

be provided by the methoxy substituents is not sufficient to overcome the lethargic nature of the leaving group.

I am greatly indebted to my excellent coworkers whose names are cited in the references for their important contributions to this work. In addition our BOC studies were markedly facilitated by the unique ability of our undergraduate "summer preps" students, Ilona Heine Thomasson, Joseph Mayo, and Fred Tibbetts, in being able to supply us with massive quantities of tert-butyl

carbazate, tert-butyl azidoformate, and tert-butyl N-hydroxycarbamate. I also wish to credit a few fascinating comments by Professor R. C. Fuson during his "advanced organic chemistry" course at the University of Illinois in 1950 regarding the difficulty of preparing tert-butyl esters by the usual techniques as the spark which first led us to the idea of using the BOC group as a substitute for the carbobenzyoxy function. Financial support for our work has been generously provided by the Research Corporation, the National Science Foundation, the U. S. Army Research Office, the Petroleum Research Fund, administered by the American Chemical Society, the Air Force Office of Scientific Research, and the National Institutes of Health.

From Kinetics to the Synthesis of Chiral Tetraorganotin Compounds

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Organometallic chemistry has been for many years a puzzling area with its own peculiar rules. For example, the reactivity of Grignard reagents, which are quite sensitive to water and to air, very strongly depends on the presence of traces of impurities. Quantitative information is therefore hard to get in this field. Only a few elements, M, give R_nM compounds (R = alkyl, aryl) which are stable toward air and water; tin, mercury, and lead belong to this category.

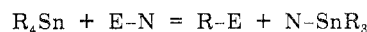
The cleavage and the formation of carbon-metal bonds are the most important reaction types in organometallic chemistry.¹ We therefore started our studies in physical organometallic chemistry by investigating kinetic aspects of the cleavage reactions of carbon-tin bonds. Precise information on their mechanisms would hopefully prove to be sufficiently general to apply to analogous reactions involving less stable organometallic species.

If one defines an organometallic derivative as a molecule which contains at least one carbon-metal bond, and if a metal is defined as an element which is less electronegative than carbon, then the expected polarity of the carbon-metal bond $C^{\delta-}-M^{\delta+2}$ suggests that organometallic compounds might be good substrates for studying both electrophilic substitution at carbon³ and nucleophilic substitution at the metal atom.⁴

Cleavage of the sp^3 Carbon to Tin Bond

Symmetric Tetraalkyltins, R_4Sn . Symmetric tetraorganotin compounds, R_4Sn , react with various

electrophiles (symbolized E-N) with the following stoichiometry



The kinetics of cleavage reactions induced by certain electrophiles have been thoroughly investigated.⁵ The most significant data⁶ are summarized in Table I.⁷⁻¹³

The first striking feature of these data is that the reactivity sequence is reversed as the nucleophilicity of the solvent decreases from methanol to carbon tetrachloride¹⁴ and as the nucleophilicity of E-N in-

(1) M. Gielen and J. Nasielski in "Organotin Compounds," A. K. Sawyer, Ed., Vol. 3, Marcel Dekker Inc., New York, N. Y., 1972, pp 625-825; M. Gielen, *Ind. Chim. Belg.*, **38**, 20, 138 (1973).

(2) R. Gupta and B. Majee, *J. Organometal. Chem.*, **40**, 107 (1972).

(3) M. Gielen, C. Dehouck, and B. De Poorter, *Chem. Weekbl.*, **68** (41), 17 (1972).

(4) M. Gielen, C. Dehouck, H. Mokhtar-Jamai, and J. Topart, *Rev. Si, Ge, Sn, Pb Compounds*, **1**, 9 (1972); M. Gielen, C. Dehouck, and B. De Poorter, *Chem. Weekbl.*, **68** (42), 15 (1972).

(5) M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 32 (1962); *Recl. Trav. Chim. Pays-Bas*, **82**, 228 (1963).

(6) M. Gielen, S. Boué, M. De Clercq, and B. De Poorter, *Rev. Si, Ge, Sn, Pb Compounds*, in press.

(7) M. H. Abraham and G. F. Johnston, *J. Chem. Soc. A*, 193 (1970).

(8) M. Gielen and J. Nasielski, *J. Organometal. Chem.*, **7**, 273 (1967).

(9) M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 601 (1962).

(10) C. Deblandre, M. Gielen, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **73**, 214 (1964).

