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HALOMETHYL—METAL COMPOUNDS

LXXII*. THE PREPARATION OF α-HALOCYCLOPROPYL DERIVATIVES OF LITHIUM AND THEIR APPLICATION IN THE SYNTHESIS OF α-HALOCYCLOPROPYL COMPOUNDS OF SILICON, GERMANIUM, TIN, LEAD, AND MERCURY. A NOVEL ISOMERIZATION OF *syn*-7-BROMO-*anti*-7-LITHIONORCARANE TO THE *anti*-7-BROMO-*syn*-7-LITHIO ISOMER

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Summary

A number of α-bromocyclopropyllithium reagents have been prepared at low temperature (—90° to —100°) in THF or THF/Et_2O medium by reaction of n-butyllithium with the respective *gem*-dibromocyclopropane. Reactions of these new lithium reagents with concentrated HCl, trimethylchlorosilane, dimethyldichlorosilane, trimethyltin chloride, dimethyltin dichloride, dimethyldichlorogermane, trimethyllead bromide, mercuric chloride and some other organometallic halides are described. A novel isomerization of *syn*-7-bromo-*anti*-7-lithionorcarane to *anti*-7-bromo-*syn*-7-lithionorcarane, induced by the presence of a slight excess of 7,7-dibromonorcarane, is described.

Introduction

In earlier papers of this series we have reported the preparation of diverse α-haloalkyl derivatives of heavy metals, principally of mercury, and their utilization as divalent carbon transfer reagents°. In the following series of papers we describe our studies aimed at extending this general approach to the generation of cyclopropylidene intermediates. Previous work in these laboratories had

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* For part LXXI see ref. 1.

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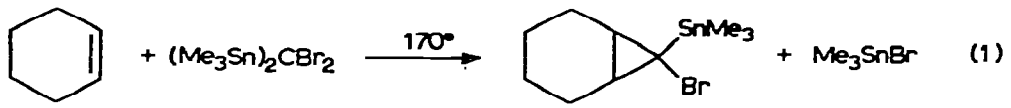
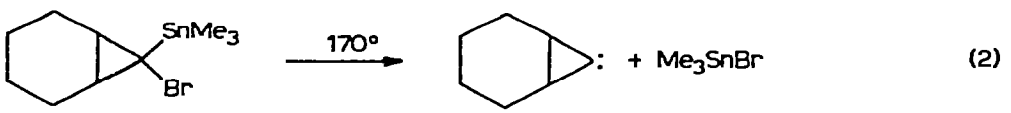
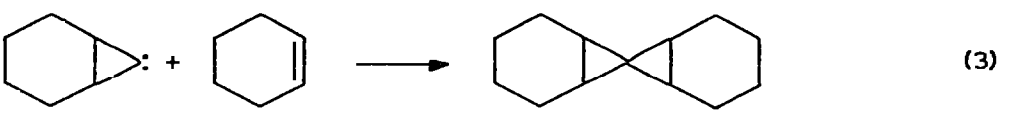
° Several recent reviews of this area are given in ref. 2.

provided some indication that this approach merited detailed examination. Thus, the high temperature reaction of $(Me_3Sn)_2CBr_2$ with cyclohexene gave a product mixture containing the spiro compound I, in low yield, which presumably was formed via the route shown [3].

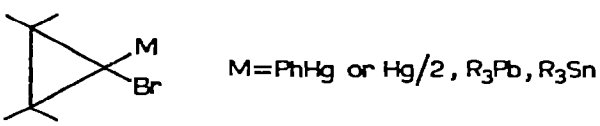






(I)

Compounds of type II were required for these investigations and it was



(II)

decided to assess the utility of organolithium and organomagnesium routes in their preparation.

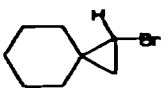
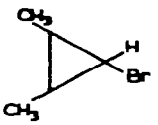
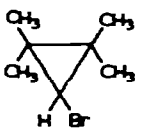
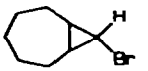
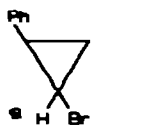
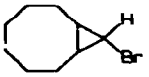
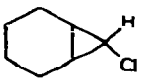
When this work was initiated, there had been many reports of the chemistry resulting from interaction of *gem*-dihalocyclopropanes with organolithium reagents [4], methylmagnesium bromide [5] and metallic magnesium [6]. However, in all this work the reaction temperatures used appeared to have been above the estimated decomposition temperatures (—100° to —50°) of the presumed *gem*-halometallocyclopropane intermediates. At the outset of our work, there had been only one report of a well-defined lithium reagent of this type, 7-chloro-7-lithionorcarane [7]. Our projected appraoch, however, required α-bromocyclopropyllithium reagents. In this paper we report the successful synthesis of several such reagents.

Results and discussion

Since α-bromocyclopropyllithium reagents were expected (and found) to be stable only at low temperatures, the low temperature techniques employed in our previous investigations of α-haloalkyllithium chemistry (e.g., ref. 8) were used. In most cases, the *gem*-dihalocyclopropane was dissolved in THF or THF—diethyl ether mixtures to obtain a 0.5 *M* to 1.0 *M* solution which was cooled to —95° or lower, and n-butyllithium in hexane then was added slowly

TABLE 1

MONOBROMOCYCLOPROPANES PREPARED BY HYDROLYSIS OF α-BROMOCYCLOPROPYLLITHIUM REAGENTS

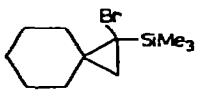
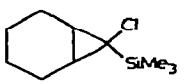
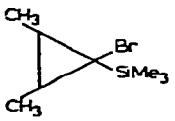
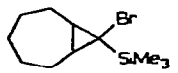
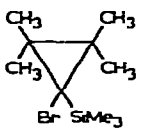
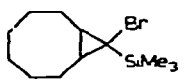
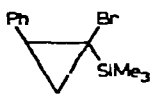
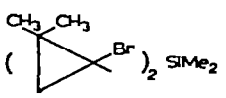
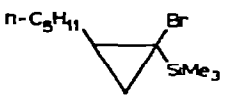
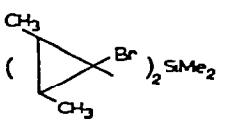
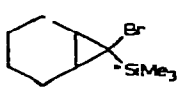
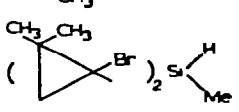
Compound	Yield (%)	*syn*-Br/*anti*-Br isomer ratio	Compound	Yield (%)	*syn*-Br/*anti*-Br isomer ratio
	61			50	1/1.5
	68	1/21		79	1/3.2[a]
	76			84	1/12
	84	1/10		66	1/3.1
				62	1/2.4[b]

[a] With inverse addition of 7,7-dibromonorcarane to the n-BuLi solution, the 7-bromonorcarane was produced in 79% yield, with a *syn*-Br/*anti* Br isomer ratio of 1/4.4. [b] From mixed isomers of 7-bromo-7-chloronorcarane, *syn*-Cl/*anti*-Cl isomer ratio.

by allowing it to run down the wall of the reaction flask. This method of addition served to cool the butyllithium solution before it mixed with the dihalocyclopropane solution. The exchange reaction appeared to be very rapid, as judged by the immediate development of a constant color, usually pale yellow. Normally, short addition times (5-10 min) were satisfactory when partial immersion of the reaction flask in a liquid nitrogen bath was used to maintain the low temperatures. The time required for consumption of the α-bromocyclopropyllithium reagent depended upon the substrate used. The addition of hydrochloric acid discharged the yellow color rapidly. Reaction with trimethyltin chloride required longer reaction times and trimethylchlorosilane reacted still more slowly. The results of our initial experiments, in which the lithium reagents were treated with hydrochloric acid, are summarized in Table 1. The assignments of configuration were performed using by now well-developed NMR procedures [9]. The reaction of n-butyllithium with 7-bromo-7-chloronorcarane apparently formed no 7-bromo-7-lithionorcarane, since 7-bromonorcarane was absent in the product. No effort was made to optimize the product yields since they were quite satisfactory. If one makes the reasonable assumption that the protolysis of α-bromocyclopropyllithiums is a stereospecific process, it is apparent that whenever two isomeric (*syn* or *anti*) reagents can be formed, it is the more hindered (at lithium) *syn*-lithio-*anti*-bromocyclopropane which is formed in higher yield, a point which will receive further attention

TABLE 2

α-BROMOCYCLOPROPYLSILANES PREPARED USING α-BROMOCYCLOPROPYLLITHIUM REAGENTS

Compound	Yield (%)	*syn*-Br/*anti*-Br isomer ratio	Compound	Yield (%)	*syn*-Br/*anti*-Br isomer ratio
	75			70	1.45/1[a]
	67	1/1		87	1/12.5
	31			65	1/2.3
	73	1/5.9		48	
	78	1/1.2		36	
	74	1/3.2		49	

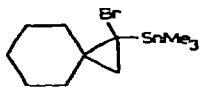
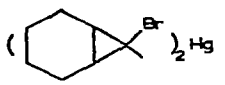
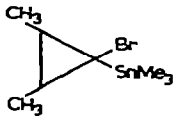
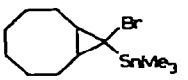
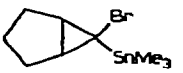
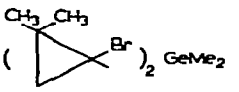
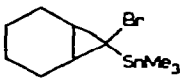
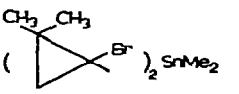
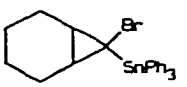
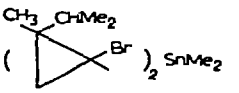
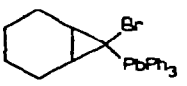
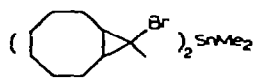
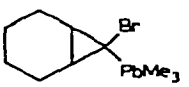
[a] From mixed isomers of 7-bromo-7-chloronorcarane; *syn*-Cl/*anti*-Cl isomer ratio.

below. We note also that this procedure for the reduction of *gem*-dibromo- or *gem*-bromochlorocyclopropanes is a useful complement to the reduction of these compounds with tri-n-butyltin hydride, in which the reversed preferential formation of isomers is observed. For instance, in the reduction of 6,6-dibromobicyclo[3.1.0]hexane by the organolithium procedure the ratio of *syn*-6-bromobicyclo[3.1.0]hexane to the *anti* isomer was 1/1.5. In contrast, the tri-n-butyltin hydride reduction of 6,6-dibromobicyclo[3.1.0]hexane gave the monobromide with a *syn/anti* ratio of 1.3/1.

