solution showed the presence of cyclooctane and 11.7 mg (70%) of tricyclooctane (**2**),[37] and no other components (limit of detection about 2%).

Acknowledgments. We would like to express our appreciation to Dr. A. S. Mehta for preliminary experiments, to Mr. H. L. Mitchell for running mass spectra, and to Professor John Baldwin (University of Oregon) for a helpful discussion.

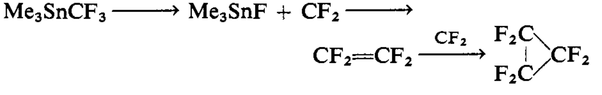
Halomethyl-Metal Compounds. XXV. α-Polyhaloalkyltin Compounds as Halocarbene Precursors[1]

Dietmar Seyferth and Frank M. Armbrecht, Jr.[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 18, 1968*

Abstract: The thermolysis of a number of halomethyl–tin compounds in the presence of olefins has been investigated. Trimethyl(trichloromethyl)tin was found to be an effective CCl_2 transfer agent at 140°, and the action of sodium iodide in 1,2-dimethoxyethane at 85° induced CCl_2 transfer from this tin compound in fair yield. Trimethyl(bromodichloromethyl)tin transferred CCl_2 to olefins very slowly at 80°, rapidly at 140°, but a small amount of decomposition to give Me_3SnCl and CClBr also was noted. In contrast, trimethyl(dichloromethyl)tin proved to be very stable thermally and it did not transfer CHCl at 140°. Trimethyl(α,α-dichlorobenzyl)tin appeared to transfer PhCCl to tetramethylethylene, but the initially formed cyclopropane was not isolated. Instead, 2,4-dimethyl-3-phenylpenta-1,3-diene, a product derived from ring opening of the latter and subsequent loss of hydrogen chloride, was obtained in 34% yield. When trimethyl(α,α-dichlorobenzyl)tin was pyrolyzed in the presence of cyclohexene, the major products were dimethyltin dichloride and styrene, and their formation could be explained in terms of a (Me → C, Cl → Sn) interchange in Me_3SnCCl_2Ph before α elimination of a tin chloride. In the pyrolysis of bis(trimethyltin)bromochloromethane in the presence of cyclohexene at *ca.* 170°, the formation in low yield of 7-chloro-7-trimethyltinnorcarane, bis(3-cyclohexenyl)methane, and 7,7′-bi(bicyclo[4.1.0]heptane) spoke for trimethyltinhalocarbene intermediates in the decomposition process. A similar reaction with bis(trimethyltin)dibromomethane gave only 7,7′-bi(bicyclo[4.1.0]heptane), while bis(trimethyltin)dichloromethane was quite stable thermally.

Our previous investigations have demonstrated the outstanding utility of halomethyl–mercury compounds as divalent carbon transfer agents. Using the appropriate mercurials, CCl_2,[3] CClBr,[3] CBr_2,[3] CClF,[4] CHCl,[5,6] CHBr,[6] CH_2,[7] and Me_3SiCCl[8] could be added to C═C double bonds or inserted into various element–element single bonds. Such divalent carbon transfer from halomethyl–metal compounds appears to be a general reaction.[9] In order to find out more concerning the factors which affect the nature of the divalent carbon transfer process, we have examined in some detail the thermolysis of a number of halomethyl–tin compounds in the presence of olefins which could serve as reactive carbene traps. Organotin compounds were chosen as the subject for this study for several reasons. (1) Taking into account all that is known to date concerning such α-elimination reactions of metal halides from halomethyl–metal compounds,[9] we would expect that the halomethyl–tin/olefin reaction would proceed by way of halocarbene intermediates, rather than a bimolecular reaction between the organometallic and the olefin. (2) Organotin starting materials for such a study can be prepared by a number of different routes.[10–13] (3) The organotin halides produced in α elimination from halomethyltin compounds are easily removed from the reaction mixture by precipitation as the fluorides or as the ammonia adducts. (4) At the time this study was begun, the thermolysis of trimethyl(trifluoromethyl)tin had already been reported[14] (eq 1) and we ourselves had made



(1)

this method for CF_2 generation more useful by appli-

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[1] (a) Part XXIV: D. C. Mueller and D. Seyferth, *J. Am. Chem. Soc.*, **91**, 1754 (1969); (b) preliminary communication: D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, *J. Organometal. Chem.* (Amsterdam), **6**, 573 (1966).

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

[3] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

[4] D. Seyferth and K. V. Darragh, *J. Organometal. Chem.* (Amsterdam), **11**, P9 (1968).

[5] D. Seyferth, H. D. Simmons, Jr., and L. J. Todd, *ibid.*, **2**, 282 (1964).

[6] D. Seyferth, H. D. Simmons, Jr., and G. Singh, *ibid.*, **3**, 337 (1965).

[7] D. Seyferth, M. A. Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 121 (1964).

[8] D. Seyferth and E. M. Hanson, *ibid.*, **90**, 2438 (1968).

[9] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, **89**, 4953 (1967).

[10] D. Seyferth and F. M. Armbrecht, Jr., *J. Organometal. Chem.* (Amsterdam), **16**, 249 (1969).

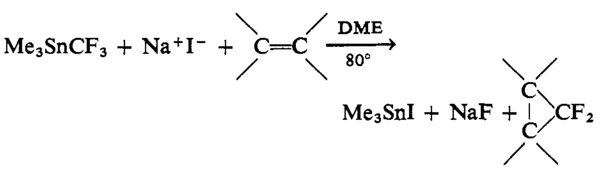
[11] A. G. Davies and W. R. Symes, *ibid.*, **5**, 394 (1966).

[12] A. G. Davies and T. N. Mitchell, *ibid.*, **6**, 568 (1966).

[13] T. Chivers and B. David, *ibid.*, 13, 177 (1968).

[14] H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

cation of the sodium iodide procedure (eq 2).[15] Thus



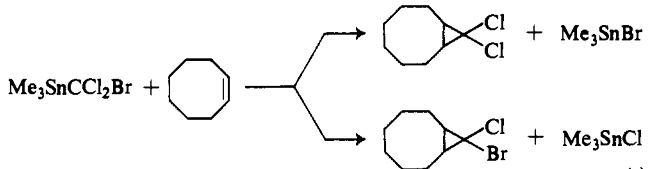
(2)

further extension to chloromethyl- and bromomethyl tin derivatives seemed promising.