(11) M. Gielen and J. Nasielski, *J. Organometal. Chem.*, **1**, 173 (1963). The halodemetalations of tetraalkyltins in chlorobenzene are in fact better described by $v = k_2 \exp[R_4Sn][X_2] + k_3 \exp[R_4Sn][X_2]^2$; the third-order term contribution is, however, not very important up to tetrapropyltin, but becomes very important for tetraisopropyltin; see, for instance, ref 12.

(12) S. Boué, M. Gielen, and J. Nasielski, *J. Organometal. Chem.*, **9**, 443 (1967).

(13) J. Nasielski, *Mem. Acad. Roy. Sci. Belg.*, **39**, 4 (1971); "Organometallic Chemistry V (Plenary and Section Lectures presented at the 5th International Conference on Organometallic Chemistry)," Z. N. Parnes, Ed., Butterworths, London, 1972; *Pure Appl. Chem.*, **30**, 449 (1972).

(14) Completely analogous behavior has been reported for tetraalkyllead compounds^{8,15} and for alkylmercury derivatives.⁵

(15) M. Gielen, J. Nasielski, J. E. Dubois, and P. Fresnet, *Bull. Soc. Chim. Belg.*, **73**, 293 (1964).

Professor Gielen's research is in the area of physical organometallic chemistry, particularly in reaction mechanisms, including kinetics and stereochemistry, and topological graphic and matrix representations of reactions. In 1963 he received his Ph.D from the French Free University in Brussels for work on electrophilic aliphatic substitution carried out under the direction of Professor J. Nasielski. Since 1969 he has been Full Professor at the Flemish Free University of Brussels.

Table I
Rate Constants (l. mol⁻¹ sec⁻¹) for Reactions at Saturated Carbon of Symmetric R₄Sn Derivatives at 20

| Substrate | Me ₄ Sn | Et ₄ Sn | Pr ₄ Sn |
|--|--------------------|--------------------|--------------------|
| k ₂ ^{exp} (HgCl ₂ -MeOH); 25° ⁷ | 3.8 | 0.012 | 0.002 |
| k ₂ ^{exp} (I ₂ -DMSO) ⁸ | 0.48 | 0.021 | |
| k ₂ ^{exp} (I ₂ -MeOH) ⁵ | 6.8 | 0.8 | 0.1 |
| k ₂ ^{exp} (I ₂ -AcOH) ⁹ | 0.22 | 0.082 | 0.009 |
| k ₂ ^{app} (Br ₂ -DMF) ^b ⁹ | 0.014 | 0.006 | 0.001 |
| k ₂ ^{exp} (Br ₂ -AcOH) ⁹ | 10.0 | 8.0 | 1.2 |
| k ₂ ^{exp} (CrO ₃ -AcOH) ¹⁰ | 0.04 | 5.4 | 3.6 |
| 10 ⁴ k ₂ ^{exp} (I ₂ -C ₆ H ₅ Cl) ¹¹ | 1.67 | 10.0 | 1.3 |
| k ₂ ^{exp} (Br ₂ -C ₆ H ₅ Cl) ¹¹ | 0.12 | 1.4 | 0.54 |
| 10 ⁴ k ₂ ^{exp} (Br-CCl ₄) ¹¹ | 1.8 | 170 | 80 |
| 10 ⁴ k ₂ ^{exp} (HCl-C ₆ H ₆) ¹³ | 1.0 | 7.5 | 3.0 |

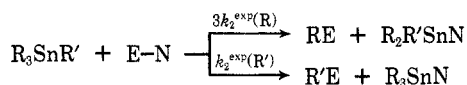
^a Dimethyl sulfoxide. ^b Dimethylformamide.

creases from I₂ to CrO₃. These results may readily be accommodated by assuming two different mechanisms:⁵ when the solvent is the strongest nucleophile present in solution (I₂ in methanol, for instance), the reaction may be described as going through an open transition state^{7,16} (SE2o; see Figure 1) and the reactivity sequence is governed by steric factors as for SN2 reactions at saturated carbon;¹⁷ when the nucleophilic pole of the reagent is the strongest nucleophile present in solution (I₂ in CCl₄ or CrO₃ in acetic acid, for instance), the transition state may be described as a cyclic one (SE2c; see Figure 2).

A critical test for this assumption involved the addition of increasing amounts of a nucleophilic solvent to a nonpolar one. It was observed that the addition of acetic acid to chlorobenzene catalyzes the reaction of bromine with tetramethyltin, and the catalyzed reaction turns out to be first order in monomeric acid.⁶ Furthermore, the influence of the solvent on kinetics [named "X"^{8,11}] parallels the nucleophilicity scale toward trimethyltin chloride (ΔJ) obtained by nmr.^{6,11}

With symmetrical R-SnR₃ derivatives, the change in chemical behavior between two compounds results from a simultaneous change of both the attacked and the leaving group. Therefore, a careful kinetic analysis of the cleavage reactions of mixed tetraalkyltin compounds (R'SnR₃) was performed.

