

The Reactivity of Nucleophilic Organotin Species

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Espécies nucleofílicas estaniladas do tipo R_3Sn^- , onde R = arila ou alquila, são bastante interessantes na obtenção de inúmeros compostos, embora mecanismos de reação competitivos possam levar a mais de um produto. A preparação desses nucleófilos é aqui descrita, bem como seu uso em reações envolvendo vários substratos. Uma aplicação importante foi a preparação por este método da trifenilestanildifenilfosfina, Ph_2PSnPh_3 , e o estudo de seu comportamento em reação com $SnCl_4$.

Nucleophilic stannylated species of the type R_3Sn^- , where R = aryl or alkyl, are very interesting for the preparation of numerous compounds, although competitive reaction mechanisms may lead to more than one product. The preparation of these nucleophiles is described here, as well as their use in reactions involving several substrates. An important application of this method was the preparation of triphenylstannyldiphenylphosphine, Ph_2PSnPh_3 , and the study of its behavior in relation to $SnCl_4$.

Keywords: nucleophilic tin, tin organometallics, triphenylstannyldiphenylphosphine

Introduction

Organotin chemistry is a field of research that has been growing quickly over the last few decades¹. Most of the work described in the literature involves electrophilic species such as organotin halides. We have conducted a series of experiments dealing with the production of nucleophilic organotin species of the type R_3Sn^- (R = aryl, alkyl), and their use in several reactions. These species show great potential in the area of synthetic chemistry, with many possibilities for practical applications, such as in the preparation of heterobimetallic complexes containing a Sn-transition metal linkage, by replacing a ligand such as Cl^- with R_3Sn^- . These heterobimetallics are important in a number of ways, especially in catalytic studies². We also used the nucleophile Ph_3Sn^- in a new route for the preparation of Ph_2PSnPh_3 , an interesting compound chosen for the presence of a basic and an acidic site next to each other. This phosphine, in its turn, was reacted with $SnCl_4$, leading to a noteworthy case of chemical rearrangement.

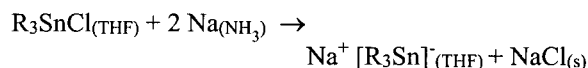
Experimental

The manipulation of air-sensitive compounds was undertaken using Schlenk techniques under pure dry N_2 .

Solvents were purified by standard methods³. I.R. spectra were run in a 283 B Perkin-Elmer instrument using either CsI pellets or nujol mulls between CsI windows. ¹¹⁹Sn Mössbauer spectra were obtained from a constant acceleration spectrometer moving a $^{119}SnO_3$ source at room temperature. The samples were analyzed at 85 K with respect to that source, and the spectra were computer-fitted, assuming Lorentzian single lines. ¹H-NMR spectra were run in CCl_4 in an 80 MHz Bruker instrument, using TMS as an internal standard.

Preparation of $Na^+[R_3Sn]^-$ (R = Ph, Bu, Me)

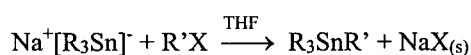
An excess of freshly cut sodium was added to a Schlenk tube containing a solution of R_3SnCl in dry peroxide-free THF. The tube was saturated with $NH_{3(g)}$ and immersed in a Dewar containing liquid N_2 , maintaining the flow of $NH_{3(g)}$. The tube was removed from the Dewar, and the mixture magnetically stirred until a bronze dispersion of ammonia in sodium developed. The ensuing reaction can be described by:



The excess NH_3 was evaporated from the resulting pale yellow solution, which was then filtered under N_2 . These solutions of $\text{Na}^+[\text{R}_3\text{Sn}]^-$ are very reactive and must be used within a few hours. The nucleophiles were well characterized by the next set of reactions.

Reactions of $\text{Na}^+[\text{R}_3\text{Sn}]^-$ with organic and organotin halides

These are well-known reactions involving the organotin nucleophiles and several organic or organotin halides⁴, and were performed as a means of identifying the nucleophiles by the reactions, as well as for comparison with the other experiments described further on. The reactions can be described by:



$\text{R} = \text{Ph}, \text{Me}$

$\text{R}' = \text{Me}, \text{Bu}^n, \text{Ph}_3\text{Sn}, \text{Bu}^n_3\text{Sn}$

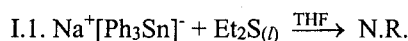
$\text{X} = \text{Cl}, \text{I}$

The products were characterized by their m.p. [except Me_4Sn and $(\text{Bu}_3\text{Sn})_2$, which are liquid], and by their I.R. and $^1\text{H-NMR}$ spectra, which conformed to the literature data^{5,6}, or were compared with spectra from commercial samples from our laboratory.

