

axis) were calculated with the aid of the program MIRAGE⁷⁷ to be the following: $x = -0.02194$, $y = 0.37230$, $z = 0.29447$; H(1'), $x = 0.02194$, $y = 0.37230$, $z = 0.20553$. Based on these coordinates, the one independent H(1)···Cl(3) distance is 2.69 Å, about 0.3 Å shorter than a normal van der Waals contact.^{46b} The capability of halogenated hydrocarbon compounds in forming hydrogen bonds is well known,⁷⁸ and in our laboratories an example was found in which the interaction between the hydrogen atom of CHCl₃ and a sulfur atom of a Co₄(h⁵-C₅H₅)₄S₆ molecule gave rise to distinct molecular distortions of part of the Co₄S₆ system.²⁹ The H(1)···Cl(3)-Fe(4) bond angle of 98.3° in the {[Fe(h⁵-C₅H₅)(CO)₂]₃SbCl₂}[FeCl₄]·CH₂Cl₂ compound is close enough to a regular tetrahedral angle to secure an interaction between a normally nonbonding electron pair from each of two chlorine atoms of the [FeCl₄]²⁻ anion with the corresponding hydrogen atom of the associated CH₂Cl₂ molecule. This interaction

(77) J. Calabrese, "Program MIRAGE," Ph.D. Thesis, University of Wisconsin (Madison), 1971.

(78) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1959, pp 197-200.

should lessen the population of the 1t₂ molecular orbitals of the [FeCl₄]²⁻ anion (assumed in these bonding arguments to still conform to T_d cubic symmetry) and thereby weaken the Fe-Cl bonds. The longer independent Fe(4)-Cl(3) bond length of 2.320 (5) Å relative to the independent Fe(4)-Cl(2) bond length of 2.284 (4) Å is an indication of such a bond weakening. Hence, the distortion of the [FeCl₄]²⁻ anion appears to be due partially to weak hydrogen bonding of the CH₂Cl₂ molecule.

Acknowledgments. This work was accomplished by the financial support of the National Science Foundation (Grant No. GP-4919). T.-T. gratefully expresses his sincere appreciation to the Agency for International Development for a predoctoral fellowship (PIO/P No. 730/90111). The use of the UNIVAC 1108 and CDC 3600 Computers at the University of Wisconsin Computing Center was made possible through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation through the University Research Committee.

Diastereotopic Nonequivalence in Asymmetric Tin Compounds. Inversion and Halogen Exchange¹

Dennis V. Stynes² and A. L. Allred*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received August 6, 1970

Abstract: The factors influencing the magnitude of diastereotopic nonequivalence in the nmr spectra of asymmetric tin compounds are discussed. A comparison of a wide variety of asymmetric tin compounds indicates that the large anisotropy of the phenyl ring is important in establishing a sufficient difference in shielding for diastereotopic nonequivalence to be observed. All three diastereotopic groups in benzylmethylneophyltin chloride are observably anisochronous in nonpolar solvents. Analysis of the coalescence of all three sets of diastereotopic peaks provides definitive evidence for a rapid inversion of configuration of the asymmetric tin center in trialkyltin halides. The concentration dependence of the mean lifetime of the asymmetric tin center indicates a second-order process. A five-coordinate halogen-bridged intermediate is proposed to explain the observed halogen exchange accompanying inversion.

The interpretation of diastereotopic nonequivalence in the nmr spectra of asymmetric molecules is complicated by a number of factors.³ Magnetic nonequivalence arises from very subtle differences in shielding which depend on the magnetic anisotropy of all the other groups in the molecule and their orientations with respect to each of the diastereotopic nuclei. Thus the shielding differences will be influenced by any factor which changes the conformation of the molecule.⁴ In addition, any molecular motion resulting

in an interchange of the magnetic environments of the diastereotopic nuclei, such as an inversion of configuration, will also affect the magnitude of the observed splitting.

Recently, diastereotopic nonequivalence has been applied to organotin compounds.^{5,6} Peddle and Redl⁶ reported two distinct peaks for the diastereotopic methyl groups in the nmr spectrum of methylneophylphenyltin chloride (1). Coalescence of the signals could be produced by increasing the concentration, increasing the temperature, increasing the solvent polarity, or adding a small amount of a Lewis base. The observed line broad-

(1) (a) This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center; (b) presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) National Institutes of Health Predoctoral Research Fellow.

(3) M. van Gorkom and G. E. Hall, *Quart. Rev., Chem. Soc.*, **22**, 14 (1968).

(4) The chemical shift difference between the diastereotopic nuclei is given by the equation $\Delta_{ab} = \Delta_{cp} + \Delta_{id}$, where Δ_{cp} is a temperature-dependent contribution due to unequal conformer populations and

Δ_{id} is a temperature independent contribution due to the intrinsic diastereotopic nonequivalence: M. Raban, *Tetrahedron Lett.*, 3105 (1966).

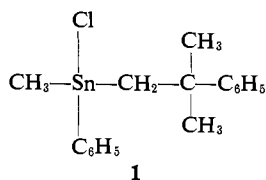
(5) (a) F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Amer. Chem. Soc.*, **89**, 5068 (1967); (b) F. P. Boer, G. A. Doorakian, H. H. Freedman, and S. V. McKinley, *ibid.*, **92**, 1225 (1970).