Mixed Tetraalkyltins. The relative reactivities of alkyl groups are such that the overall reaction generally yields a mixture according to



The most significant data¹² are given in Table II for typical nucleophilic and nonnucleophilic solvents, such as methanol and chlorobenzene.

In *methanol*, the steric sequence of reactivity obtained with a constant SnMe₃ leaving group is identical with the one described for the R₄Sn series: Me ≫ Et ≫ *i*-Pr ≫ *t*-Bu. Furthermore, the selectivity is high.

In *chlorobenzene*, the observed sequence of reactivities (and of selectivities) is no longer a homoge-

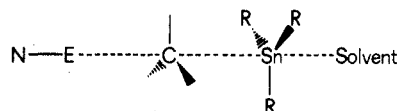


Figure 1. SE2o (inversion).

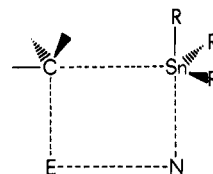


Figure 2. SE2c (retention).

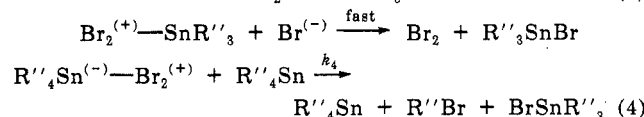
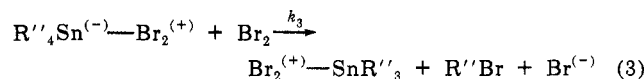
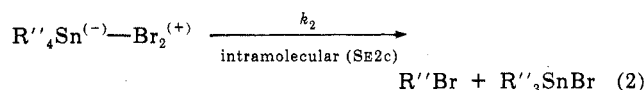
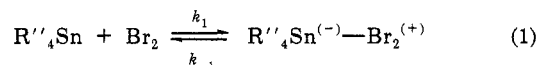
Table II
Second-Order Rate Constants (l. mol⁻¹ sec⁻¹) for the Halogenodemetalation of Me₃SnR Derivatives

| R | In methanol | | In chlorobenzene | |
|--------------|---|--|--|--|
| | 10 ² k ₂ ^{exp} (R), I ₂ (20°) ¹² | k ₂ ^{exp} (R)/k ₂ ^{exp} (Me) (selectivity) | 10 ² k ₂ ^{exp} (R), (R), Br ₂ (20°) ^{12,18} | k ₂ ^{exp} (R)/k ₂ ^{exp} (Me) (selectivity) |
| Me | 1.77 | 1.00 | 2.85 | 1.00 |
| Et | 0.26 | 0.11 | 2.08 | 0.38 |
| <i>i</i> -Pr | 0.01 | 0.0066 | 2.06 | 0.35 |
| <i>t</i> -Bu | 0.00 | 0.0000 | 5.50 | 1.38 |

neous one: *t*-Bu > Me > Et ≈ *i*-Pr. Furthermore, the selectivity is *low*.

The Mixing Effect. The selectivity $k(R')/k(R)$ for the reaction R₃SnR' + Br₂ in chlorobenzene is significantly modified by the addition of another organotin molecule R''₄Sn. This has been called the "mixing effect."¹⁸ Representative data are displayed in Table III.

This can be explained only¹⁹ by assuming that the disturber R''₄Sn reacts with bromine to yield an intermediate R''₄SnBr₂ having a finite lifetime.



Making the steady-state assumption with respect to R''₄Sn⁽⁻⁾-Br₂⁽⁺⁾, one gets

$$v = \frac{k_1[R''_4Sn][Br_2](k_2 + k_3[Br_2] + k_4[R''_4Sn])}{k_{-1} + k_2 + k_3[Br_2] + k_4[R''_4Sn]} \quad (5)$$

(18) Here, also, the third-order term¹¹ is negligible. These experiments show that the difference between the reactivity of tetraethyltin and of tetramethyltin in nonpolar solvents is not due to a higher intrinsic reactivity of the ethyl groups [$k_{Me,MeSnMe_2}^{Br_2,PhCl} = k_2^{exp}(Me_4Sn)/4 = 0.03$ (see Table I); $k_{Et,EtSnMe_3}^{Br_2,PhCl} = 0.02$ (see Table II)] and that the stabilization of the leaving stannocation by the alkyl groups fixed on it plays an important role [$k_{Et,EtSnMe_3}^{Br_2,PhCl} = 0.02$; $k_{Et,EtSnEt_3}^{Br_2,PhCl} = k_2^{exp}(Et_4Sn)/4 = 0.35$].