Available for study during the course of this investigation were the following compounds: Me_3SnCCl_3,[10] Me_3SnCCl_2Br,[10] Me_3SnCCl_2H,[10] Me_3SnCCl_2Ph,[10] $Me_3SnCCl_2SnMe_3$,[16] $Me_3SnCClBrSnMe_3$,[16] and $Me_3SnCBr_2SnMe_3$.[16]

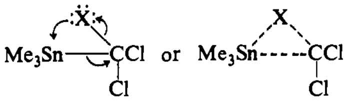
Results and Discussion

Trimethyl(trihalomethyl)tin Compounds. In view of the outstanding superiority of $PhHgCCl_2Br$ as a CCl_2 source (*vs.* $PhHgCCl_3$),[3] our first experiments were carried out using trimethyl(bromodichloromethyl)tin. The higher thermal stability of the tin compound (compared to $PhHgCCl_2Br$) was immediately apparent. When Me_3SnCCl_2Br was heated in refluxing cyclohexene (*ca.* 80°), only a slow decomposition was observable, and after 92 hr of heating, 8% of the starting tin compound still remained. Transfer of CCl_2 had occurred, as shown by the formation of 7,7-dichloronorcarane in 42% yield. Trimethyltin bromide also was present, as expected, and trace yields of trimethyltin chloride and 7-bromo-7-chloronorcarane also had been formed. A much faster reaction occurred at 140°. Decomposition of trimethyl(bromodichloromethyl)tin was complete within 3 hr when it was heated in refluxing cyclooctene solution. 9,9-Dichlorobicyclo[6.1.0]nonane was produced in 66% yield, but also present was 9-bromo-9-chlorobicyclo[6.1.0]nonane (5% yield) (eq 3). Thus we note two advantages of phenyl(bromodichloromethyl)mercury over trimethyl(bromodichloromethyl)tin: (1) it transfers dichlorocarbene to olefins rapidly at significantly lower temperatures, and (2) it transfers CCl_2 exclusively, whereas the tin compound does not. Furthermore, the tin compound is quite reactive toward atmospheric moisture, but the mercury compound is stable hydrolytically.



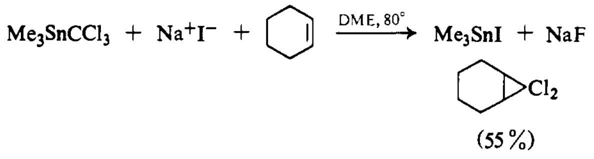
(3)

When trimethyl(trichloromethyl)tin was heated at reflux with cyclooctene (140°) for 3 hr, the expected 9,9-dichlorobicyclo[6.1.0]nonane was formed in 94% yield. In order to obtain further information concerning the nature of the Me_3SnCCl_3–olefin reaction, the reaction of this tin compound with vinyl acetate (1:5 molar ratio) in chlorobenzene at reflux was examined. This olefin has served usefully in past studies to provide preliminary indication of the intermediates involved in CCl_2 transfer systems. If the trichloromethyl anion is an intermediate (*e.g.*, as is the case for sodium trichloroacetate pyrolysis[17] and the $PhHgCCl_3$–NaI system[18]), then the CCl_3^- trapping product, $CH_3CO_2CH(Me)CCl_3$, is obtained in yields comparable to those of the expected 2,2-dichlorocyclopropyl acetate. If the trichloromethyl radical is an intermediate, then telomeric, polymeric, and chain-transfer products would be expected when vinyl acetate is the olefinic substrate. If, on the other hand, CCl_2 is formed directly from the CCl_2 transfer reagent (as is the case with $PhHgCCl_2Br$[3,9]), then the CCl_2 trapping product, 2,2-dichlorocyclopropyl acetate, is the only product formed. The Me_3SnCCl_3–vinyl acetate reaction gave *only* 2,2-dichlorocyclopropyl acetate (58% yield). None of the CCl_3^- addition product was observed, nor was there a change in the color or viscosity of the solution during the reaction. No nonvolatiles were produced. On the basis of this result, we suggest that the mechanism of the Me_3SnCCl_2X–olefin reaction involves a CCl_2 intermediate and that the CCl_2 extrusion from the Me_3SnCCl_2X reagent is similar to the process suggested for CX_2 extrusion from $PhHgCX_2Br$.[9] The transition state one would draw for such extrusion, I, resembles the interaction between halogen and tin postulated to occur during S_N2 displacements of halomethyltin compounds.[19,20] An appropriate kinetic study is contemplated in order to confirm or reject this suggestion concerning mechanism.



I

A second method for generating dihalocarbenes from phenyl(trihalomethyl)mercury compounds, which occurs under milder conditions than the thermolytic process but has the disadvantage of involving trihalomethyl anion intermediates, is the sodium iodide procedure.[18] This procedure could be applied successfully to CCl_2 transfer from trimethyl(trichloromethyl)tin (eq 4). An improvement in the yield of this reaction should in principle be possible, but our discovery of the utility of triorganotin trichloroacetates as CCl_2 transfer agents[1b,21,22] has obviated any further work with the very hydrolytically



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[15] D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, **32**, 2980 (1967).

[16] D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, in press.

[17] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

[18] D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967).

[19] R. G. Kostyanovskii and A. K. Prokof'ev, *Dokl. Akad. Nauk SSSR*, **164**, 1054 (1965).

[20] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Organometal. Chem.* (Amsterdam), **5**, 233 (1966).

[21] D. Seyferth, B. Prokai, and R. J. Cross, *ibid.*, **13**, 169 (1968).

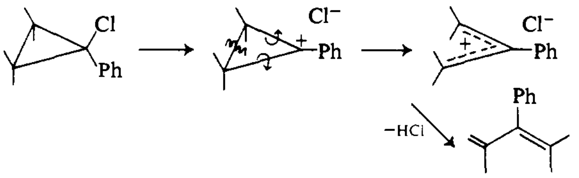
[22] F. M. Armbrecht, Jr., W. Tronich, and D. Seyferth, paper in preparation.

unstable and hard-to-handle trimethyl(trihalomethyl)tin compounds.

Trimethyl(dichloromethyl)tin. In contrast to phenyl(dichloromethyl)mercury, which reacted with cyclohexene in a sealed tube at 145° (60 hr) to give a mixture of the 7-chloronorcarane isomers in 60% yield,[5] trimethyl(dichloromethyl)tin survived a 10-day reflux (140°) period in cyclooctene solution. No trace of 9-chlorobicyclo[6.1.0]nonane could be detected by gas chromatography. The sodium iodide procedure also was not applicable. When sodium iodide (10% excess) was added to a refluxing solution of trimethyl(dichloromethyl)tin and cyclohexene in 1,2-dimethoxyethane (DME), nucleophilic displacement occurred at carbon, not at tin, and trimethyl(chloroiodomethyl)tin, $Me_3SnCHClI$ (62%), and trimethyl(diiodomethyl)tin, Me_3SnCHI_2 (22%), were produced. A similar observation of I^- attack at carbon rather than at the metal atom had been made previously in the case of $PhHgCHCl_2$ and PhHgCHClBr.[23]

Trimethyl(α,α-dichlorobenzyl)tin. The possible application of trimethyl(α,α-dichlorobenzyl)tin as a precursor for phenylchlorocarbene was of special interest, since a mercurial route to this carbene still was lacking. An indirect, mercurial-based procedure had been reported[24] ($PhHgCCl_2Br + Ph_3B \rightarrow Ph_2BCCl_2Ph$; $Ph_2BCCl_2Ph + {>}C{=}C{<} \rightarrow Ph_2BCl$ + *gem*-chlorophenylcyclopropane, but the product yields were low as a result of a competing side reaction in the first step. Other known methods of PhCCl transfer involve the action of strong bases (*t*-BuOK,[25,26] methyllithium,[27] *n*-butyllithium[28]) on benzal chloride. The thermolysis of trimethyl(α,α-dichlorobenzyl)tin was studied in the presence of two different olefins. In neither instance were the expected phenylchlorocarbene adducts obtained.

