TSN toward the ZnX_2 salts studied indicates that the ability of a tripod system to chelate is not determined by the presence of an apical functional atom. However, should there be an apical functional atom present, as in the cases of tren and its derivatives, it may find itself fortuitously close enough to the central metal atom, by virtue of ligand geometry, to become involved in coordination.

In complexes of TTN with $ZnCl_2$ and $ZnBr_2$ we conclude that the zinc atom has a coordination number of four due to the sterically controlled bidentate behavior of TTN. This restricted chelating ability of TTN is a manifestation of critical steric interactions that arise from neighboring N-methyl groups during complex formation. The coordination geometry of the zinc atom is most probably a slightly distorted tetrahedron. The bidentate coordination of TTN to the zinc atom gives rise to one six-membered chelate ring and an uncoordinated amine group (Figure 5). The chelate ring adopts a frozen pseudo-chair conformation at room temperature, the rigidity no doubt being due to the bulky substituents on the ring. The striking similarity between the ^1H nmr data of these systems and structurally analogous nitrogen-containing heterocycles indicates that the zinc(II) nucleus, though chemically different from the carbon atom, does not produce any conformational change in these systems. The fact that the ionic radius of zinc(II), 0.74 Å, is very similar to the covalent radius of carbon, 0.77 Å, probably accounts for the above results.

The postulated structures of the complexes can rationally account for all similarities and differences in physical data. Presently temperature-dependent ^1H nmr and three-dimensional X-ray studies are in progress in order to gain complete insight into the discrete molecular structures and properties of these complexes.

Acknowledgment. We wish to acknowledge the help received from Dr. J. R. Phillips and Professor Galen D. Stucky through reliable discussions.

Halomethyl–Metal Compounds. XXVI. Concerning the Mechanism of Dichlorocarbene Transfer from Trimethyltin Trichloroacetate to Olefins[1]

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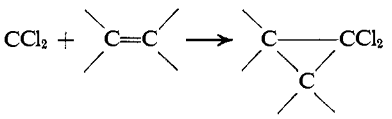
Received December 4, 1968

Abstract: An nmr investigation has shown that the CCl_2 transfer from trimethyltin trichloroacetate to olefins proceeds *via* intermediate trimethyl(trichloromethyl)tin and that the decarboxylation of the organotin ester is an autocatalytic process. The catalytic agent most probably is trimethyltin chloride. Conditions have been defined for the synthesis in high yield of 9,9-dichlorobicyclo[6.1.0]nonane by the reaction of trimethyltin trichloroacetate and cyclooctene in diglyme solution.

In a previous, brief study we investigated the possible utility of triorganotin trihaloacetates as CX_2 transfer agents.[4] It was found that trimethyltin and triphenyltin trichloroacetate did indeed decompose with carbon dioxide evolution on being heated at *ca.* 140°, and if such decomposition was carried out in the presence of an olefin, the expected *gem*-dichlorocyclopropane was formed. The product yields were only fair (40–55%), and no attempts were made to optimize this reaction for preparative purposes. A mechanism involving (trichloromethyl)tin intermediates was proposed (eq 1–3), but this suggestion was not backed up by experiment. It was known from other work in these laboratories[1,5] that trimethyl(trichloromethyl)tin serves as an effective CCl_2 transfer agent under exactly these conditions and that this transfer process most likely involves dichlorocarbene as an intermediate. However, this was not sufficient evidence and a clear demonstration was required that a triorgano(trichloromethyl)tin compound was indeed an intermediate rather than that the CCl_2 transfer from $R_3SnO_2CCCl_3$ to olefin was a concerted, one-step process. Nmr spectroscopy has served excellently to answer this question and to define the experimental conditions under which the $Me_3SnO_2CCCl_3$–olefin reaction is a high-yield process.

$$R_3SnO_2CCCl_3 \longrightarrow R_3SnCCl_3 + CO_2 \qquad (1)$$

$$R_3SnCCl_3 \rightleftharpoons R_3SnCl + CCl_2 \qquad (2)$$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[1] Part XXV: D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, **91**, 2616 (1969).