(16) M. H. Abraham and F. Behbahany, *J. Chem. Soc. A*, 1469 (1971); M. H. Abraham and T. R. Spalding, *ibid.*, 2530 (1968).

(17) F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4048 (1971).

(19) S. Boué, M. Gielen, and J. Nasielski, *J. Organometal. Chem.*, **9**, 481 (1967); Abstracts of Papers of the First IUPAC Conference on Physical Organic Chemistry, Crans, 1972, No. 9, pp 27-29.

Table III
Mixing Effect on the Bromodestannylation of $R'SnMe_3$ in Chlorobenzene at 20°

| Substrate $R'SnMe_3$ | $[R'SnMe_3]$, mol. l. ⁻¹ | Disturber R''_4Sn | $[R''_4Sn]$, mol. l. ⁻¹ | $k_2^{exp}(R')/k_2^{exp}(Me)$ |
|-------------------------------|--------------------------------------|------------------------------|-------------------------------------|-------------------------------|
| <i>i</i> -PrSnMe ₃ | 0.154 | None | | 0.39 |
| | 0.154 | Et ₄ Sn | 0.086 | 0.54 |
| | 0.154 | Et ₄ Sn | 0.171 | 1.09 |
| <i>n</i> -PrSnMe ₃ | 0.145 | None | | 0.17 ₄ |
| | 0.582 | None | | 0.17 ⁷ |
| | 0.243 | Et ₄ Sn | 0.128 | 0.23 |
| | 0.243 | <i>i</i> -Pr ₄ Sn | 0.138 | 0.37 |

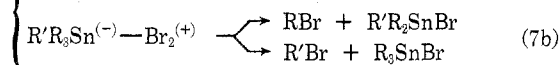
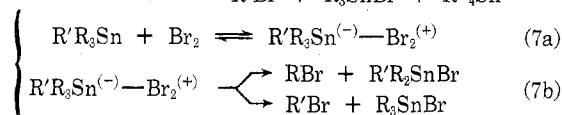
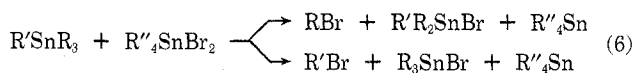
Table IV
Magnitude of the "Mixing Effect" as a Function of the Nature of Both Substrate and Disturber^a

| Substrate (S) | Disturber (D) | k_2^{exp} (S) | k_3^{exp} (D) | $k_3^{exp}(D)/k_2^{exp}(S)$ | Experimental perturbation |
|-------------------------------|-------------------------------|-----------------|-----------------|-----------------------------|---------------------------|
| <i>n</i> -PrSnMe ₃ | <i>n</i> -PrSnMe ₃ | 0.19 | <5 | <25 | - |
| <i>i</i> -PrSnEt ₃ | Me ₄ Sn | 1.5 | <10 | <7 | -19 |
| <i>i</i> -PrSnMe ₃ | Et ₄ Sn | 0.19 | 100 | 525 | ++ |
| EtSnMe ₃ | <i>i</i> -Pr ₄ Sn | 0.19 | ~400 | ~2000 | ++19 |

^a For the pure substrate, one has $v(S) = k_2^{exp}(S)[S][Br_2]$ if $S = R'SnMe_3$;¹¹ for the pure disturber, one has $v(D) = k_2^{exp}(D)[D][Br_2] + k_3^{exp}(D)[D][Br_2]^2$.

If $k_4[R''_4Sn]$ (responsible for the mixing effect) and $k_3[Br_2]$ (responsible for the third-order term) are much smaller than k_2 (responsible for the second-order term), eq 5 simplifies to the experimental rate equation characterizing the bromodemetalation of alkyltrimethyltin compounds [$k_2^{exp} = k_1k_2/(k_1 + k_2)$ and $k_3^{exp} \approx 0$].¹¹ If $k_{-1} \gg k_3[Br_2] \gg k_4[R''_4Sn]$, one gets the experimental rate equation obtained for tetraisopropyltin [$k_2^{exp} = k_1k_2/(k_{-1} + k_2)$ and $k_3^{exp} = k_1k_3/(k_{-1} + k_2)$].¹¹

The mixing effect can thus be understood as the result of competition between a reaction in which R''_4SnBr_2 behaves like a modified halogen toward $R'SnR_3$ (eq 6) and the "normal" bromodemetalation reaction of $R'SnR_3$ (eq 7).



