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HALOMETHYL—METAL COMPOUNDS

LXXVI.* α-BROMOCYCLOPROPYL DERIVATIVES OF TIN AND LEAD AS CYCLOPROPYLIDENE PRECURSORS

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Summary

The thermolysis of 1-bromo-1-trimethyltin-*cis*-2,3-dimethylcyclopropane (both isomers), *anti*-6-bromo-*syn*-6-trimethyltinbicyclo[3.1.0]hexane, 7-bromo-7-trimethyltinnorcarane, and also the 7-triphenyltin-, 7- trimethyllead- and 7-triphenyllead- derivatives (both isomers), 1-bromo-1-trimethyltinspiro[2.5]-octane and 9-bromo-9-trimethyltinbicyclo[6.1.0]nonane (both isomers) has been studied. Under the conditions used, the *syn*-Me_3Sn isomers decomposed, while the *anti*-Me_3Sn isomers were quite stable. Only the norcarane system showed useful intermolecular divalent carbon transfer reactions.

Introduction

During the course of a previous study devoted to an investigation of the synthesis of α-haloalkyltin compounds [2] and their utilization as divalent carbon transfer agents [3] the compounds $(Me_3Sn)_2CClBr$ and $(Me_3Sn)_2CBr_2$ were prepared [2b,c] and investigated [3] as potential sources of trimethyltinhalocarbenes, Me_3SnCX (X = Cl, Br). It was found that when either of these compounds was heated with cyclohexene at 160-180°, one of the products formed was the spiropentane derivative I. The formation of I was believed to have occurred as shown in Scheme 1.

The yields of I were very low, and in the case of $(Me_3Sn)_2CClBr$ two other products were isolated in low yield: bis(3-cyclohexenyl)methane and

* Part LXXV: ref. 1.

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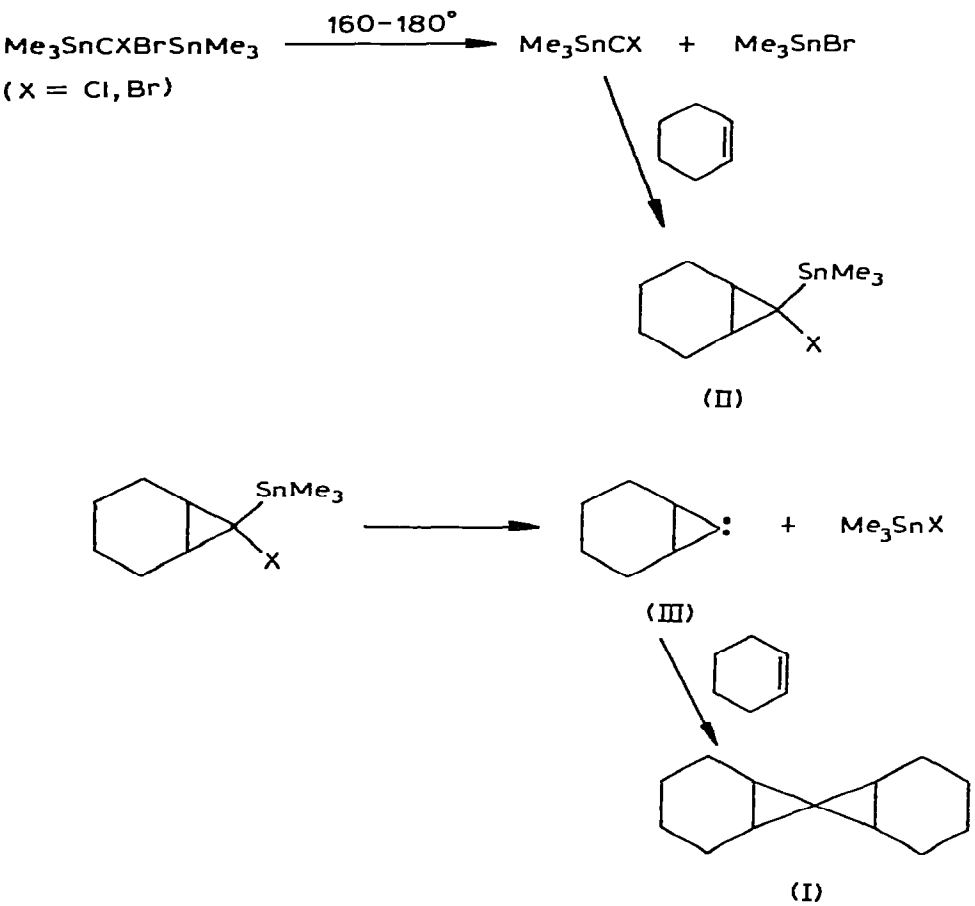
SCHEME 1

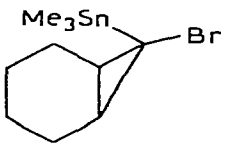


II (X = Cl). The fact that the 7-halo-7-trimethyltinnorcaranes underwent thermolysis with apparent release of the carbene III was of interest. However, the reaction conditions appeared to be too harsh to permit any synthetic application of this chemistry.