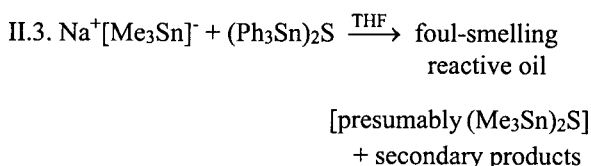
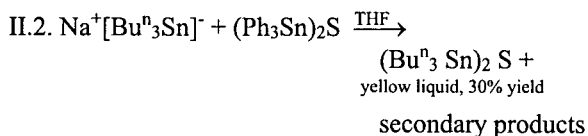
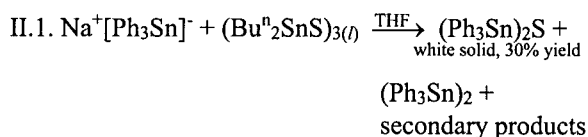
Reactions of $\text{Na}^+[\text{R}_3\text{Sn}]^-$ with sulfides

These are novel reactions which can be separated into three groups:

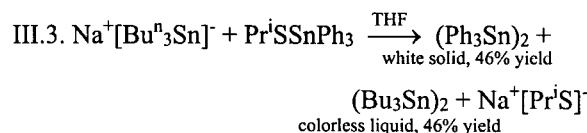
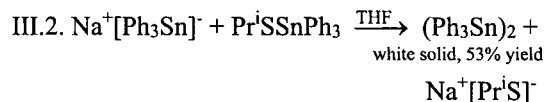
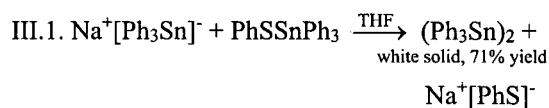
I. Reaction with organic sulfides



II. Reaction with organotin sulfides



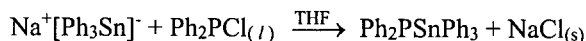
III. Reaction with mixed sulfides



In the above reactions, $(\text{Bu}^n_2\text{SnS})_3$ was a commercial product, and $(\text{Ph}_3\text{Sn})_2\text{S}$ was prepared according to the literature⁷, as were the mixed sulfides $\text{R}'\text{SSnPh}_3$ ⁸. The reactions of the nucleophiles with the sulfides were carried out as follows: a solution of $\text{Na}^+[\text{R}_3\text{Sn}]^-$ in THF, prepared from R_3SnCl (3.80 mmole) as previously described, was transferred under N_2 to a Schlenk tube containing the sulfide reagent (1.90 mmole of Sn) in 15 mL of Et_2O . The pale yellow solution discolored quickly and evaporation yielded the products after mechanical separation and extraction with Et_2O , MeOH and Me_2CO . The products were characterized by comparison with either commercial samples or with samples previously prepared in the laboratory by standard methods, using their m.p., I.R. and $^1\text{H-NMR}$ spectra.

Preparation and reactivity of triphenylstannyldiphenylphosphine, $\text{Ph}_2\text{PSnPh}_3$

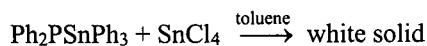
This compound and its preparation are only scantily described in the literature^{9,12}. We have devised a new way of preparing it by means of an organotin nucleophile, as shown by the equation:



A solution of $\text{Na}^+[\text{Ph}_3\text{Sn}]^-$ in THF, prepared from Ph_3SnCl (0.91 mmole) was slowly added under N_2 to Ph_2PCl (2.20 mmole) under stirring. A white precipitate formed, and was identified as a mixture of NaCl and the by-product $(\text{Ph}_3\text{Sn})_2$. Evaporation of the mixture was followed by three extractions with EtOH . The EtOH fractions were slowly evaporated, yielding white crystals which were mechanically picked and washed with *n*-heptane. The yield of the air-stable product $\text{Ph}_2\text{PSnPh}_3$ was 45%. The literature⁹ describes an unsuccessful attempt to obtain $\text{Ph}_2\text{PSnPh}_3$ by a similar method which only produced $(\text{Ph}_3\text{Sn})_2$. Analysis of our product yielded: exp., C, 70.7; H, 4.9%; calcd. for $\text{Ph}_2\text{PSnPh}_3$, C, 67.3, H, 4.7% (m.p. = 127 - 130 °C). The ^{119}Sn Mössbauer spectrum of the product showed one absorption, with $\delta = 1.27(1) \text{ mms}^{-1}$ and $\Delta = 3.17(1) \text{ mms}^{-1}$, which was totally different from the data

obtained in this laboratory for $(\text{Ph}_3\text{Sn})_2$ ($\delta = 1.396$ (7) mms^{-1} , $\Delta = 0$ mms^{-1}).