[2] National Institutes of Health Predoctoral Fellow, 1964–1968.

[3] Postdoctoral Research Associate, 1968–1969.

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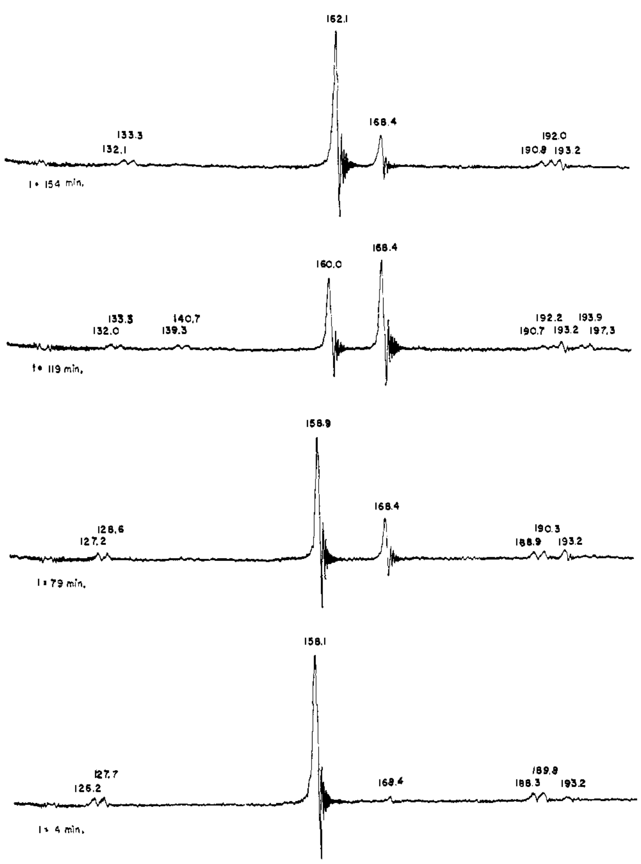


Figure 1. Nmr study of the thermolysis of trimethyltin trichloroacetate in diglyme at 89.5°.

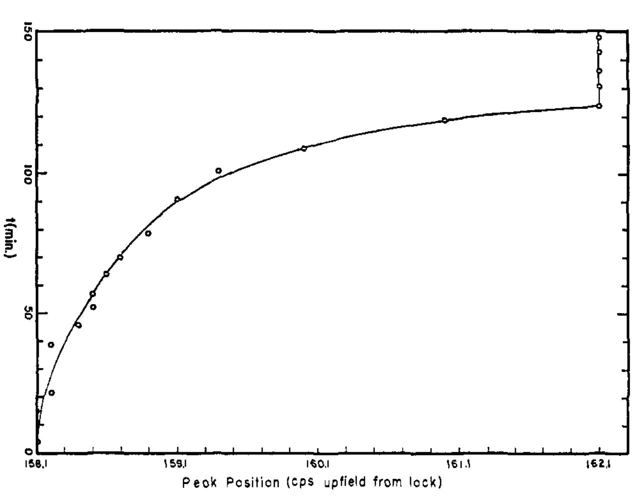
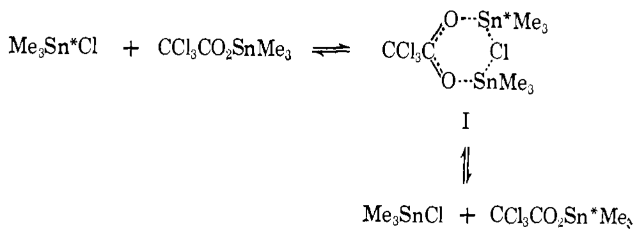


Figure 2. Nmr study of the thermolysis of trimethyltin trichloroacetate: shift in the lower field resonance with time.