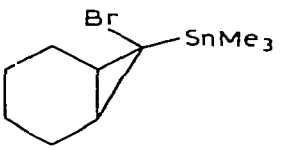
In order to examine the applicability of α-halocyclopropyl compounds of heavy metals as cyclopropylidene sources, we prepared a number of such derivatives of tin, lead and mercury [4,5]. In this paper we report concerning their utility as divalent carbon transfer reagents. Prior to our work in this area, certain aspects of the chemistry of cyclopropylidenes had been investigated intensively [6] and three types of reactions of this class of carbenes had clearly emerged. The first of these is the addition to an olefin to form a spiropentane derivative [7-11], the second, the intramolecular insertion into a C—H bond to form a polycyclic derivative [8,10,12] and the third, cyclopropane ring opening to form an allene [9,10,13,17]. Quite a few of the routes to these cyclopropylidene intermediates involve the formation of unstable α-halocyclopropyl-lithium, -magnesium or -sodium intermediates by reactions of *gem*-dihalocyclopropanes with organolithium reagents, with Grignard reagents, with metallic magnesium, or with sodium on alumina [6]. Stereochemical

studies had not been carried out, indeed, were not possible with these intermediates under these conditions. Thus, it was not known whether the generation of 7-norcaranylidene was faster from *syn*-7-bromo-*anti*-7-lithionorcarane or from the *anti*-7-bromo-*syn*-7-lithio isomer; in fact, it was not known if both isomers decomposed in the same fashion to give 7-norcaranylidene.

For some of the α-bromocyclopropyltin compounds which we had prepared we had either a mixture of isomers of known stereochemistry available, e.g., a 4/1 mixture of IVa and IVb, or, in some cases, one or both of the pure isomer. Thus it was possible to examine differences in type, as well as in



(IVa)



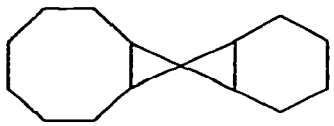
(IVb)

rate, of reactions of isomeric α-bromocyclopropyl compounds of heavy metals.

Results and discussion

In our initial experiments we examined the relative reaction rates and the effectiveness of divalent carbon transfer for reactions of several 7-bromo-7-norcaranyl derivatives of tin and lead, the 7-Me_3Sn, -Ph_3Sn, -Me_3Pb and -Ph_3Pb compounds. These had been prepared by the low temperature reaction of 7-bromo-7-lithionorcarane with the respective organometallic halide [4]. Characterization included, in the case of the trimethylmetal derivatives, a determination of the configuration of each of the isomers by cleavage of the cyclopropyl-to-metal bond with anhydrous hydrogen chloride in chloroform. The reaction of hydrogen bromide with substituted cyclopropyltrimethyltin compounds had been shown to proceed with retention of configuration at carbon [18], so the stereochemistry of the bromocyclopropane produced in our cleavage reaction was taken to indicate the stereochemistry of our starting α-bromocyclopropylmetal compound. The configurations of the respective isomeric bromocyclopropanes were known from earlier studies in these laboratories [19].

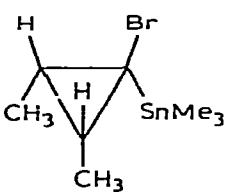
The α-bromocyclopropyl-tin and -lead compounds were heated under nitrogen in cyclooctene solution at reflux until complete decomposition had occurred. The progress of such decompositions of 7-bromo-7-norcaranyltrimethyl-tin and -lead could be followed by NMR spectroscopy, while the extent of similar reactions of 7-bromo-7-norcaranyltriphenyl-tin and -lead was estimated by noting the amount of solid triphenylmetal bromide which precipitated when the reaction mixture was cooled quickly. The divalent carbon transfer to cyclooctene gave spiro(bicyclo[6.1.0]nonane-9,7'-bicyclo[4.1.0]-heptane) (V) which was isolated; lower boiling products of intramolecular norcaranylidene reactions [7,8] were not. The lead compounds were much more labile than the tin compounds. Thus 7-bromo-7-triphenyltinnorcarane was completely con-



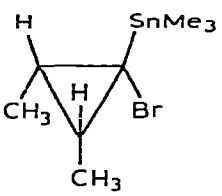
(V)

sumed after 7 days in refluxing cyclooctene, giving V in 22% yield, but a 13 h reflux period sufficed in the case of the corresponding lead compound and V was obtained in 61% yield. For 7-bromo-7-trimethyltinnorcarane the time required for complete consumption under these conditions was 18 h (46% yield of V), but 7-bromo-7-trimethylleadnorcarane required only 2 h (29% V). Although the lead derivatives appeared to be the more reactive, the tin compounds are much easier to prepare, so all further work was done using α-bromocyclopropyltin compounds.

The tin compounds which we studied included IVa and IVb, as well VIa/VIb, VII, VIII and IXa/IXb. The relative stabilities of IV, VII, VIII and IX were assessed by heating either the isomerically pure compounds or the mixed isomers at reflux in cyclohexene solution until the compound or at least one of its isomers had decomposed completely. The progress of the reactions was monitored by measuring the relative peak heights of the methyltin proton NMR resonances of the starting material and of the trimethyltin bromide formed. The results of these experiments are shown in Figs. 1-4. We



(VIa)



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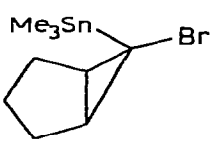
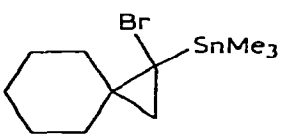


(VII)



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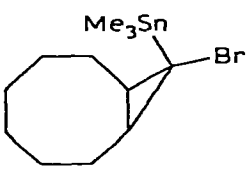
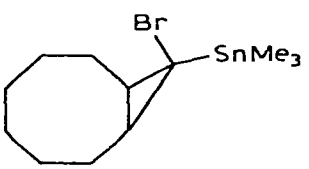


(IXa)



(IXb)

note that in all cases the isomer with the trimethyltin group in the more hindered *syn* position decomposed faster, while the absolute reaction rates varied considerably with the structure of the starting tin compound. The decompositions appeared to be first order with respect to the compound or isomer involved. Another more subtle feature became apparent after the concentration of the more hindered isomer had decreased below the concentration of the other isomer in the case of IVa/IVb and IXa/IXb: after this point it becomes obvious that there is no interconversion of isomers, i.e., *if* the decomposition involves carbene extrusion, then the reverse reaction of carbene in-