Table 2 lists the results of reactions of various α-bromocyclopropyllithiums with trimethylchlorosilane and other chlorosilanes. Again, both possible isomers were formed and the product yields were quite good. Other reactions of these α-bromocyclopropyllithiums with heavy metal halides were carried out (Table 3), and the divalent carbon transfer chemistry of these products, which has been studied in some detail, will be the subject of a later paper. It was observed in all cases where two geometrical isomers are possible for

TABLE 3

α-BROMOCYCLOPROPYLMETAL COMPOUNDS PREPARED USING α-BROMOCYCLOPROPYLLITHIUM REAGENTS

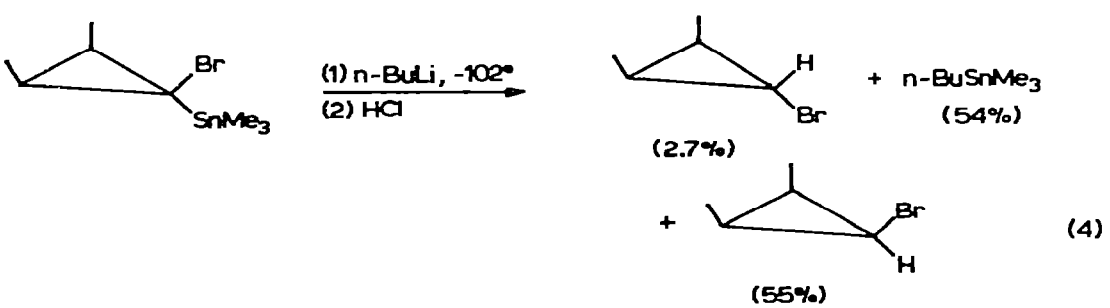
Compound	Yield (%)	*syn*-Br/*anti*-Br isomer ratio	Compound	Yield (%)	*syn* Br/*anti* Br isomer ratio
	79			62	
	66	1/2		57	1/4.8
	23	0/1		70	
	71	1/4		65	
	19			55	
	20			23	
	75	1/25			

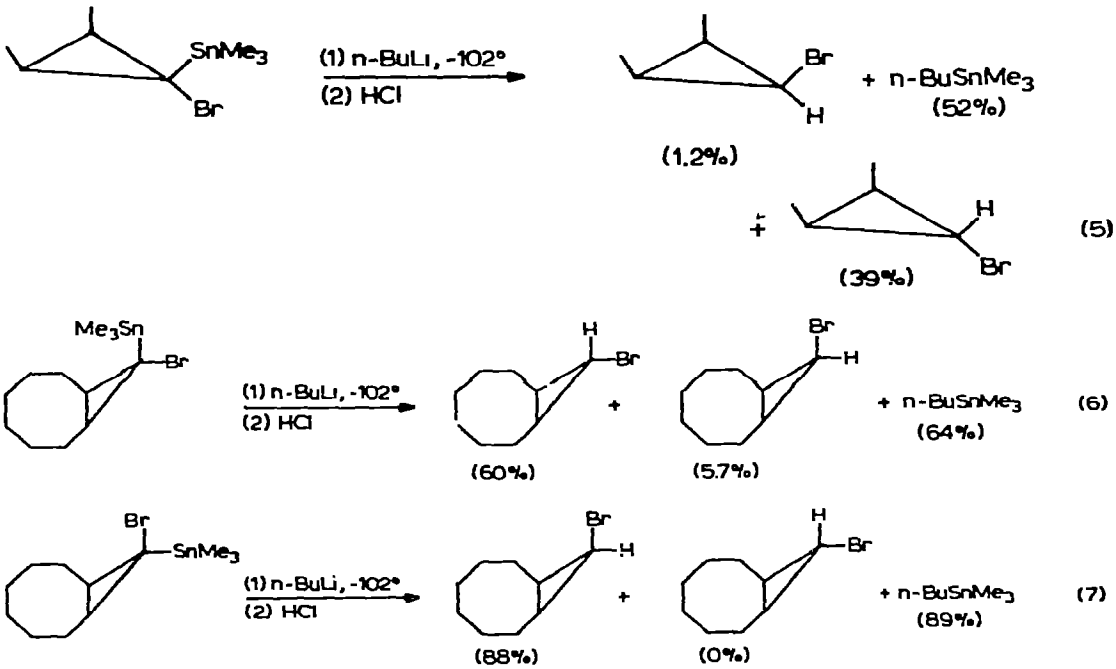
products derived from trimethylchlorosilane and trimethyltin chloride, that the isomer with the more hindered (*syn*) $(CH_3)_3M$ group showed its CH_3—M proton resonance at a lower field position than the *anti*-$(CH_3)_3M$ isomer. A similar observation had been made in the case of the two isomers of 7-trimethylsilylnorcarane [10]. Inspection of Tables 1, 2 and 3 shows that on the whole, the *syn/anti* product ratios obtained for a given lithium reagent do not change much with substrate. Furthermore, it may be noted that the mixture of 9-bromo-9-trimethylsilylbicyclo[6.1.0]nonane isomers (Table 2) was converted to the Grignard reagent which was subsequently hydrolyzed. The resulting 9-trimethylsilylbicyclo[6.1.0]nonane isomers were isolated and characterized. The observed *syn/anti*-trimethylsilyl isomer ratio was about 1/2. A particularly noteworthy result which bears on the stereochemical question was the successful isolation of *anti*-9-bromo-*syn*-9-trimethylstannylbicyclo[6.1.0]nonane as a solid, m.p. 58°, by crystallization from the mixture of isomers produced when

trimethyltin chloride was added to the appropriate lithium reagent. Cleavage of this solid with gaseous HCl gave only *anti*-9-bromobicyclo[6.1.0]nonane. This is decisive with regard to our stereochemical assignment, since such cleavage of cyclopropyltin compounds has been shown to proceed with retention of configuration at carbon [11].

The product yields in these reactions (Tables 2 and 3) were reasonably good, with some exceptions. The low yield obtained for 6-bromo-6-trimethylstannylbicyclo[3.1.0]hexane probably is a reflection of the thermal instability of the lithium reagent. There was a considerable amount of organic soluble residue left after distillation of the product which may have been oligomers of (C_6H_8) [12] which were formed by decomposition of the lithium reagent. The presence of only the *syn*-trimethyltin isomer may be due to the possibly greater instability of the *anti*-lithium reagent. Similarly, the low yield of 1-bromotetramethylcyclopropyltrimethylsilane very likely is a consequence of the low stability of 1-bromotetramethylcyclopropyllithium.

Having demonstrated that α-bromocyclopropyllithiums are useful reagents at low temperatures, we also investigated their configurational stability. It had been shown that nonhalogenated cyclopropyllithiums are configurationally stable [13-15]. In the case of α-bromocyclopropyllithiums, we chose to prepare them via the transmetalation reaction in order to assess their configurational stability, since preparation of organolithiums by this route has been demonstrated to occur without change of configuration at carbon [16]. It had been possible to obtain *anti*-1-bromo-*syn*-1-trimethylstannyl-*cis*-2,3-dimethylcyclopropane as a crystalline solid and to isolate the pure *syn*-bromo-*anti*-trimethyltin isomer (a liquid) by selective thermal decomposition of the *anti*-bromo-*syn*-trimethyltin isomer in a mixture of both isomers, and this made such a study feasible. Both isomers were treated separately with n-butyllithium at low temperature, using the same conditions for each. Each reaction mixture was hydrolyzed with hydrochloric acid and the yields of the products were determined by GLC. The results, summarized in eqns. 4 and 5, demonstrate that the lithium reagents in question are configurationally stable. The good correspondence between n-butyltrimethyltin yields and product yields provides good evidence that it is hydrolysis of the lithium reagent, not protolysis of the organotin starting compound, which is responsible for the formation of the monobromocyclopropane. Similar results were obtained with the two isomers of 9-bromo-9-trimethylstannylbicyclo[6.1.0]nonane. As mentioned above, the *anti*-bromo-*syn*-trimethyltin isomer of this compound could be isolated as a crystalline solid, and a sample of the other isomer of 90% isomeric purity also was obtained. Equations 6 and 7 summarize the results obtained with these compounds.



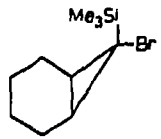
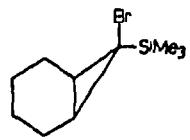
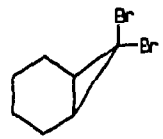


The configurational stability of these α-bromocyclopropyllithium reagents at −100° in THF medium having been established, investigations into the selective decomposition of 7-bromo-7-lithionorcarane then were undertaken. After a few otherwise unremarkable reactions in which the mixture of lithium reagents was warmed to various temperatures from −95° for varying lengths of time and then hydrolyzed, an inconsistent result was obtained in which the only apparent lithium reagent in solution was *anti*-7-bromo-*syn*-7-lithionorcarane. Closer investigation revealed that about 1.2% of unconverted dibromonorcarane was present as well; in previous reactions this starting material had been completely consumed. Further experiments in which reactant stoichiometry and the reaction temperature were varied were carried out and these are summarized in Table 4. In each of these experiments 7,7-dibromonorcarane was treated with an excess or with a deficiency of n-butyllithium. In the first three experiments the initial temperature was about −95° and after the reactants had been mixed, the reaction mixture was allowed to warm to and maintained at about −85° for 30 min. The mixture then was cooled to −95° to −100°, again, and one equivalent of trimethylchlorosilane was added. In the fourth experiment the temperature was lowered to about −117° rather than raised to −85°.

The *anti*-7-bromo-*syn*-7-trimethylsilylnorcarane isomer was obtained as exclusive product only when a slight deficiency of n-butyllithium was used and when a somewhat warmer temperature (−85°) than the usual −95° to −100° was used; both conditions were essential. One may assume that the formation of only *anti*-7-bromo-*syn*-7-trimethylsilylnorcarane in the fourth experiment indicates that only (or almost exclusively) the *anti*-7-bromo-*syn*-7-lithionorcarane isomer was present at the time trimethylchlorosilane was added. The essential constancy of silylated product yields in these experiments suggests

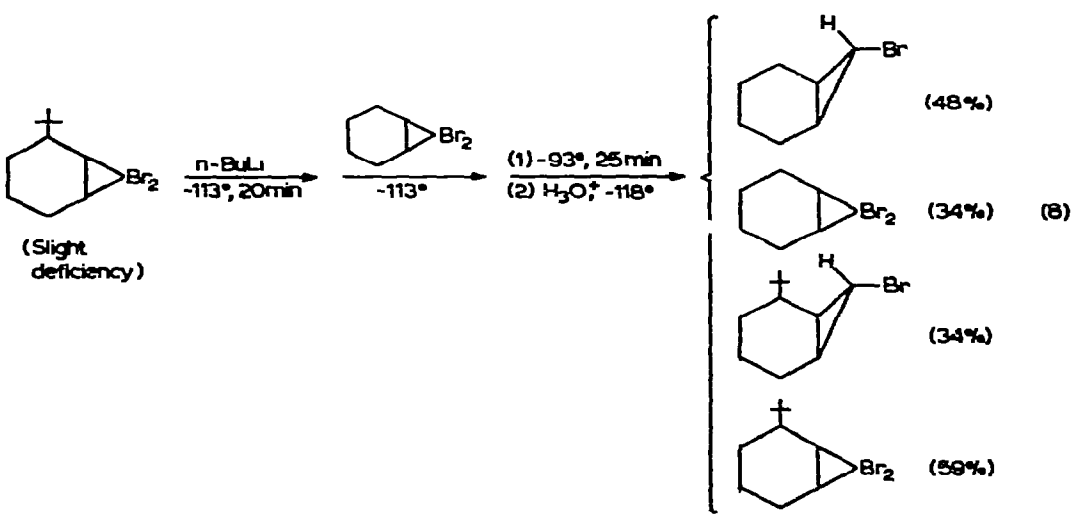
TABLE 4

EXPERIMENTS WITH 7-BROMO-7-LITHIONORCARANE

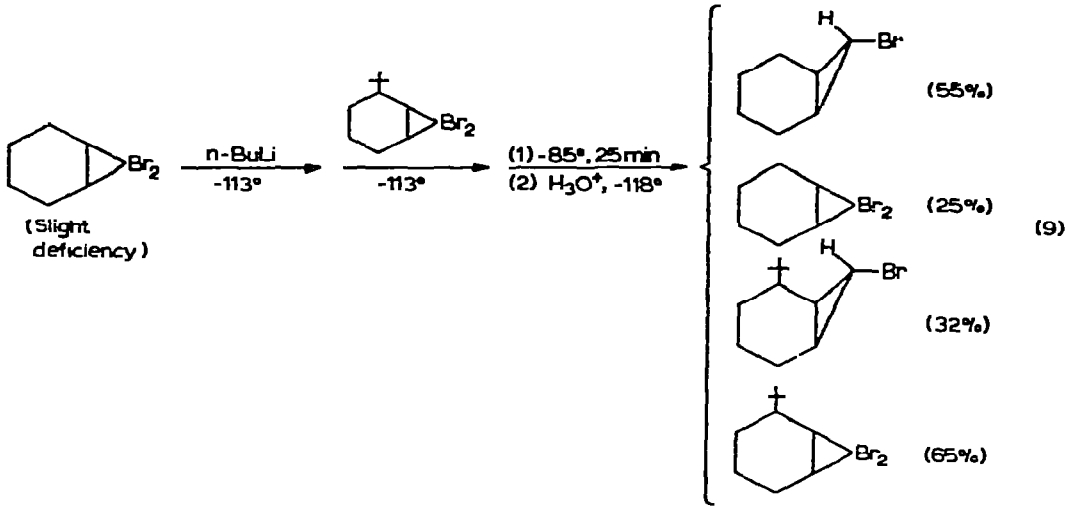
Experiment number	 (1 molar equivalent)	x n-BuLi (THF/Et_2O) at -95°	stir at °C	y Me_3SiCl	Products obtained (%) 			 (*syn*-Br/*anti*-Br)
1		1.3 (3/1)	−85	1.1	42	12	0	24 (1/1.2)
2		1.05 (3/1)	−85	1.0	61	16	0	6 (1/1.9)
3		0.95 (3/1)	−85	1.0	76	0	4	5 (1/2.5)
4		0.95 (1/1)	−117	1.0	55	17	trace	7 (1/3.4)

that we are not dealing with selective decomposition of the *syn*-7-bromo-*anti*-7-lithionorcarane but rather with its isomerization to the *anti*-bromo-*syn*-lithio isomer. It should be appreciated that temperature measurement and control in these temperature ranges is not especially straightforward, so that in some experiments a mixture of isomers will result when only the *anti*-7-bromo-*syn*-7-lithionorcarane isomer is desired. However, any operations which tend in the indicated directions of stoichiometry and temperature control will serve to increase the *syn*/*anti*-lithium reagent ratio.