During a thermolysis of trimethyltin trichloroacetate carried out in diglyme solution in an nmr tube at 89.5°, the pmr signal of the tin trichloroacetate, 158.1 Hz upfield from the lock signal of the diglyme and approximately 0.67 ppm downfield from internal tetramethylsilane, slowly decreased in amplitude. Simultaneously, a new signal appeared at 168.4 Hz (upfield from diglyme), which was *not* due to trimethyltin chloride, the organotin end product of trimethyltin trichloroacetate decomposition. As the $Me_3SnO_2CCCl_3$ signal diminished in intensity, it also began to shift slowly upfield. The new signal at 168.4 Hz reached its maximum intensity approximately 120 min from the start of the experiment and then decreased rapidly. As this signal decreased, a new trimethyltin resonance at 162.1 Hz rose to a peak height equal to that of the starting material. It was established that trimethyltin chloride was responsible for this signal. A series of such nmr spectra is shown in Figure 1. It is clearly apparent that an intermediate, the compound responsible for the 168.4 Hz resonance, is involved in the $Me_3SnO_2CCCl_3$ to Me_3SnCl conversion.

This reaction occurs much faster at 140°; when carried out in an nmr tube at this temperature in the presence of cyclooctene, it was shown to be complete within 30 min. Subsequent glpc analysis showed that 9,9-dichlorobicyclo[6.1.0]nonane had been produced in quantitative yield. During another experiment at 136°, the progress of the reaction was monitored by nmr spectroscopy and the reaction occurring in the sample tube was stopped by chilling the reaction mixture to −80° at a time when significant quantities of the intermediate whose Me_3Sn resonance occurs at 168.4 Hz were present. Glpc analysis of the reaction mixture at this point and subsequent isolation of the intermediate and measurement of its infrared spectrum showed it to be trimethyl(trichloromethyl)tin, a compound already known to us.[5,6] Thus the reaction course proposed (eq 1–3) was indeed the correct one.

It is significant that at no time were separate resonances seen for trimethyltin trichloroacetate and trimethyltin chloride when both should have been present in the reaction mixture.[7] This observation is consistent only with an exchange phenomenon which occurs rapidly enough to average the environments of the protons of the trimethyltin moieties seen by the spectrometer. A lower limit of 50 sec^{-1} for the rate of exchange can be set using the relationship $2\pi\tau(\nu_a - \nu_b) = 0.5$ for environmental averaging in nmr,[8] where τ is the half-lifetime at either site and $\nu_a - \nu_b$ is the difference in the resonance. A simple intermediate, I, which need never be present in significant concentration, may be proposed for this exchange process



It will be noted that trimethyltin trichloroacetate is represented as a monomer. In diglyme solution the magnitude of $J(^{119}Sn-^{1}H) = 66.0$ Hz for this compound indicates that it is for the most part unassociated but strongly solvated, since it comes close to the value observed for the pentacoordinate trimethyltin chloride-pyridine complex (68.3 Hz).[9]

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(6) D. Seyferth and F. M. Armbrecht, Jr., *J. Organometal Chem.*, **16**, 249 (1969).

(7) This observation was verified with synthetic mixtures of trimethyltin chloride and trichloroacetate in diglyme.

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

(9) P. B. Simons and W. A. G. Graham, *J. Organometal. Chem.*, **10**, 457 (1967).