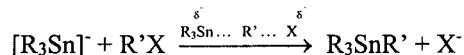
The reaction of $\text{Ph}_2\text{PSnPh}_3$ with SnCl_4 can be described by:



SnCl_4 (0.052 mmole) in toluene was added under N_2 to a solution of $\text{Ph}_2\text{PSnPh}_3$ (0.056 mmole) in toluene. A compact white solid formed immediately. The liquid phase was removed with a transfer needle, and the solid was dissolved in CHCl_3 and reprecipitated with n-hexane. Washing with n-hexane followed by petroleum ether in an ultrasonic bath yielded a loose white powder. This powder presented an m.p. of 62-66 °C, and was analyzed for C (46.2%) and H (3.45%). Its I.R. spectrum in a CsI pellet produced an absorption at 272 cm^{-1} , characteristic of the Sn-Cl linkage. The ^{119}Sn Mössbauer spectrum showed a single line ($\Delta = 0$) with $\delta = 0.221(8)$ mms^{-1} .

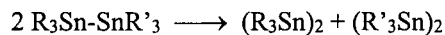
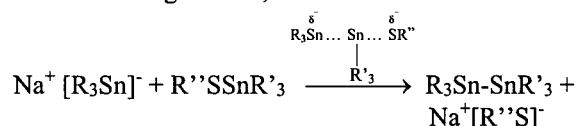
Results and Discussion

The reactions with organic and organotin halides proceeded quickly and involved a strong nucleophile dissolved in a low-polarity solvent, usually THF, conditions which favor $\text{S}_{\text{N}}2$ processes¹³:

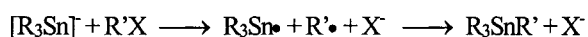


However, considering the reactions with the sulfides, another type of process must be invoked in order to explain the results.

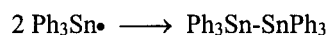
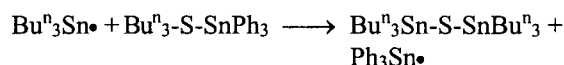
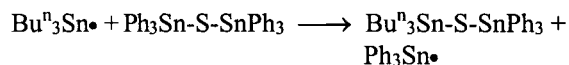
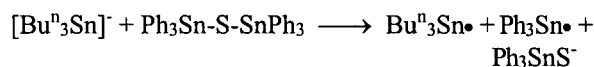
If we analyze reactions III.1 to III.3, it can be assumed that they proceed by an $\text{S}_{\text{N}}2$ mechanism, followed by a symbiotic rearrangement¹⁴, as in the case of III.3:



Reaction I.1 did not proceed, presumably for lack of suitable conditions. Reactions II.1 to II.3 gave more than one product, suggesting a more complex pathway. These reactions presented an exchange between R_3Sn^- and the organotin residue bonded to S. The formation of $(\text{Ph}_3\text{Sn})_2\text{S}$ in reaction II.1 involved the cyclic trimer $(\text{Bu}^n_2\text{SnS})_3$ ¹, which can hardly be thought of as generating an electrophilic moiety. Comparison with reactions III.1 to III.3 shows that in the latter the electrophilic site is Sn, not S. As a consequence, reactions II.1 to II.3 are likely to involve an alternative mechanism, or mechanisms. Such a mechanism could be of a free-radical type, as in the following process¹⁵:

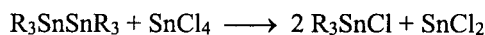
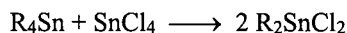


Of course, a free-radical process could also account for reactions III.1 to III.3. The situation is far from resolved and can be summarized as follows in reactions III.1 to III.3, in which any of the two processes ($\text{S}_{\text{N}}2$ or free-radical), or a combination of both, lead to the same results, whereas in reactions II.1 to II.3 free-radical formation must be assumed in order to explain the formation of the observed products, as shown in the following example:

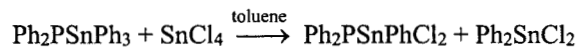


The preparation of the phosphine $\text{Ph}_2\text{PSnPh}_3$ gave additional evidence that both $\text{S}_{\text{N}}2$ and free-radical processes can be operative in a given reaction. Indeed, when Ph_2PCl was added to $\text{Na}^+[\text{Ph}_3\text{Sn}]^-$, only $\text{Ph}_3\text{Sn-SnPh}_3$ was isolated, which could not have been formed by an $\text{S}_{\text{N}}2$ pathway, but rather by a free-radical mechanism. Inverting the sequence of the addition of the reagents, *i.e.*, slowly adding $\text{Na}^+[\text{Ph}_3\text{Sn}]^-$ to Ph_2PCl in order to keep a large excess of Ph_2PCl at all times, the desired stannylated phosphine, $\text{Ph}_2\text{PSnPh}_3$, was obtained, as described in the experimental section, in addition to $\text{Ph}_3\text{Sn-SnPh}_3$ (minor product). The different behavior observed in the two cases seems to validate the aforementioned occurrence of two competitive pathways.