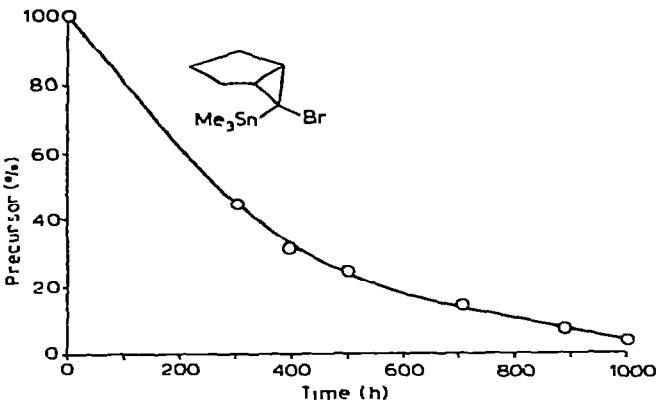


Fig. 1. Decomposition of *anti*-6-bromo-*syn*-6-trimethyltinbicyclo[3.1.0]hexane in cyclohexene.

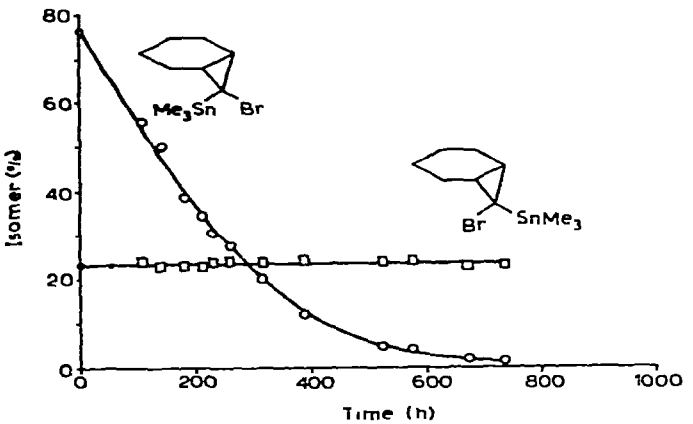


Fig. 2. Decomposition of 7-bromo-7-trimethyltinnorcarane in cyclohexene.

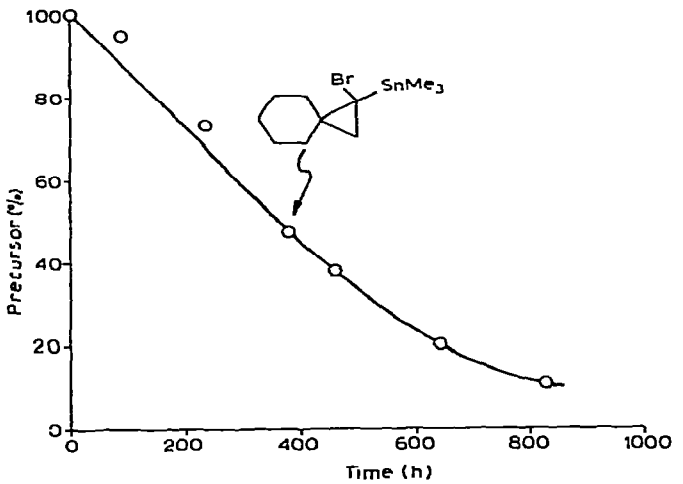


Fig. 3. Decomposition of 1-bromo-1-trimethyltinspiro[2.5]octane in cyclohexene.

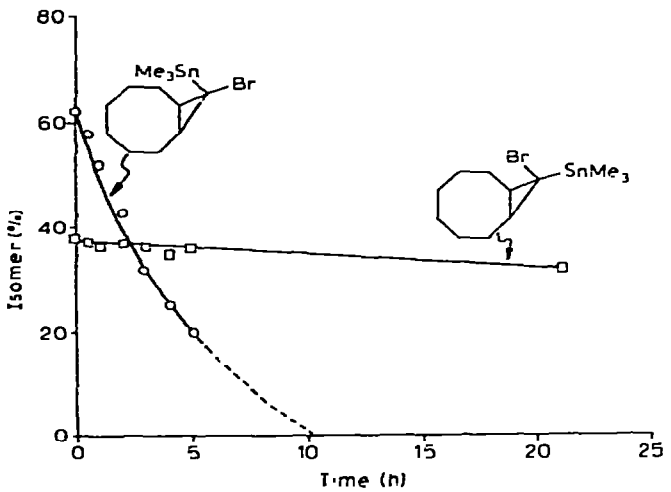
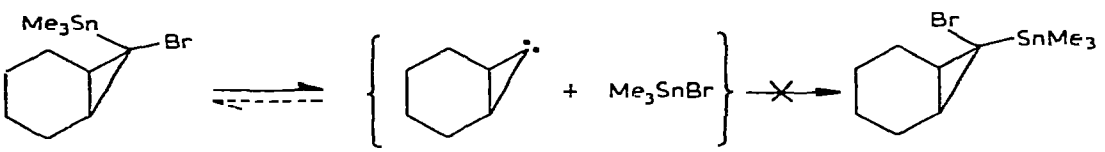


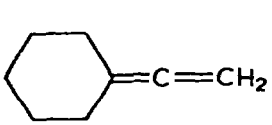
Fig. 4. Decomposition of 9-bromo-9-trimethyltinbicyclo[6.1.0]nonane in refluxing chlorobenzene.

sertion into the Sn—Br bond of trimethyltin bromide either is stereospecific or it does not occur at all:

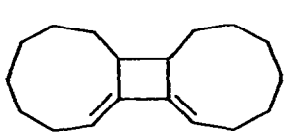


We shall return to this point later in the discussion.

