

Second Edition

SYNTHESIS AND TECHNIQUE IN INORGANIC CHEMISTRY

Robert J. Angelici

Department of Chemistry
Iowa State University
Ames, Iowa

Copyright © 1986 by University Science Books
Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permissions of the copyright owner is unlawful. Requests for permissions or further information should be addressed to the Permissions Department, University Science Books.

Library of Congress Catalog Card Number: 86-050811

ISBN 0-935702-53-9

Printed in the United States of America

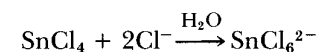
10 9 8 7 6 5 4 3 2 1

University Science Books
20 Edgehill Road
Mill Valley, CA 94941

Experiment 17

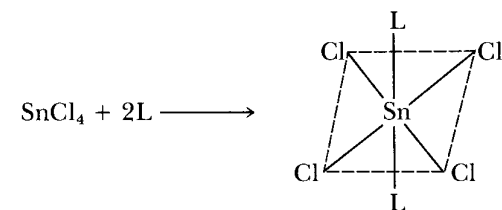
$\text{Sn}(\text{C}_2\text{H}_5)_4$, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, and $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$

As a member of the group IV elements, tin forms a tetrahedral SnCl_4 structure analogous to that of CCl_4 . At room temperature both compounds are colorless liquids whose boiling points at atmospheric pressure are 114° and 77°C , respectively. Beyond these comparisons, their chemistries differ considerably. These differences depend to a large extent on the larger size of the Sn atom compared with that of C and on the availability of relatively low energy 5d orbitals on Sn. Both of these factors favor the tendency of Sn to bond to more than four Cl atoms. This is evidenced by the reaction of SnCl_4 with Cl^- in water to form the octahedral anion, SnCl_6^{2-} .



Obviously CCl_4 does not undergo an analogous reaction.

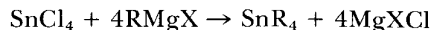
The tendency of SnCl_4 to expand its coordination number might also be illustrated by its reactions with numerous donor ligands, L:



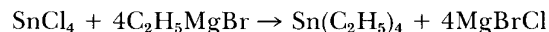
where $\text{L} = (\text{CH}_3)_3\text{N}$, $(\text{C}_2\text{H}_5)_2\text{O}$, or $(\text{C}_2\text{H}_5)_2\text{S}$. While infrared studies suggest that these complexes have a *trans* structure, other L groups are known to give compounds with the *cis* geometry. In moist air, SnCl_4 readily fumes to form the compound $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, whose structure is

unknown but is probably not a simple coordination complex of the preceding type.

In addition to complex formation, SnCl_4 forms numerous organotin compounds by reaction with Grignard reagents:



This type of reaction is not limited to SnCl_4 but has also been used in the preparation of SiR_4 , GeR_4 , BR_3 , AlR_3 , PR_3 , AsR_3 , and SbR_3 from SiCl_4 , GeCl_4 , BCl_3 , AlCl_3 , PCl_3 , AsCl_3 , and SbCl_3 , respectively. The specific reaction that will be carried out in this experiment is



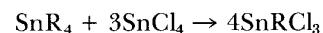
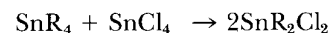
The product, tetraethyltin, is a colorless liquid that is stable in air and boils at 180°C . Unlike SnCl_4 , SnR_4 does not form stable 6-coordinated complexes. In general, the tendency to form such complexes decreases as Cl is replaced by R in the compounds $\text{SnCl}_y\text{R}_{4-y}$: $\text{SnCl}_4 > \text{SnCl}_3\text{R} > \text{SnCl}_2\text{R}_2 > \text{SnClR}_3 > \text{SnR}_4$. Because the Sn-C vibrations occur at frequencies below 650 cm^{-1} , the infrared spectrum of $\text{Sn}(\text{C}_2\text{H}_5)_4$ simply consists of C_2H_5 vibrational absorptions that reveal very little about the composition or structure of the compound. Its nmr spectrum is too complex for interpretation without a detailed treatment of nmr spectroscopy. The reason for this complexity is the presence of the isotopes ^{117}Sn and ^{119}Sn (see Appendix 7), which have nuclear spins of $\frac{1}{2}$ and which couple with the ^1H to give a complicated nmr spectrum.