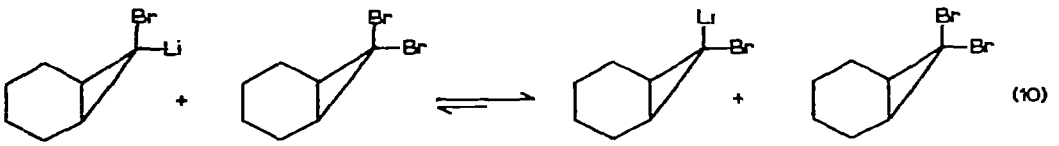
The nature of this novel isomerization reaction was of interest. The requirement that a slight excess of 7,7-dibromonorcarane be present suggested that an intermolecular process was operative. In order to obtain more information bearing on this question, experiments utilizing 2-t-butyl-7,7-dibromonorcarane were carried out*. Approximately one equivalent of 7,7-dibromonorcarane and one equivalent of n-butyllithium were allowed to react, presumably as completely as possible within stoichiometric limits, at −105° for 20 min. Then one equivalent of t-butyl-labelled 7,7-dibromonorcarane was added and the mixture was warmed to −85° for 25 min. The reaction mixture then was treated with concentrated hydrochloric acid at −110°. The procedure was repeated, but with the order of introduction of the two dibromonorcaranes interchanged. The results of these experiments are presented in eqns. 8 and 9. These results not only verify an isomerization mechanism involving intermolecular exchange with "unreacted" dibromonorcarane, but indicate that there is a preference for the lithium atom to be attached to the ring system without the t-butyl group. Even when all of the lithium atoms are attached initially to the ring system containing the t-butyl group, most are exchanged to the other ring system. At this point one must amend the original conclusion that α-bromocyclopropyllithiums are configurationally stable to include (at least in the case of the norcaranyl system) the necessary absence of a *gem*-dibromocyclopropane. This may not be true at very low temperatures, but this point was not examined further.



* Obtained by CBr_2 addition to 3-t-butylcyclohexene as a 98/2 mixture of isomers in which the predominant one undoubtedly was the *trans* isomer.



The occurrence of reaction 10 may be understood in terms of the operation

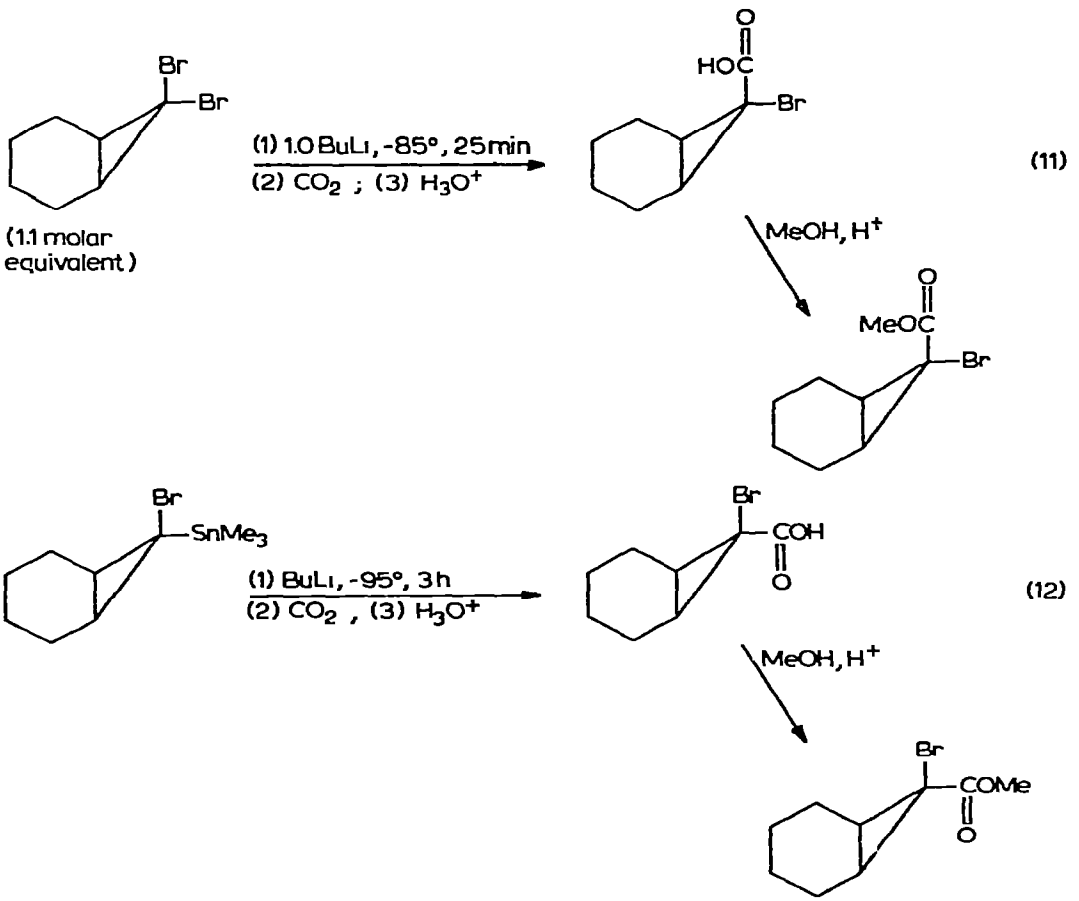


of steric effects. The *syn*-lithium is more sterically hindered, hence less reactive, than the *anti*-lithium, and this should result in the accumulation of *anti*-7-bromo-*syn*-7-lithionorcarane at the expense of the *syn*-7-bromo-*anti*-7-lithio isomer. One might expect to observe similar isomerization reactions in the case of other 2,3-disubstituted or more highly substituted 1-bromocyclopropyllithium compounds, but this point has not been investigated in a systematic manner, the emphasis of our research in this area at least temporarily having shifted in other directions.

Some immediate applications of the above results were the preparation of *anti*-7-bromo-*syn*-7-trimethylstannylnorcarane (63%), bis(*anti*-7-bromo-*syn*-7-norcaranyl)dimethyltin (54%) and bis(*anti*-7-bromo-*syn*-7-norcaranyl)dimethylgermane (48%) by appropriate reactions with trimethyltin chloride, dimethyltin dichloride and dimethyldichlorogermane, respectively, as well as the preparation of bis(*anti*-7-bromo-*syn*-7-norcaranyl)dimethylsilane [22].

These procedures for the preparation of isomerically pure α-halocyclopropyllithium reagents found useful application in other projects. For example, there was a need to know the configurations of the isomers which were formed in the addition of $PhHgCBr_2CO_2CH_3$-derived bromocarbomethoxycarbene to cyclohexene [17]. Carboxylation of such an *anti*-7-bromo-*syn*-7-lithionorcarane solution followed by acid hydrolysis gave the *syn*-carboxylic acid in 76% yield. Treatment of the latter with methanol in the presence of acid produced the methyl ester in 80% yield (eqn. 11). In similar fashion, transmetalation of *syn*-7-bromo-*anti*-7-trimethylstannylnorcarane with n-butyllithium followed by carboxylation yielded the *anti*-carboxylic acid in 60% yield and this was esterified with methanol in 84% yield (eqn. 12) [24]. IR and NMR

spectroscopic studies established the isomeric purity of each ester and confirmed that the *syn*-7-bromo-*anti*-7-carbomethoxynorcarane isomer was the major product in the $PhHgCBr_2CO_2CH_3$-cyclohexene reaction.



The procedures developed in this study also made possible the preparation for the first time of the pure isomers of 7-bromo-7-chloronorcarane. All bromochlorocarbene additions to cyclohexene give a mixture of both isomers [18]. The best separation of these was achieved under analytical conditions and only partial resolution was possible [19]. The chlorination of the *anti*-7-bromo-*syn*-7-lithio- and *syn*-7-bromo-*anti*-7-lithionorcarane isomers with hexachloroethane [20] at low temperature gave the respective bromochloronorcaranes. That different isomers were formed when the lithium reagents were generated as shown in eqns. 11 and 12 and then chlorinated was indicated by the IR spectra of the bromochloronorcaranes produced in the 740-790 cm^{-1} region, as shown in Fig. 1. A 1/1 mixture of the pure isomers produced a spectrum essentially identical with that of a sample prepared by the $HCClBr_2$—Me_3COK procedure. Further convincing evidence that isomerically pure products had been produced was obtained when their reactions with n-butyllithium were examined. In one reaction, the *anti*-7-bromo-*syn*-7-chloro isomer was added to a slight excess of n-butyllithium during a one-minute period at —95° and the mixture then

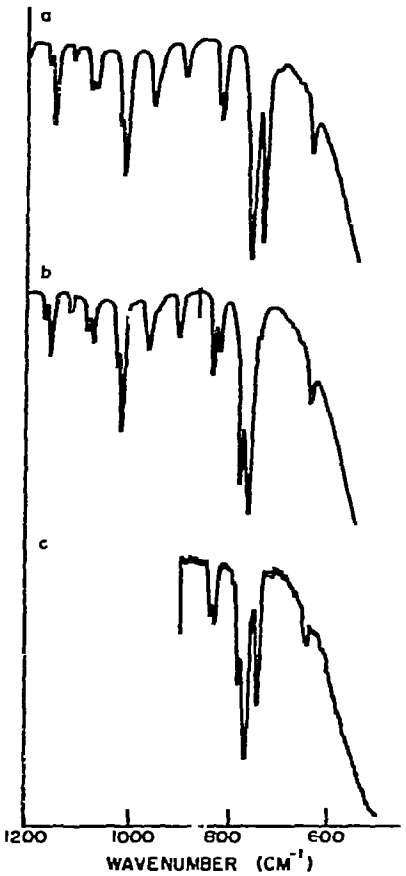


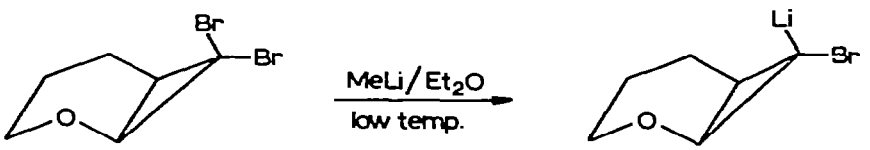
Fig. 1. Infrared spectra of the isomers of 7-bromo-7-chloronorcarane: (a) *anti*-7-bromo-*syn*-7-chloronorcarane; (b) *syn*-7-bromo-*anti*-7-chloronorcarane and (c) 1/1 mixture of both isomers.

was treated with concentrated hydrochloric acid. A mixture of *syn*-7-chloronorcarane (57%) and the *anti*-7-chloro isomer (18%) was obtained, which indicates the occurrence of about 25% isomerization. However, by increasing the excess of *n*-butyllithium used to 5/1 and using a more rapid (15 sec) addition time, the formation of only *syn*-7-chloronorcarane in 69% yield was effected. When such a lithium reagent was treated with trimethylchlorosilane, *syn*-7-chloro-*anti*-7-trimethylsilylnorcarane, isomerically pure, was produced in 81% yield. Similar treatment of *syn*-7-bromo-*anti*-7-chloronorcarane with 5 molar equivalents of *n*-butyllithium (10 sec addition time) at —95°, followed by addition of concentrated HCl gave only *anti*-7-chloronorcarane (84%), and treatment of the lithium reagent with trimethylchlorosilane resulted in *anti*-7-chloro-*syn*-7-trimethylsilylnorcarane.