Reaction between $\text{Ph}_2\text{PSnPh}_3$ and SnCl_4 gave a compound whose analysis seemed to indicate the formation of an adduct such as $\text{Ph}_2\text{PSnPh}_3 \cdot \text{SnCl}_4$ (Calcd.: C, 45.2, H, 3.2%; exp.: C, 46.2, H, 3.5%). However, as previously indicated, the ^{119}Sn Mössbauer spectrum only showed a single absorption, with $\delta = 0.221(8)$ mms^{-1} . Therefore an adduct such as the one written above is precluded, since it would necessarily contain two different Mössbauer sites. A well-known rearrangement is given by the comproportionation, or Kocheskov, reaction¹:



If we assume a similar rearrangement in our reaction, we can reconcile both the analytical data and the single Mössbauer absorption. The low value of the latter is also in line with what would be expected from compounds containing Sn-P linkages¹⁶. In addition, the proposed molecular structure also presents Sn-Cl bonds in agreement with the observed I.R. band at 272 cm^{-1} . The reaction is then likely to be:



The calculated molecular composition of $\text{Ph}_2\text{PSnPhCl}_2$ (C, 47.8; H, 3.3%) agrees with our data, within experimental error.

The reactions described in this work show that rearrangements are a key feature in organotin chemistry. The use of both nucleophilic and electrophilic species can lead to new preparative reactions, as well as to new compounds. It is important to always be aware that competitive mechanisms may be at play, and delicate balances may favor one or another among different possible products.

Acknowledgments

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References

- Omae, I.; *Organotin Chemistry - J. Organomet. Chem. Library 21*; Elsevier; Amsterdam, 1989.
- Gomez, M.; Muller, G.; Sainz, D.; Sales, J.; *Organometallics* **1991**, *10*, 4036.
- Riddick, J.A.; Bunger, W.B.; *Organic Solvents - Physical Properties and Methods of Purification*; Wiley - Interscience; New York, 3rd. ed., 1970.
- Ingham, R.K.; *Chem. Rev.* **1960**, *60*, 459.
- Pouchert, C.J.; *The Aldrich Library of FT-IR Spectra*; Aldrich Chemical Company; Milwaukee, 1985.
- Pouchert, C.J.; Campbell, J.R.; *The Aldrich Library of NMR Spectra*; Aldrich Chemical Company; Milwaukee, 1974.
- Midgal, S.; Gertner, D.; Zilkha, A.; *Can. J. Chem.* **1967**, *45*, 2987.
- Schumann, H.; Schumann-Ruidisch, I.; Schmidt, M.; *Organotin Compounds with Sn-S, Sn-Se and Sn-Te Bonds* In A.K. Sawyer, Ed.; *Organotin Compounds*; Marcel Dekker, New York, 1971; Vol. 2, .
- Campbell, I.G.M.; Fowles, G.W.A.; Nixon, L.A.; *J. Chem. Soc.* **1964**, 1389.
- Schumann, H.; Köpf, H.; Schmidt, M.; *J. Organomet. Chem.* **1964**, *2*, 159.
- Schumann, H.; Jutzi, P.; Roth, A.; Schwabe, P.; Schauer, W.; *J. Organomet. Chem.* **1967**, *10*, 71.
- Dakternieks, D.; Hoskins, B.F.; Rolls, C.L.; *Aust. J. Chem.* **1986**, *39*, 1221.
- Kuivila, H.G.; Alnajjar, M.S.; *J. Amer. Chem. Soc.* **1982**, *104*, 6144.
- Bulten, E.J.; Budding, H.A.; *J. Organomet. Chem.* **1974**, *78*, 385.
- Ashby, E.C.; De Priest, R.; *J. Amer. Chem. Soc.* **1982**, *104*, 6144.
- Passos, B.F.T.; De Jesus Filho, M.F.; Filgueiras, C.A.L.; Abras, A.; Galvão da Silva, E.; *Hyperfine Interactions*, **1990**, *53*, 379.