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An unexpected Sn–Ph cleavage by mercaptoacetic acid

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Abstract

The reaction of triphenyltin chloride and mercaptoacetic acid under mild reaction conditions in the presence of an amine resulted in the cleavage of a Sn–Ph bond. This cleavage reaction was not observed when triphenyltin hydroxide or other triorganotin chlorides were employed. A possible pathway was proposed for the Sn–Ph cleavage. This is a first report of a mercaptoacetate ligand cleavaging Sn–Ph bonds under mild reaction conditions. It is also the first report of using $^{3}J(^{119}Sn–^{1}H)$ (–Sn–S–CH_2) coupling constants to differentiate sulfur containing organotin compounds.

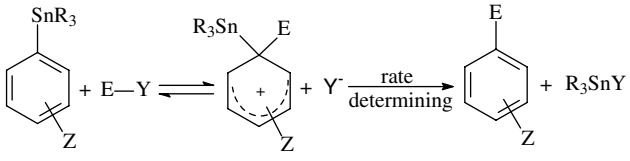
Keywords: Sn–C cleavage; Mercaptoacetic acid; Crystal structure; Coupling constants

Tin–carbon bonds may be cleaved in both heterolytic and homolytic processes. A wide range of tin–carbon bonds are cleaved in heterolytic reactions by various electrophilic reagents such as halogens (e.g., Br_2 [1] or I_2 [2]), protic acids (e.g., hydrogen halides [3] and carboxylic acids [4]), metal halides (e.g., SnX_4 [5], HgX_2 [6], BX_3 [7] and PdX_3 [8]) and sulfur dioxide [9]. Heterolytic cleavage has also been reported to occur with basic nucleophilic reagents, such as alcoholic alkali [10], alkoxide [10], alkali metals [10] and alkyl- or phenyllithium [11]. These cleavage reactions are used for both the syntheses of organotin compounds, R_nSnY_{4-n} (especially when Y = halide or carboxylate), as well as organic compounds, R^1–E, where E is an electrophile (Eq. (1)). The order of cleavage by electrophilic reagents is: allyl > phenyl > benzyl > vinyl > methyl > higher alkyl [12]

$$R_3Sn–R^1 + E–Y \rightarrow R_3Sn–Y + R^1–E \quad (1)$$

Organotin compounds can also transfer organic groups to electrophilic carbons in transition metal-catalyzed cross-coupling reactions with organic halides or esters. A well-known example is the Stille reaction [8]. It is still the method of choice for forming carbon–carbon bonds due to its mild characteristic and the functional tolerability of both substrates and reagents. This is a useful protocol in various preparative reactions as well as in the synthesis of bioactive substances [13].

Aryl cleavages by electrophiles are typical electrophilic aromatic substitutions [14] as shown in Eq. (2). However, a strong electrophilic reagent is normally needed in such a cleavage reaction, e.g., $FOSO_4^-Cs^+$, [15] F_2 [16], NO–Cl [17], etc. More electron-releazing substituents (Z) lead to faster reactions [18]



(2)

The relative ease of cleavage can be predicted on the basis of mechanistic studies such as kinetic data, substituent effects, solvent isotopic effects and stereochemistry [18].

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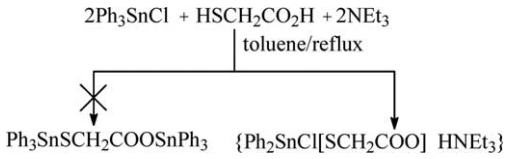
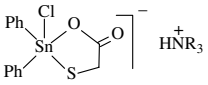
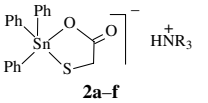
In an attempt to synthesize $Ph_3SnSCH_2COOSnPh_3$ according to Scheme 1, an unexpected tin-phenyl cleavage reaction occurred and resulted in the formation of the ionic tin complex $\{[Ph_2SnCl(\mu^2\text{-}SCH_2COO)][HNEt_3]\}$ (Table 1; **1a**). Its structure was confirmed by X-ray crystallography (Fig. 1) as well as ^1H, ^{13}C and ^{119}Sn NMR spectroscopies.

The tin-phenyl cleavage was also observed when different amines were used under the same reaction conditions resulting in the formation of an analogous series of compounds, **1a–g**, with the general formula $\{[Ph_2SnCl(\mu^2\text{-}SCH_2COO–)]\ [HNR_3]\}$ as given in Table 1. Their structures were deduced by multiple NMR (^1H, ^{13}C, ^{119}Sn), and the structure of **1g** was also confirmed by X-ray crystallography (Fig. 2).



Scheme 1.