These results not only demonstrate the isomeric purity of the individual 7-bromo-7-chloronorcaranes, but yield the more important result that bromine—lithium exchange in these reactions is stereospecific. These reactions also permit the assignment of the absolute configuration to the isomers of 7-chloro-7-trimethylsilylnorcarane, one of which had been prepared previously, isolated and otherwise characterized [21].

The availability of α-bromocyclopropylmetal compounds of type II via the procedures developed allowed an examination of their thermolysis and the results of these studies will be reported in a later paper. The preparation of bis(α-bromocyclopropyl)dimethylsilanes during the course of this study provided the key intermediates for the preparation of the first silacyclopropanes [22]. Other workers have developed useful synthetic chemistry from their studies of the reactions of α-bromocyclopropyllithium reagents with organic carbonyl compounds [23]. Thus the new organolithium reagents described here and reported first in preliminary communications [22,24] have found useful application in synthesis very quickly.

Finally, we note that a stereospecific conversion of a *gem*-dibromocyclopropane to a *gem*-bromolithiocyclopropane has been reported by Taylor et al. [25] (eqn. 13). This result, however, was rationalized in terms of intramolecular coordination of the lithium to the oxygen atom, a bonding feature which is not possible in the other isomer.



(13)

Experimental

General comments

All reactions involving organometallic compounds were carried out under an atmosphere of prepurified nitrogen. The apparatus generally was assembled and then flame-dried with a stream of nitrogen passing through it. Transfers involving air-sensitive solutions were carried out with syringes and/or cannulae. All solvents used were anhydrous. Workup procedures included rotary evaporation at water aspirator pressure and trap-to-trap distillation to separate volatile products from nonvolatiles. The conditions given (temperature/mmHg) are the maximum required to heat the distillation apparatus. Trap-to-trap distillations generally were done with an open-to-pump system transfer apparatus with liquid nitrogen traps. Gas—liquid chromatography (GLC) was used for both the isolation of samples and yield determinations. The commercial instruments used included F&M models 700, 720, 5754 and 776. An MIT isothermal unit was also used for preparative isolations. Yields were determined using the internal standard method.

Infrared spectra were recorded using Perkin—Elmer 337, 257 or 457A spectrophotometers. Samples of liquids were taken as a film between sodium chloride discs; samples of solids as KBr pellets or Nujol mulls. 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.

A few general comments concerning the carrying out of such reactions at low temperature are in order. The most important consideration is temperature control, which is accomplished with a Dewar flask only partially filled with liquid nitrogen, although with larger flasks (2 or 3 liter) a polyurethane

bucket served adequately. The surface of the liquid nitrogen is kept just below the bottom of the reaction flask and the Dewar flask is usually positioned so that the reaction flask is as far inside the Dewar flask as possible. These criteria are readily met if one uses a laboratory jack to continually readjust the Dewar flask as the level of the liquid nitrogen decreases. Whenever heat must be removed from the reaction, the Dewar flask may be raised to surround the reaction flask with liquid nitrogen, which extracts heat at a very convenient rate for most reactions. The addition of reagents generally requires considerable heat extraction to keep the temperature under control. Although these procedures require a considerable amount of continuous attention to the reaction and a certain amount of manual dexterity during the addition operations, the use of liquid nitrogen permits very rapid (1-15 min) additions of reagents that would take much longer using a cryostatic bath. The temperatures cited in the experimental detail for various reactions are the stem temperatures observed with the particular apparatus described and are probably 5-10° higher than actual. The pentane thermometers used (Walter H. Kessler Co., Inc., +30° to −200°C) were apparently a total immersion thermometer and found to read −71° (bulb immersion) versus −77° (total immersion) in a dry ice—acetone bath. Since most of the procedures described involved only bulb immersion, the temperatures are probably somewhat high.

Finally, it is preferable to avoid as much freezing of the reaction mixture as possible. If the glass stirrer shaft protrudes very far out of the bearing, then a suddenly freezing or asymmetric lumpy mixture may result in a stirrer shaft snapping off. A second reason is that it is difficult to completely melt a frozen solution, or portion of a solution, without the liquid phase warming appreciably, at, or near to a decomposition temperature. The best method for avoiding freezing is to use an adequate solvent system, either a THF—Et_2O or THF—Me_2O system [26] which has a low enough freezing point.

gem-Dibromocyclopropanes were prepared by reaction of the bromoform/potassium t-butoxide reagent with the respective olefins [27]. Methylenecyclohexane was obtained by the method of Villieras [28]. The other olefins were commercial products, as were the chlorosilanes (Union Carbide Corp.), the organotin halides (M&T Chemicals, Inc.), triphenyllead chloride (Deutsche Advance Produktion GmbH), n-butyllithium and methyllithium (Alfa/Ventron).

The preparation and hydrolysis of α-halocyclopropyllithiums

Preparation of 1-bromospiro[2,5]octane. This preparation is fully described as an example of the procedure used for the preparation and protonation of *gem*-halolithiocyclopropanes.

Into a flamed-out 1 liter standard low temperature reaction apparatus was charged 27.83 g (104 mmol) of 1,1-dibromospiro[2.5]octane and 200 ml of freshly distilled THF. After the mixture had been cooled to −95 ± 3°, 70 ml (112 mmol) of 1.6 *M* n-butyllithium was added by syringe during a 5-min period. After it had been stirred for an additional 30 min, the reaction mixture was quenched with 10 ml of concentrated hydrochloric acid added by syringe and the temperature of the reaction was maintained below −70° for 1 h. After the reaction mixture had been warmed to room temperature, the resulting organic layer was washed with 50 ml of water and the organic layer was distilled through

a 30 cm Vigreux column to remove solvents. After the head temperature had reached 71°, the cooled pot residue was trap-to-trap distilled (60°/0.05 mmHg). The distillate was redistilled at reduced pressure through a short path head to yield two fractions: (1) 1.5 g boiling range 50-85°/20 mmHg and (2) 12.07 g (61%) of b.p. 87-89°/20 mmHg. Analytical sample was isolated by preparative GLC (10% UC-W98, 165°), n_D^{25} 1.5004. Fraction 2 was about 96% pure as distilled. Anal. found: C, 51.11; H, 6.86; Br, 41.81. $C_8H_{13}Br$ calcd.: C, 50.82; H, 6.93; Br, 42.25%. NMR (CCl_4, CH_2Cl_2): δ 2.72 (dd, 1H, *J* 4.0, 6.0 Hz, CHBr), 2.3-1.0 (m, 10H, C_5H_{10} bridge), and 1.0-0.40 ppm (m, 2H, cyclopropyl H).

Other reductions are summarized in Table 5.

Preparation of α-halocyclopropylsilanes

Preparation of 1-bromo-1-trimethylsilylspiro[2.5]octane. This preparation is fully described as an example of the procedure used for the silylation of *gem*-halolithiocyclopropanes.

Into a flamed-out 500 ml standard low temperature reaction apparatus was charged 13.4 g (50 mmol) of 1,1-dibromospiro[2.5]octane and 100 ml of THF. The mixture was cooled to −95 ± 2° and then 35 ml (56 mmol) of 1.6 *M* n-butyllithium was added during a 5-min period. After the mixture had been stirred for 50 min, 8.0 ml (62 mmol) of trimethylchlorosilane was added and the mixture was stirred for an additional 2 h before it was allowed to warm to room temperature. The mixture was hydrolyzed with 100 ml of water (back extraction with 50 ml hexane) and the organic layers were combined and concentrated by distilling most of the solvents through a 30 cm Vigreux column. The pot residue was vacuum distilled through a short path head to yield 9.83 g (75%) of 1-bromo-1-trimethylsilylspiro[2.5]octane of b.p. 51-52°/0.10 mmHg, n_D^{25} 1.4994. An analytical sample was obtained by redistillation. Anal. found.: C, 50.39; H, 8.14; Br, 30.95. $C_{11}H_{21}BrSi$ calcd.: C, 50.56; H, 8.10; Br, 30.58%. NMR (CCl_4, $CHCl_3$): δ 2.0-1.4 (m, 10H, $(CH_2)_5$), 0.93 (s, 2H, cyclopropyl H) and 0.25 ppm (s, 9H, Me_3Si). IR (film): 3050w, 2990(sh), 2960(sh), 2930vs, 2910(sh), 2860s, 2670w, 1560w, 1450m, 1445m, 1410w, 1375w, 1321w, 1315w, 1282w, 1267m, 1253vs, 1210w, 1150w, 1140w, 1123m, 1055m, 1040m, 1003w, 960m, 938m, 925m, 892w, 860vs, 845vs, 770m, 735w, 707m, 697m.

Other reactions leading to trimethylsilyl derivatives are summarized in Table 6.

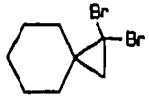
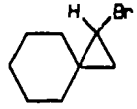
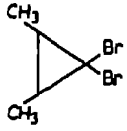
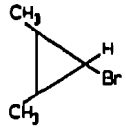
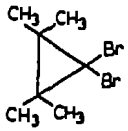
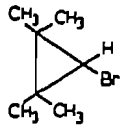
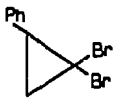
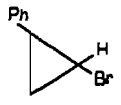
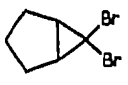
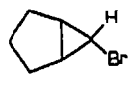
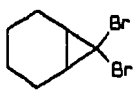
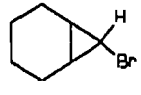
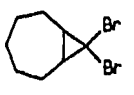
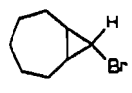
Reduction of α-bromocyclopropyltrimethylsilanes via Grignard intermediates

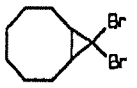
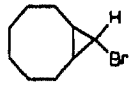
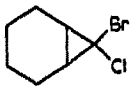
Into a 50 ml, three-necked flask equipped with a mechanical stirrer, reflux condenser (nitrogen inlet tube), and an addition funnel was placed 0.33 g (13.6 mmol) of magnesium turnings and the apparatus was flamed out. After cooling, 2 ml of THF was added to the magnesium and the addition funnel was charged with a solution of 2.16 g (8.7 mmol) of *syn*-7-bromo-*anti*-7-trimethylsilylnorcarane in 8 ml of THF. After a few drops of the solution had been added, the reaction was initiated by addition of 40 μl (0.4 mmol) 1,2-dibromoethane and the rest of the solution was added dropwise. After the reaction mixture had cooled to room temperature, it was hydrolyzed with saturated ammo-

(continued on p. 272)

TABLE 5

PREPARATION OF MONOHALOCYCLOPROPANES: EXPERIMENTAL DETAILS

gem-Dihalocyclopropane (mmol)		Mmol n-BuLi; solvents (ml)	Exchange time (min); temp. (°C)	Concentrated HCl (mmol)	Monohalocyclopropane [a] (% yield)		B.p. (°C/mmHg)	Literature reference
	(104)	112; THF (200)	30; −95	115		(61)	87-89 (20)	
	(100)	110 [b]; THF (150), Et_2O (50)	20; −105	112		(68)	119-125 (atm)	29
	(53)	56; THF (150), Et_2O (50)	15; −103	56		(76)	86-88 (100)	9d
	(100)	104; THF (150), Et_2O (50)	20; −98	100		(84)	50-51 (0.2)	9d
	(50)	53; THF (75), Et_2O (25)	20; −109	50		(50) [c]	56-58 (22)	
	(50)	56; THF (75), Et_2O (25)	30; −106	50		(79) [d]	84-86 (23)	9d
	(50)	53; THF (75), Et_2O (25)	20; −100	50		(84)	55-58 (1.0)	30