The thermal decomposition of Me_3SnCCl_2Ph in tetramethylethylene solution was carried out in a sealed tube at 140–160° for 9 hr, milder conditions being insufficient for reagent decomposition. Although 1-chloro-1-phenyl-2,2,3,3-tetramethylcyclopropane was not obtained, the product which was isolated in 34% yield, 2,4-dimethyl-3-phenylpenta-1,3-diene (II), undoubtedly was produced from the expected cyclopropane by the process shown in eq 5. The rotation of the electrocyclic ring opening (disrotatory, as required by the Woodward–Hoffmann rules) produces such crowding of the methyl groups that the preferred method of steric strain release is loss of a proton from the incipient tertiary allylic carbonium ion and formation of a butadiene structure.[29] Many examples of such thermolyses of halocyclopropanes are known. As a closely related example, we may cite the pyrolysis of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, which gives 2,4-dimethyl-3-chloropenta-1,3-diene.[30,31] In another study,[32] we found that the mild Lewis acid, zinc chloride, was required to induce trimethylchlorosilane elimination and ring opening of trimethylsilylmethyl-substituted *gem*-dihalocyclopropanes (to give 2-halobuta-1,3-dienes) under reasonable conditions, but that the elimination of trimethyltin chloride from 1,1-dichloro-2-(trimethyltinmethyl)cyclopropane occurred readily under comparable conditions in the absence of this catalyst. It was suggested that the decomposition of the tin compound was an autocatalytic process, the trimethyltin chloride (known to be a Lewis acid toward chloride ion[33,34]) produced serving as the required catalyst. In the present case, we may also be dealing with a trimethyltin chloride assisted C–Cl ionization and ring-opening process.



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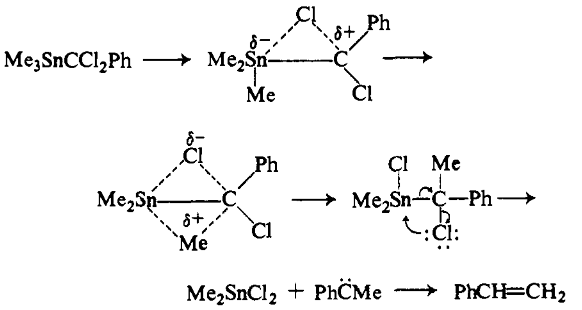
Even more interesting in terms of deviation from expected chemistry was the thermal decomposition of trimethyl(α,α-dichlorobenzyl)tin in the presence of cyclohexene at 150°. A myriad of products resulted, and among them may have been the expected 7-chloro-7-phenylnorcarane in very low yield. (A component in the reaction mixture had the expected glpc retention time and its infrared and nmr spectra, while not dissimilar, were not exactly identical with those of authentic material). In any case, Jensen and Patterson[35] have pointed out the thermal instability of 7-chloro-7-phenylnorcarane, so its virtual absence in this reaction mixture is not surprising. Noteworthy in this reaction were the low (11%) trimethyltin chloride yield, the formation of dimethyltin dichloride (26% yield) and the presence of styrene (identified by its infrared, nmr and mass spectra) (41% yield) among the volatile products. The formation of dimethyltin dichloride and styrene can be rationalized in terms of a variation of the concerted carbene extrusion transition state I as follows. As the chlorine begins its nucleophilic attack, *i.e.*, its migration from carbon to tin, the partial positive charge which develops on the α-carbon atom is stabilized by the phenyl substituent to such an extent that it need not be satisfied immediately by cleavage of the Sn–C bond. Instead, an alternate process, migration of a methyl group from tin to the α-carbon atom is preferred (eq 6). The migration of a second chlorine to tin then occurs *via* the usual α-elimination



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(23) D. Seyferth and H. D. Simmons, Jr., *J. Organometal. Chem.* (Amsterdam), **6**, 306 (1966).

(24) D. Seyferth and B. Prokai, *J. Am. Chem. Soc.*, **88**, 1834 (1966).

(25) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2586 (1959).

(26) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(27) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).

(28) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4147 (1965).

(29) S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967), and references cited therein.

(30) J. W. Engelsma, *Rec. Trav. Chim.*, **84**, 187 (1965).

(31) G. C. Robinson, *J. Org. Chem.*, **33**, 607 (1968).

(32) D. Seyferth and T. F. Jula, *J. Am. Chem. Soc.*, **90**, 2938 (1968).

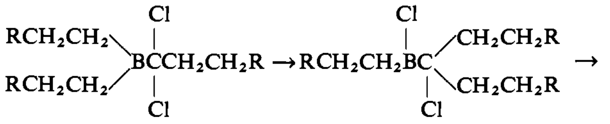
(33) P. Pfeiffer, *Ann. Chem.*, **376**, 310 (1910).

(34) D. Seyferth, U. S. Patent 3,070,614 (Dec 25, 1962); *Chem. Abstr.*, **58**, 11399 (1963).

(35) F. R. Jensen and D. B. Patterson, *Tetrahedron Letters*, 3837 (1966).

pathway to give dimethyltin dichloride and phenylmethylcarbene, the rearrangement of which by hydrogen migration produces the observed styrene. Such a process was suggested as an explanation of the formation of higher internal olefins during the reaction of phenyl(bromodichloromethyl)mercury with trialkylboranes[24] (eq 7 and 8). A further case somewhat analogous to

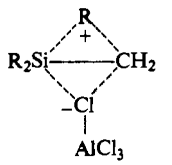
$$(RCH_2CH_2)_3B \xrightarrow{\text{PhHgCCl}^2\text{Br}} (RCH_2CH_2)_2BCCl_2CH_2CH_2R \quad (7)$$



$$RCH_2CH_2BCl_2 + (RCH_2CH_2)_2C \rightarrow$$

$$RCH_2CH_2CH{=}CHCH_2R \quad (8)$$

these (but without final carbene elimination) is the aluminum chloride catalyzed rearrangement of Me_3SiCH_2Cl to $Me_2EtSiCl$ (Me → C, Cl → Si interchange).[36] It will be noted that in this example the substituent exchange is promoted by $AlCl_3$, a Lewis acid, and a transition state III has been suggested[37] for this process;



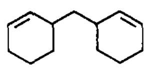
III

R group relative migratory aptitudes decreased in the order Ph > Me_3Si > *n*-Pr > Et > Me > CH_2Cl.[37,38] In the $R_2BCCl_2R \rightarrow RClBCClR_2$ case the chloroboranes formed in that and subsequent steps could act as promoters for chloride migration in a similar fashion. In the case of the decomposition of trimethyl(α,α-dichlorobenzyl)tin, two main factors probably operate to make the observed mode of decomposition favorable: (1) the chlorine atom on the α-carbon atom has a high migratory aptitude, and (2) the dimethyltin dichloride formed very likely is acting as a Lewis acid and promoting chloride migration. This point concerning the Lewis acidity of methyltin chlorides had already been made earlier in this discussion for trimethyltin chloride, and it should be pointed out that dimethyltin dichloride should be a stronger Lewis acid toward chloride ion than trimethyltin chloride.[39]

Dimethyltin dichloride also was formed during the thermolysis of trimethyl(α,α-dichlorobenzyl)tin in the presence of tetramethylethylene, so it is likely that the alternate decomposition to give Me_2SnCl_2 and styrene also had occurred to some extent. The reaction work-up, however, was such that any styrene formed would have escaped detection. The decomposition reactions of R_3SnCX_2R' compounds are receiving further study in these laboratories.

