalent silicon and tin compounds[a]

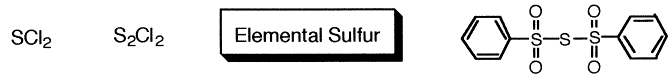
ENTRY NO	Si or Sn COMPOUND (mmol)	SULFUR REAGENT (mmol)	CsF[b] (mmol)	T (°C)	SOLVENT	TIME (hr)	PRODUCTS	YIELD (%)[c]
1	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		130	DMF	22	PhSSPh	99
2	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		130	DMF	5.5	PhSSPh	99
3	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		130	DMF	1.0	PhSSPh	86
4	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		130	DMSO	1.5	PhSSPh	80
5	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		100	DMF	22	PhSSPh	< 43
6	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		50	DMF	27	PhSSPh	17
7	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.93)		22	THF	48	PhSSPh	0
8	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (0.64)		130	DMF	5.5	PhSSPh	58
9	$nBu_4N\ (Ph_3SnF_2)$ (0.63)	Sulfur (0.63)		130	DMF	23	PhSSPh	16
10	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (1.90)		130	DMF	24	PhSSPh	99
11	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	Sulfur (1.90)	CsF (1.0)	130	DMF	24	PhSSPh	50
12	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	SCl_2 (0.47)		65	THF	25	PhSSPh	30
13	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	S_2Cl_2 (0.35)		130	DMF	23	PhSSPh	80[d]
14	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	$(PhSO_2)_2S$ (0.35)		130	DMF	8.25	PhSSPh	75
15	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	$(PhSO_2)_2S$ (0.35)		130	DMSO	8.5	PhSSPh	0
16	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	$(PhSO_2)_2S$ (0.35)		130	DMF	1.5	PhSSPh	23
17	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	$(PhSO_2)_2S$ (0.64)		130	DMF	16	PhSSPh	80
18	$nBu_4N\ (Ph_3SnF_2)$ (0.32)	$(PhSO_2)_2S$ (0.35)		90	DMF	8	PhSSPh	0
19	Cy_3SnCl (0.50)	Sulfur (1.50)	CsF (1.0)	130	DMF	20	CySSCy	40
20	Cy_3SnCl (0.50)	Sulfur (1.00)	CsF (1.6)	130	DMF	48	CySSCy	10
21	Cy_3SnCl (0.50)	Sulfur (1.56)	CsF (1.25)	130	DMF	48	CySSCy	80
22	Cy_3SnCl (0.50)	$(PhSO_2)_2S$ (0.50)	CsF (1.25)	130	DMF	24	CySSCy	0
23	$nBu_4N\ (Ph_3SiF_2)$ (0.43)	Sulfur (1.29)		130	DMF	24	PhSSPh	0
24	$nBu_4N\ (Ph_3SiF_2)$ (0.43)	SCl_2 (0.43)		0	THF	20	PhSSPh	0

a: Products were characterized by ^1H NMR and GC/MS

b: Dried CsF

c: Isolated yields, purity > 95% as checked by GC

d: 20% PhSPh



5 **6** **7** **8**

Figure 2. List of electrophilic sulfur reagents used

As shown in Table 1, all of the sulfur reagents react with hypervalent organotins. In contrast, organosilicon complexes seem to decompose into triphenylsilyl fluoride.[8] On no occasion, have they led to a significant amount of sulfurated organics. The optimized conditions with **1** could not be reproduced with organosilicon **2** and sulfur. Sulfur dichloride **5** also gave negative results. Apparently, the reactivity of the C–Si bond does not surpass its decomposition. These findings represent a case where the chemical properties between **1** and **2** are very different, when thay are compared as nucleophilic fluorinating agents. The C–Sn bond is longer, more polarizable and has a richer electronic density than the C–Si bond. As a consequence, organotin complexes behave as better nucleophiles towards electrophilic sulfur species.

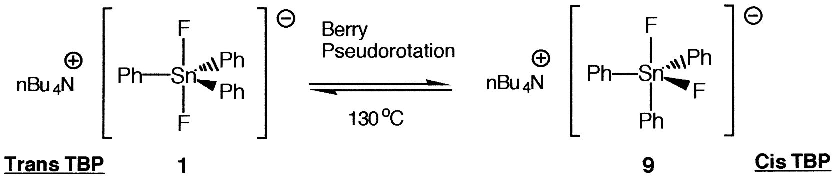
Several experimental parameters were optimized with organotins and elemental sulfur (Table 1). We found slow kinetics at 50°C with **1**, but the reaction proceeded well at 120–130°C. Completion of the reaction was estimated between at 2–5 h at 130°C in DMF (entries 2, 3). A variation in the sulfur/organotin molar ratio was verified and a 3:1 ratio gave the best results. A lower ratio has a negative effect on the yields. These results are highly dependent on temperature and solvent: DMSO and DMF provide the best results, but THF was inadequate. Interestingly, the cyclohexyl group can be transferred from tin, if the hypervalent complex is generated in situ with CsF (1.25 equiv.) in DMF at 130°C for 48 h (sulfur/organotin: 3:1). However, reagent **8** did not lead to a significant amount of disulfide. Starting with nBu_3F (1.0 equiv.), some reactions were attempted with CsF (3.0 equiv.) and sulfur (1.0 equiv.). Complex **4** and its isomer are thought to be generated in situ, because of the GC/MS detection of some n-butyl disulfide. However, due to its volatility, the isolation and quantification were difficult.

Freshly distilled sulfur dichloride gave poor yields of disulfide, in spite of many assays at various temperatures and molar ratios. Sulfur monochloride **6** could be useful as an alternative reagent to sulfur powder (entry 13, 80% yield). Even if reagent **8** usually supplies monosulfide in a reaction with Grignard reagents, it gave us unexpected disulfide formation. The best conditions used a **8**/organotin molar ratio of 2:1, at 130°C, in less than 16 h (80% yield). Surprisingly, DMSO cannot be utilized with **8** (entry 15, 0% yield).

Overall, the reactions of hypervalent compounds produced organic disulfides in a selective manner. Many precautions were taken for detecting organic thiols by GC/MS or TLC but it has always failed, even when using inert gas techniques. Entry 11 shows that forcing conditions, by the addition of CsF or an excess of sulfur powder under prolonged heating, do not lead to more than one ligand transfer. This fact is distinctive of hypervalent compounds, where one apical group is the most reactive in trigonal bipyramidal (TBP) complexes.

At this stage, we cannot delineate an exact mechanism for those sulfurations. However, because organotin compounds can accommodate some C–Sn bond insertion reactions (for instance with SO_2), one could hypothesize that sulfur could be introduced in this way, rather than going through an ionic mechanism. If it were so, one would expect the detection of thiols, from a release of carbanions, as in Scheme 1. Moreover, organomagnesiums reacting with **8** usually produce organic monosulfides, in contrast to our results. Because most sulfur reagents lead to a selective production of disulfides, we are questioning the possibility of generating a common radical intermediate, leading to a dimerisation of RS.

Through a Berry pseudorotation (Scheme 2), the dynamic stereochemistry of the hypervalent species might exist as an equilibrium between *cis*/*trans* TBP complexes; the *cis* complex being the most reactive one, because of apical alkyl or aryl groups.



Scheme 2.

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