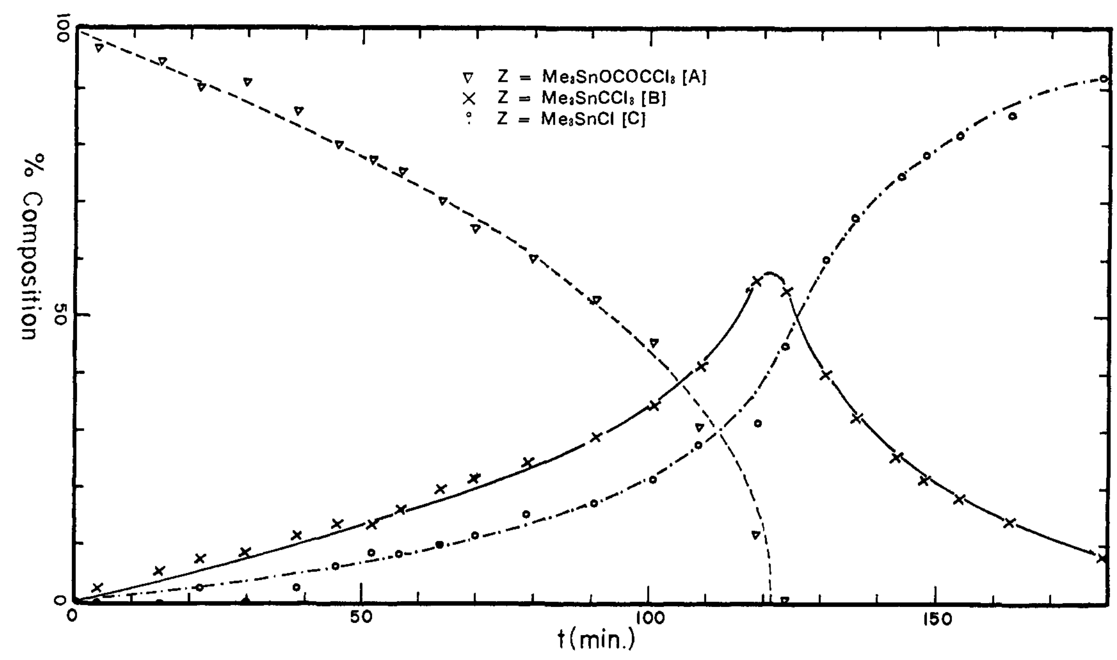

Figure 3. Per cent composition of the reaction mixture with time at 89.5° [*Z*/(*A* + *B* + *C*)].

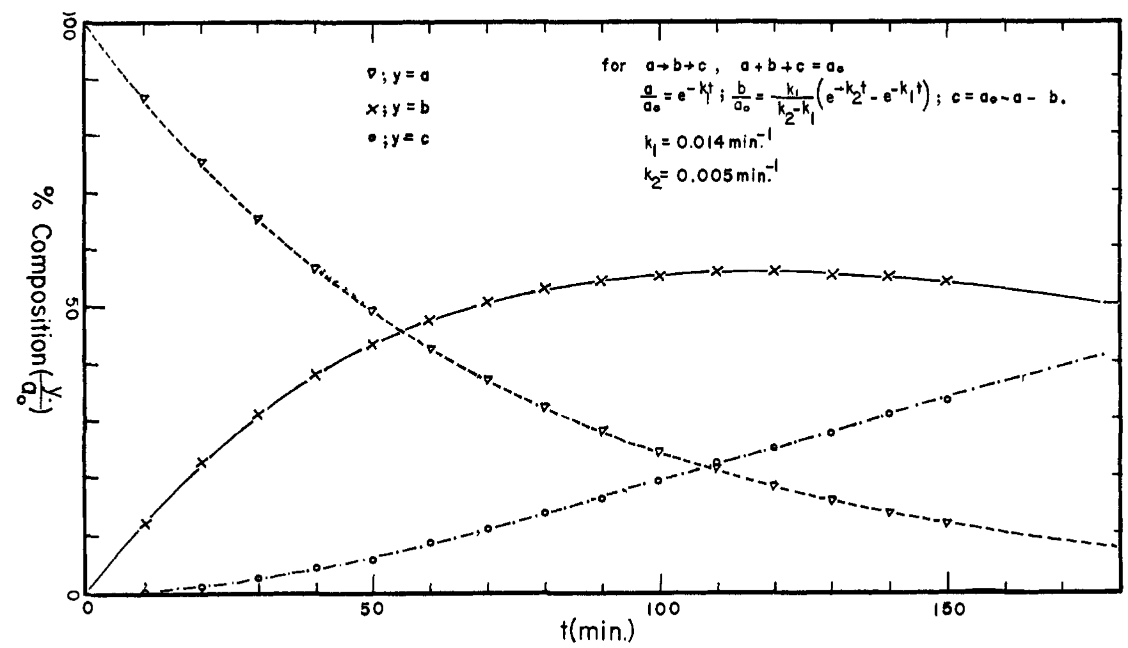

Figure 4. Calculated curves for two first-order reactions in series.