Table 1
Three series of organotin compounds with mercaptoacetate ligand

1a	R_3N=NEt_3	
1b	R_3N=$HNEt_2$	
1c	R_3N=$HN(CHMe_2)_2$	
1d	R_3N=$HNPr_2$	
1e	R_3N=$HNBu^n_2$	**1a–g**
1f	R_3N=$HNCy_2$	
1g	R_3N=α-methyl pyridine	
2a	R_3N=NEt_3	
2b	R_3N=$HNEt_2$	
2c	R_3N=$HN(CHMe_2)_2$	
2d	R_3N=$HNPr_2$	
2e	R_3N=$HNBu^n_2$	**2a–f**
2f	R_3N=$HNCy_2$	
3a	R = butyl	$R_3SnSCH_2COOSnR_3$ **3a–c**
3b	R = *cyclo*hexyl	
3c	R = neophyl[a]	

[a] Neophyl = 2-methyl-2-phenylpropyl.

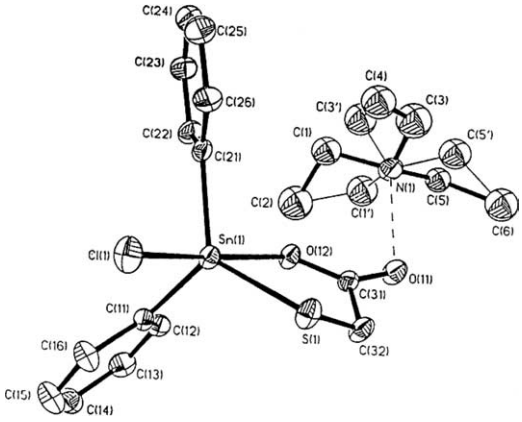


Fig. 1. Molecular structure of **1a**. Selected bond lengths (Å) and bond angles (°): Sn–Cl = 2.470(2), Sn–S = 2.399(2), Sn–O = 2.228(4), Sn–C(1) = 2.133(7), Sn–C(2) = 2.126(6) and C(1)–Sn–C(2) = 118.4(2), S–Sn–O = 81.3(1).

However, when triphenyltin hydroxide was used instead of triphenyltin chloride, no Sn–C cleavage resulted and a second series of triorganotin compound, **2a–f**, $[Ph_3Sn(\mu^2\text{-}SCH_2COO–)]\ [HNR_3]$, resulted (Table 1). Replacing the phenyl group with either cyclohexyl, butyl or neophyl resulted in the formation of a third series of compound, **3a–c**, $R_3SnSCH_2COOSnR_3$, again with no Sn–C cleavage as shown in Table 1.

The tin-phenyl cleavage reaction was then reinvestigated under different experimental conditions to confirm the validation of the reaction. The reaction conditions and results are given in Table 2. Tin-phenyl cleavage was observed in all cases, except in Experiment 8, when no amine was added to the reaction.

The data indicated that the amine is necessary for the cleavage reaction to occur. A possible pathway was proposed for the Sn–Ph cleavage reaction as shown in Scheme 2.

The reaction is believed to involve an intermediate species, $[Ph_3SnSCH_2COOH \cdot NR_3]$, which further reacts with $NR \cdot HCl$ to give the Sn–Ph cleavage product. The

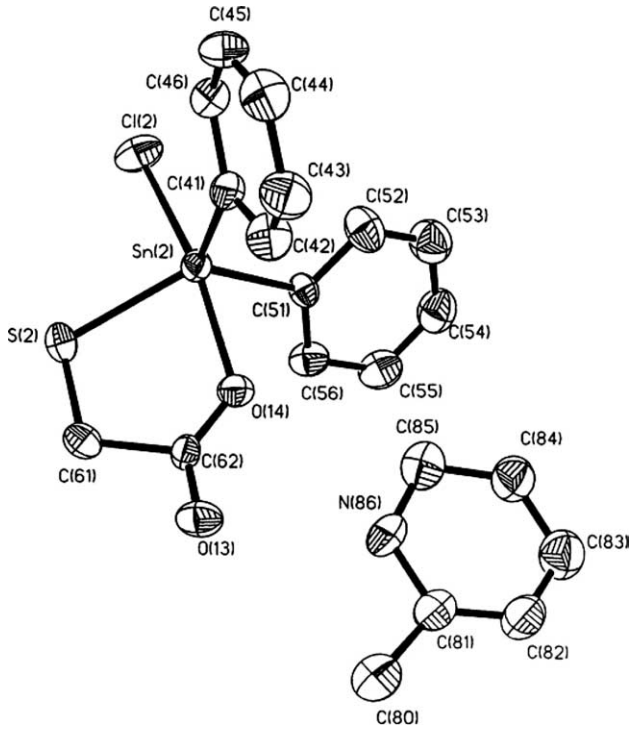


Fig. 2. Molecular structure of **1g** selected bond lengths (Å) and bond angles (°): Sn–Cl = 2.102(7), 2.138(8); Sn–S = 2.396(6), 2.402(6); Sn–O = 2.247(8), 2.181(9); Sn–C(1) = 2.120(7), 2.148(7); Sn–C(2) = 2.482(6), 2.459(7) and C(1)–Sn–C(2) = 117.4(4), 113.7(6); S–Sn–O = 82.0(3), 79.4(3).