Bis(trimethyltin)dichloromethane. Bis(trimethyltin)dichloromethane proved to be very stable thermally. A pure sample showed almost no sign of decomposition after it had been heated in a sealed tube at 145° for 40 hr. This compound was decomposed to the extent of 36% on being heated at 180° for 4 days in the presence of an excess of cyclohexene, but the only volatile materials present at the end of this time were the olefin and trimethyltin chloride.

Bis(trimethyltin)bromochloromethane. In view of the high stability of bis(trimethyltin)dichloromethane, further experiments were carried out with bis(trimethyltin)bromochloromethane, in the well-grounded hope that elimination of trimethyltin bromide from such a structure might be more facile. This compound also was quite stable, only trace decomposition occurring when it was heated in the presence of an excess of tetramethylethylene for 20 hr at 130°. However, pyrolysis at 190–200° for 24 hr served to destroy almost all of a sample of this compound; trimethyltin bromide and trimethyltin chloride were the only volatile products found. The results obtained when $(Me_3Sn)_2CClBr$ was heated in a sealed tube in the presence of an excess of cyclohexene for 4 days at 160–180° provided the first clear evidence for the thermal extrusion of trimethyltinhalocarbenes from $(Me_3Sn)_2CX_2$ compounds. The product mixture was complex: trimethyltin bromide (63.5% yield); trimethyltin chloride (45%); dimethyltin dichloride (10%); a small amount of dimethyltin dibromide (identification tentative); bis(trimethyltin)chloromethane (4%); bis(trimethyltin)bromomethane (3%); starting material (5.4%); an olefin tentatively identified as bis(3-cyclohexenyl)methane (IV); 7,7′-bi(bicyclo[4.1.0]heptane) (V) (6%); 7-chloro-7-trimethyltinnorcarane (VI) (2%). At first sight it would appear that a rather unselective elimination of trimethyltin bromide and trimethyltin chloride from $(Me_3Sn)_2CClBr$ has occurred. Further discussion will show that this need not be the correct interpretation of the observed yield figures. The formation of 7-chloro-7-trimethyltinnorcarane can most certainly be attributed to the addition of Me_3SnCCl to cyclohexene. The rather high temperatures used in this reaction serve to explain the formation of the two wholly organic products, IV and V. 7-Chloro-7-trimethyltinnorcarane is itself an α-chloroalkyltin compound, hence would be expected to undergo thermal α elimination of the type discussed in this paper. Such elimination of trimethyltin chloride from VI would produce the carbene VII, the reactions of which with cyclohexene would result in formation of the spiropentane V *via* C=C addition, and at these high temperatures, also of the C–H insertion product VIII. Thermal rearrangement of the latter could then give the observed IV. The spiropentane V had been isolated earlier by



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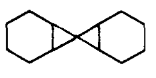

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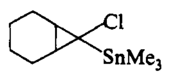

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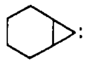

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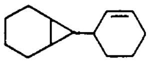

VIII

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(36) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).

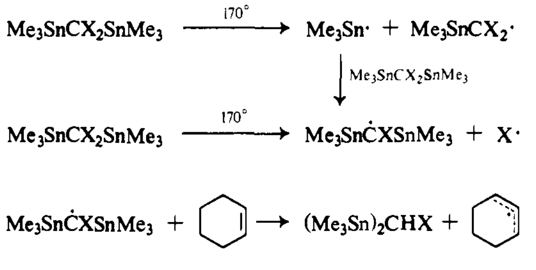
(37) R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometal. Chem.* (Amsterdam), **3**, 455 (1965).

(38) O. W. Steward, W. J. Uhl, and B. W. Sands, *ibid.*, **15**, 329 (1968).

(39) G. Tagliavini, P. Zanella, and M. Fiorani, *Coord. Chem. Rev.*, **1**, 249 (1966).

Moore and Ward[40] as a product of the reaction of 7,7-dibromonorcarane and methyllithium in the presence of cyclohexene.

From this discussion it will now be appreciated that all (or most) of the trimethyltin bromide produced could have derived from decomposition of $(Me_3Sn)_2CClBr$, while all (or most) of the trimethyltin chloride obtained could have resulted from thermolysis of VI. We have no way of telling which interpretation of the yield data is correct but we prefer the latter interpretation in view of the high selectivity for trimethyltin bromide elimination observed in the case of Me_3SnCCl_2Br. The bis(trimethyltin)monohalomethanes probably were formed in competing homolytic reactions (eq 9–11).



$$Me_3SnCX_2SnMe_3 \xrightarrow{170^\circ} Me_3Sn\cdot + Me_3SnCX_2\cdot \quad (9)$$

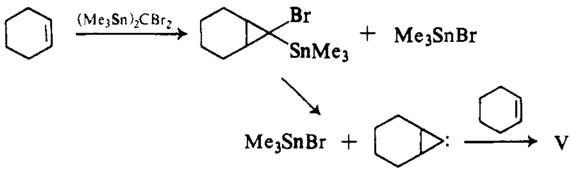
$$Me_3SnCX_2SnMe_3 \xrightarrow{170^\circ} Me_3Sn\dot{C}XSnMe_3 + X\cdot \quad (10)$$

(11)

It will be noted that dimethyltin dichloride and possibly dimethyltin dibromide were among the products of this reaction. It is possible that these derive from a substituent-exchange process analogous to that observed in the case of trimethyl(α,α-dichlorobenzyl)tin, but the other expected product from such a process, trimethylvinyltin, was not identified in the product mixture. This, however, does not speak against the simultaneous occurrence of the substituent exchange reaction with any degree of finality, since trimethylvinyltin could have been decomposed or otherwise consumed during the heating period.

The successful application of the sodium iodide procedure to dichlorocarbene generation from trimethyl(trichloromethyl)tin led us to explore the applicability of this method to carbene release from bis(trimethyltin)bromochloromethane. A reaction between this tin compound and sodium iodide in DME at 85° in the presence of cyclohexene appeared to proceed exclusively by way of iodide ion attack at carbon, giving sodium bromide and bis(trimethyltin)chloroiodomethane in 63% yield.

Bis(trimethyltin)dibromomethane. When bis(trimethyltin)dibromomethane was heated at 160–180° in the presence of cyclohexene in a sealed tube for 4 days, an 83.5% yield of trimethyltin bromide (based on the elimination of 2 mol of Me_3SnBr/mol of $(Me_3Sn)_2CBr_2$) was obtained. Among the several higher boiling products the only one present in greater than 1% yield was the spiropentane V (4.3%). Thus in this case it would seem that the process shown in eq 12 proceeded nearly to completion under the conditions of the experiment.