(6) G. J. D. Peddle and G. Redl, *ibid.*, **92**, 365 (1970).

Table I. Comparison of Chemical Shifts^a for Neophyl and Isobutyl Derivatives of Organotin Compounds

Compound	Neophyl				Isobutyl			
	Me	CH ₂ C(CH ₃) ₂ Ph	CH ₂ C(CH ₃) ₂ Ph	-CH ₂ Ph	Me	CH ₂ C(CH ₃) ₂ H	CH ₂ C(CH ₃) ₂ H	-CH ₂ Ph
MePhBzSnR	0.17	1.78	1.45	2.37 ^b	0.18	1.03	0.90	2.43
MePhISnR	0.23	2.00	1.33		0.78	1.37	0.83	
MePhClSnR	0.23	2.07	1.42 ^b		0.67	1.38	0.90	
MePh ₂ SnR	0.12	1.78	1.37		0.47	1.28	0.95	
MeBzISnR	0.17	2.00	1.33	2.47 ^b	0.63	1.35	0.88	2.82
MeBzClSnR	-0.03	1.80 ^b	1.30 ^b	2.33 ^b	0.43	1.25	0.92	2.75

^a All shifts (δ) refer to 60-MHz spectra of dilute solutions in carbon tetrachloride using TMS as an internal standard. ^b Diastereotopic nonequivalence observed; average shift reported.



ening and eventual coalescence of the diastereotopic peaks on addition of a Lewis base or on increasing the concentration was attributed to a rapid interchange of the different magnetic environments of the diastereotopic nuclei resulting in a time-averaged signal. Such an interchange is equivalent to an inversion of the asymmetric tin center.

During the course of our investigations of asymmetric tin compounds, we synthesized methylphenylbenzyltin iodide, methylphenylisobutyltin iodide, methylphenylisopropyltin iodide, and methylphenylbenzylisobutyltin. None of the diastereotopic groups in these compounds showed observable magnetic nonequivalence in the nmr. Even in **1**, for which the methyl groups were reported to be observably anisochronous, the neophyl methylene protons were unresolved under all the conditions employed.

We undertook this investigation to achieve a better understanding of the factors which influence the magnitude of the diastereotopic splitting in asymmetric tin compounds and also to investigate possible mechanisms for the inversion of asymmetric tin compounds.

Results and Discussion

Structural Factors. A wide variety of asymmetric tin compounds was prepared in order to assess the factors which contribute to observable splittings of the diastereotopic groups in the nmr spectra. The benzyl, neophyl, isobutyl, and isopropyl groups all contain protons which are diastereotopic if an asymmetric center is present in the molecule. Fifteen asymmetric tin compounds containing one or more of these groups were prepared. Diastereotopic nonequivalence was only observed in cases where a neophyl group was present in the molecule.

A comparison of compounds containing an isobutyl group with those containing a neophyl group gives some insight into the unique shielding ability of the neophyl group. The chemical shifts for dilute carbon tetrachloride solutions of the compounds using TMS as an internal standard are shown in Table I. Those protons having observable diastereotopic nonequivalence are designated.

In general, the upfield shift of the protons in the CH₃-Sn group is much greater in the neophyl derivatives than in the isobutyl derivatives. The shifts are

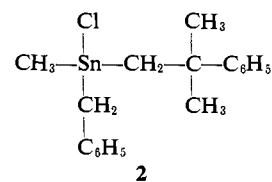
too great to be explained by an inductive effect since the phenyl group is three bonds removed from tin. Thus the large upfield shifts must be due to the tin-bonded methyl group being oriented over the plane of the phenyl ring. In such an orientation the methyl group experiences a lower magnetic field due to a ring current effect and therefore exhibits an upfield shift. A similar effect is observed with the benzylic protons.

The opposite effect is observed with the γ -methyl protons and the methylene protons of the neophyl group. Molecular models indicate that those conformations which result in large upfield shifts of the CH₃-Sn resonance place these protons in the plane of the phenyl rings. Thus they experience a downfield shift.

Compounds with the largest upfield shifts for the methyl and benzyl protons and with the largest downfield shifts of the γ and α protons show the greatest diastereotopic nonequivalence. This is consistent with the interpretation that the large diamagnetic anisotropy of the phenyl rings is responsible for the large shielding differences in the molecules and the consequent observations of nonequivalence in the nmr spectra. In any case, the shielding effects which result in an observable magnetic nonequivalence are very subtle and cannot be predicted. One can say, however, that the presence of groups of large anisotropy in the molecule favors the chances of observing diastereotopic splitting.

Second-Order Effects. For cases of geminal nonequivalence, second-order effects due to the coupling of the nonequivalent protons can have a large effect on the spectrum. Coupling constants for geminal protons on sp³-hybridized carbon are generally around 12 Hz.⁷

The 90-MHz spectrum of benzylmethylneophyltin chloride (**2**) is shown in Figure 1. All three diastereo-



topic groups are observably anisochronous in a 10% carbon tetrachloride solution at room temperature. The assignments for the diastereotopic protons are given in Table II. Second-order effects are clearly evident in the spectrum of the benzylic protons. The inner lines are separated by 9.3 Hz, with two smaller lines at 12.1 Hz on either side of the inner lines and of roughly one-third the intensity of the inner lines.