It has been shown¹⁹ that the magnitude of the perturbation should depend on the ratio between the third-order term for the disturber and the second-order term for the substrate. This fully agrees with the experimental perturbation reported in Table IV.

It is predictable that, in nucleophilic media like methanol, the solvent itself will attack the metal and usurp the role of the first bromine molecule complexing the metal atom, thus preventing the formation of the halogenated complex. Therefore the mixing effect is no longer expected to occur and indeed was never detected in methanol, nor was the third-order term in the rate equation (eq 5), which de-

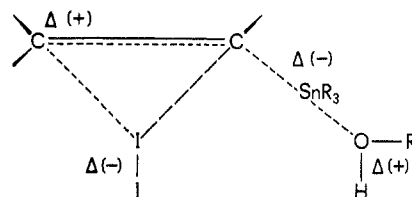


Figure 3. Transition state for bimolecular electrophilic olefinic substitution.

creases and soon vanishes on addition of small amounts of methanol.²⁰

Stereochemistry of the SE_2 Reaction at Saturated Carbon

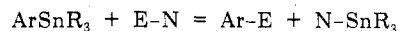
The only available information about the stereochemistry at carbon of the cleavage of a C-Sn bond has been given by Jensen,¹⁷ who studied the bromodestannylation of $(S)(+)$ -*sec*-butyltriisopentyltin and found an inversion of configuration in methanol. Older results had indicated that retention of configuration is frequently encountered in SE_2 reactions of organomercury compounds.²² Recent data on bimolecular electrophilic substitutions of organoboranes²³ suggest the following hypotheses:³ for SE_2 reactions without any particular constraint, the preferred stereochemistry is inversion of configuration (for instance, for SE_2o reactions, see Figure 1); for SE_2 reactions for which the structure of the transition state or of the substrate makes the inversion impossible, the stereochemistry is retention of configuration (for instance, SE_2c reactions—see Figure 2—or SE_2o reactions on cyclopropyltin compounds²⁴).

Cleavage of the sp^2 Carbon to Tin Bond

Olefinic Derivatives of Tin. The rate constant for iododemetalation of vinyltin compounds is very sensitive to the presence of substituents on the double bond²⁵ (see Table V).

A transition state which accounts for both these kinetic data and the stereochemistry of the reaction, which is retention of configuration,²⁵ is given in Figure 3.

Aryltin Compounds. In bimolecular aromatic electrophilic substitutions like



(20) When equimolecular amounts of bromine and of tetraalkyltin compounds—especially tetraisopropyltin¹¹—are mixed in nonpolar solvents, one gets, besides the expected trialkyltin bromide, unreacted tetraalkyltin (sometimes up to 25%) and dialkyltin dibromide, and it has been shown that R_2SnBr_2 is not formed from R_3SnBr .²¹ This might also be due to the third-order term in the rate equation. In polar solvents such as methanol, bromodemetalation proceeds cleanly to the single monobromotrialkyltin compound.

(21) M. Gielen and G. Mayence, *J. Organometal. Chem.*, **12**, 363 (1968).
(22) R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950); S. Winstein and T. G. Traylor, *ibid.*, **77**, 3741 (1955); E. D. Hughes, C. Ingold, *et al.*, *J. Chem. Soc.*, 2523, 2530 (1959); 1121, 1133, 1142, 2359 (1961); D. Curtin and W. Koehl, *J. Amer. Chem. Soc.*, **84**, 1967 (1962); M. Gielen and J. Nasielski, *Ind. Chim. Belg.*, **29**, 767 (1964), and references cited therein; O. A. Reutov, "Fundamentals of Theoretical Organic Chemistry," North-Holland Publishing Co., Amsterdam, 1967, pp 105-164, and the references cited therein; F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, and references cited therein.

(23) H. C. Brown and C. F. Lane, *Chem. Commun.*, 521 (1971).
(24) P. Baekelmans, M. Gielen, and J. Nasielski, *Tetrahedron Lett.*, 1149 (1967); *J. Organometal. Chem.*, **34**, 329 (1971); K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, **33** (1967); K. Sisido, T. Miyajima, T. Isida, and S. Kozima, *J. Organometal. Chem.*, **23**, 117 (1970); K. Sisido, K. Ban, and T. Isida, *ibid.*, **29**, C7 (1971).
(25) P. Baekelmans, M. Gielen, P. Malfroid, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **77**, 85 (1968).