(12)

Conclusions

From the work discussed above, it is obvious that halomethyltin compounds (at least the ones studied at this time) are not particularly useful divalent carbon transfer agents. The trimethyl(trihalomethyl)tin compounds do transfer CX_2 to olefins in high yield, but the temperatures required to do so at a reasonable rate are rather high. Furthermore, these compounds suffer from an extreme sensitivity to moisture. The side reactions occasioned by the weak Lewis acidity of the organotin halides produced in these reactions also represent an undesired complication; for instance, they make trimethyl(α,α-dichlorobenzyl)tin essentially unusable as a transfer agent for phenylchlorocarbene. The high temperatures required for decomposition of the $Me_3SnCXBrSnMe_3$ (X = Cl, Br) compounds in the presence of olefins also are sufficiently high so as to almost completely destroy the Me_3SnCX–olefin adducts which are formed.[41] All in all, halomethylmercury compounds are far superior to halomethyltin compounds as halocarbene precursors.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Elemental analyses were performed by Dr. S. M. Nagy (MIT), the Galbraith Laboratories, Knoxville, Tenn. and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were recorded using a Perkin-Elmer 337 grating infrared spectrophotometer, nmr spectra using either a Varian A-60 or HA/HR60 high resolution spectrometer. Chemical shifts are recorded in δ units (parts per million) downfield from internal tetramethylsilane. Mass spectra were measured using either a Consolidated Electrodyanmics Co. 130 or a Hitachi Perkin-Elmer RMU6D mass spectrometer. Gas-liquid partition chromatography (glpc) was used for product separation and yield analysis. The gas chromatographs and the columns used were as follows: column A, 4 ft aluminum, 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb P (F & M 700); column B, 4 ft glass, 20% SE-30 on Chromosorb P, analytical (MIT, isothermal); column C, 8 ft glass, otherwise identical with column B; column D, 4 ft aluminium, LAC 728 on Chromosorb W (F & M 720); column E, 6 ft aluminum, Carbowax W on Chromosorb W (F & M 700); column F, 6 ft aluminum, Dow Corning Corp. DC-200 silicone oil on Chromosorb W (F & M 700); column G, 6 ft aluminum, General Electric Co. XE-60 nitrile silicone gum on Chromosorb W (F & M 700). The internal standard method of yield analysis was used.

The organotin compounds studied were prepared as described in previous papers of this series.[10,16]

Reaction of Trimethyl(bromodichloromethyl)tin with Cyclohexene. Into a dry, 10-ml flask with side arm and no-air stopper, equipped with reflux condenser and gas inlet tube and under 1 atm of prepurified nitrogen, was charged 0.226 g (0.65 mmol) of the tin compound and 3 ml of cyclohexene (distilled from calcium hydride). During the 92-hr reflux period (80°), aliquot samples were taken periodically and analyzed by glpc as a means of following the progress of the reaction. At the end of the heating period, glpc analysis (column B, 85°, benzotrichloride internal standard) showed the presence of 7,7-dichloronorcarane (42% yield), trimethyl(bromodichloromethyl)tin (8% recovery), trimethyltin bromide (yield not determined), trimethyltin chloride (trace), and 7-bromo-7-chloronorcarane (trace), all identified by comparison of their glpc retention times and the infrared spectra with those of authentic samples. No tetrachloroethylene was observed.

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[40] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

[41] One would expect a $PhHgCX_2SnMe_3$ compound to be a much better Me_3SnCX precursor, and we are working in this direction.

Reaction of Trimethyl(bromodichloromethyl)tin with Cyclooctene. Into a dry, 50-ml flask equipped with a magnetic stirring assembly and a reflux condenser was charged under an atmosphere of prepurified nitrogen 2.37 g (7.27 mmol) of the tin compound and 16 ml of cyclooctene (distilled from calcium hydride and passed through Woelm neutral activated alumina immediately before use). The mixture was heated at reflux (140°), with stirring, for 3 hr. At the end of this time, glpc analysis showed that none of the starting tin compound remained. The solution was trap-to-trap distilled at 0.03 mm; two fractions were collected: (a) pot temperature to 25°, 12.95 g; (b) pot temperature to 100°, 1.17 g. Fraction 2 was analyzed by glpc (column B, 160°, 1-iodonaphthalene internal standard) after filtration of a small amount of flocculent white solid. The presence of 9,9-dichlorobicyclo[6.1.0]nonane[18] (66%) and 9-bromo-9-chlorobicyclo[6.1.0]nonane (5%) was demonstrated; these products were identified by comparison of their glpc retention times and infrared spectra with those of authentic samples.

An authentic sample of 9-bromo-9-chlorobicyclo[6.1.0]nonane was prepared by reaction at 80° in benzene solution of 2 mmol of phenyl(dibromochloromethyl)mercury and 5.0 mmol of cyclooctene in 10 ml of benzene using our standard procedure.[3] The yield of phenylmercuric bromide was 94%, and 9-bromo-9-chlorobicyclo[6.1.0]nonane, $n^{25}\text{D}$ 1.5263 (mixed isomers) was obtained in 91% yield; no 9,9-dibromobicyclo[6.1.0]nonane was observed.

Anal. Calcd for $C_9H_{14}BrCl$: C, 45.50; H, 5.94; AgX expected from a 9.890-mg sample, 13.76 mg. Found: C, 45.58; H, 6.09; AgX, 13.80 mg.

Reaction of Trimethyl(trichloromethyl)tin with Cyclooctene. The same procedure was used in the reaction of 2.17 g (7.70 mmol) of this tin compound with cyclooctene (20 ml) for 3 hr at reflux. At the end of this time, the tin compound had been completely consumed and the reaction mixture was trap-to-trap distilled in two fractions at 0.03 mm: 18.64 g, pot temperature to 25°; 1.24 g, pot temperature to 100°. The second fraction was pure 9,9-dichlorobicyclo[6.1.0]nonane (83% yield), identified by comparison of its infrared spectrum and glpc retention time with those of an authentic sample. Analysis of the first fraction by glpc (column B, 160°, 1-iodonaphthalene internal standard) for additional product raised the yield to 94%.

Reaction of Trimethyl(trichloromethyl)tin with Vinyl Acetate. A mixture of 2.29 g (8.12 mmol) of the tin compound and 3.46 g (4.02 mmol) of vinyl acetate in 20 ml of freshly distilled chlorobenzene was heated for 24 hr at reflux. At the end of this time the solution had not changed in viscosity or color. The reaction mixture was trap-to-trap distilled at 0.1 mm (pot temperature to 55°) and the filtrate was analyzed by glpc (column A, 75–125°, *o*-dichlorobenzene internal standard). Trimethyltin chloride was identified and 2,2-dichlorocyclopropyl acetate was found to be present in 57.5% yield. The latter was identified by comparison of its glpc retention time and infrared spectrum with those of an authentic sample.[3]

Reaction of Trimethyl(trichloromethyl)tin with Sodium Iodide in the Presence of Cyclohexene. Into a dry, 100-ml, three-necked flask equipped with reflux condenser, dropping funnel, magnetic stirring assembly and gas inlet tube was charged under an atmosphere of prepurified nitrogen (1.76 g 6.25 mmol) of trimethyl(trichloromethyl)tin, 2.47 g (30 mmol) of cyclohexene and 40 ml of DME (doubly distilled from potassium immediately before use). The solution was heated to reflux and 1.65 g (11.0 mmol) of sodium iodide (dried at 100° (1 mm) for 100 hr) in 15 ml of DME was added dropwise over a 55-min period. A white solid began to form immediately. After a 4-hr reflux period, the mixture was cooled and filtered to remove 0.45 g of sodium chloride. The filtrate was trap-to-trap distilled in two fractions: 0.03 mm, pot temperature to 25°; 46.41 g, 0.0007 mm, pot heated with an infrared lamp, 2.17 g. The two products, collected by glpc, were shown by comparison of their infrared spectra with those of authentic samples to be trimethyltin iodide (shorter retention time) and 7,7-dichloronorcarane, the latter in 55% yield (by glpc analysis, column B, 95°, *n*-dodecane internal standard).