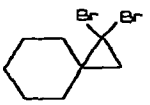
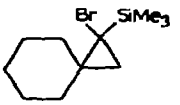
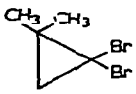
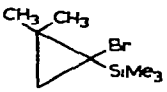
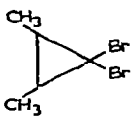
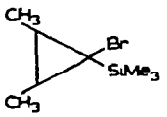
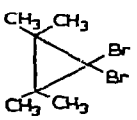
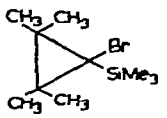
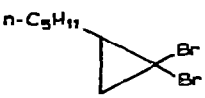
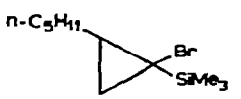
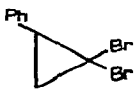
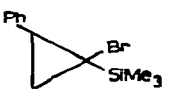
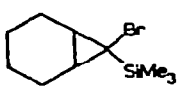
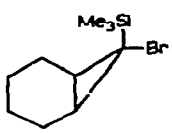
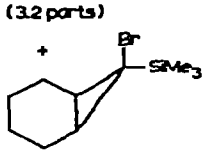
	(50)	53; THF (75), Et_2O (25)	20; −102	50		(66)	61-64 (1.0)	9d
	(53)	48; THF (75), Et_2O (25)	25; −85	50		(62)	73-75 (23)	9d

[a] For *syn*-Br/*anti*-Br isomer ratios, see Table 1. [b] t-butyllithium. [c] An authentic sample of a mixture of both isomers was prepared by tri-n-butyltin hydride reduction [9d] of 6,6-dibromobicyclo[3.1.0]hexane in 54% yield, b.p. 46-49° at 10 mmHg. The NMR spectrum of the distilled product showed inter alia two triplets at δ 3.30 (J 7.5 Hz) and 2.46 ppm (J 1.5 Hz), in a relative area ratio of 1.3/1. On the basis of relative H—H coupling constants [9], the more abundant isomer is assigned as *syn*-6-bromobicyclo[3.1.0]hexane and the minor isomer as the *anti*-6-bromo derivative). (Found (isomer mixture): C, 44.54; H, 5.56; Br, 49.95. C_6H_9Br calcd.: C, 44.75; H, 5.62; Br, 49.63%.) [d] Use of a slight excess of 7,7-dibromobicyclo[4.1.0]hexane in this reaction gave a *syn*/*anti* isomer ratio of 1/12 in one experiment.

nium chloride solution. The organic layer was decanted and the solid cake was dissolved in 1 *M* hydrochloric acid and 20 ml of Et_2O. The combined ether layers were dried over sodium sulfate and then most of the solvents were removed by distillation through a 20 cm Vigreux column. The pot residue was trap-to-trap distilled (room temp./0.06 mmHg) to yield 1.85 g of distillate which was analyzed by GLC (20% DC-200, 155°) and found to contain 1.79

TABLE 6

PREPARATION OF α-BROMOCYCLOPROPYLTRIMETHYLSILANES: EXPERIMENTAL DETAILS

gem Dihalocyclopropane (*mmol*)	Mmol n-BuLi: solvents (ml)	Exchange time (min): temp. (°C)	Me_3SiCl (mmol)	Product [a] (% yield)
 (50)	56: THF (100)	50: −95	62	 (75)
 (400)	400: THF (500)	50: −95	400	 (67)
 (100)	112: THF (150), Et_2O (50)	30: −102	117	 (47)
 (51)	56: THF (150) Et_2O (50)	20: −105	62	 (31)
 (50)	56: THF (100)	20: −95	55	 (78)
 (150)	160: THF (225), Et_2O (75)	25: −102	150	 (73)
 (100)	112: THF (150)	15; −95	120	 composed of: (74)  (3.2 parts) +  (1 part)

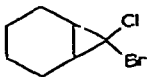
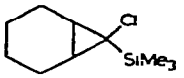
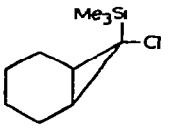
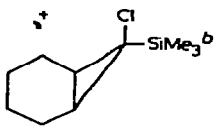
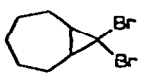
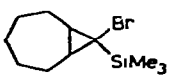
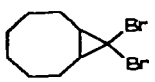
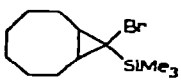
mmol (21%) of *syn*-7-trimethylsilylnorcarane and 5.41 mmol (63%) of *anti*-7-trimethylsilylnorcarane. Samples were isolated by preparative GLC (column as above, 140°) and identified by comparison of their NMR spectra with those of authentic samples [10].

The same procedure, work-up and yield determination were used in the analogous reaction of *anti*-7-bromo-*syn*-7-trimethylsilylbicyclo[4.1.0]heptane,

B.p. (°C, mmHg)	n_D^{25}	Analysis found (calcd.) (%)			NMR spectrum, δ (ppm in CCl_4)
		C	H	Br	
51-52 (0.10)	1.4994	50.39 (50.56)	8.14 (8.10)	30.95 (30.58)	2.0-1.4 (m, 10H, $(CH_2)_5$) 0.93 (s, 2H, cyclopropyl H) 0.25 (s, 9H, Me_3Si)
60-62 (8.0)	1.4717	43.01 (43.43)	7.61 (7.75)	35.60 (36.12)	1.46 (s, 3H, CH_3C) 1.02 (s, 3H, CH_3C) 0.95 (s, 2H, cyclopropyl H) 0.22 (s, 9H, Me_3Si)
72-75 (15)		43.81 (43.43)	7.75 (7.75)	36.27 (36.12)	1.80-1.40 (m, 2H, cyclopropyl H) 1.14 (d, J 6 Hz, 6H, CH_3C) 0.10, 0.25 (s, 9H, Me_3Si; ~1/1 height ratio)
m.p. 87-88 (sublimes)		48.40 (48.18)	8.46 (8.49)	32.50 (32.05)	2.32 (s, 6H, CH_3C) 2.27 (s, 6H, CH_3C) 0.32 (s, 9H, Me_3Si)
66-68 (1.0)		50.50 (50.20)	8.88 (8.80)	30.24 (30.33)	1.9-0.50 (m, 14H, C_5H_{11} + cyclopropyl H) 0.18, 0.07 (s, 9H, Me_3Si; 1.2/1 height ratio
60-62 (0.10) 53-54 (0.4)		53.67 (53.52)	6.58 (6.36)	29.24 (29.67)	7.3 (broad s, 5H, Ph) 2.90 (t, J 4 Hz, 1H, Ph—C—H) 1.48 (d of d, 2H, J 2 and 4 Hz, cyclopropyl H) 0.18, −0.12 (s, 9H, Me_3Si; 1/6 height ratio)
	1.5102	48.92 (48.58)	7.62 (7.74)	32.53 (32.32)	2.4-1.0 (m, 10H, $(CH_2)_4$ and cyclopropyl H) 0.20 (s, 9H, Me_3Si)
	1.4995	48.64 (48.58)	7.71 (7.74)	32.39 (32.32)	2.4-0.5 (m, 10H, $(CH_2)_4$ and cyclopropyl H) 0.07 (s, 9H, Me_3Si)

(Table continued)

TABLE 6 (continued)

gem-Dihalocyclopropane (mmol)		Mmol n-BuLi; solvents (ml) temp. (°C)	Exchange time (min);	Me_3SiCl (mmol)	Product [a] (% yield)	
	(53)	56: THF (75), Et_2O (25)	30; −95	62	 composed of:  (1 part)  (145 parts)	(70)
	(50)	56: THF (75), Et_2O (25)	20; −102	62		(67)
	(101)	112: THF (150), Et_2O (50)	25; −100	117		(65)

[a] For *syn*-Br/*anti*-Br isomer ratio, see Table 2. [b] This isomer had been prepared before in these laboratories by Me_3SiCCl transfer to cyclohexene using the $(Me_3SiCCl_2)_2Hg/Ph_2Hg$ reagent [21]. It was characterized, but in the absence of the other isomer, its structural assignment as the above isomer was only tentative.

except that 0.23 g (9.5 mmol) of magnesium and 0.51 g (2.07 mmol) of *anti*-7-bromo-*syn*-7-trimethylsilylnorcarane in 6 ml of THF were used as reagents. GLC analysis of the trap-to-trap distillate (0.72 g) showed the presence of 0.40 mmol (19%) of *syn*-7-trimethylsilylnorcarane and 1.01 mmol (49%) of *anti*-7-trimethylsilylnorcarane.

A mixture of 9-bromo-9-trimethylsilylbicyclo[6.1.0]nonane isomers (2.3/1 *syn*-Br/*anti*-Br ratio) was converted to a mixture of *syn*- and *anti*-9-trimethylsilylbicyclo[6.1.0]nonane by conversion to the Grignard reagent and hydrolysis of the latter by reaction of 53 mmol of magnesium turnings and 40 mmol of the isomer mixture in 30 ml of THF using the procedure described for the reduction of the 7-bromo-7-trimethylsilylnorcaranes. The organic layer was distilled (after an initial trap-to-trap distillation) to give 9-trimethylsilylbicyclo-[6.1.0]nonane in 55% yield, b.p. 48°/0.4 mmHg. The isomers were separated by GLC (20% UC-W98, 150°). Their structures were assigned on the basis of their $J(H_{1,8})$—$J(H_9)$ coupling constants [10]. Anal. found (mixed isomers): C, 73.27; H, 12.22. $C_{12}H_{24}Si$ calcd.: C, 73.38; H, 12.32%. The first isomer to be eluted was *anti*-9-trimethylsilylbicyclo[6.1.0]nonane; n_D^{25} 1.4670; NMR (CCl_4,

TABLE 6 (continued)

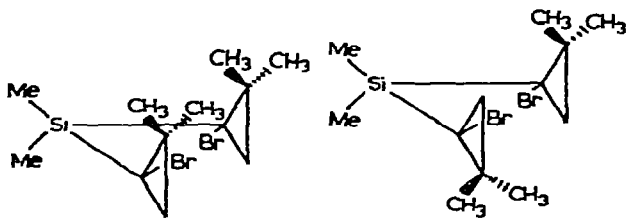
B.p. (°C, mmHg)	n_D^{25}	Analysis found (calcd.) (%)			NMR spectrum, δ (ppm in CCl_4)
		C	H	Br	
61-65 (1.2)		59.27 (59.23)	9.49 (9.44)	17.38 (17.48)	
					2.3-1.1 (m, 10H, $(CH_2)_4$ and cyclopropyl H) 0.30 (s, 9H, Me_3Si)
					2.2-0.9 (m, 10H, $(CH_2)_4$ and cyclopropyl H) 0.08 (s, 9H, Me_3Si)
56-61 (0.1)		50.92 (50.56)	8.15 (8.10)	30.98 (30.58)	2.4-0.7 (m, 12H, $(CH_2)_5$ and cyclopropyl H) 0.30, 0.06 } (s, 9H, Me_3Si; 12.5/1 height ratio)
70-73 (0.05)		52.62 (52.36)	8.14 (8.36)		2.3-0.6 (m, $(CH_2)_6$ and cyclopropyl H) 0.28, 0.09 } (s, 9H, Me_3Si; 2.3/1 height ratio)

$CHCl_3$): δ 2.1-0.2 (m, 14H, $(CH_2)_6$ and $H_{1,8}$), −0.08 (s, 9H, Me_3Si) and −1.0 ppm (t, 1H, *J* 6.0 Hz, H_9). The second isomer to be eluted was the *syn*-9-trimethylsilyl compound; n_D^{25} 1.4778; NMR (CCl_4, $CHCl_3$): δ 2.1-0.7 (m, 14H, $(CH_2)_6$ and $H_{1,8}$), 0.05 (s, 9H, Me_3Si) and −0.20 to −0.60 ppm (m, 1H, H_9).