(7) J. A. Pople and A-A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

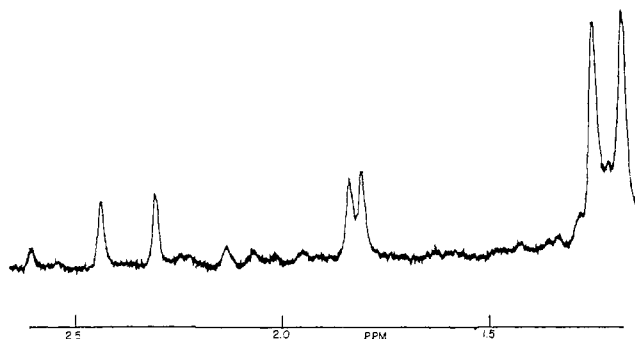


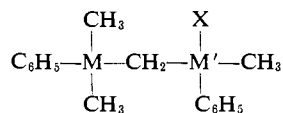
Figure 1. The 90-MHz nmr spectrum of a 10% solution of benzylmethylneophyltin chloride (**2**) showing the diastereotopic splitting of the benzylic, neophyl-methylene, and neophyl-methyl protons. Assignments are given in Table II.

Analysis of the line positions in terms of an AB pattern gives a chemical shift difference of 17.7 Hz and a coupling constant of 12.1 Hz.⁸

Table II. Chemical Shift Data (90 MHz) for the Diastereotopic Groups in Benzylmethylneophyltin Chloride in Carbon Tetrachloride

Position, Hz	Assignment
223.9	
211.8	AB quartet due to benzylic protons
202.5	$\delta_{AB} = 17.7 \text{ Hz}, J_{AB} = 12.1 \text{ Hz}$
190.5	
169.0	Inner lines of AB quartet due to neophyl-methylene protons
167.0	
126.8	Neophyl-methyl groups
121.7	

The observed splitting of the neophyl-methylene protons is of interest. It is reported⁶ that the chemical shift difference between the diastereotopic methyl groups is always much greater than that of the methylene protons for compounds of the type



where M = C, Si, Sn; M' = C, Si, Ge, Sn; and X = Cl, H. This was attributed to a greater contact of the methyl groups with the asymmetric center.

In **2** the two observable neophyl-methylene peaks appear to be split by 2.0 Hz at 90 MHz. However, the protons are coupled to each other. The coupling constant should be similar to that of the benzylic protons. If a coupling of 12.1 Hz is assumed,⁹ the

(8) The 60-MHz spectrum of the compound verifies the calculated chemical shift difference. The benzylic protons appear as a doublet separated by 4.8 Hz. In this case the outer lines of the AB quartet are too weak to observe. Using $J = 12.1 \text{ Hz}$ from the 90-MHz spectrum we calculate a chemical shift difference of 11.8 Hz, 0.197 ppm. This agrees with the calculated shift difference at the higher field strength.

(9) In principle, one can calculate the spectral parameters from only the inner lines if accurate data are available at two different field strengths. The coupling constant is given by $J = \frac{1}{4}[(D_2^2 - H_2^2 D_1^2 / H_1^2) / (H_2^2 D_1 / H_1^2 - D_2)]$, where D_1 and D_2 are the separation of the inner lines of the AB spectrum at field strengths H_1 and H_2 , respectively. A small change in the line positions is reflected by a large change in the calculated coupling constant. Therefore, very accurate chemical shifts for the inner lines are required. An accurate value of the coupling constant is favored by large chemical shift differences and a large difference in the two field strengths.

actual chemical shift differences between the diastereotopic protons is calculated to be 7.2 Hz. Thus, in this case, the asymmetric shielding of the methylene protons is actually greater than that of the methyl groups which are only split by 5.1 Hz.

It is imperative in cases of geminal nonequivalence to treat the spectrum as second order. In most cases of diastereotopic nonequivalence, where the chemical shift differences are small, the outer lines will be extremely weak. For the neophyl-methylene protons in **2**, which had a separation of the inner lines of the AB pattern of 2.0 Hz, the intensity of the outer lines is calculated to be $1/13$ th the intensity of the inner lines. The outer lines were lost in the base-line noise and could not be detected.

In general for small chemical shift differences, between geminal protons, the outer lines of the AB quartet will be very weak. However, even when the outer lines are too weak to detect, the effect of second-order splitting on the spectrum must be considered if an accurate estimate of the chemical shift difference is desired.

Inversion vs. Conformational Change. The major problem in interpreting the magnitude of the diastereotopic splitting in asymmetric tin compounds is to distinguish coalescence due to a rapid inversion of the tin center from that due to a decrease in chemical shift difference because of a change in the conformation of the molecule. For large splittings the two processes may be distinguished from line width considerations. For inversion, the lines will broaden due to exchange broadening while in the case of a conformational change there should be no line broadening (assuming inversion is much slower than any conformational change). If both processes are occurring at the same time, or if the lines are overlapped preventing an estimate of the line widths, distinction between the two processes is usually impossible.