Of somewhat greater value and interest is the mass spectrum of $\text{Sn}(\text{C}_2\text{H}_5)_4$. For a discussion of mass spectrometry, see Experiment 14, p. 140. The large number of stable isotopes of Sn sometimes aids in the assignment of peaks to ion fragments containing Sn, but also can make complex spectra more difficult to interpret. The isotopes of Sn and their natural abundances are:

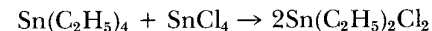
Isotope	Natural Abundance
^{112}Sn	0.95 per cent
^{114}Sn	0.65 per cent
^{115}Sn	0.34 per cent
^{116}Sn	14.2 per cent
^{117}Sn	7.6 per cent
^{118}Sn	24.0 per cent
^{119}Sn	8.6 per cent
^{120}Sn	33.0 per cent
^{122}Sn	4.7 per cent
^{124}Sn	6.0 per cent

Carbon occurs as 98.89 per cent ^{12}C and 1.11 per cent ^{13}C . The tendency of $\text{Sn}(\text{C}_2\text{H}_5)_4$ to fragment with the loss of ethylene, C_2H_4 , and the formation of Sn-H ions should be noted.

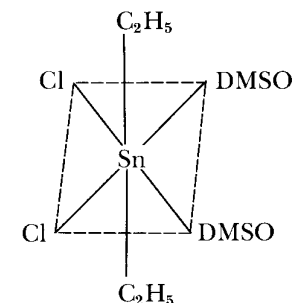
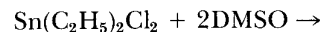
In principle, it is possible to synthesize the mixed compounds $\text{SnR}_y\text{Cl}_{4-y}$ by reacting various ratios of SnCl_4 and RMgX . In practice, a mixture of compounds that are difficult to separate is obtained. The best method for their preparation is frequently the reaction of stoichiometric amounts of SnR_4 and SnCl_4 until exchange of R and Cl has occurred. The equations for these reactions are:



Yields of SnR_3Cl , SnR_2Cl_2 , and SnRCl_3 prepared by this method are generally very high. The compound $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ will be synthesized in this experiment from the reaction:

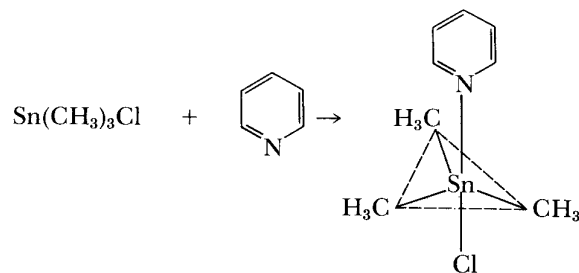


The product is a white crystalline solid that melts at 85° . The presence of Cl allows this compound, as contrasted with $\text{Sn}(\text{C}_2\text{H}_5)_4$, to form adduct complexes. Thus, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ (m.p., 64°) precipitates upon mixing ether solutions of $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ and dimethyl sulfoxide (DMSO):



Infrared studies suggest that the product has the geometry shown above. Dimethyl sulfoxide coordinates with certain metals through the S atom, and with others through the O atom. By examining the infrared spectrum, in particular the S-O stretching frequency, the mode of coordination in $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ will be established in this experiment.

Not all organotin halides form octahedral complexes. A five-coordinated compound is generated from the reaction of $\text{Sn}(\text{CH}_3)_3\text{Cl}$ with pyridine:



An x-ray diffraction study of the solid indicates that the compound has the trigonal bipyramidal structure shown. Thus tetrahedral, octahedral, and trigonal bipyramidal geometries dominate the structural chemistry of tetravalent tin. The endless variety of organotin complexes that may be prepared makes tin chemistry a fascinating area of research.