Some other α-bromocyclopropylsilanes were prepared using this general procedure.

Bis(1-bromo-2,2-dimethylcyclopropyl)dimethylsilane. By reaction of 1.0 mol of 1,1-dibromo-2,2-dimethylcyclopropane with 1.0 mol of n-butyllithium (in hexane) (1.1 liter THF, exchange time 40 min at −95°), followed by addition of 0.47 mol of dimethyldichlorosilane (1.5 h reaction time). The work-up involved concentration of the reaction mixture to about 300 ml by distillation, separation of the liquid phase of the residue and trap-to-trap distillation (room temp./0.01 mmHg) and fractional distillation. Two products were obtained: (a) 30.1 g (25%), b.p. 65-67°/10 mmHg, whose NMR spectrum suggested that it was 1-bromo-2,2-dimethylcyclopropyldimethylchlorosilane. This material was not further characterized. NMR (CCl_4, $CHCl_3$): δ 1.48 and 1.39 (s, each 3H, CH_3C), 1.30 1.17, 1.02, 0.92, 0.81, 0.75 (all s, 2H, cyclopropyl CH_2) and 0.70, 0.60 ppm (s, 6H, Me_2ClSi). (b) 85.0 g, b.p. 75-78°/0.01 mmHg, redistilled 63-64° at 0.02 mm, n_D^{25} 1.5184, the title compound.

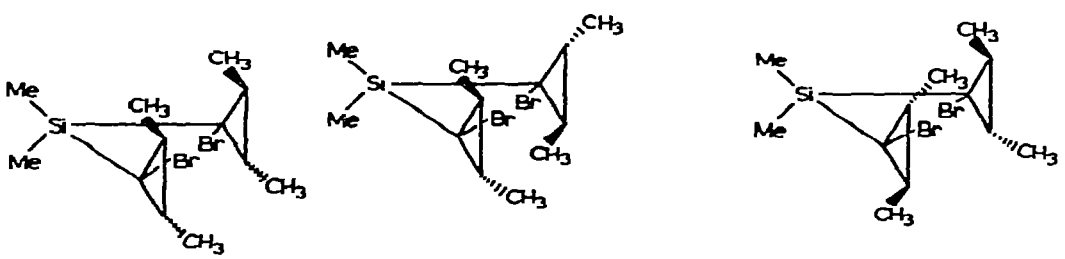
Anal. found: C, 40.53; H, 6.28; Br, 45.15. $C_{12}H_{22}Br_2Si$ calcd.: C, 40.69; H, 6.26; Br, 45.12). NMR (CCl_4, $CHCl_3$): δ 1.50 and 1.30 (s, each 6H, CH_3C), 1.10 (t, J 3.0 Hz, 4H, cyclopropyl CH_2), 0.32 (s, 3H, Me_2Si) and 0.28 ppm (two s separated by 5 Hz, 3H, Me_2Si). For this compound there are three possible isomers, *d*, *l* and *meso* (formulas below), and the NMR spectrum indicates that all three may have been formed. These, however, could not be separated by GLC since the compounds decomposed under the experimental conditions.



"meso" "d" "l"

Bis(1-bromo-trans-2,3-dimethylcyclopropyl)dimethylsilane. By reaction of 0.20 mol of 1,1-dibromo-*trans*-2,3-dimethylcyclopropane and 0.20 mol of n-butyllithium (250 ml THF, exchange time 15 min at —95°), followed by addition of 0.10 mol of dimethyldichlorosilane. Subsequent hydrolysis (100 ml of water), concentration of the organic layer, extraction of the latter with 200 ml of hexane and evaporation of the hexane extracts followed. The residue was crystallized from methanol with cooling only to room temperature. The first crop, 4.1 g (11%), had m.p. 95-97° and was characterized as one of the possible isomers of the title compound. Anal. found: C, 40.90; H, 6.33; Br, 45.22. $C_{12}H_{22}Br_2Si$ calcd.: C, 40.69; H, 6.26; Br, 45.12%. NMR (CCl_4, $CHCl_3$): δ 1.36, 1.27, 1.16, 1.13 (s, 12H total, CH_3C), 1.0-0.5 (m, 4H, cyclopropyl H) and 0.22 ppm (s, 6H, Me_2Si).

The mother liquor gave another 9.4 g of solid in three crops, which all had lower, long melting ranges, 56-64°. NMR spectra showed these crops to be an apparent mixture of isomers, *meso*, *d* and *l* (formulas below), with another CH_3Si resonance at δ 0.13 ppm in addition to the 0.22 ppm signal. Attempts to fractionally crystallize these mixtures from methanol failed.



"meso" "d" "l"

Bis(1-bromo-2,2-dimethylcyclopropyl)methylsilane. By reaction of 200 mmol of 1,1-dibromo-2,2-dimethylcyclopropane and 207 mmol of n-butyllithium (250 ml THF, exchange time 30 min at —95°) followed by addition of 100 mmol of methyldichlorosilane. Product in 49% yield, b.p. 71-73°/0.10

mmHg. Anal. found: C, 39.01; H, 5.99; Br, 46.26. $C_{11}H_{20}Br_2Si$ calcd.: C, 38.83; H, 5.92; Br, 46.99%. IR: ν(Si—H) at 2145 cm^{-1}. NMR (CCl_4, $CHCl_3$): δ 4.35 (q, 1H, J 3.5 Hz, SiH), 1.50, 1.35 (s, 12H, CH_3C), 1.30-1.00 (m, 4H, cyclopropyl H) and 0.50-0.40 (m, 3H, MeSi).

Preparation of other α-bromocyclopropylmetal compounds (Table 3)

Preparation of 1-bromo-1-trimethylstannylspiro[2.5]octane. This preparation is fully described as an example of the procedure used in the preparation of *gem*-heavy-metal derivatives of bromocyclopropanes.

Into a flamed-out 500 ml standard low temperature reaction apparatus was charged 13.4 g (50 mmol) of 1,1-dibromospiro[2.5]octane and 100 ml of freshly distilled THF. After the mixture had been cooled to —90 ± 2°, 35 ml (56 mmol) of 1.6 *M* n-butyllithium was added during a 5-min period and then the mixture was stirred at —95 ± 5° for the remainder of the reaction time. After the mixture had been stirred for 20 min, it was treated with a solution of 10.0 g (50 mmol) of trimethyltin chloride dissolved in 25 ml of THF. The mixture was stirred for an addition hour, and then allowed to warm to room temperature. The solvents were removed on a rotary evaporator (room temp./ca. 20 mmHg) and the residue was dissolved in a mixture of 100 ml water/125 ml hexane. The hexane layer was filter-dried though anhydrous sodium sulfate and evaporated to yield a light yellow oil. The oil was trap-to-trap distilled (65°/0.05 mmHg) and then redistilled through a short path fractionating head to yield 13.9 g (79%) of 1-bromo-1-trimethylstannylspiro[2.5]octane of b.p. 63-64°/0.05 mmHg, n_D^{25} 1.5335.

1-Bromo-1-trimethylstannyl-cis-2,3-dimethylcyclopropane. By reaction of 100 mmol of 1,1-dibromo-*cis*-2,3-dimethylcyclopropane with 105 mmol of n-butyllithium (200 ml THF, 50 ml Et_2O, exchange time 20 min at —100°), followed by addition of 100 mmol of Me_3SnCl in 70 ml THF. Product in 66% yield, b.p. 51-52°/1.3 mmHg, *syn*-Br/*anti*-Br isomer ratio 1/2 (by NMR integration of the Me_3Sn resonances at δ 0.13 and 0.27 ppm, respectively).

In another experiment (100 mmol of the dibromocyclopropane, 96 mmol of n-butyllithium, 200 ml THF, 5 min at —98°, 15 min at —88°, 87 mmol Me_3SnCl) the organic layer was evaporated, treated with 100 ml each of pentane and water. The dried pentane layer was concentrated and chilled to give a white solid which was recrystallized twice from warm methanol to give 2.5 g of white needles, m.p. 89-91°, dec. at 142°. Anal. found: C, 30.33; H, 5.40; Br, 25.18. $C_8H_{17}BrSn$ calcd.: C, 30.82; H, 5.49; Br, 25.62%. NMR (CCl_4, $CHCl_3$): δ 1.9-1.4 (m, 2H, cyclopropyl H), 1.2-1.0 (asym. d, J 6.0 Hz, CH_3C) and 0.27 ppm (s, 9H, $J(^{117,119}Sn—H)$ 53, 55 Hz, Me_3Sn). Cleavage of this solid with anhydrous hydrogen chloride in chloroform gave only *anti*-1-bromo-*cis*-2,3-dimethylcyclopropane and thus the solid is *anti*-1-bromo-*syn*-1-trimethylstannyl-*cis*-2,3-dimethylcyclopropane.

The preparations of other α-bromocyclopropylmetal compounds are summarized in Table 7.

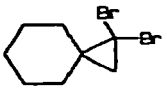
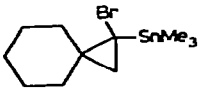
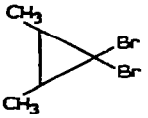
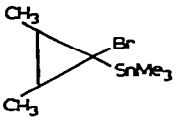
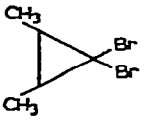
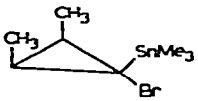
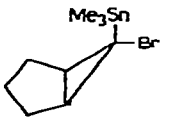
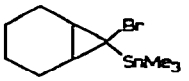
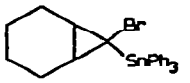
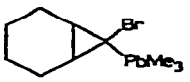
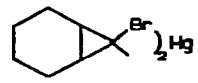
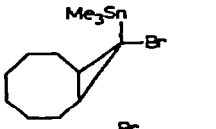
Preparation of 2-t-butyl-anti-7-bromonorcarane

Into a flamed-out 500 ml standard low temperature reaction apparatus

(continued on p. 282)

TABLE 7

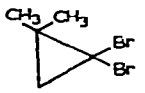
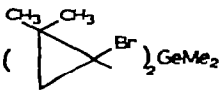
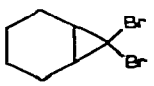
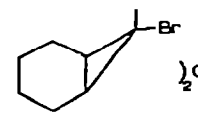
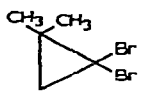
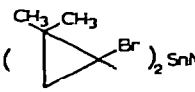
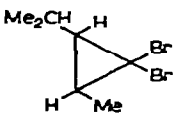
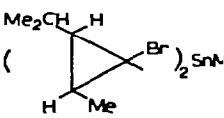
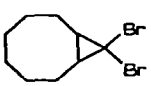
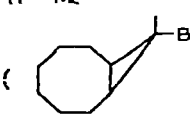
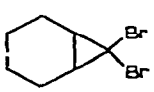
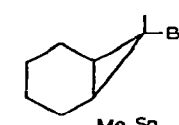
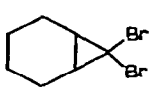
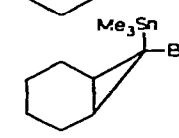
PREPARATION OF α-BROMOCYCLOPROPYLMETAL COMPOUNDS: EXPERIMENTAL DETAILS

gem-Dihalocyclopropane (mmol)		Mmol n-BuLi solvents (ml)	Exchange time (min); temp. (°C)	Metal halide (mmol)	Product [a] (% yield)	
	(50)	56: THF (150)	20; −95	Me_3SnCl (50) (in 25 ml THF)		(79)
	(100)	150: THF (200); Et_2O (50)	20; −100	Me_3SnCl (100) (in 70 ml THF)		(66)
	(100)	96: THF (200)	5; −98 and 15; −88	Me_3SnCl (87) (in 50 ml THF)		
	(200)	208: THF (300)	25; −98	Me_3SnCl (195) [b] (in 60 ml THF)		(23)
	(100)	112: THF (150)	15; −95	Me_3SnCl (80) (in 100 ml THF)		(71)
	(100)[c]	112: THF (150)	60; −95	Ph_3SnCl (90) (in 75 ml THF) [d]		(19)
	(100)	104: THF (150)	25; −95	Ph_3PbCl (93) (in 150 ml THF) [e]		(20)
	(100)	104: THF (200); Et_2O (50)	20; −103	Me_3PbBr (100) (in 60 ml THF) [f]		(75)[g]
	(214)	213: THF (500)	25; −95	$HgCl_2$ (100) [h] (in 50 ml THF)		(62)
	(200)	208: THF (350)	30; −98	Me_3SnCl (195) (in 10 ml THF)		(48)[i] (10)