Table V
Reactivities of Vinyltin Derivatives with Iodine in Methanol at 20°

| Organotin compound | k_2 , l. mol ⁻¹ sec ⁻¹ |
|---|--|
| CH ₂ =CHSnMe ₃ | 310 |
| CH ₂ =C(Et)SnMe ₃ | 155 |
| MeCH=C(Me)SnMe ₃ | 14,600 (trans), 53,000 (cis) |
| Me ₂ C=CHSnMe ₃ | 1.0 × 10 ⁸ |

Table VI
Relative Reactivities of Substituted Phenyltrimethyltins
YC₆H₄ + SnMe₃

| Y | I ₂ -MeOH | AcOH | Br ₂ -MeOH | I ₂ -MeCN | I ₂ -PhCl |
|------------------------------|----------------------|------------------------|-----------------------|------------------------|----------------------|
| <i>p</i> -OMe | 64 | 71 | 74 | 175 | |
| <i>p</i> -Me | 5.0 | 5.2 | 5.4 | 6.3 | 5.7 |
| <i>m</i> -Me | 1.50 | 1.40 | 1.62 | 1.33 | 0.92 |
| H | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| <i>p</i> -Br | 0.24 | 0.29 | 0.22 | 0.29 | 0.24 |
| $k_2(\text{H})_{\text{abs}}$ | 507 | 4.3 × 10 ⁻⁵ | 4.9 × 10 ⁴ | 6.0 × 10 ⁻⁵ | 4.8 |

it has been shown that electron-donating substituents on Ar accelerate the reaction;¹³ see Table VI.

The acceleration caused by a *o*-methyl substituent (factor <5) in aromatic substitution is very different from the acceleration caused by a β -methyl substituent in olefinic substitution (see Table V). Therefore, the transition states must be very different for those two reactions. The kinetic data of Table VI and the observed solvent isotope effect in acetolysis¹³ allow one to depict the transition state as in Figure 4.²⁵

Synthesis of Racemic and Optically Active Tetraorganotins, RR'R''SnY

Racemic Tetraorganotins. It seemed interesting to make use of the kinetic data for the purpose of synthesis of organotin compounds in which the central atom is surrounded by four different organic ligands. If one recalls that the bromodemetalation of tetraalkyltin compounds in nonpolar solvents yields a mixture of R₄Sn, R₃SnBr, and R₂SnBr₂, and if one recalls the poor selectivity obtained in these solvents,²⁶ one understands why it has been rather tedious so far to synthesize a pure racemic organotin compound in good yields, since most of the previous halogenodemetalations employed in organotin synthesis were carried out in nonpolar solvents.

Based on the observation that in methanol the bromodemetalation proceeds cleanly to the single monobromotrialkyltin with a high selectivity, it was possible to achieve a fast high-yield synthesis of very pure racemic tetraalkyltin compounds,²⁷ as shown in Scheme I.²⁸

(26) One may add to these two points the fact that the reaction rate of SE₂ reactions in nonpolar solvents is low enough to allow a parallel photochemically induced radical reaction (Br₂ + R₄Sn), which occurs with a reversed low selectivity,⁶ to compete with the SE₂ reactions; see, for instance, S. Boué, M. Gielen, and J. Nasielski, *J. Organometal. Chem.*, **9**, 461 (1967).

(27) S. Boué, M. Gielen, and J. Nasielski, *Tetrahedron Lett.*, 1047 (1968); S. Boué, M. Gielen, J. Nasielski, J. P. Lieutenant, and R. Spielmann, *Bull. Soc. Chim. Belg.*, **78**, 135 (1969). The structures of all these organotin compounds have been checked by mass spectrometry; see also M. Gielen and J. Nasielski, *ibid.*, **77**, 5 (1968); S. Boué, M. Gielen, and J. Nasielski, *ibid.*, **77**, 43 (1968); M. Gielen, M. R. Barthels, M. De Clercq, and J. Nasielski, *ibid.*, **80**, 189 (1971); M. Gielen and G. Mayence, *J. Organometal. Chem.*, **46**, 281 (1972).