EXPERIMENTAL PROCEDURE

Organotin compounds have different toxicities, depending upon the number and type of organo-groups bound to the tin. In general, they are not exceedingly dangerous. If they are handled in a *hood*, they will present no serious hazard. Their relatively low volatilities also minimize any toxic effects that the compounds might have. These preparations should be carried out in a properly functioning hood.

Tetraethyltin, $\text{Sn}(\text{C}_2\text{H}_5)_4$

As in any Grignard reaction, the reaction vessels should be thoroughly cleaned and oven-dried. This should be done the day before the experiment is actually performed. Put 15.0 g (0.61 mole) of Mg turnings into the 500 ml 3-neck round-bottom flask, and assemble the apparatus as shown in Figure 17-1, which includes a CaCl_2 drying tube to protect the reaction mixture from atmospheric moisture. (Grease the ground glass joints, and lubricate the ground glass stirrer bearing with glycerin.)

Add 53 ml (75 g, 0.69 mole) of $\text{C}_2\text{H}_5\text{Br}$ to the addition funnel and 5 ml of diethyl ether to the Mg turnings. Turn on the cool water in the condenser. Then run 5 to 10 ml of the $\text{C}_2\text{H}_5\text{Br}$ onto the Mg turnings. Grignard formation should occur fairly soon, as evidenced by the formation of bubbles on the surface of the Mg. If the reaction does not start, momentarily remove the addition funnel and add one or two drops of

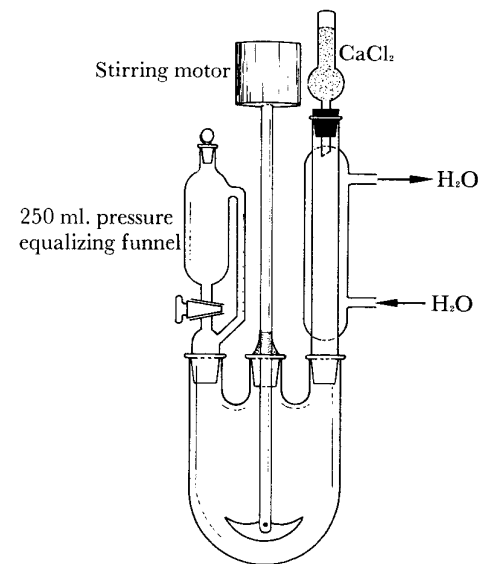


Figure 17-1

Br_2 to the solution. The reaction should then start. When the reaction starts, add 45 ml of ether to the flask, stir the Mg turnings, and add the $\text{C}_2\text{H}_5\text{Br}$ dropwise, cooling the flask with an ice bath. This addition will require about 30 minutes. After all of the $\text{C}_2\text{H}_5\text{Br}$ has been added, remove the ice bath and continue stirring until the mixture is at room temperature.

Remove, clean, and dry the addition funnel and add 10 ml (23 g, 0.090 mole) of anhydrous SnCl_4 to it. (It is important that the addition funnel be free of ether because of its rapid reaction with SnCl_4 to form the solid complex, $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, discussed earlier. It will be noted that the volatility of ether, even at 0°C , is sufficient to cause some of this complex formation in the funnel. The formation of large amounts of the complex will clog the addition funnel.) Cool the reaction flask to 0°C in an ice bath. Add the SnCl_4 dropwise to the cooled Grignard solution with continuous stirring over a period of 10 to 15 minutes. This will result in the immediate formation of white $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, and the ether will begin to reflux again. Stir the thick mixture as long as possible. After all of the SnCl_4 has been added, remove the ice bath and allow the mixture to come to room temperature.