M.p. (°C) or b.p. (°C, mmHg)	Analysis found (calcd.) (%)			NMR spectrum, δ (ppm in CCl_4)
	C	H	Br	
63-64 (0.05) [n_D^{25} 1.5335]	37.62 (37.55)	6.00 (6.02)	23.10 (22.71)	1.8-1.0 (m, 10H, $(CH_2)_5$) 0.90 (s, 2H, cyclopropyl H) 0.23 (s, 9H, Me_3Sn, $J(^{117,119}Sn-H)$ 52,54 Hz
51-52 (1.3)	(individual isomers analyzed)			1.9-1.4 (m, 2H, cyclopropyl H) 1.2-1.0 (asym, d, 6H, CH_3C) 0.13 0.27 } (s, 9H, Me_3Sn, $J(^{117,119}Sn-H)$ 53, 55 Hz; height ratio 1/2.03)
m.p. 89-91	30.33 (30.82)	5.40 (5.49)	25.18 (25.62)	0.27 (s, 9H, Me_3Sn)
50.5-51.5 (0.03)	33.44 (33.38)	5.28 (5.29)	24.81 (24.68)	2.1-1.9 (m, 8H, $(CH_2)_3$ and cyclopropyl H) 0.30 (s, 9H, Me_3Sn, $J(^{117,119}Sn-H)$ 52, 55 Hz)
	(isomers characterized separately)			-0.34 0.10 } (s, 9H, Me_3Sn, with $^{117,119}Sn$ satellites; height ratio 4.3/1)
m.p. 121.5-123	57.25 (57.29)	4.82 (4.81)	15.68 (15.25)	8.3-7.2 (m, 15H, Ph) 2.3-0.7 (m, 10H, $(CH_2)_4$ and cyclopropyl H)
m.p. 108-109.5	49.05 (49.02)	4.10 (4.08)		7.8-6.9 (m, 15H, Ph) 2.3-0.7 (m, 10H, $(CH_2)_4$ and cyclopropyl H)
74-75 (0.07)	28.63 (28.17)	4.64 (4.49)		2.2-0.9 (m, 10H, $(CH_2)_4$ and cyclopropyl H) 1.01 0.81 } (s, 9H, Me_3Pb, $J(^{207}Pb-H)$ 61 Hz, height ratio 2.5/1)
m.p. 94-96	30.66 (30.64)	3.65 (3.67)		2.6-0.8 (all H, maxima at 1.90 and 2.43 ppm)
m.p. 58-59.5 (from MeOH)	39.33 (39.39)	6.19 (6.34)	22.04 (21.84)	2.3-0.8 (m, 14H, $(CH_2)_6$ and cyclopropyl H) 0.27 (s, 9H, Me_3Sn, $J(^{117,119}Sn-H)$ 52, 55 Hz)
liquid	(not characterized [f])			0.15 (s, 9H, Me_3Sn, $J(^{117,119}Sn-H)$ 52, 55 Hz)

(Table continued)

TABLE 7 (continued)

gem-Dihalocyclopropane (mmol)		Mmol n-Bu-Li solvents (ml)	Exchange time (min). temp. (°C)	Metal halide (mmol)	Product [a] (% yield)	
	(182)	180: THF (400)	120: −95	Me_2GeCl_2 (84) (in 60 ml THF)		(70) [k]
	(197)	190: THF (250)	5: −95 and 25: −85	Me_2GeCl_2 (90) (added at −100)		(48) [m]
	(77)	75: THF (150)	60: −95	Me_2SnCl_2 (35) (in 50 ml THF)		(65) [n,o]
	(85.5) [p]	83: THF (150)	30: −100	Me_2SnCl_2 (37) (in 50 ml THF)		(55) [q]
	(175)	170: THF (200)	5, −95 and 40: −85	Me_2SnCl_2 (80) (in 50 ml THF, added at −95)		(23)
	(216)	200, THF (300)	5: −95 and 25: −85	Me_2SnCl_2 (100) [r] (in 40 ml THF, added at −98)		(54)
	(209)	200: THF (400)	10: −95 and 30: −85	Me_3SnCl (200) [s] (in 80 ml THF, added at −100)		(63)

[a] For *syn*-Br/*anti*-Br isomer, see Table 3. [b] Residue after rotary evaporation was treated with ca. 500 ml of 10% potassium fluoride solution (back extraction with 400 ml of hexane). The organic solvents were evaporated and the balance of the usual procedure was followed. [c] Experiment by Marcia J. Keyes. [d] The solid residue left after rotary evaporation of the solvents was shaken with 50 ml of 10% potassium fluoride solution and the liquid was decanted. The residual solid was crystallized from 2/1 hexane/chloroform. [e] The solid residue left after rotary evaporation of solvent was recrystallized from hot hexane. [f] The solvents were removed by rotary evaporation without heating. The residue was treated with 250 ml of water, 250 ml of hexane, and 50 ml of 10% potassium fluoride solution. The hexane was removed by rotary evaporation. The resulting pale yellow oil was trap-to-trap distilled (0.05 mm) using an oil bath at 90°. The distillate was redistilled without water cooling. [g] A sample of the mixture was dissolved in $CDCl_3$ in an NMR tube and treated with hydrogen chloride. The resulting NMR spectrum had resonances for both *syn*- and *anti*-7-bromonorcarane in the ratio of 1.0/2.8, respectively. [h] The solid residue after rotary evaporation was partitioned between 500 ml of benzene and 200 ml of water. The benzene was evaporated and the resulting oil was recrystallized from 150 ml of hot hexane. [i] The distillate solidified partially; solid was recrystallized from absolute methanol to yield 22.1 g (30%) of one isomer; residue redistilled to yield 19.1 g (27%) of b.p. 90-94°/0.1 mmHg. Further crystallization of the distillate gave another 18% of solid. The yield of the other isomer was estimated on the basis of the relative heights of the trimethyltin resonances in the distillate at δ 0.28 and 0.15 ppm, respectively. The solid isomer was cleaved with HCl to *anti*-9-bromobicyclo-[6.1.0]nonane. [j] Characterized in later studies; to be published. [k] A forecut, b.p. 70-78° (0.04 mmHg) contained (GLC, NMR) Me_2GeBr_2 and dimethyl(1-bromo-2,3-dimethylcyclopropyl)bromogermane. At-

TABLE 7 (continued)

M.p. (°C) or b.p. (°C, mmHg)	Analysis found (calcd.) (%)			NMR spectrum, δ (ppm in CCl_4)
	C	H	Br	
78-80 (0.04) [n_D^{25} 1.5322]	36.03 (36.14)	5.52 (5.56)	40.03 (40.08)	1.46, 1.27 } (s, each 6H, CH_3 C) [l] 0.47, 0.42 } (s, 6H, Me_2Ge)
m.p. 116-117 (from MeOH)	42.53 (42.62)	5.81 (5.81)	35.33 (35.46)	2.5-1.1 (m, 20H, $(CH_2)_3$ and cyclopropyl H) 0.63 (s, 6H, Me_2Ge)
95-96 (0.02) [n_D^{25} 1.5437]	32.82 (32.40)	5.04 (4.98)	36.68 (35.93)	2.53, 2.15 } (s, each 6H, CH_3C) 0.43 (2s, 1 Hz separation, Me—Sn) 0.33 (s, Me—Sn)
115-116 (0.02) [n_D^{25} 1.5203]	38.25 (38.36)	5.96 (6.04)	32.49 (31.91)	
m.p. 124-125 (from MeOH)	43.41 (43.40)	6.14 (6.20)	28.78 (28.90)	2.5-0.8 (m, $(CH_2)_6$ and cyclopropyl H) 0.43 (s, 9H, Me_3Sn)
m.p. 99-100	38.58 (38.67)	5.29 (5.27)	32.45 (32.16)	2.2-0.9 (m, 20H, $(CH_2)_3$ and cyclopropyl H) 0.56 (s, 6H, Me_2Sn, $J(^{117,119}Sn—H)$ 50, 53 Hz)
52-53 (0.01) [n_D^{25} 1.5480]	35.95 (35.55)	5.71 (5.67)	23.82 (23.65)	2.1-0.9 (m, 10H, $(CH_2)_3$ and cyclopropyl H) 0.32 (s, 9H, Me_3Sn, $J(^{117,119}Sn—H)$ 52, 55 Hz)

tempted purification and isolation of the latter by distillation or GLC failed, α-elimination giving Me_2GeBr_2 and $Me_2C{=}C{=}CH_2$ (ν(C=C=C) 1965 cm^{-1}, δ(CH_2) at 4.46 ppm). [l] The NMR spectrum suggests the presence of isomers, as in the case of the reaction of this lithium reagent with Me_2SiCl_2. [m] In another very similar experiment, this compound was isolated in 27% yield. In addition, distillation of the mother liquor gave another 11% of product, b.p. 147-148° at 0.05 mmHg, which contained this compound (3 parts) and the corresponding isomer (2 parts) with one 7-*syn*-bromonorcaranyl and one 7-*anti*-bromonorcaranyl substituent (δ(CH_3—Ge) 0.44 ppm). [n] In another experiment (290 mmol, 1,1-dibromo-2,2-dimethylcyclopropane), the prolonged application of heat during distillation (130° oil bath) resulted in considerable α-elimination giving $Me_2C{=}C{=}CH_2$, b.p. 40-41°, n_D^{25} 1.4158, in 60% yield, as well as Me_2SnBr_2. The desired product was isolated in 24% yield. [o] The NMR spectrum suggests the presence of isomers, as in the case of the similar reactions of this lithium reagent with Me_2SiCl_2 and Me_2GeCl_2. [p] Prepared from *trans*-4-methyl-2-pentene by the Doering—Hoffmann procedure in 75% yield, b.p. 94-95° (36 mmHg), n_D^{25} 1.4916, correct analysis for C, H and Br. [q] The complex NMR spectrum indicates the presence of a mixture of isomers. [r] The solid residue was dissolved in a mixture of 200 ml of chloroform and 100 ml of water. The organic layer was treated with 50 ml of 10% potassium fluoride solution. The organic layer was separated and the solvents were rotary evaporated. The residue was treated with methanol and the evaporation was continued. The final residue was dissolved in a mixture of hot acetone—methanol and set in a freezer to crystallize. [s] The residue was treated with 50 ml of 10% potassium fluoride solution, 200 ml of water, 200 ml of methylene chloride, and 100 ml of carbon tetrachloride. The organic layer was rotary evaporated and then the residue was trap-to-trap distilled (50°/0.01 mmHg).

was placed 8.0 g (25.8 mmol) of 2-t-butyl-7,7-dibromonorcarane*, 25 ml of Et_2O, and 75 ml of THF and the mixture was cooled to −101 ± 2°. Then 14.5 ml (23.2 mmol) of 1.6 *M* n-butyllithium was added to the mixture and it was then stirred at −85 ± 3° for 20 min. The mixture then was cooled to −105 ± 2° and treated with 2.0 ml (25 mmol) of concentrated hydrochloric acid. After the mixture had been stirred for an additional 15 min, it was allowed to warm. The solution was extracted with 2 × 25 ml of water (back extraction with 30 ml of hexane), filtered, dried over sodium sulfate, and the solvents were removed by rotary evaporation. The residue was vacuum distilled through a short path head to yield 3.67 g (68%) of 2-t-butyl-*anti*-7-bromonorcarane of b.p. 66-68°/0.9 mmHg, n_D^{25} 1.4958. The isomer assignment was based on the results of the next reaction. Anal. found: C, 57.05; H, 8.19; Br, 34.58. $C_{11}H_{19}Br$ calcd.: C, 57.10; H, 8.28; Br, 34.62%. NMR (CCl_4, $CHCl_3$): δ 2.48 (t, 1H, *J* 3.0 Hz, bromocyclopropyl H), 2.4-0.7 (m, 9H, cyclohexyl) and 1.02 ppm (s, 9H, $(CH_3)_3C$).