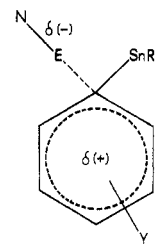
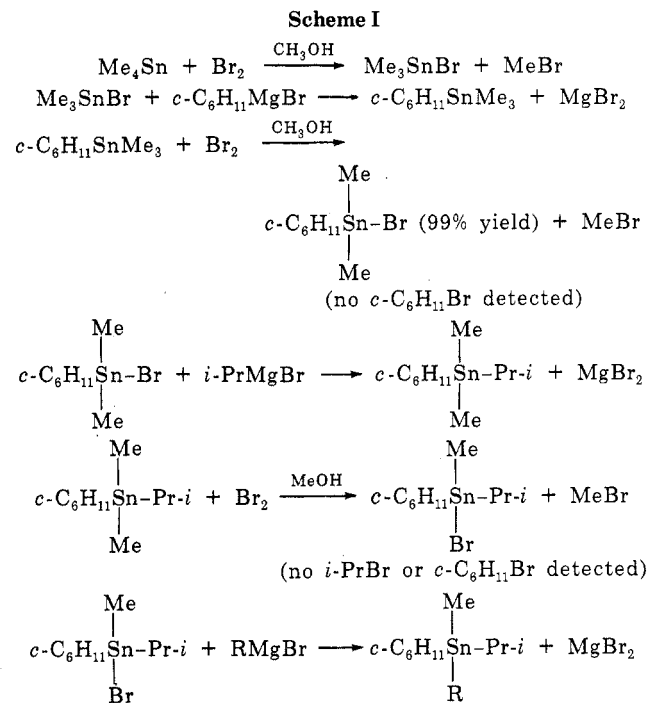


Figure 4. Transition state for electrophilic bimolecular aromatic substitution.



A further treatment with iodine in methanol causes better than 99% Me-Sn cleavage and opens the way to racemic tetraalkyltin compounds containing no methyl substituents. In contrast, the iododestannylation in chlorobenzene of methylethylisopropylcyclohexyltin yields, as expected²⁹ a mixture of about equal amounts of methyl, ethyl, isopropyl, and cyclohexyl iodides.

The synthetic scheme (Scheme I) has been generalized and was applied to *n*-Bu₄Sn:³⁰ by successive brominations in 2-propanol⁶ and condensations with the appropriate Grignard reagents, one easily gets *n*-butylcyclohexylisopropyltin bromide which readily affords any of the desired racemic tetraalkyltin compounds. However, some precautions in handling the trialkyltin halides are required to keep the system clean.^{6,30}

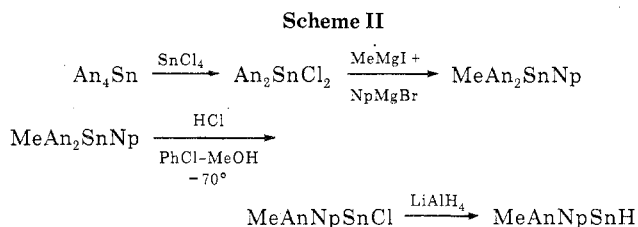
This method of synthesis has also been applied starting from tetraphenyltin, since bromodephenylation at tin remains by far the fastest process. Suitable conditions³¹ allowed to keep the dibromination contribution below 1%; thus one readily ends up

(28) An analogous method has since been used in organogermanium chemistry; cf. E. Bulten, H. A. Budding, and J. G. Noltes, *J. Organometal. Chem.*, **22**, C5 (1970).

(29) S. Boué, M. Gielen, J. Nasielski, J. Autin, and M. Limbourg, *J. Organometal. Chem.*, **15**, 267 (1968).

(30) M. Gielen, B. De Poorter, M. T. Sciort, and J. Topart, *Bull. Soc. Chim. Belg.*, **82**, 271 (1973).

(31) M. Gielen, J. Nasielski, and J. Topart, *Recl. Trav. Chim. Pays-Bas*, **87**, 1051 (1968).



with Me-*i*-PrPhSnBr which can be transformed into a series of racemic tetraorganotins Me-*i*-PrPhSnR.

Optically Active Tetraorganotins. In order to synthesize optically active tetraorganotin compounds, it was advisable to put two different aryl groups on tin. This is why we started from the very reactive tetra-*p*-anisyltin since the *p*-anisyl group is cleaved much faster than the other aromatic groups; see Table VI.^{6,12} We used Scheme II (in which An stands for *p*-anisyl and Np for 1-naphthyl) to prepare and isolate the first optically active tin derivative in which the metal is the only chiral center.³² The addition of this racemic triorganotin hydride to (-)-methyl acrylate yields two diastereoisomers which can be distinguished by nmr and separated. One of these, with $[\alpha]_D -24^\circ$, reacted with methylmagnesium iodide to give the corresponding chiral alcohol MeAnNpSnCH₂CH₂CMe₂OH, $[\alpha]_D +9^\circ$,⁶ which is optically stable, as expected.^{33,34}