In the case of the trimethyltin trichloroacetate–trimethyltin chloride system, it is a valid assumption that the position of the averaged resonance will be intermediate between the position of the resonances of the individual species and in direct proportion to the relative quantities of each in the mixture at the moment of observation. Thus, analysis of the gradual shift of the trimethyltin resonance between 158.1 and 162.1 Hz reveals the changing proportions of the starting material and trimethyltin chloride during the course of the reaction. Figure 2 shows the shift in the resonance (and therefore the per cent composition of the two components) with time for the trimethyltin trichloroacetate decomposition reaction at 89.5°. These values then were used to calculate the per cent composition of the reaction mixture at various times (Table I; Figure 3).

An interesting feature with regard to the kinetics of this process should be pointed out. The equation sequence 1–2 might lead one to assume that the over-all reaction may be treated as two consecutive, first-order reactions. This is not the case Figure 3 shows the per cent of each of the components—$Me_3SnO_2CCCl_3$, Me_3SnCCl_3 and Me_3SnCl—present in the reaction mixture as a function of time. Figure 4 shows the behavior of composition curves calculated assuming consecutive first-order kinetics to fit the time and amplitude of the maximum point of the experimental concentration curve for the intermediate as seen in Figure 3. Inspection of Figure 4 reveals that the rate of disappearance of starting material decreases with time, as is the usual case for first-order decomposition. The experimental curve (Figure 3), on the other hand, shows an *increase* in rate with time. This behavior can only be explained by assuming that the first reaction is autocatalyzed, *i.e.*, that some product in the reaction sequence catalyzes the decarboxylation of trimethyltin trichloroacetate. The autocatalytic agent most likely is trimethyltin chloride, and the proposed interaction between it and trimethyltin trichloroacetate (intermediate I) very likely accounts for the observed autocatalysis. Decarboxylation *via* intermediate I could represent a lower energy pathway than that available to the uncomplexed trimethyltin trichloroacetate. In I the Sn–O bond and C–O bond both should be weakened and the incipient positive charge on tin should be stabilized by the chlorine bridge. Further work is, however, required to put these ideas on a firm experimental basis.

The second half of the experimental curves in Figure 3, *i.e.*, after the total disappearance of the starting material, may be interpreted as a first-order decomposition of trimethyl(trichloromethyl)tin. The slight deviation from linearity in the standard first-order plot of log concentration *vs.* time (Figure 5) is expected if one considers the rate-determining step to be reversible (eq 2). That dichlorocarbene can indeed insert into tin–halogen bonds has been demonstrated during the course of our work on the preparation of trimethyl(trihalomethyl)tin compounds.[6]

Since this nmr study had indicated that the decomposition of trimethyltin trichloroacetate to trimethyltin chloride proceeds rapidly at *ca.* 140° and that when this decomposition is carried out in the presence of cyclooctene the dichlorocarbene interception by the olefin is quantitative, another assessment of the practical utility of trimethyltin trichloroacetate as a dichlorocarbene transfer agent seemed in order. When a mixture of 0.1 mole each of this tin compound and cyclooctene in 80 ml of diglyme was heated under nitrogen in an oil bath at 140°, gas evolution ceased after 20 min, and subsequent distillation gave 9,9-dichlorobicyclo[6.1.0]nonane in 88% yield. Thus, as this nmr investigation had predicted, trimethyltin trichloroacetate serves excellently in the preparation of *gem*-dichlorocyclopropanes.

A similar reassessment of the usefulness of triphenyltin trichloroacetate as a dichlorocarbene source confirmed the results of our previous study.[4] The yield of 9,9-dichlorobicyclo[6.1.0]nonane was only moderate when thermolysis of this compound was carried out in the presence of cyclooctene, and major amounts of benzene were formed in a side reaction, the nature of which is not known. Furthermore, the temperature and the rate at which triphenyltin trichloroacetate decomposition occurred appeared to be very dependent upon the purity of the starting tin compound.