The Thermolysis of Trimethyl(dichloromethyl)tin in the Presence of Cyclooctene. In the usual manner, a mixture of 1.44 g (5.21 mmol) of trimethyl(dichloromethyl)tin, 20 ml of cyclooctene, and 1.0 g (6.67 mmol) of 7,7-dichloronorcarane (internal standard) was heated at reflux (140°) for 10 days. Aliquot samples were taken at various intermediate times and analyzed by glpc (column A, 90–140°). No change in the composition of the reaction mixture was apparent at any time and recovery of the starting tin compound was essentially quantitative (97% by glpc).

Preparation of an Authentic Sample of 9-Chlorobicyclo[6.1.0]-nonane. In order to have an authentic sample of 9-chlorobicyclo-[6.1.0]nonane, the product expected in a possible trimethyl(dichloromethyl)tin–cyclooctene reaction, this compound was prepared by the mercurial procedure.[6] Into a 50-ml flask equipped with condenser, magnetic stirring assembly, and gas inlet tube was charged under 1 atm of prepurified nitrogen 2.29 g (5.64 mmol) of phenyl-(bromochloromethyl)mercury[23] and 22 ml of cyclooctene. The resulting mixture was heated for 4 hr at reflux, cooled, and filtered to remove 1.91 g (96%) of phenylmercuric bromide. Trap-to-trap distillation at 10^{-5} mm gave a mixture of *syn*- (all cyclopropyl protons *cis*) and *anti*-9-chlorobicyclo[6.1.0]nonanes. The total yield of the two isomers by glpc (column A, 125–181°, 9,9-dichlorobicyclo[6.1.0]nonane internal standard) was 92%; the *anti:syn* ratio was 1:2.3. The structure of the isomers was assigned on the basis of their nmr spectra; in particular, the isomer in which the 7-proton is *anti* to the tetramethylene bridge (*syn* isomer) should be the less highly shielded.[42] Furthermore, it should be noted that the cyclopropyl proton coupling constant of 7.5 cps observed in the case of the presumed *syn* isomer is in the range of *cis*-proton coupling in cyclopropanes.[43]

Anal. Calcd for $C_9H_{15}Cl$: C, 68.12; H, 9.53. Found (mixed isomers): C, 68.49; H, 9.67. Found (*syn* isomer): C, 68.27; H, 9.57.

Spectral results for the *anti* isomer were: ir (CS_2) 3015 (w), 2990 (m), 2910 (vs), 2840 (s), 2670 (w), 1400 (w), 1352 (w), 1300 (w), 1274 (m), 1244 (m), 1212 (w), 1150 (w), 1075 (w), 1058 (w), 1025 (m), 982 (m), 966 (w), 935 (w), 899 (w), 868 (sh), 856 (m), 817 (m), 778 (w), 765 (m), 755 (m), 740 (w), and 705 (m) cm^{-1}; *nmr* (CS_2) δ 0.85–1.15 multiplet (~4 H), 0.50–2.20 multiplet (~8 H), and 1.90–2.40 multiplet (~3 H).

Spectral results for the *syn* isomer were: ir 3035 (m), 2975 (s), 2955 (sh), 2915 (vs), 2850 (vs), 2675 (w), 1395 (vw), 1370 (w), 1355 (w), 1276 (s), 1245 (sh), 1230 (m), 1215 (m), 1185 (w), 1147 (s), 1103 (w), 1028 (sh), 1017 (m), 984 (w), 923 (w), 855 (w), 840 (w), 790 (m), 770 (w), 755 (m), 742 (s), 728 (m), and 675 (s) cm^{-1}; nmr (CS_2) δ 0.50–2.00 multiplet (~12 H), 0.70–1.10 multiplet (~2 H), and 3.18 triplet ($J = 7.5$ cps) (1 H).

Reaction of Trimethyl(dichloromethyl)tin with Sodium Iodide in the Presence of Cyclohexene. A procedure similar to that followed in the analogous reaction of trimethyl(trichloromethyl)tin was used in the reaction of 2.50 g (10.1 mmol) of trimethyl(dichloromethyl)-tin and 1.65 g (11.0 mmol) of sodium iodide in a mixture of 3.79 g of cyclohexene and 10 ml of DME. The solution gradually turned yellow and a white powder precipitated during the 8-hr reflux period. The latter (0.72 g) was removed by filtration and the filtrate was trap-to-trap distilled in two fractions: (a) 39.88 g, at 0.03 mm (pot temperature to 25°); (b) 3.37 g, at 0.003 mm (pot temperature to 100°). Glpc analysis (column A, 90–196°, ethyl cinnamate internal standard) showed the presence of trimethyl-(chloroiodomethyl)tin (62%), trimethyl(diiodomethyl)tin (22%), and starting material (22%). Analytical samples of the products were isolated by glpc (column B, 100°). Both compounds appear to be slightly heat and/or air sensitive; loss of iodine appeared to occur at higher temperatures during gas chromatography or upon exposure to the atmosphere.

$Me_3SnCClIH$ gave the following spectral properties: ir (CS_2) 2980 (s), 2905 (s), 2760 (w), 2350 (w), 1720 (vw) 1700 (vw), 1380 (m), 1257 (w), 1198 (sh), 1191 (m), 1154 (m), 1068 (w), 1015 (m), 771 (vs), 718 (sh), 700 (s), 582 (s), and 530 (s) cm^{-1}; nmr (CS_2) δ 0.32 singlet ($J_{^{117}Sn-^1H} = 53$ cps; $J_{^{119}Sn-^1H} = 57$ cps) (9 H) and 5.25 singlet (J_{Sn-H} not discernible) (1 H).

Anal. Calcd for $C_4H_{10}SnClI$: C, 14.16; H, 2.97; total halide, 47.87. Found: C, 14.42; H, 3.06; total halide, 46.70.

Me_3SnCI_2H gave the following spectral properties: ir (film) 2975 (w), 2900 (w), 1480 (w), 1196 (sh), 1188 (w), 1061 (m), 1010 (w), 770 (s), 736 (sh), 711 (w), 596 (m), 542 (m), and 530 (m) cm^{-1}; nmr (CS_2) δ 0.45 singlet ($J_{^{119}Sn-^1H} = 54.5$; $J_{^{117}Sn-^1H} = 52.5$) (9 H) and 4.35 singlet ($J_{Sn-^1H} = 22$ cps) (1 H).

Anal. Calcd for $C_4H_{10}SnI_2$: C, 11.16; H, 2.34; I, 58.94. Found: C, 11.51; H, 2.58; I, 58.16.

Reaction of Trimethyl(α,α-dichlorobenzyl)tin with Tetramethylethylene. A dry, 8-in., thick-walled Pyrex combustion tube (1 in. o.d. with $^3/_8$ in. o.d. neck) was charged with 2.90 g (8.95 mmol)

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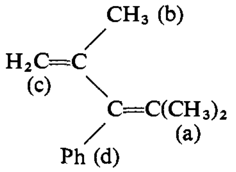
(42) D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, **90**, 1080 (1968), and references cited therein.