In all reactions a search was made for carbene-derived products. Only in the reaction of IVa/IVb was a cyclohexene adduct, I, obtained; the yield of this product was 33%. No attempt was made to detect intramolecular C—H insertion products of norcaranylidene. The decomposition of VII in cyclohexene gave a very low yield of material which had the same GLC retention time as the expected spiropentane derivative, spiro(bicyclo[4.1.0]heptane-7,6'-bicyclo[3.1.0]hexane). However, this system was not investigated further because the preparation of the starting tin compound was rather difficult as a result of the poor stability of the required organolithium reagent [4]. The decomposition of the other tin compounds in the presence of cyclohexene resulted in formation of allenes. 1-Bromo-1-trimethyltinspiro[2.5]octane gave 1,1-cyclopentamethylenepropadiene, X, in 70% yield. When IXa was decomposed in chlorobenzene solution in the presence of cyclohexene the only products isolated were 1,2-cyclononadiene (16%) and some material (46%) which probably was the dimer of this cyclic allene, XI [20,21]. Finally, decomposi-



(X)



(XI)

tion of 1-bromo-1-trimethyltin-*cis*-2,3-dimethylcyclopropane, VIa/VIb, in the presence of cyclohexene gave only 1,3-dimethylallene (52%) and no trace of any olefin addition product. In this case also it was the *syn*-Me_3Sn isomer VIa which was consumed; VIb decomposed only to a minor extent.

The trend in all these reactions is to form an allene when it would not be severely strained; this intramolecular rearrangement of the intermediate carbene was very much faster than the intermolecular reaction with an olefin in the cases of VI, VIII and IX. In the case of IV, the allene is very strained and so the rearrangement occurs more slowly than does the reaction of the carbene with cyclohexene. These trends are substantially what one observes for the reactions of *gem*-dihalocyclopropanes with alkyllithiums in the presence of olefins [7-17].

The fact that one isomer in each of the isomer mixtures IVa/IVb, VIa/VIb and IXa/IXb is so much more stable than the other can be turned to good advantage and used to prepare isomerically pure compounds in which the trimethyltin substituent is in the less hindered *anti* position. Thus, after a mixture of VIa and VIb had been heated in cyclohexene at reflux for 84 h, the mixture could be distilled to give pure VIb. Similarly, pure IXb was obtained after a IXa/IXb mixture had been heated for 8 h at 135° in chlorobenzene solution. A less destructive isomer separation is possible in both of these cases. In each system the isomer in which the trimethyltin group is in the more hindered *syn* position (VIa, IXa) is a solid which may be separated from the isomer mixture by crystallization from methanol. The remaining material, rich in the *anti*-Me_3Sn isomer (VIb or IXb) then can be heated until the remaining VIa or IXa is destroyed. The availability of both geometric isomers as pure compounds in these systems, and very likely in others, may be very useful for mechanistic studies.

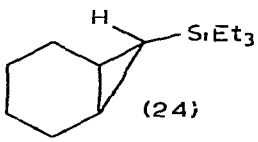
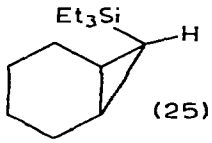
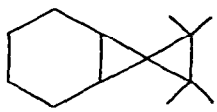
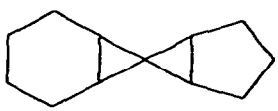
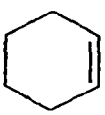
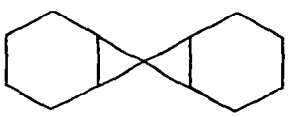
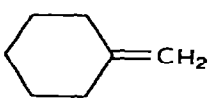
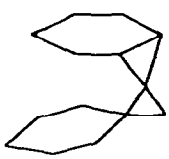
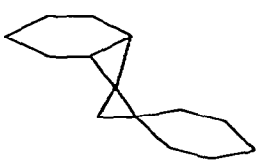
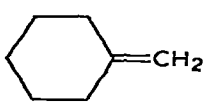
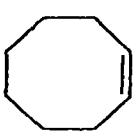
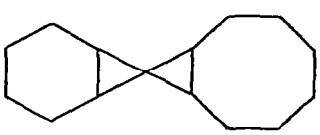
Further work was devoted to the divalent carbon transfer chemistry of 7-bromo-7-trimethyltinnorcarane. The results are summarized in Table 1. Several comments are appropriate. The product yields in general are not high. Since in most experiments the *syn/anti*-Me_3Sn isomer ratio of the 7-bromo-7-trimethyltinnorcarane used was 3/4, it is obvious that a large part of the 7-norcaranylidene is consumed in reactions other than olefin addition. The formation of a spiropentane derivative in the reaction with tetramethylethylene is noteworthy; the 7,7-dibromonorcarane/methyllithium reaction carried out in the presence of this olefin failed to give this adduct [7]. The reactions with methylenecyclohexane and with triethylsilane resulted in formation of a pair of separable isomers in each case. That the product isomer ratio was close to unity in both reactions is surprising in view of the asymmetric reaction site of the 7-norcaranylidene. In a number of these reactions, another product, a hydrocarbon which may be the formal dimer of 1,2-cycloheptadiene, was obtained as well in yields of 5-12%. Finally, as might be expected on the basis of the result shown in Fig. 2, the use of an isomer mixture less rich in the *syn*-Me_3Sn isomer results in rather low yields of intermolecular product.*

The availability of both 7-bromo-7-trimethyltinnorcarane isomers as

* The 1/1.3 *syn/anti*-Me_3Sn isomer mixture used was obtained in 71% yield by brominolysis of 7,7-bis(trimethyltin)norcarane [5] in carbon tetrachloride at 0°.