Experimental Section

Starting Materials. Trimethyltin trichloroacetate was prepared by reaction of trichloroacetic acid with trimethyltin hydroxide; mp 174–176° (lit.[9] mp 175–176°). A similar reaction with triphenyltin hydroxide served in the preparation of triphenyltin trichloroacetate. The melting point of the latter after one crystallization was 90–91°; after four recrystallizations from hexane, mp 105–106°, decomposition above 155°. *Anal.* Calcd for $C_{20}H_{15}O_2Cl_3Sn$: C, 46.88; H, 2.95; Cl, 20.75. Found: C, 46.47; H, 3.11; Cl, 20.52.

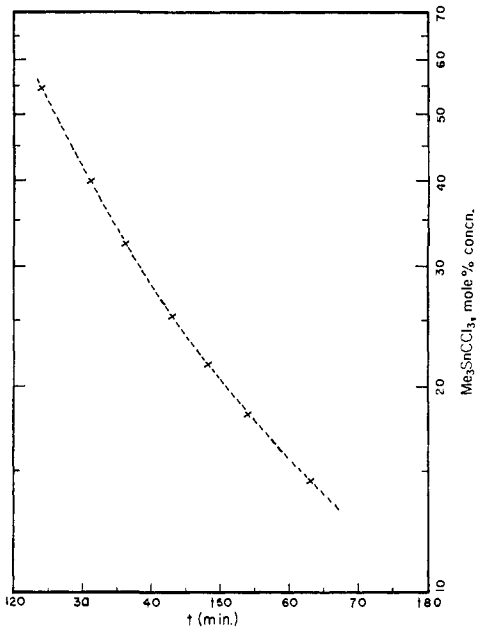

Figure 5. Rate of decomposition of trimethyl(trichloromethyl)tin

The diglyme used was dried over solid KOH and distilled *at reduced pressure* from lithium aluminum hydride.

Thermolysis of Trimethyltin Trichloroacetate at 89.5°. Into a dry, weighed nmr tube were charged under an atmosphere of dry nitrogen 34.7 mg (0.106 mmole) of trimethyltin trichloroacetate, 300 µl of diglyme, and 43 µl of cyclooctene. The tube, closed with a pressure-holding cap, was placed in a variable-temperature probe in a Varian Associates HA-60 spectrometer. The diglyme solvent signal was used as the internal lock and the auto-shim was used to stabilize the *Y*-gradient. Twenty-seven sweeps of the Me_3Sn resonance region were made during 204 min. The results are given in Table I, and several of the nmr spectra are reproduced in Figure 1. The temperature was measured by the standard method of measuring the difference in Hz (59.0 Hz; 89.5°) between the methylene and hydroxyl resonance of ethylene glycol.

Isolation of the Intermediate in the Decarboxylation of Trimethyltin Trichloroacetate. Into a dry, weighed nmr tube under an atmosphere of dry nitrogen were charged 75.9 mg (0.23 mmole) of the tin compound and 400 µl of diglyme. A pressure cap was placed on the tube, and the tube was heated to 140° in the variable-temperature probe of an A-60 nmr spectrometer. The progress of the reaction was followed by scanning the 0.0–0.1-ppm range. The reaction was stopped by chilling the tube in a Dry Ice–acetone bath when the intermediate was present in about 25% yield. The contents of the tube were transferred under nitrogen to a small, dry 10-mm tube with a no-air stopper. Samples then were withdrawn from this tube with a syringe and were analyzed by glpc (MIT isothermal unit, 4-ft glass column, 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb P, at 100°). Other than solvent, the samples analyzed contained trimethyltin chloride and trimethyl(trichloromethyl)tin. The latter was identified by comparison of its glpc retention time and the infrared spectrum of a sample isolated by glpc with those of authentic material.[6]

Thermolysis of Trimethyltin Trichloroacetate in the Presence of Cyclooctene. (a) Nmr Tube Experiment. Into a dried, weighed nmr tube under an atmosphere of dry nitrogen were charged 0.1243 g (0.38 mmole) of trimethyltin trichloroacetate, 400 µl of cyclooctene, and 1.0 ml of dry diglyme. The tube, sealed with a pressure cap, was heated at 144° in a variable-temperature probe in an A-60 nmr spectrometer. The progress of the reaction, which was completed in 30 min, was followed by nmr. The tube was allowed to cool to room temperature and 57.5 mg of *n*-dodecane was added as an internal standard to the weighed solution. Glpc analysis (same instrument and column, at 98°) showed that 9,9-dichlorobicyclo[6.1.0]nonane had been produced in quantitative yield.