The presence of more than one diastereotopic group in **2** allows us to make a distinction between conformational and configurational changes. A change in conformation will cause a change in the chemical shifts of each of the diastereotopic protons in an unpredictable fashion. A change in the rate of inversion will change each of the diastereotopic splittings in a predictable way. From the separation of the diastereotopic peaks and the chemical shift difference between the diastereotopic protons in the limit of slow inversion, the mean lifetime, τ , of the inverting species may be calculated.¹⁰ In order to obtain accurate values of τ , it was necessary to compare observed spectra with computer-simulated spectra.^{11,12} The benzylic and methylene protons were treated as A_2 to AB systems, while for the neophyl-methyl groups coupling was neglected. The relaxation time was obtained from the width of the $\text{CH}_3\text{---Sn}$ line. Chemical shifts and coupling constants were obtained from very dilute solutions where the rate of inversion is slow. Coalescence was deemed to be consistent with an inversion of the asymmetric tin center only if the estimate of τ was the same for each set of diastereotopic peaks in the spectrum.

(10) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(11) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

(12) We thank J. B. Lambert for the computer program.

Table III. Temperature Dependence of the Diastereotopic Splittings^a in Benzylmethylneophyltin Chloride in TMS Solution

Temp, °C	Benzyl		Methyl	Methylene	
	a	b		a	b
20% Solution					
20	4.2	10.9	2.3	0.8	4.5
10	4.6	11.5	2.6	1.0	5.0
0	5.5	12.8	3.4	1.2	5.4
-10	6.0	13.5	3.6	1.8	6.8
-20	6.0	13.5	3.6	1.8	6.8
10% Solution					
20	4.2	10.9	3.5	1.0	5.0
10	4.6	11.5	3.6	1.2	5.4
0	5.4	12.7	3.8	1.8	6.8
-10	5.9	13.3	3.8	2.0	7.2
-20	6.8	14.5	4.0	2.2	7.6

^a The splittings are reported for 60-MHz spectra in hertz. For the benzyl and methylene protons where coupling is important, the separation observed (a) is the separation of the inner peaks of the AB pattern. The apparent chemical shift differences (b) are obtained by a second-order treatment with $J = 12.1$ Hz. These may or may not correspond to actual chemical shift differences depending upon the lifetime, τ , of the asymmetric center.

The effects of temperature, concentration, and solvent were considered. Table III shows the diastereotopic splittings for solutions of benzylmethylneophyltin chloride in TMS solution as a function of temperature. The change in the separation of the diastereotopic peaks with temperature is not consistent with an increase in the rate of inversion of the asymmetric tin center. Therefore the changes must be due to a conformational change.

The changes in splitting due to an increase in concentration are shown in Table IV. The results are

Table IV. Concentration Dependence of the Diastereotopic Splittings^a in Benzylmethylneophyltin Chloride in Carbon Tetrachloride Solution at 37°

Concn, % w/w	Benzyl		Methyl	τ
	a	b		
11	3.6	10.0	2.4	0.60
15	3.6	10.0	2.4	0.40
18	3.5	9.8	2.4	0.35
20	3.5	9.8	2.4	0.30
27	3.4	9.6	0.0	0.15
35	3.2	9.3	0.0	0.06

^a See footnote a, Table III. The neophyl-methylene splittings were not well resolved.

entirely consistent with an increase in the rate of inversion of the asymmetric tin center as the concentration is increased. The values of τ estimated from a comparison of computer-simulated spectra with experimental spectra are given. The experimental peak separations and line shapes for each set of diastereotopic protons are reproduced by a computer simulation using the values of τ in Table IV. The excellent agreement between the observed and calculated spectra for each set of diastereotopic protons confirms the hypothesis that the coalescence of the diastereotopic signals with an increase in concentration is due to an inversion of the asymmetric tin center. The results would also rule out the possibility of a slow conformational change giving rise to the splitting, since such a change would

not be expected to affect each of the diastereotopic groups equally.

Solvent polarity also has a considerable effect on the rate of inversion of the asymmetric tin center. While all three diastereotopic groups are observably anisochronous in dilute carbon tetrachloride (ϵ 2.24) solution, none of the groups are split in dichloromethane (ϵ 9.08) solution. The sharpness of the peaks would indicate that rapid inversion is taking place. In pentachloroethane (ϵ 3.73) an intermediate rate of inversion is observed. The diastereotopic benzylic protons are split by 15 Hz, the splitting of the methylene protons is just barely detectable at 90 MHz, and the methyl groups appear as a broad singlet. For this to occur, the value of τ must be close to 0.03 sec. An increase in temperature can cause coalescence of all the diastereotopic peaks of **2** in pentachloroethane solution. The methylene protons coalesce at 350°K while the benzylic protons coalesce at 365°K.

The coalescence occurring as the concentration is increased may be due to two factors. The increase in the rate of inversion could be caused by an increase in the polarity of the solution as trialkyltin halide is added. A decrease in τ would also be expected for a second-order rate process where the mean lifetime is inversely proportional to the concentration. For a first-order process, the mean lifetime is independent of the concentration.

The product of the mean lifetime and the concentration of **2** is constant for concentrations up to 20%, indicative of a second-order reaction. For higher concentrations a correction for the increase in rate due to the polarity of the solution is necessary to interpret the rate of inversion.

Halogen Exchange. Although halogen exchange was postulated as a possible mechanism for inversion of the asymmetric tin center in trialkyltin halides,⁶ no definitive evidence for such a mechanism has been presented. (Evidence of halogen-to-tin intramolecular coordination has recently been presented.^{5b,13}) The nmr spectrum of mixtures of trialkyltin halides was examined to determine if halogen exchange is important in the inversion. The spectrum of a mixture of benzylmethylneophyltin iodide and benzylmethylneophyltin chloride is shown in Figure 2. Diastereotopic splitting of the benzylic protons on both the iodide and the chloride is evident. The lines are broadened due to exchange. The extent of the broadening depends on the concentration, temperature, and solvent. A similar dependence is observed on the rate of inversion of the asymmetric tin center in both the iodide and the chloride as determined from the coalescence of the diastereotopic peaks.