TABLE 1

DIVALENT CARBON TRANSFER REACTIONS OF 7-BROMO-7-TRIMETHYLTINNORCARANE

Carbenophile	*syn/anti*-Me_3Sn isomer ratio	Products (% yield)	
Et_3SiH	4.0	 (24)	 (25)
Et_3SiH	0.76	(8)	(7)
$Me_2C{=}CMe_2$	2.9	 (25)	
	2.9	 (26)	
	4.0	 (33)	
	4.0	 (19)	 (18)
	0.76	(10)	(9)
	2.9	 (46)	

pure compounds [4,5] allowed the examination of the divalent carbon transfer reactivity of each individually during the later stages of this work. The decomposition of pure IVa in refluxing cyclooctene during 6 h gave 76% yield. In contrast, a similar reaction of the other isomer, IVb, after 23 h gave V in only 40% yield. Obviously, IVb does decompose at this higher temperature

(in contrast to the about 80° reaction temperature in Fig. 2), but much more slowly than IVa.

The mechanism of a divalent carbon transfer reaction from an organometallic precursor is never obvious and qualitative observations can be misleading. We do not have enough experimental basis for reasonable speculation in the present instance. A carbene mechanism may be operative in the decomposition of IV and VI-IX but there is the disturbing feature that the less reactive isomer with the trimethyltin group in the *anti* position is not formed in a back-reaction of the carbene with trimethyltin bromide. Either the carbene extrusion is not reversible or the back-reaction is completely stereospecific, giving only the *syn*-Me_3Sn isomer. Neither alternative is intuitively pleasing. A further possibility is that a noncarbene process is operative, perhaps a direct transfer such as has been found for the ICH_2ZnI/olefin reaction [22]. An objection to this is that one would not expect to obtain a ca. 1/1 ratio of hindered to unhindered product isomer ratio in reactions of 7-norcaranylidene with methylenecyclohexane and triethylsilane in view of the known [22] steric demands of the transition state of such bimolecular transfer processes. At the present writing the question of mechanism clearly is not resolved and further experimental attention to this problem is required. Such studies, however, are beyond the scope of our present interests.

Experimental

General comments

All reactions involving organometallic compounds were carried out under an atmosphere of pre-purified nitrogen. The apparatus generally was assembled and then flame-dried with a stream of dry nitrogen passing through it. Gas-liquid chromatography (GLC) was used both for the isolation of samples and for yield determinations. The commercial instruments used included Hewlett—Packard F&M Model 700, 720, 5754 and 776 gas chromatographs. An MIT isothermal unit also was used for preparative isolations. Yields were determined using the internal standard method.

Infrared spectra were recorded using a Perkin—Elmer 257 or 457A spectrophotometer. Samples of liquids were taken as a film between sodium chloride discs. Proton NMR spectra were recorded on a Varian Associates T60 spectrometer. Chemical shifts are given in δ units, ppm downfield from TMS. Mass spectra were obtained with a Hitachi—Perkin—Elmer model RMU-6D instrument operating at 70 eV.

The preparation of the starting materials used in these studies is described in ref. 4 and 5.

Initial experiments with 7-norcaranylidene precursors

A flame-dried 100 ml three-necked flask equipped with a magnetic stirring unit, a reflux condenser and a nitrogen inlet tube was charged with 5.54 g (9.1 mmol) of 7-bromo-7-triphenylleadnorcarane and 20 ml of cyclooctene which had been freshly distilled from sodium prior to use. The mixture was stirred at reflux for 13 h and then was allowed to cool to room temperature. A voluminous precipitate formed while the mixture cooled and this was fil-

tered to give 3.1 g of white needles, m.p. 168-170°. The filtrate was trap-to-trap distilled (80°/0.02 Torr). GLC analysis (10% UC W98, 190°) showed only two high boiling components to be present, in about 20/1 ratio. The major product was isolated and identified as V, n_D^{25} 1.5111. (Found: C, 88.00; H, 11.71. $C_{15}H_{24}$ calcd.: C, 88.16; H, 11.84%). Its NMR spectrum (in CCl_4) showed a multiplet from δ 2.2 to 0.50 ppm with maxima at 0.97 and 0.66 ppm. The yield of this product as determined by GLC was 61%. The total yield of solid residue was 4.2 g (87%), m.p. 168-170°. The m.p. of a mixture with authentic triphenyllead bromide was not depressed.

A similar reaction of 4.8 mmol of 7-bromo-7-triphenyltinnorcarane with 50 ml of cyclooctene (7 days at reflux) gave V in 22% yield and triphenyltin bromide. The reaction of 7-bromo-7-trimethylleadnorcarane (*syn/anti*-Me_3Pb isomer ratio = 2.5) (14.5 mmol) in 20 ml of cyclooctene at reflux was monitored by NMR. Within 2 h the CH_3-Pb resonances of the starting material had disappeared and two new ones at δ 1.6 and 0.7 ppm had developed. Trap-to-trap distillation and GLC analysis of the distillate showed that V was present in 29% yield. The reaction of 7-bromo-7-trimethyltinnorcarane (*syn/anti*-Me_3Sn isomer ratio = 2.9) (5.4 mmol) with 20 ml of cyclooctene was carried out in similar fashion. After 18 h at reflux (pot temperature 146°) NMR showed that the starting tin compound had been consumed completely. The cooled reaction mixture was treated with 20 ml of 10% aqueous methanolic KF solution to remove trimethyltin bromide. The organic layer was separated, dried and filtered. Trap-to-trap distillation of the filtrate was followed by GLC analysis of the distillate; V was present in 46% yield.