(b) Preparative-Scale Experiment. Into a dry 250-ml three-necked flask equipped with a reflux condenser, gas-inlet tube, and magnetic stirring assembly were charged 32.5 g (0.1 mole) of tri-

Table I. Data from Decarboxylation of $Me_3SnOCOCCl_3$ at 89.5°

t, min	Peak ht (y) of intermediate	Total peak ht (a) for both resonances	% shift (Δ) of low-field peak (from Figure 2)	% Me_3SnCCl_3 (y/a)	% Me_3SnCl ($\Delta[(a - y)/a]$)	% $Me_3SnOCOCCl_3$ ($100 - \Delta[(a - y)/a]$)
4	3	110	0	2.7	0.0	97.3
15	6	115	0	5.2	0.0	94.8
22	8	104	2.5	7.7	2.31	90.0
30	10	113	0	8.9	0.0	91.1
39	13	109	2.5	11.9	2.20	85.9
46	15	110	7.5	13.6	6.48	80.0
52	14	103	10	13.6	8.56	77.7
57	19	117	10	16.2	8.38	75.5
64	22	112	12.5	19.6	10.0	70.3
70	25	115	15	21.7	11.7	65.5
79	28	115	20	24.4	15.1	60.4
91	34	116	25	29.3	17.7	53.0
101	39	113	32.5	34.5	21.9	45.6
109	48	116	47.5	41.4	27.8	30.8
119	65	115	72.5	56.5	31.6	12.0
124	56	102	100	54.9	45.1	0.0
131	44	110	100	40.0	60.0	0.0
136	37	114	100	32.4	67.6	0.0
143	29	114	100	25.4	74.6	0.0
148	25	116	100	21.6	78.4	0.0
154	21	115	100	18.3	81.7	0.0
163	17	117	100	14.5	85.5	0.0
179	9	109	100	8.3	91.7	0.0
184	7	105	100	6.7	93.3	0.0
193	6	106	100	5.7	94.3	0.0
199	5	115	100	4.3	95.7	0.0
204	5	116	100	4.3	95.7	0.0

methyltin trichloroacetate, 11.0 g (0.1 mole) of cyclooctene, and 80 ml of dry diglyme under nitrogen. The reaction mixture was stirred and heated, and the gas inlet tube was connected to a Nujol bubbler. At *ca.* 50° a homogeneous solution was obtained. The oil-bath temperature was raised to 140°, at which temperature gas evolution was brisk. After the mixture had been heated at 140° for 20 min, the gas evolution ceased. Cooling to room temperature was followed by filtration of *ca.* 0.5 g of yellowish solid and removal of most of the solvent by distillation at 25–30° (0.05 mm). The liquid residue was shaken with 50 ml of water to remove the remaining diglyme. The organic phase was diluted with diethyl ether, dried over anhydrous sodium sulfate, and distilled to give 15.8 g (88% yield) of 9,9-dichlorobicyclo[6.1.0]nonane, bp 54–56° (0.07 mm), $n^{25}D$ 1.5002, whose infrared spectrum was in complete agreement with that of an authentic sample.

Acknowledgments. The authors are grateful to the U. S. Army Research Office (Durham) for generous support of this work and to M&T Chemicals, Inc. for gifts of chemicals. This work was supported in part by Public Heath Service Fellowship 5-F1-GM-23,-742 (to F. M. A.). We also thank Dr. A. M. Leonardi-Cattolica for a valuable discussion.