Figure 3 shows a spectrum of the same solution after addition of 0.1 ml of pyridine. Only a single average peak for each group corresponding to the two halides is observed because of rapid halogen exchange. If the pyridine is added in small increments, a gradual coalescence of the peaks due to the separate halides is observed. *At the same time* the splitting of the diastereotopic benzylic protons on both the chloride and the iodide decreases.

(13) M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, **90**, 2189 (1968).

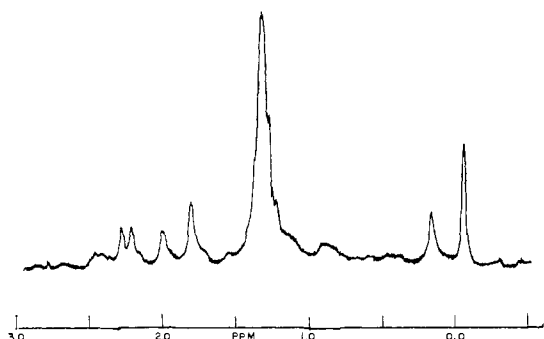


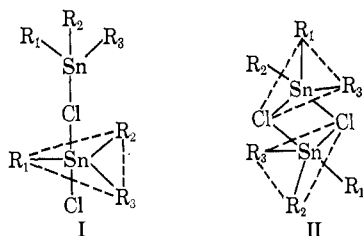
Figure 2. The 60-MHz nmr spectrum of a carbon tetrachloride solution of benzylmethylneophyltin chloride (10%) and benzylmethylneophyltin iodide (10%). For assignments, see Table I.

A similar effect is observed with an increase in temperature or with addition of dichloromethane to the solution. In no case is halogen exchange observed without coalescence of the diastereotopic peaks, and in no case was coalescence of the diastereotopic peaks due to rapid inversion of the tin center observed without a corresponding coalescence of the peaks due to the separate halides. The results indicate that inversion of configuration occurs at the same rate as halogen exchange. The wide variety of conditions where the rates are the same indicates that the two processes are closely related.

Several conceivable mechanisms for halogen exchange would be accompanied by racemization of the asymmetric tin center.

The simplest would involve a dissociation of the halide to give a trialkylstannonium ion which would be expected to racemize very rapidly. There has been considerable study on alkyltin cations in polar solvents such as water and alcohol.¹⁴ The possibility of formation of cationic species in less polar solvents would be considerably diminished. Thus a dissociation mechanism with which a great deal of charge is developed would only be favorable in highly polar solvents where the trialkylstannonium ion would be stabilized by solvation and the large electrostatic forces would be decreased due to the large dielectric constant of the medium.

In nonpolar solvents, an associative mechanism is more likely. This could take place through either one or two bridging halogen atoms. Two possible intermediates are shown in I and II. Type I is found



in the solid state for trimethyltin fluoride and trimethyltin hydroxide.¹⁵ On dissolving the hydroxide in nonpolar solvents, however, the polymer is reported to

(14) R. S. Tobias, *Organometal. Chem. Rev.*, **1**, 93 (1966).

(15) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc., London*, 85 (1963); H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 2332 (1964); N. Kasai, K. Yasuda, and R. Okawara, *J. Organometal. Chem.*, **3**, 172 (1965).

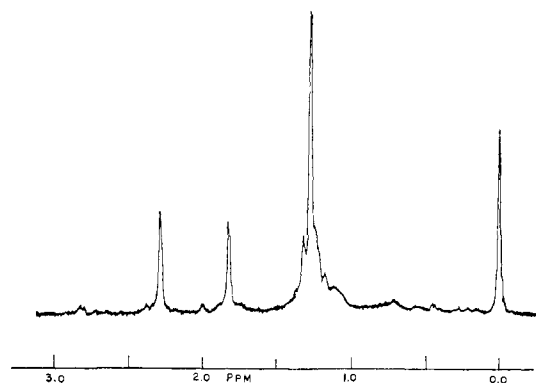


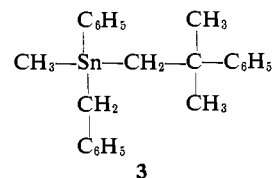
Figure 3. The 60-MHz nmr spectrum of a carbon tetrachloride solution of benzylmethylneophyltin chloride (10%) and benzylmethylneophyltin iodide (10%) after addition of 1% pyridine.

break down to give the dimer containing two OH bridges analogous to the second structure.¹⁶ Both structures involve a five-coordinate tin which would be expected to invert rapidly. Both are consistent with a bimolecular reaction which is indicated by the concentration dependence of τ .

A separate mechanism for inversion of R_3SnX in the presence of Lewis bases has been postulated.^{5b} The Lewis acidity of trialkyltin halides is well known.^{17,18} The pyridine adduct of trimethyltin chloride has a five-coordinate trigonal bipyramidal structure in which the methyl groups occupy the three equatorial positions.¹⁹ Such a structure would be expected to undergo rapid inversion as well as halogen exchange, since the tin-halogen bond is considerably weakened on coordination to a Lewis base.