A mixture of both isomers for comparison was prepared by tri-n-butyltin hydride reduction [9d] of 2-t-butyl-7,7-dibromonorcarane in 75% yield, b.p. 73-77°/0.8 mmHg, n_D^{25} 1.4998. An NMR spectrum showed an *anti/syn* ratio of 1.0/2.8, using the same criteria for isomer assignment which was used for 7-bromonorcarane [9d]. NMR (CCl_4, $CHCl_3$): δ 3.30 (t, 0.7 H, *J* 7.5 Hz, bromocyclopropyl H), 2.50 (t, 0.26H, *J* 3.0 Hz, bromocyclopropyl H), 2.2-0.4 (m, 9H, cyclohexyl) and 1.00 ppm (broadened s, 9H, $(CH_3)_3C$).

Reaction of 2-t-butyl-7,7-dibromonorcarane with a deficiency of n-butyllithium; exchange with 7,7-dibromonorcarane

Into a flamed-out 500 ml standard low temperature reaction apparatus was placed 8.00 g (25.8 mmol) of 2-t-butyl-7,7-dibromonorcarane, 25 ml of Et_2O, and 75 ml of THF. The solution was cooled to −105 ± 3° and then 16.0 ml (25.6 mmol) of 1.6 *M* n-butyllithium was added during a 1-min period. After this mixture had been stirred for 20 min, a solution of 6.80 g (26.8 mmol) of 7,7-dibromonorcarane in 15 ml of Et_2O was added during a 2-min period. Then the mixture was stirred for 25 min at −85 ± 1°. The mixture was cooled to −110 ± 2°, and then the reaction was quenched by adding 2.5 ml (31 mmol) of concentrated hydrochloric acid. The mixture was then stirred for 20 min before it was allowed to warm to room temperature. The mixture was treated with 25 ml of water and then the organic layer was extracted with another 25 ml portion of water (back extraction with 25 ml of hexane). The organic layer was filtered through sodium sulfate and the filtrate was concentrated by distilling most of the solvents through a 30 cm Vigreux column. The pot residue weighed 17.6 g. Yield analysis (10% DC200, 160°) showed the presence of *anti*-7-bromonorcarane, 12.9 mmol (48%), 7,7-dibromonorcarane, 9.0 mmol (34%), 2-t-butyl-*anti*-7-bromonorcarane, 8.7 mmol (34%), and 2-t-butyl-7,7-dibromonorcarane, 15.2 mmol (59%). There was no trace of either of the two possible *syn*-7-bromonorcaranes.

* Prepared in 88% yield by the Doering–Hoffmann procedure; b.p. 66-68°, 0.07 mmHg, n_D^{25} 1.5268.

Reaction of 7,7-dibromonorcarane with a deficiency of n-butyllithium; exchange with 2-t-butyl-7,7-dibromonorcarane

This reaction was carried out at the same time as the preceding reaction; the above procedure was followed identically, with the exception that the order of addition of the two dibromonorcaranes was interchanged. Yield analysis (same conditions) showed the presence of *anti*-7-bromonorcarane, 14.8 mmol (55%), 7,7-dibromonorcarane, 6.8 mmol (25%), 2-t-butyl-*anti*-7-bromonorcarane, 8.2 mmol (32%), and 2-t-butyl-7,7-dibromonorcarane, 16.7 mmol (65%). Again, there was no trace of either of the two possible *syn*-7-bromonorcaranes.

Preparation of anti-7-bromo-syn-7-norcaranylcarboxylic acid

Into a flamed-out 500 ml standard low temperature reaction apparatus was placed 27.7 g (109 mmol) of 7,7-dibromonorcarane and 150 ml of THF. After the mixture had been cooled to —95°, 62 ml (99 mmol) of 1.6 *M* n-butyllithium was added and the mixture was stirred at —85 ± 2° for 25 min. Then the mixture was cooled to —90 ± 3° and approx. 50 g (1.1 mol) of finely crushed (granular) dry ice was added rapidly through a side neck. The mixture was stirred for 15 min and then 10 ml (125 mmol) of concentrated hydrochloric acid was added to the mixture. The mixture was stirred vigorously while it was allowed to warm slowly (expulsion of CO_2). After it reached room temperature, the mixture was rotary evaporated to remove solvents. The residue was dissolved in a mixture of 100 ml water/100 ml chloroform and the organic layer was evaporated. The resulting residue was successively evaporated with 3 × 100 ml portions of added hexane until the residue had solidified. The latter was recrystallized from hot hexane. The white plates were filtered to yield 16.53 g (76%) of *anti*-7-bromo-*syn*-7-norcaranylcarboxylic acid of m.p. 104-106°. The acid was assigned its configuration on the basis of the isomerically pure ester it formed, based on the assumption of a stereospecific quench of a lithium reagent of known configuration. Anal. found: C, 43.93; H, 5.11; Br, 36.54. $C_8H_{11}BrO_2$ calcd.: C, 43.86; H, 5.06; Br, 36.47%. NMR (CCl_4, $CHCl_3$): δ 2.4-0.6 ppm (m, all H, maxima at 1.77, 1.19).

The methyl ester was prepared in 80% yield by esterification of the acid with methanol in the presence of a small amount of concentrated sulfuric acid. The product, *anti*-7-bromo-*syn*-7-carbomethoxynorcarane had b.p. 70-72°/0.4 mmHg, n_D^{25} 1.5043, ν(C=O) 1734 cm^{-1}. Anal. found: C, 46.45; H, 5.64; Br, 34.47. $C_9H_{13}BrO_2$ calcd.: C, 46.37; H, 5.62; Br, 34.27%. NMR (CCl_4, $CHCl_3$): 3.65 (s, 3H, CH_3—O) and 2.0-0.5 ppm (m, 10H, cyclohexyl, two maxima at 1.70 and 1.05).

Reaction of anti-7-bromo-syn-7-lithionorcarane with hexachloroethane

Into a flamed-out 500 ml standard low temperature reaction apparatus was placed 54.0 g (214 mmol) of 7,7-dibromonorcarane and 250 ml of THF. After the mixture had been cooled to —95°, 88 ml (200 mmol) of 2.3 *M* n-butyllithium was added during a 5-min period and then the mixture was stirred for 25 min at —85 ± 2°. Then the mixture was cooled to —98 ± 3° and the serum cap on the side neck was quickly replaced by a 250 ml, flame-dried addition funnel. The funnel was charged with 49.0 g (207 mmol) of hexachloro-

ethane (Eastman Kodak) and 60 ml of THF. The resulting solution was added to the flask as rapidly as possible while maintaining the temperature below —95° which required about 8 min. As the last of the hexachloroethane solution had been added, the pale yellow color of the reaction mixture faded to a colorless solution. The mixture was stirred for 30 min and then it was allowed to warm to room temperature. The reaction mixture was extracted with 2 × 100 ml of water (back extraction with 100 ml of hexane) and the combined organic layers were trap-to-trap distilled (50°/0.03 mmHg). The distillate was concentrated to ca. 100 ml by distillation of some of the solvents through a 30 cm Vigreux column. The concentrated solution was further distilled at reduced pressure (10 mmHg) through a 20 cm Vigreux column while heating the pot gently in order to sublime away unreacted hexachloroethane. After no more solid could be trapped in the receiver, a few drops were allowed to distill over. Then a new receiving flask was attached and 34.23 g (82%) of a clear liquid was obtained, b.p. 47-48°/0.9 mmHg. GLC analysis showed that this material contained about 4% 7,7-dibromonorcarane. The liquid was redistilled through a 20 cm Widmer column to yield 26.3 g (63%) of pure *anti*-7-bromo-*syn*-7-chloronorcarane, n_D^{25} 1.5293. The isomeric purity of the compound was established initially by its IR spectrum; later it was confirmed by its stereospecific conversions. IR (film): (unique bands in italics): 3020w, 2945vs, 2925(sh), 2900(sh), 2875(sh), 2860s, 2680w, 2660w, 1462m, 1447(sh), 1443s, 1437m, 1367w, 1352w, 1342m, 1334m, 1274w, 1255w, 1225w, 1180w, 1167m, 1130w, 1095m, 1083m, 1034m, 1025s, 970m, 906m, *839m*, 833m, 782(sh), 770vs, *747vs*, *652m*.

Reactions of n-butyllithium with the 7-bromo-7-chloronorcarane isomers.

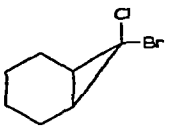
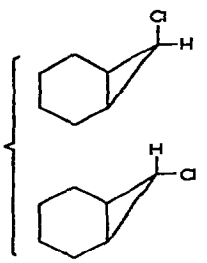
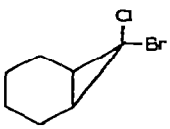
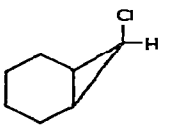
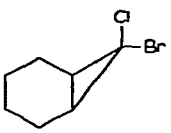
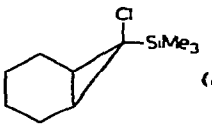
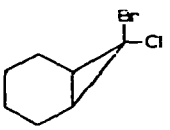
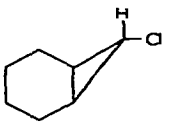
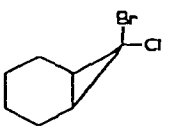
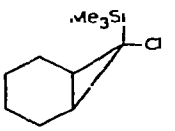
The reaction of *anti*-7-bromo-*syn*-7-chloronorcarane with n-butyllithium, followed by protolysis of the resulting lithium reagent with concentrated hydrochloric acid, is described to illustrate the procedure used.

Into a flamed-out 500 ml standard low temperature reaction apparatus was placed 100 ml of freshly distilled THF and the solvent was cooled to —80°. Then 20 ml (32 mmol) of 1.6 *M* n-butyllithium was added and the mixture was stirred at —95 ± 3° until a homogeneous solution was obtained. Then a solution of 5.00 g (25 mmol) of *anti*-7-bromo-*syn*-7-chloronorcarane in 10 ml of THF was added during a 1-min period. After the resulting mixture had been stirred for 15 min, it was treated with 3.5 ml (44 mmol) of concentrated hydrochloric acid and then it was stirred for 30 min before it was allowed to warm to room temperature. The mixture was treated with 50 ml of water, the organic layer was dried over magnesium sulfate, and the solution was filtered. The filtrate was trap-to-trap distilled (40°/0.02 mmHg) to yield 115 g of distillate, which was analyzed by GLC (10% Apiezon L, 135°) and found to contain *syn*-7-chloronorcarane, 13.6 mmol (57%) and *anti*-7-chloronorcarane, 4.4 mmol (18%).

Other reactions are summarized in Table 8.

TABLE 8

REACTIONS OF THE LITHIUM REAGENTS DERIVED FROM THE 7-BROMO-7-CHLORONORCARANE ISOMERS

7-Bromo-7-chloronorcarane (mmol)	Mmol n-BuLi solvents (ml)	Exchange time (min)/ temp. (°C)	Substrate (mmol)	Product (% yield)
 (25)	32; THF (100)	(1 min addition) 15/—95	concentrated HCl (44)	 (57) (18)
 (10)	50; THF (100)	(15 sec addition) 15/—95	concentrated HCl (62)	 (69)
 (20)	104; THF (150), Et_2O (50)	(15 sec addition) 15/—95	Me_3SiCl (115)	 (81)[a]
 (1.52)	10.4; THF (40)	(10 sec addition) 10/—95	concentrated HCl (12)	 (84)
 (2.13)	10.4; THF (40)	(10 sec addition) 10/—95	Me_3SiCl (12)	 (73)[b]

[a] B.p. 49-50.5 (0.9 mmHg); n_D^{25} 1.4795. [b] There may have been ca. 1.5% of the *syn*-Cl-*anti*-Me_3Si isomer.

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