Then add 50 ml of ether slowly through the addition funnel. Stir the mixture if possible. Replace the drying tube with an adapter (such as that shown in the left neck of the flask in Figure 15-1) and rubber tubing that leads to the back of the hood. *Very cautiously* add to the mixture first 20 ml of ice water and then 100 ml of ice cold 1.2 M HCl. *Rapid addition will produce a violent reaction.* After the addition of some water,

Diethyltin Dichloride, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$

Place 10 g of $\text{Sn}(\text{C}_2\text{H}_5)_4$ and 11.1 g of SnCl_4 (equimolar amounts) in a 100 ml round-bottom flask, and assemble the equipment shown in Figure 17-3. Turn on the cooling water and heat the mixture at 210° to 220°C in a silicone fluid bath for 15 minutes. Raise the flask from the heating bath, and allow it to cool until it can be handled conveniently. Then cool the flask further in a water bath or with running tap water. The product crystallizes as a white solid. Recrystallize the $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ by dissolving it in a minimum amount (~ 250 ml) of a boiling hydrocarbon solvent with a boiling range of approximately 110° to 140°C . While it is hot, suction-filter the solution (Figure 1-1) and allow it to cool to room temperature. Suction-filter off the white needles of $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, dry, and determine its melting point. Calculate the percentage yield of the product. Measure the infrared spectrum of the product in a Nujol mull (see Experiment 1, p. 19).

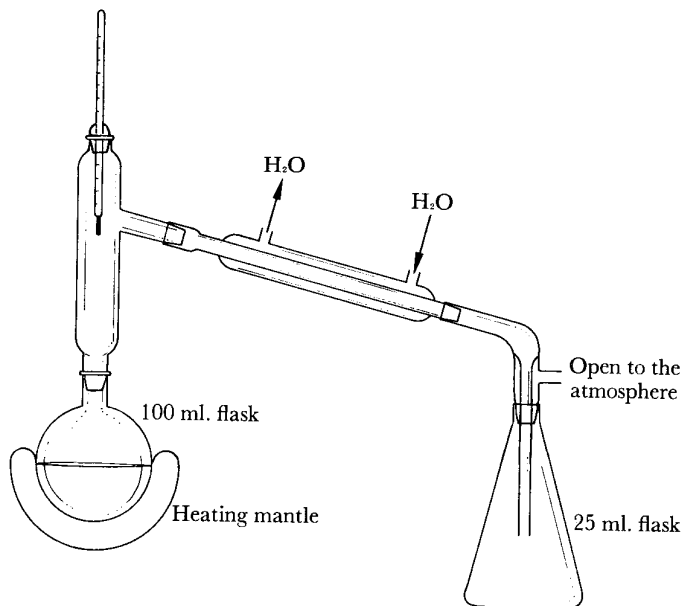


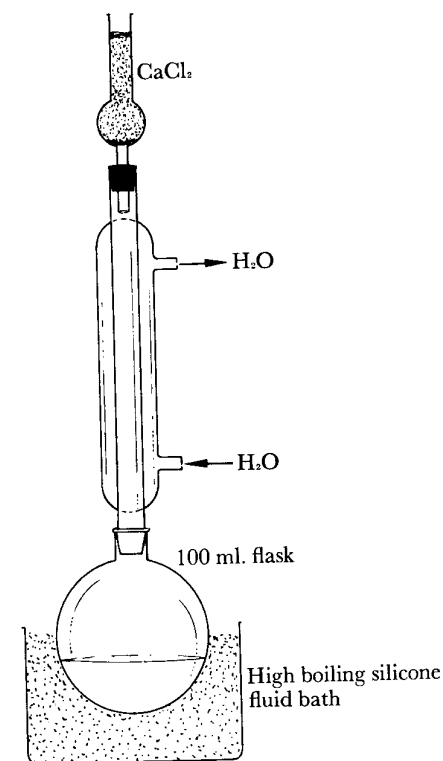
Figure 17-2

start the stirrer as soon as it can be turned by hand. Continue the stirring for 5 minutes after the HCl addition is completed. Separate the ether layer in a separatory funnel and dry it overnight over anhydrous MgSO_4 .