Tetraalkyltin Compounds. Although numerous Lewis acid-base adducts of trialkyltin halides are known, there is no evidence for any Lewis acidity in tetraalkyltin compounds. The absence of coordinating ability in tetraalkyltin compounds rules out the low-energy pathways available to trialkyltin halides for inversion of the tin center. Therefore, tetraalkyltin compounds are expected to be considerably more stable to inversion of the asymmetric tin center.

The diastereotopic benzyl protons in benzylmethylneophylphenyltin (**3**) provide the first example of an



observable diastereotopic shielding due to an asymmetric tin center with four tin-carbon bonds.²⁰ Neither of the other two diastereotopic groups in the molecule was observably anisochronous under any of the conditions studied.

The splitting was found to be temperature dependent. In dichloromethane solution the observed splitting de-

(16) R. Okawara and K. Yasuda, *ibid.*, **1**, 356 (1964).

(17) I. R. Beattie, *Quart. Rev., Chem. Soc.*, **17**, 382 (1963).

(18) R. C. Poller, *J. Organometal. Chem.*, **3**, 321 (1965).

(19) R. Hulme, *J. Chem. Soc.*, 1524 (1963).

(20) The methyl groups in (4-halo-1,2,3,4-tetraphenyl-1,3-butadienyl)-dimethylphenyltins (ref 5) and dimethylphenyl(2-phenylpropyl)tin (ref 6) are reported to be anisochronous due to the diastereotopic shielding of the asymmetric carbon in the molecule.

creased from 2.0 to 1.0 Hz as the temperature was raised from -20 to 40° . In pyridine solution the splitting decreased from 2.5 Hz at 20° to 0 Hz at 80° . It should be recalled that the splittings observed do not correspond to the actual chemical shift difference because of coupling of the nonequivalent benzyl protons. The chemical shift differences, assuming a coupling constant of 12.1 Hz, may be calculated.

It is not possible to decide whether coalescence is due to inversion at tin or merely a conformational change. The lines are quite overlapped, so line-width considerations are not possible. In view of Peddle and Redl's result⁶ with the asymmetric carbon compound, it seems likely that the coalescence is due to a very small Δ_{id} value (a similar convergence was observed by Peddle and Redl in their carbon compound although coalescence did not occur). The absence of diastereotopic splitting in all other tetrasubstituted tin compounds suggests that in general a very low Δ_{id} is typical. However, the possibility of rapid inversion of tetrasubstituted tin at high temperature cannot be ruled out on the basis of present information. This could conceivably occur through a high-energy process by either dissociation of one of the alkyl groups or association with another tin molecule possibly through alkyl bridging. The redistribution reactions of tetraalkyltin at high temperatures²¹ indicate such a pathway, although at present rapid inversion of tetraalkyltin below 200° seems unlikely. The estimate of the stereochemical stability of tetraalkyltin by Peddle and Redl is consistent with our observations.

Experimental Section

Triphenyltin chloride (Alfa Inorganics), methyl iodide (Baker), benzyl chloride (Aldrich), 3-chloro-2-methylpropene (Aldrich), isobutyl bromide (Matheson Coleman and Bell), isopropyl chloride (Matheson Coleman and Bell), tetramethylsilane (NMR Specialties), and spectroquality carbon tetrachloride (Matheson Coleman and Bell) were purchased and used without further purification. Anhydrous ethyl ether (Baker and Adamson) and tetrahydrofuran (Matheson Coleman and Bell) were distilled from lithium aluminum hydride (Metal Hydrides) immediately prior to use. *tert*-Butyllithium in pentane solution was purchased from Lithcoa and rebottled in brown bottles with septum syringe caps.

Nuclear magnetic resonance spectra were obtained with a Model HFX-10 Bruker Scientific spectrometer or a Model A60 or T60 Varian Associates, Inc., spectrometer.

Neophyl chloride was prepared (70% yield) by a published procedure.²² Purity was established by nmr.

Synthesis of Asymmetric Tin. In view of the large number of reactions and their similarity, only a few representative procedures will be given. The synthesis of other tin compounds may be inferred from the following procedures. A comprehensive review of organotin chemistry²³ provides references to a vast amount of information on techniques and procedures in organotin chemistry.

Total Synthesis of an Asymmetric Tin Compound in Four Steps.

Step 1. Synthesis of Methyltriphenyltin. Methylmagnesium iodide (2 equiv) was prepared by dropwise addition of methyl iodide (22 g) to a stirred mixture of magnesium turnings (3.75 g) in 200 ml of ether at 0° . The Grignard solution was then added over a period of 1 hr to a stirred mixture of triphenyltin chloride (60 g) in 300 ml of ether. The reaction mixture was stirred an additional 2 hr and then hydrolyzed with dilute hydrochloric acid. The ether layer was separated, dried with calcium chloride, and filtered. The ether was then stripped off on a rotary evaporator and the white solid recrystallized from methanol: yield 72%; mp 61.5 – 62.5° (lit.²⁴ 62.5 – 63.0°); nmr (dilute carbon tetrachloride) δ 0.70.

(21) G. Calingaert, H. Soroos, and V. Hnizda, *J. Amer. Chem. Soc.*, **62**, 1107 (1940).