Decomposition of 1-bromo-1-trimethyltin-cis-2,3-dimethylcyclopropane in cyclohexene

Using essentially the same procedure as described above, 2.5 g (8.1 mmol) of the tin compound (*syn/anti*-Me_3Sn isomer ratio = 2) in cyclohexene (25 ml) solution was heated at reflux under nitrogen. After 20 h the major isomer had decomposed completely and perhaps a small amount of the minor isomer had been consumed as well. The reaction mixture was distilled through a 20 cm Vigreux column into an ice-cooled receiver until the head temperature did not rise any further (80°). The distillate (4.8 g) was analyzed by GLC (10% UC W98, 30°). The only product formed was 2,3-pentadiene (52% yield, based on 67% decomposition of the tin compound), identified by its IR band at 1970 cm^{-1}, which is typical of the C=C=C structure [23], and its NMR spectrum in CCl_4: δ 4.95(quintet, J = 5.0 Hz, 2H, =CH—) and 1.65 ppm (t, J = 5.0 Hz, 6H, CH_3) (lit. [24] δ 4.89 and 1.56 ppm).

There were no high-boiling materials in the distillation pot residue (by GLC) which were not attributable to starting material.

In another experiment, selective decomposition of isomer VIa was used to prepare a pure sample of VIb. The tin compound (17.5 g, 56.1 mmol, *syn/anti*-Me_3Sn isomer ratio = 2.2) was heated at reflux in 50 ml of cyclohexene for 84 h, until VIa had been consumed. The mixture was trap-to-trap distilled (40°/0.05 Torr) and the distillate concentrated at 50 Torr. The pot residue was distilled through a short path fractionating head to give 5.51 g (79%, based on 40% isomer VIb in the VIa/VIb mixture) of VIb, b.p. 62-63°/2.8 Torr, n_D^{25}

1.5105, of 98% isomeric purity. (Found: C, 30.50; H, 5.46; Br, 25.43. $C_6H_{17}BrSn$ calcd.: C, 30.82; H, 5.49; Br, 25.62%.)

Decomposition of 6-bromo-6-trimethyltinbicyclo[3.1.0]hexane in cyclohexene

A solution of 3.81 g (11.8 mmol) of the tin compound in 30 ml of cyclohexene was heated at reflux (pot temperature 85°) under nitrogen, with stirring. The progress of the decomposition was followed by noting the decrease of the Me_3Sn signal of the starting material and the increase of the trimethyltin bromide resonance with time. The following data were recorded (time, h; % Me_3SnBr; % starting tin compound): 300, 54, 46; 397, 68, 32; 497, 76, 24; 716, 86, 14; 884, 92, 8; 1000, 96, 4. The reaction mixture then was trap-to-trap distilled (80°/0.03 Torr) and the distillate examined by GLC (10% UC W98, 180°). There were several high boiling components; coinjection of authentic spiro(bicyclo[4.1.0]heptane-7,6'-bicyclo[3.1.0]hexane) indicated that one of the minor components might be this compound. Other organic products were not examined further.

Decomposition of 7-bromo-7-trimethyltinnorcarane in cyclohexene

A solution of 2.85 g (8.4 mmol) of the tin compound in 20 ml of cyclohexene was heated at reflux under nitrogen. The *syn/anti*-Me_3Sn isomer ratio (IVa/IVb) of the starting tin compound was 3.4. The results of the NMR study of the progress of the reaction are shown in Table 2. After 830 h the reaction mixture was cooled to room temperature and treated with anhydrous hydrogen chloride. Analysis of the mixture by GLC (15% Carbowax 20M, 190°) showed that only *syn*-7-bromonorcarane was present. A sample isolated by GLC showed an NMR spectrum in agreement with that published for this compound [19].

Decomposition of 1-bromo-1-trimethyltinspiro[2.5]octane in cyclohexene

A solution of the tin compound (2.93 g, 8.33 mmol) in 20 ml of cyclohexene was stirred and heated at reflux. The study of this reaction by NMR pro-

TABLE 2

DECOMPOSITION OF 7-BROMO-7-TRIMETHYLTINNORCARANE MONITORED BY NMR

Reaction time (h)	% Me_3SnBr	%IVa	%IVb
0	0	77	23
108	20	56	24
141	27	50	23
180	38	39	23
211	42	35	23
230	45	31	24
259	49	27	24
316	56	20	24
390	64	12	24
526	71	5	24
576	72	4	24
669	75	2	23
738	76	1	23
830	75	0	19

vided the following data (time, h; % Me_3SnBr; % starting tin compound): 92, 5, 95; 236, 27, 73; 383, 52, 48; 461, 62, 38; 642, 80, 20; 825, 89, 11). At this time the reaction mixture was treated with 30 ml of 10% aqueous methanolic KF. The organic layer was dried and trap-to-trap distilled (room temp./0.05 Torr) and the distillate was examined by GLC (20% UC W98, 130°) The only product present was the allene X (70% yield) which was isolated by preparative GLC. (Found: C, 88.57; H, 11.29. C_8H_{12} calcd.: C, 88.82; H, 11.18%.) NMR (in CCl_4): δ 4.51 (quintet, J = 4.5 Hz, 2H, $=CH_2$) and 2.4-1.3 ppm (m, 10H); IR (film): 1962 cm^{-1} (allene); n_D^{25} 1.4905.