Suction-filter (Figure 1-1) the solution through a medium glass frit. Transfer the solution to the distillation apparatus illustrated in Figure 17-2, and insulate the distillation head with asbestos tape or glass wool. First distill off the ether and then collect in a 25 ml flask the $\text{Sn}(\text{C}_2\text{H}_5)_4$ boiling at approximately 180° to 182°C at atmospheric pressure. Calculate the percentage yield of the product.

As noted in the earlier discussion, infrared and nmr spectroscopy are not convenient methods of characterizing $\text{Sn}(\text{C}_2\text{H}_5)_4$. The mass spectrum, however, is interesting. If it is not possible to have a mass spectrum run on your sample, analyze the spectrum (Figure E) in the section on NMR and Mass Spectra near the end of the book. Using the isotopic abundances listed earlier, make ion assignments to all the peaks in the spectrum in a manner similar to that outlined in Experiment 14, p. 141. In interpreting the mass spectrum, you should keep in mind that $(\text{C}_2\text{H}_5)_3\text{SnCl}$ is a possible impurity in $\text{Sn}(\text{C}_2\text{H}_5)_4$. [The naturally occurring isotopes of Cl and their abundances are ^{35}Cl (75.4 per cent) and ^{37}Cl (24.6 per cent); see Appendix 7.]

Figure 17-3



Sn(C₂H₅)₂Cl₂·2(CH₃)₂SO

Dissolve 5 g (19 mmoles) of Sn(C₂H₅)₂Cl₂ in a minimum (~45 ml) of anhydrous ether. Pour this solution into a solution of 3.2 g (41 mmoles) of dimethyl sulfoxide in 5 ml of ether. When the solution is left standing, a white precipitate of Sn(C₂H₅)₂Cl₂·2DMSO separates. Suction-filter, and dry the precipitate on the frit. Calculate the percentage yield and determine the melting point of the product. Record its infrared spectrum in a Nujol mull and compare it with that of Sn(C₂H₅)₂Cl₂. The S—O stretching mode of uncoordinated (CH₃)₂SO occurs at approximately 1100 cm⁻¹. Try to locate the S—O absorption in the spectrum of your complex. From the change in frequency from free (CH₃)₂SO, suggest whether DMSO is coordinated to Sn through the S or O atom.

REPORT

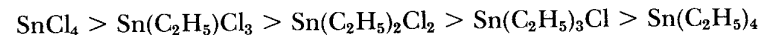
Include the following:

1. Yield and interpretation of the mass spectrum of Sn(C₂H₅)₄. (Make a line drawing spectrum of Sn(C₂H₅)₄ that contains only one isotope of Sn.)
2. Yield, melting range, and infrared spectrum of Sn(C₂H₅)₂Cl₂.
3. Yield, melting point, and infrared spectrum of Sn(C₂H₅)₂Cl₂·2DMSO.
4. Comparison of infrared spectra of Sn(C₂H₅)₂Cl₂ and Sn(C₂H₅)₂Cl₂·2DMSO.
5. Interpretation of DMSO bonding to Sn in Sn(C₂H₅)₂Cl₂·2(CH₃)₂SO.

QUESTIONS

1. Determinations of S or O bonding of (CH₃)₂SO to metals are based on whether the S—O stretching frequency of DMSO in the complex is higher or lower than that of free DMSO. Sulfur bonding is suggested by higher frequencies and oxygen bonding by lower frequencies. What is the basis for interpreting frequencies in this manner?
2. Draw all possible structural and optical (if any) isomers of Sn(C₂H₅)₂Cl₂·2DMSO.
3. Suggest methods of analyzing Sn(C₂H₅)₂Cl₂ for its percentage Sn and Cl content.
4. Why are H₂O and also HCl added to the reaction mixture during the isolation of Sn(C₂H₅)₄? What reaction occurs during the addition of the H₂O?
5. What reactions could be used to prepare Sn(CH₃)Cl₃ from SnCl₄?
6. Suggest a method for preparing P(C₂H₅)₃.