(22) W. T. Smith, Jr., and J. T. Sellas, *Org. Syn.*, **32**, 90 (1952).

(23) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

Integrated intensities were within experimental error of the expected ratio for methyl:phenyl of 3:15. Splitting of the methyl absorption due to ^1H – ^{117}Sn and ^1H – ^{119}Sn coupling was observed.

Step 2. Synthesis of Methylphenyltin Iodide. A solution of iodine (35.6 g) in 2 l. of chloroform was added dropwise to a solution of methyltriphenyltin (50 g) in 500 ml of chloroform over a period of 5 hr. At various stages of the addition it was necessary to strip off solvent on a rotary evaporator to prevent the volume of the solution from becoming unwieldy. The red color of the iodine solution was rapidly decolorized on dropping into the methyltriphenyltin solution. Thus the extent of the reaction could be easily followed from the rate of disappearance of the color. On completion of the reaction, addition of a small amount of iodine resulted in a persistence of the red color. At this point solvent was pumped off and phenyl iodide was removed with an oil pump at 80° . The phenyl iodide was identified by comparison of its nmr spectrum with that of a known sample. A heavy clear liquid (54 g) was obtained. The nmr spectrum of the product in dilute carbon tetrachloride showed a sharp singlet at δ 1.07 with the side bands expected for a tin–methyl bond. The only other peak in the spectrum is a complex pattern due to the phenyl protons at low field. Attempts to obtain crystals from a variety of solvents even at low temperatures failed.

Step 3. Synthesis of Methylphenylbenzyltin. Benzylmagnesium chloride (2 equiv) was prepared by the dropwise addition of benzyl chloride (30.8 g) to a stirred mixture of magnesium turnings (5.8 g) in 200 ml of ether at 0° . A solution of methylphenyltin iodide (52 g) in 20 ml of ether was added dropwise to the stirred Grignard solution over a period of 1 hr. The reaction mixture was stirred an additional 5 hr and hydrolyzed with dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride, and filtered. The ether was then stripped off on a rotary evaporator and other volatile side products were removed at 80° with an oil pump. A heavy liquid (43 g) was obtained. The nmr spectrum of the product contained a resonance due to methyl (with the corresponding peaks due to coupling with tin) at δ 0.35, a peak due to the benzylic protons at δ 2.67, and a complex pattern due to phenyl protons. Integration of the spectrum confirmed the ratios methyl:benzyl:phenyl of 3:2:15.

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{Sn}$: C, 63.94; H, 5.28. Found: C, 63.40; H, 5.38.

Step 4. Synthesis of Methylphenylbenzyltin Iodide. A solution of iodine (13.5 g) in 1 l. of chloroform was added dropwise to a solution of methylphenylbenzyltin (20 g) in 25 ml of chloroform over a period of 7 hr. Volatiles were pumped off at 80° . The product, a heavy liquid, was the stoichiometric amount (22.8 g) expected. The nmr spectrum of the product contains a sharp singlet at δ 0.82 due to the methyl group (coupling due to ^{117}Sn and ^{119}Sn was observed), a sharp singlet at δ 2.92 due to the benzylic protons, and a complex pattern at low field due to the phenyl protons. Integration of the spectrum confirmed the expected ratio methyl:benzyl:phenyl of 3:2:10.

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{SnI}$: C, 39.22; H, 3.50. Found: C, 39.46; H, 3.72.

Benzylmethylneophylphenyltin. Neophylmagnesium chloride (2 equiv) was prepared by the dropwise addition of neophyl chloride (8.8 g) to a stirred mixture of magnesium turnings (1.3 g) in 100 ml of anhydrous ether. A mixture of benzylmethylphenyltin iodide (10 g) in 25 ml of ethyl ether was added dropwise. The reaction mixture was stirred for an additional 2 hr and was then hydrolyzed with dilute hydrochloric acid. The ether layer was extracted, dried over calcium chloride, and filtered. The solvent was pumped off at 80° with an oil pump. About 5 g of a heavy liquid was obtained which contained an impurity as shown by nmr. The liquid was chromatographed on a silica gel column with hexane. The first fraction contained predominantly the coupled product 2,5-diphenyl-2,5-dimethylhexane, as determined by nmr. The remainder of the liquid was the expected product, methylneophylphenyltin. The compound was characterized by nmr (Table I). Integration of the spectrum gave the expected ratios methyl:neophyl methyl:neophyl methylene:benzyl:aromatic of 3:6:2:2:15.

The synthesis was also accomplished by reaction of methylneophylphenyltin iodide with two equivalents of benzylmagnesium chloride. The product was identical with that obtained above.

Benzylmethylneophyltin Iodide. A solution of iodine (1.0 g) in 100 ml of chloroform was added dropwise to a solution of benzylmethylneophylphenyltin (2.0 g) in 10 ml of chloroform. On

(24) M. Dub, "Organometallic Compounds," Vol. 2, Springer-Verlag, New York, N. Y., 1967, p 181.

completion of the addition, the chloroform and other volatiles were pumped off at 80°. The remaining liquid was identified as methylneophylbenzyltin iodide from its nmr spectrum (Table I). Integration of the spectrum confirmed the ratio methyl:neophyl methyl:neophyl methylene:benzyl:aromatic of 3:6:2:2:10.