Decomposition of 9-bromo-9-trimethyltinbicyclo[6.1.0]nonane in chlorobenzene

A solution of the tin compound (2.31 g, 6.3 mmol, *syn/anti*-Me_3Sn isomer (IXa/IXb) ratio = 1.6) in 20 ml of chlorobenzene was stirred and heated under nitrogen at reflux. The results of the examination of the progress of the decomposition by NMR are given in Table 3. In order to ascertain if decomposition of IXa results in a trappable carbene, its decomposition was carried out in the presence of cyclohexene. The sample of IXa was obtained by crystallization of a IXa/IXb mixture from methanol to give solid IXa, m.p. 58-59.5°; cleavage of a sample with anhydrous HCl in CCl_4 gave only *anti*-9-bromobicyclo[6.1.0]-nonane, an authentic sample of which was available [19], thus confirming the assignment of stereochemistry.

A solution of 3.50 g (12.2 mmol) of IXa in 4 ml of cyclohexene and 20 ml of chlorobenzene was stirred and heated at reflux (pot temperature 116°) for 36 h. At this time the Me_3Sn resonances of the starting material no longer were apparent in the NMRspectrum of the reaction mixture. The mixture was treated with 50 ml of KF solution and the filtered organic layer was dried and concentrated by distillation until the head temperature reached 133°. The residue was trap-to-trap distilled (room temp./0.03 Torr). The distillate was examined by GLC (10% UC W98, 155°) and found to contain 1,2-cyclononadiene (16%), n_D^{25} 1.5046 (lit. [25] 1.5045); IR: 1955 cm^{-1} (allene); NMR, vinylic to aliphatic proton ratio, 2/12. The trap-to-trap distillation pot contained a considerable amount of solid which was recrystallized from methanol/acetone to give 0.56 g (46%) of a material with a melting range of 70-76°. This appeared to be a mix-

TABLE 3

DECOMPOSITION OF 9-BROMO-9-TRIMETHYLTINBICYCLO[6.1.0]NONANE IN CHLOROBENZENE MONITORED BY NMR

Reaction time (h)	% Me_3SnBr	% IXa	% IXb
0	0	62	38
0.5	5	58	37
1	12	52	36
2	20	43	37
3	32	32	36
4	40	25	35
5	44	20	36
21	68	~0	32

ture of the dimers of 1,2-cyclononadiene, (lit. [20] m.p. 64-76°). The NMR spectrum (in $CDCl_3$) showed δ 5.60 (t, J = 8.5 Hz, 1H) and 3.2-0.8 ppm (m, ca. 12H).

Divalent carbon transfer reactions of 7-bromo-7-trimethyltinnorcarane

(a). With triethylsilane. A solution of 6.78 g (20.0 mmol, *syn/anti*-Me_3Sn isomer ratio = 4.0) of the tin compound and 6.85 g (59 mmol) of triethylsilane (PCR Inc.) in 20 ml of chlorobenzene was stirred and heated at reflux (pot temperature 125-128°) under nitrogen for 40 h. The progress of the reaction was followed by GLC. The reaction mixture was treated with 60 ml of 10% KF solution and the organic layer was filtered and the filtrate concentrated by distillation to a head temperature of 133°. The residue was trap-to-trap distilled (85°/0.05 Torr) and the distillate (4.17 g) was examined by GLC (20% UC W98, 200°). Two major components were present and were collected by preparative GLC. The first to be eluted was *anti*-7-triethylsilylnorcarane (24% yield), n_D^{25} 1.4743. (Found: C, 74.20; H, 12.27. $C_{13}H_{26}Si$ calcd.: C, 74.20; H, 12.45). NMR (in CCl_4): δ 2.3-0.1 (m, 25H, maxima at 1.7, 0.94, 0.83, 0.60, 0.50, 0.38) and −0.75 ppm (t, J = 7.0 Hz, 1H, 7-H). The second compound to be eluted was *syn*-7-triethylsilylnorcarane (25% yield), n_D^{25} 1.4876. (Found: C, 73.96; H, 12.17. $C_{13}H_{26}Si$ calcd.: C, 74.20; H, 12.45%.) NMR (in CCl_4): δ 2.4-0.2 (m, 25 H, maxima at 1.57, 1.30, 1.00, 0.90, 0.66) and −0.47 ppm (t, J = 10.0 Hz, 1H, 7-H).

Also present was a hydrocarbon tentatively identified (by IR) as the dimer of 1,2-cycloheptadiene, in 12% yield.

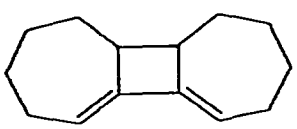
(b). With tetramethylethylene. A solution of 3.91 g (11.6 mmol) of the tin compound (*syn/anti*-Me_3Sn isomer ratio = 2.9) and 3.22 g (38.3 mmol) of tetramethylethylene in 15 ml of chlorobenzene was stirred and heated at reflux (112-115°) under nitrogen; the progress of the reaction was monitored by NMR. The decomposition of the starting tin compound was almost complete after 19 h, but heating was continued for a total of 88 h. The reaction mixture was treated with 10% KF solution and the dried organic layer was concentrated by distillation to a head temperature of 135°. The pot residue was trap-to-trap distilled at 50°/0.02 Torr to give 2.46 g of clear distillate which GLC (10% UC W98, 195°) showed to contain only one major high-boiling component in 25% yield. A sample was isolated by GLC and identified as 2′,2′,3′,3′-tetramethylspiro(bicyclo[4.1.0]heptane-7,1′-cyclopropane), n_D^{25} 1.4754. (Found: C, 87.56; H, 12.55. $C_{13}H_{22}$ calcd.: C, 87.56; H, 12.44%.) NMR (in CCl_4): δ 1.9-0.8 (m, 10 H, cyclohexyl H), 1.16 (s, 6H, CH_3), and 0.93 ppm (s, 6H, CH_3).