(43) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

of the tin compound and 10 ml of tetramethylethylene (freshly distilled from lithium aluminum hydride), under 1 atm of prepurified nitrogen, cooled to −78° and sealed at 640 mm. The tube then was heated (140–160°) for 9 hr while being agitated using a mechanical shaker. After the tube had been cooled to −78°, it was opened and the contents were filtered, under nitrogen, to remove 0.65 g of white solid, mp 105–106°. The latter was identified as dimethyltin dichloride (lit.[44] mp 107.5–108°) by mixture melting point with an authentic sample. The filtrate was saturated with gaseous ammonia, causing a voluminous, white precipitate to appear. This solid, 1.25 g, did not melt below 280°, but sublimed slowly above 150°. The filtrate from this treatment was concentrated at reduced pressure and the liquid residue was trap-to-trap distilled at 0.03 mm (pot temperature to 110°). Glpc analysis (column B, 90–183°, *n*-decane internal standard) indicated the presence of 2,4-dimethyl-3-phenylpenta-1,3-diene in 35% yield. A second, higher boiling component or, more likely, mixture of components (5–10%), was not identified. Analytical samples of the diene were obtained by preparative glpc: ir (film) 3065 (m), 3045 (sh), 3010 (w), 2975 (m), 2955 (m), 2915 (sh), 2900 (m), 2845 (m), 2710 (vw), 1935 (vw), 1870 (vw), 1790 (vw), 1620 (m), 1590 (w), 1560 (vw), 1490 (m), 1440 (m), 1370 (m), 1202 (vw), 1190 (vw), 1179 (w), 1089 (m), 1069 (m), 1030 (w), 1000 (w), 983 (w), 960 (w), 912 (sh), 893 (s), 865 (w), 800 (m), 785 (w), 760 (s), 720 (m), and 698 (vs) cm^{-1}; nmr (TMS) (a) δ 1.58 singlet (6 H); (b) 1.83 singlet (3 H); (c) 4.8–5.1 multiplet (2 H); (d) 7.12 singlet (5 H).



Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C 90.97; H, 9.19.

Thermal Decomposition of Trimethyl(α,α-dichlorobenzyl)tin in the Presence of Cyclohexene. The tin compound (3.11 g, 9.62 mmol) and 8.66 g (105 mmol) of cyclohexene were sealed at −196° (600 mm) in a 12-in. combustion tube. The tube was placed in a steel casing and heated between 140 and 160° for 13.5 hr, during which time the contents changed from colorless to red brown. Upon cooling, a grey solid precipitated. The tube was opened at −196° and the contents subsequently were filtered. Addition of pentane to the filtrate caused more solid to precipitate. The combined solids, 0.83 g, were identified as dimethyltin dichloride (26% yield), mp 105–107°. The filtrate was trap-to-trap distilled from room temperature to 130° (0.0015–0.00013 mm) to give 5.29 g of clear, pale yellow distillate and 0.18 g of tarry residue. Glpc analysis (column B, 55°, toluene internal standard) showed the presence of cyclohexene, pentane, styrene (41% yield), trimethyltin chloride (11% yield), and small amounts of dimethyltin dichloride and α,α-dichlorotoluene. Approximately 14 other minor components were apparent upon glpc analysis using column B (65–200°), but only one could be isolated in purity sufficient for even partial analysis. Its infrared and nmr spectra, not dissimilar nor exactly identical with those of 7-chloro-7-phenylnorcarane, are: ir (CS$_2$) 3080 (m), 3055 (s), 3020 (s), 3000 (s), 2930 (vs), 2910 (sh), 2865 (sh), 2850 (s), 2650 (w), 1950 (sh), 1935 (w), 1875 (w), 1795 (w), 1598 (m), 1395 (vw), 1375 (vw), 1350 (m), 1335 (m), 1305 (vw), 1270 (w), 1257 (m), 1212 (m), 1195 (vw), 1175 (m), 1155 (m), 1130 (w), 1091 (s), 1072 (s), 1020 (s), 984 (m), 971 (m), 905 (w), 885 (vw), 844 (s), 828 (s), 805 (vw), 775 (s), 752 (vw), 734 (vs), 705 (vs), 650 (vw), and 631 (s) cm^{-1}; nmr (CS$_2$) δ 1.0–2.8 broad multiplet (40 units), 6.2–6.5 (?) multiplet (4 units), and 6.7–7.8 broad multiplet (26 units).

The styrene produced was identified conclusively by comparison of its infrared, nmr and mass spectra with those of an authentic sample.

Thermal Decomposition of Bis(trimethyltin)bromochloromethane in the Presence of Cyclohexene. A dry, 35-ml, thick-walled Pyrex combustion tube was charged with 3.39 g (7.46 mmol) of the tin compound and 8.88 g (108 mmol) of cyclohexene under an atmosphere of dry, oxygen-free argon. The tube was cooled to −196°, sealed at 650 mm pressure and then placed in a 1.4-l. autoclave bomb. Benzene (240 ml) was placed around the tube to equalize the internal pressure on the glass tube. The apparatus was heated at 170 ± 10° for 96 hr. At the end of this period, the yellow contents of the tube were transferred to a distilling flask (the tube being washed out with cyclohexene) and trap-to-trap distilled in two fractions at 0.03 mm: (a) 9.21 g (pot temperature to 25°); (b) 1.26 g (pot temperature to 120°); (c) 0.33 g, a brown, very viscous residue. Fraction a consisted of cyclohexene, trimethyltin bromide, and trimethyltin chloride. Fraction b was very complex and was collected in six major peaks by glpc (column A, 100–200°) and these are listed below.

(a) Peak 1 consisted of a mixture of trimethyltin chloride and bromide. These were separated using column F at 75° and were identified by means of their glpc retention times and infrared spectra.

(b) Peak 2 was mainly dimethyltin dichloride containing a small amount of an impurity with slightly longer retention time, thought to be dimethyltin dibromide.

(c) Peak 3 represented a minor component, an unstable and unidentifiable liquid.

(d) Peak 4 could be further separated using column E into two major and several minor components. The first was identified as **bis(trimethyltin)chloromethane**: ir (CS$_2$) 2980 (s), 2910 (s), 2360–2280 (w), 1690 (w), 1188 (m), 1130 (w), 940 (m), 765 (vs), 712 (s), 665 (w), 625 (s), and 525 (vs) cm^{-1}; nmr (CS$_2$) δ 0.2 singlet ($J_{^{117}Sn-^1H}$ = 51.5 cps; $J_{^{119}Sn-^1H}$ = 54 cps) (∼20 H) and 3.07 singlet ($J_{^{117}Sn-^1H}$ = 33 cps; $J_{^{119}Sn-^1H}$ = 34 cps) (1 H).

Anal. Calcd for $C_7H_{19}Sn_2Cl$: C, 22.35; H, 5.09. Found: C, 22.52; H, 5.14.

The mass spectrum also was in agreement with this structure and is given in the Ph.D. thesis (MIT, 1968) of F. M. A.

The second major component of peak 4 was an unsaturated hydrocarbon which we believe to be **bis(3-cyclohexenyl)methane**: ir (CS$_2$) 3520 (w), 3010 (s), 2925 (vs), 2850 (s), 2825 (s), 2645 (w), 1690 (m), 1650 (m), 1420 (w), 1390 (w), 1340 (m), 1320 (sh), 1310 (m), 1295 (sh), 1255 (vw), 1188 (vw), 1172 (vw), 1165 (vw), 1140 (m), 1130 (m), 1100 (vw), 1092 (vw), 1053 (w), 1020 (w), 980 (w), 948 (w), 919 (w), 898 (m), 871 (m), 865 (sh), 780 (w), 765 (w), 741 (sh), 730 (sh), 721 (s), 715 (sh), 701 (m), 695 (m), and 635 (m) cm^{-1}; nmr (CS$_2$) δ 1.0–2.4 broad multiplet (16 H) and 5.5–5.75 narrow multiplet (4 H).

Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.77; H, 11.13.

Its mass spectrum also is recorded in the thesis of F. M. A.

(e) Peak 5 could be separated into five components on column E. The first was bis(trimethyltin)chloromethane, the second **bis(trimethyltin)bromomethane**: ir (in CS$_2$) 2980 (s), 2910 (s), 2355 (w), 1715 (w), 1695 (w), 1390 (m), 1195 (sh), 1187 (s), 1078 (m), 942 (s), 878 (w), 770 (vs), 710 (vs), and 622 (vs) cm^{-1}; nmr (in CS$_2$) singlets at δ 0.20 ($J_{^{117}Sn-^1H}$ = 51.5 cps; $J_{^{119}Sn-^1H}$ = 53.5 cps; 18 H) and 2.60 ppm (J_{Sn-H} = 35 cps; 1 H).

Anal. Calcd for $C_7H_{19}BrSn_2$: C, 19.99; H, 4.55. Found: C, 20.50; H, 4.77.

Relative side-to-center band peak heights indicated that the 2.60-ppm singlet was being split by two tin nucleii. The mass spectrum (Ph.D. thesis of F. M. A.) was in agreement with the structure indicated.

The third peak of separated peak 5 appeared as a single component on columns A, D, and E. However, differential mass spectrometry, a technique by which one takes a mass spectrum, pumps out the inlet system, and reintroduces the sample, showed the presence of two components of very slightly different volatility. The mass spectra obtained were highly indicative of a mixture of 7,7′-spirobi(bicyclo[4.1.0]heptane) (V) and 7-chloro-7-trimethyltinnorcarane. Separation finally was achieved using column G, and the two components could be isolated and identified. The component with shorter retention time was shown to be the spiropentane derivative V by comparison of its infrared spectrum with that of an authentic sample[40] (obtained from Professor W. R. Moore of this department). The infrared and nmr spectra of the second component were in agreement with those to be expected for 7-chloro-7-trimethyltinnorcarane. Although this product could not be isolated in a quantity sufficient for a combustion analysis, its mass spectrum at 70 V indicated that this was the correct structure, since the correct molecular ion with the appropriate ratios for the tin and chlorine isotopic composition was observed (*cf.* Table I): ir (CS$_2$) 2975 (s), 2920 (vs), 2845 (s), 2640 (vw), 2340 (vw), 1720 (vs), 1698 (vw), 1378 (m), 1350 (m),

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[44] R. A. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

Table I. Mass Spectrum of 7-Chloro-7-trimethyltinnorcarane

Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass no.	%	Mass calcd
27	12	51	5.4	68	1.3	94	56	120	4.6	146	2.0	157	3.8	169	5.9	187	8.7	290	0.29	0.22
28	3.6	52	3.9	75	1.3	95	6.7	121	2.8	147	2.3	159	2.0	170	1.7	189	4.3	291	0.17	0.12
29	5.7	53	8.7	77	16	105	2.6	131	6.2	148	3.2	161	14	176	1.3	191	1.2	292	0.61	0.45
38	1.3	54	3.5	78	4.2	107	1.7	132	4.1	149	2.6	162	7.5	177	1.2	198	1.2	293	0.29	0.17
39	21	55	5.2	79	100[a]	108	1.4	133	9.7	150	4.1	163	22	181	8.4	201	1.0	294	0.62	0.62[a]
40	4.5	56	1.1	80	8.6	109	2.0	134	4.3	151	4.3	164	8.4	182	4.9	239	1.9	295	0.16	0.04
41	18	63	2.3	81	3.3	116	2.0	135	12	152	2.0	165	29	183	17	240	1.0	296	0.25	0.24
42	2.5	65	9.4	91	12	117	2.2	137	1.9	153	6.1	166	1.6	184	6.7	241	3.5	298	0.16	0.16
43	1.2	66	11	92	2.8	118	3.5	139	2.3	154	2.9	167	4.9	185	24	242	1.9			
50	1.6	67	7.8	93	23	119	3.0	145	1.7	155	8.4	168	1.6	186	2.3	243	5.1			

[a] Set arbitrarily.

1341 (m), 1331 (m), 1270 (w), 1258 (w), 1224 (vw), 1188 (s), 1162 (w), 1130 (w), 1082 (w), 1070 (w), 1032 (w), 1028 (sh), 980 (m), 960 (m), 907 (m), 830 (sh), 780 (vs), 760 (vs), 720 (sh), 705 (s), 648 (m), and 524 (vs) cm^{-1}; nmr (CS_2) δ 0.13 singlet ($J_{^{117}Sn-^{1}H}$ = 51.5 cps; $J_{^{119}Sn-^{1}H}$ = 54 cps) (9 H) and 0.75–2.15 broad multiplet (~10 H).

The nmr spectrum and the infrared spectrum in the C–H stretching region at 3000–2800 cm^{-1} of 7-chloro-7-trimethyltinnorcarane were very similar to those of its silicon analog, 7-chloro-7-trimethylsilylnorcarane.[8]

(f) Peak 6 was shown to be starting bis(trimethyltin)bromochloromethane by comparison of its infrared spectrum with that of an authentic sample.

The yields of these various components are listed below. The yields of the higher boiling materials are only approximate due to the separation problems experienced. Me_3SnCl (45%), Me_3SnBr (64%), Me_2SnCl_2 (10%), $(Me_3Sn)_2CClH$ (4%), $(Me_3Sn)_2CBrH$ (3%), olefin IV (3%), spiropentane V (6.3%), 7-chloro-7-trimethyltinnorcarane (2%), and recovered $(Me_3Sn)_2CClBr$ (5%).

Thermal Decomposition of Bis(trimethyltin)dibromomethane in the Presence of Cyclohexene. This reaction, between 3.78 g (7.56 mmol) of the tin compound and 7.91 g (96.5 mmol) of cyclohexene, was carried out at 170 ± 10° for 96 hr in the same manner as described in the previous experiment. At the end of the reaction period, the yellow-brown contents of the bomb tube were trap-to-trap distilled in two fractions at 0.03 mm: (a) 8.37 g (pot temperature to 25°), cyclohexene and a minor amount of trimethyltin bromide (by glpc); (b) 1.70 g (pot temperature to 120°), which contained several higher boiling materials. These were collected by glpc (column A, 100–220°) and identified as trimethyltin bromide (84%), a trace of dimethyltin dibromide, the starting tin compound (1.3%), and the spiropentane V (4.3%). All products were identified by comparison of their glpc retention times and infrared spectra with those of authentic samples.

Attempts to isolate material from the 0.30-g distillation residue by low-temperature recrystallization of the oil from pentane gave small amounts of a brown powder, mp 190–210°, with decomposition.

Acknowledgments. The authors are grateful to the 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 Health Fellowship 5-F1-GM-23,742 (to F. M. A.). Thanks are due to Professor W. R. Moore for the infrared spectrum of spiropentane (V) and for valuable discussions.