Benzylmethylneophyltin Chloride. Benzylmethylneophyltin iodide (5.0 g) was dissolved in 100 ml of ether. The ether solution was shaken with 50 ml of a 5 M aqueous solution of potassium hydroxide. The KOH layer was separated and the ether layer

shaken with 50 ml of 3 M hydrochloric acid for 10 min. The ether layer was separated, dried over calcium chloride, and filtered. The ether was removed on a rotary evaporator. The resulting product was identified by its nmr spectrum (Table II). Integration of the spectrum confirmed the ratio methyl:neophyl methyl:neophyl methylene:benzyl:aromatic of 3:6:2:2:10.

Acknowledgment. We thank Dan Netzel for obtaining the 90-MHz spectra.

Complexes of Cyclic 2-Oxacarbenes. I. A Spontaneous Cyclization to Form a Complex of 2-Oxacyclopentylidene¹

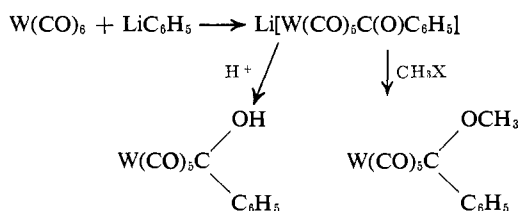
F. A. Cotton* and C. M. Lukehart²

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received October 29, 1970

Abstract: When (pentahaptocyclopentadienyl)(tricarbonyl)(3-bromo-*n*-propyl)molybdenum (**1**) reacts with triphenylphosphine, the *cis* and *trans* isomers of the cation (pentahaptocyclopentadienyl)(dicarbonyl)(triphenylphosphine)(2-oxacyclopentylidene)molybdenum (**2**) are formed. Closer observation indicates that the *cis* isomer is produced under kinetic control as the initial product and that this rearranges unimolecularly to the *trans* isomer. The equilibrium constant, [*trans*]/[*cis*], at 27° in chloroform has the value 42 ± 5, and the rate constant for the *cis*-to-*trans* conversion is 1.3 × 10⁻⁵ sec⁻¹. It appears that the preparative reaction involves attack by P(C₆H₅)₃ on Mo to form the acyl derivative BrCH₂CH₂CH₂C(O)Mo(*h*⁵-C₅H₅)(PPh₃)(CO)₂ in the *cis* configuration, which promptly and spontaneously undergoes internal nucleophilic attack of the acyl oxygen atom on the γ-carbon atom to displace Br⁻ and generate the *cis* form of the cation. The presence of the coordinated carbene, 2-oxacyclopentylidene,

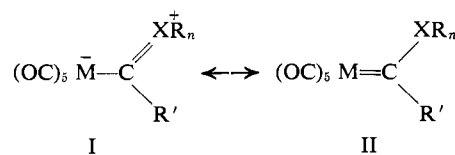
$\text{:COCH}_2\text{CH}_2\text{CH}_2$, is demonstrated by infrared and pmr spectra and by the formation of γ-butyrolactone when **2** is treated with pyridine *N*-oxide.

The possibility of stabilizing carbenes by causing them to be coordinated to low-valent metal atoms appears to have been first knowingly accomplished by Fischer and Maasbol³ in 1964 by way of reaction sequences such as



Subsequent chemical studies⁴ showed that the -OR group of the carbene can be replaced by -NR'R'' groups. X-Ray crystallographic studies⁵ of several chromium compounds containing the :C(OR)R' and :C(NRR')R'' types of carbenes have validated the idea that these compounds can realistically be regarded as carbene complexes whose electronic structures may be represented as resonance hybrids of I and II. The relative contributions of I and II vary significantly as the group XR_n is changed, but in all cases the contribution of I is substantial. Indeed, the only complexes

so far reported are those in which an XR_n group capable of participating in a structure such as I is present. More recently, the attack of alcohols or primary amines



on isocyanides coordinated to platinum(II) has been shown to afford complexes of the type PtX₂(PR₃)[C(R)NHR'], where R = OCH₃, OC₂H₅, OC₃H₇, NHC₆H₅, and NHC(CH₃)₂C₂H₅ and R' = C₆H₅.⁶ An X-ray crystallographic examination of the compound PtCl₂[P(C₂H₅)₃][C(OC₂H₅)NH(C₆H₅)] confirmed the structural formulation of these compounds.

While the work reported here was in progress, still another route leading to *in situ* formation of coordinated carbene moieties was reported.⁷ Attack of an alcohol on a coordinated acetylene leads, apparently through a coordinated vinyl ether intermediate, to a C(OR)-CHR'R'' type of carbene complex. Of direct relevance to the studies we are reporting here was Chisholm and Clark's observation of the following particular reaction (where L = As(CH₃)₃ or P(CH₃)₂C₆H₅), in which an intramolecular cyclization has occurred.

(1) Supported in part by the National Science Foundation.

(2) National Science Foundation Trainee, 1969-1970.

(3) E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).

(4) U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, **89**, 7141 (1967).

(5) Cf. J. A. Connor and O. S. Mills, *J. Chem. Soc. A*, 335 (1969), and references therein to earlier work by Mills and his coworkers.

(6) M. E. Badley, J. Chatt, R. L. Richards, and G. R. Sim, *Chem. Commun.*, 1322 (1969).

(7) M. H. Chisholm and H. C. Clark, *ibid.*, 763 (1970).