(c) With cyclopentene. Essentially the same reaction and work-up procedure was used in the reaction of 3.04 g (9.0 mmol) of the tin compound (*syn/anti*-Me_3Sn isomer ratio = 2.9) and 2.21 g (32.5 mmol) of cyclopentene in 25 ml of chlorobenzene at reflux (117°) for 62 h. The final trap-to-trap distillate was examined by GLC (20% UC W98, 210°) and found to contain two high-boiling components which then were isolated by preparative GLC. The first to be eluted was the expected spiropentane derivative, spiro(bicyclo[4.1.0]-heptane-7,6′-bicyclo[3.1.0]hexane), 26% yield, n_D^{25} 1.5041. (Found: C, 88.59; H, 11.27. $C_{12}H_{18}$ calcd.: C, 88.82; H, 11.18%.) NMR (in CCl_4): δ 2.1-0.6 ppm (m, maxima at 1.65, 1.30 and 1.05). The second component was tentatively identified as the dimer of C_7H_{10} (by IR), 13% yield.

(d). With cyclohexene. A flame-dried Pyrex bomb tube of about 20 ml capacity was charged with 4.46 g (13.2 mmol) of the tin compound (*syn/anti*-Me_3Sn isomer ratio = 4.0) and 10 ml of cyclohexene. The tube was sealed under reduced pressure and placed in a rocking autoclave at 170± 5° for 4 days. Upon completion of the reaction the mixture was distilled. The fraction with b.p. 60°/0.30 Torr contained only a single component (33% yield) which was identified as 7,7'-bis(bicyclo[4.1.0]heptane) which was identified by comparison of its spectral properties with those of this compound as prepared by Moore et al. [7,8]. In the 70 eV mass spectrum of the product the highest detectable ion cluster was seen at *m/e* 175(1), 176(13), 177(2), which is consistent with $C_{13}H_{20}$ = 176.

(e). With methylenecyclohexane. The reaction and work-up procedure detailed in (*c*) was used in the reaction of 3.74 g (11.0 mmol) of the tin compound (*syn/anti*-Me_3Sn isomer ratio = 4.0) and 3.38 g (34.2 mmol) of methylenecyclohexane in 20 ml of chlorobenzene at reflux (128°) for 16 h. The final trap-to-trap distillate contained three high-boiling components which were separated by GLC; that with the longest retention time using a 20% UC W98 column at 200°, the other two using a 10% UC W98 column at 190°.

The first compound to be eluted was one of the expected isomeric spiropentanes, n_D^{25} 1.4973, in 18% yield. (Found: C, 88.30; H, 11.53. $C_{14}H_{22}$ calcd.: 88.35; H, 11.65%.) NMR (in CCl_4): δ 2.2-0.8 (m, 20H, maxima at 1.40 and 1.26) and 0.40 ppm (s, 2H, cyclopropyl CH_2). The second compound to be eluted was the other isomeric spiropentane derivative, n_D^{25} 1.5034, in 19% yield. (Found: C, 88.56; H, 11.66. $C_{14}H_{22}$ calcd.: C, 88.35; H, 11.65%.) NMR (in CCl_4): δ 2.2-0.8 (m, 20H, maxima at 1.65, 1.30 and 1.15) and 0.40 ppm (s, 2H, cyclopropyl CH_2). The highest boiling component was identified tentatively as tricyclo[2.5.0.$0^{2,5}$]tetradeca-7,9-diene (XII) on the basis of its spectral simi-



(XII)

larity to the thermal dimers of 1,2-cyclononadiene [21] and the presence of an IR band at 1660 cm^{-1}. NMR (in CCl_4): δ 5.68 (broad t, J = 5.5 Hz, 2H) and 2.6-0.8 (m, 18H). The yield of this material was 5%.

(f). With cyclooctene. Separate reactions were carried out with the two isomers of the organotin compound.

A solution of 7.51 g (22.2 mmol) of *anti*-7-bromo-*syn*-7-trimethyltinnorcarane in 20 ml of cyclooctene was stirred and heated at reflux for 6 h. Vacuum distillation of the reaction mixture gave 3.45 g of a fraction with b.p. 68-71°/0.05 Torr which contained ca 10% lower-boiling impurities. The main component, present in 76% yield by GLC (10% UC W98 at 190°), was isolated and identified as the spiropentane derivative V.

A similar reaction with the other isomer of the tin compound (38.9 mmol in 25 ml of cyclooctene) required a reflux period of 23 h to completely consume the tin compound and give V, b.p. 83-85°/0.1 Torr, in 40% yield.

Reaction of 7,7-bis(trimethyltin)norcarane with bromine

Into a flamed-out 100 ml, three-necked flask equipped with a mechanical stirrer, nitrogen inlet tube, and an addition funnel were placed 6.50 g (15.4 mmol) of 7,7-bis(trimethyltin)norcarane and 15 ml of reagent grade carbon tetrachloride. The reaction flask was cooled with an ice bath. In the addition funnel was placed a solution of 2.71 g (16.9 mmol) of reagent grade bromine (Mallinckrodt) in 25 ml of CCl_4. The bromine solution was added dropwise during a 90 min period. The color of the bromine was discharged immediately as each drop was added. The reaction mixture was treated with 25 ml of 10% potassium floride solution and the resulting heterogeneous mixture was stirred for 10 min and then filtered. After the solid had been washed with hexane, the organic layer was dried over sodium sulfate and the solvents were evaporated on a steam bath. The pot residue was vacuum distilled to yield 3.69 g (71%) of 7-bromo-7-trimethyltinnorcarane, b.p. 83-85°/0.4 Torr. An NMR spectrum of this mixture shows a *syn/anti*-Me_3Sn ratio of 1.0/2.0. This reaction was repeated under slightly different conditions (the bromine was added during a 30 min period) on a 100 mmol scale to yield material with a 1.0/1.3 isomer ratio.

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