Optical Stability of Organotin Compounds. Optically active organotin compounds containing a chiral tin atom might normally be expected to be of

some use for the study of the stereochemistry of S_N2 reactions at the metal atom, much as in organosilicon or organogermanium chemistry.^{4,35} However, it has been shown by the coalescence of diastereotopic signals that triorganotin halides are not optically stable.^{33,34} Their ready conversion³⁶ into stereochemically nonrigid^{37,38} pentacoordinate structures might account for this optical instability. This means that the study of the stereochemistry at tin in the halogen cleavage of carbon-tin bonds will be very difficult, if one does not find a way to reduce the optical instability of RR'R''SnX compounds. To do this, one may either try to slow down the formation of pentacoordinate complexes or the stereomutation processes by which they interconvert, or introduce constraints into the chemical system to avoid at least those stereomutations which are responsible for their optical instability, and which are best visualized on topological (graphical or matrix) representations.^{4,37,38} This is the reason why we started several studies on sterically hindered organotin compounds³⁹ and on stannetanes,⁴⁰ which, we hope, will make it possible to obtain optically stable triorganotin halides⁴¹ and hydrides.⁴²

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(35) M. Gielen, *Ind. Chim. Belg.*, **36**, 185 (1971).

(36) M. Gielen and N. Sprecher, *Organometal. Chem. Rev.*, **1**, 455 (1966).

(37) M. Gielen, *Meded. Vlaam. Chem. Ver.*, **31**, 185 (1969); M. Gielen and N. Van Lautem, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970); J. Brocas and M. Gielen, *ibid.*, **80**, 207 (1971); M. Gielen, J. Brocas, M. De Clercq, G. Mayence, and J. Topart, *Proc. Symp. Coord. Chem.*, **3rd**, **1**, 495 (1970); **2**, 281 (1971).

(38) M. Gielen in "Applications of Graph Theory to Chemistry," A. T. Balaban, Ed., Academic Press, New York, N. Y., in press.

(39) M. Gielen and M. De Clercq, *J. Organometal. Chem.*, **47**, 351 (1973); M. Gielen, M. De Clercq, and B. De Poorter, *ibid.*, **34**, 305 (1972).

(40) M. Gielen and J. Topart, *J. Organometal. Chem.*, in press; M. Gielen and J. Topart, *Bull. Soc. Chim. Belg.*, **80**, 655 (1971).

(41) N. Goffin and M. Gielen, unpublished results.

(42) S. Simon and M. Gielen, unpublished results.

(32) H. Mokhtar-Jamai, C. Dehouck, S. Boué, and M. Gielen, *Proc. 5th Int. Conf. Organometal. Chem., Moscow*, **1**, 523 (1971); **2**, 359 (1971); H. Mokhtar-Jamai and M. Gielen, *Bull. Soc. Chim. Fr.*, **9B**, 32 (1972).

(33) M. Gielen, M. De Clercq, G. Mayence, J. Nasielski, J. Topart, and H. Vanwuytswinkel, *Recl. Trav. Chim. Pays-Bas*, **88**, 1337 (1969).

(34) G. J. Peddle and G. Redl, *J. Amer. Chem. Soc.*, **92**, 365 (1970); F. D. Boer, G. A. Dorakian, H. H. Freedman, and S. V. Mc. Kinley, *ibid.*, **92**, 1225 (1970); D. V. Stynes and A. L. Allred, *ibid.*, **93**, 2666 (1971); C. E. Holloway, S. A. Kandil, and I. M. Walker, *ibid.*, **94**, 4027 (1972). A reinvestigation of a reported resolution of methylethylpropyltin iodide showed Pope and Peachey's results to be erroneous; see G. Redl, *J. Organometal. Chem.*, **22**, 139 (1970).

Some Aspects of Organoplatinum Chemistry. Significance of Metal-Induced Carbonium Ions

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The commercial importance of homogeneous and heterogeneous transition-metal-catalyzed reactions of olefins and acetylenes has generated tremendous interest in the activation of unsaturated molecules by transition-metal complexes. Noteworthy examples are (a) the hydroformylation of olefins to aldehydes, catalyzed by cobalt tetracarbonyl hydride,¹ (b) the hydrogenation of olefins catalyzed by [P(C₆H₅)₃]₃RhCl,² and (c) the oxidation of ethylene to acetal-

(1) D. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960).