7. The tendency for Sn(C₂H₅)_yCl_{4-y} to coordinate additional ligands decreases as follows:



Explain.

8. Based on reactions that you carried out in this experiment, which ligand do you believe is the stronger Lewis base toward Sn(C₂H₅)₂Cl₂—(C₂H₅)₂O or DMSO?

INDEPENDENT STUDIES

- A. Prepare and characterize Sn(C₂H₅)₃Cl or Sn(C₂H₅)Cl₃.
- B. Prepare and characterize Sn(C₂H₅)₂F₂ obtained from the reaction of Sn(C₂H₅)₂Cl₂ and aqueous HF. (L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 43 (1972).)
- C. Prepare and characterize the pyridine (py) adducts SnCl₄·2py and Sn(C₂H₅)₂Cl₂·2py.
- D. Prepare and characterize triphenyltin hydride, (C₆H₅)₃SnH. (C. W. Allen, *J. Chem. Educ.*, **47**, 479 (1970).)
- E. Prepare and characterize SnCl₂(acetylacetonate)₂ obtained from SnCl₄ and acetylacetone. (D. W. Thompson, D. E. Kranbuehl, and M. D. Schiavelli, *J. Chem. Educ.*, **49**, 569 (1972).)

REFERENCES

Sn(C₂H₅)₄, Sn(C₂H₅)₂Cl₂, and Sn(C₂H₅)₂Cl₂·2(CH₃)₂SO

- D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. (A)*, 1759 (1967). Mass spectrum of Sn(C₂H₅)₄ and other organotin compounds.
- A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. (A)*, 2862 (1970). An x-ray structural study of Sn(CH₃)₂Cl₂.
- E. Heldt, K. Höppner, and K. H. Krebs, *Z. anorg. allg. Chem.*, **347**, 95 (1966). Mass spectra of the compounds Sn(C₂H₅)_y(CH₃)_{4-y}.
- N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. (A)*, 1257 (1970). An x-ray structural study of Sn(CH₃)₂Cl₂·2(CH₃)₂SO.
- K. A. Kozeschkow, *Chem. Ber.*, **66**, 1661 (1933). Preparation of Sn(C₂H₅)₂Cl₂.
- T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967). Preparation and infrared spectra of adducts of SnCl₄ and SnR₂Cl₂.
- G. J. M. VanDerKerk and J. G. A. Luijten, *Org. Syntheses*, **36**, 86 (1956). Preparation of Sn(C₂H₅)₄.

Organotin Chemistry

- J. M. Barnes and L. Magos, *Organometal Chem. Revs.*, **3**, 137 (1968). Toxicology of organometallic compounds.
- I. R. Beattie, *Quart. Revs.*, **17**, 382 (1963). Adducts of quadrivalent Si, Ge, Sn, and Pb compounds.
- I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964). Infrared studies of SnCl₄ adducts.

- G. E. Coates and K. Wade, *Organometallic Compounds, Vol. 1*, Methuen and Co., Ltd., London, 1967, Organometallic chemistry of the nontransition metals.
- R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Revs.*, 60, 459 (1960). Comprehensive review of organotin compounds.
- K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Ed., John Wiley and Sons, New York, 1970, p. 210. Infrared spectra of DMSO complexes.
- R. Okawara and M. Wada in *Advances in Organometallic Chemistry, Vol. 5*, F. G. A. Stone and R. West, Eds., Academic Press, New York, 1967, p. 137.
- R. C. Poller, *The Chemistry of Organotin Compounds*, Academic Press, New York, 1970.
- W. L. Reynolds, *Progress in Inorganic Chemistry*, 12, 1 (1970). Dimethyl sulfoxide in inorganic chemistry; primarily metal complexes.
- A. K. Sawyer, Ed., *Organotin Compounds*, Marcel Dekker, New York, 1971. A series of volumes.