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THE ELUSIVE GERMA- AND STANNACYCLOPROPANES. ATTEMPTED PREPARATION BY THE REACTION OF 1,3-DIHALIDES WITH MAGNESIUM

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Summary

The attempted isolation of germacyclopropanes and stannacyclopropanes by the action of magnesium in THF on bis(1-bromocyclopropyl)germanium and -tin compounds was not successful. Although ring closure did appear to occur in the case of dimethylbis(7-*anti*-bromobicyclo[4.1.0]hept-7-yl)germane and -tin, the product which was isolated was *anti*-7,7′-bis(norcaranylidene). In the case of dimethylbis(1-bromo-2,2-dimethylcyclopropyl)germane and -tin, reduction of the C—Br bonds occurred in THF medium, but in diethyl ether another product, dimethyl-3,3-dimethylcyclopropenyl-2,2-dimethylcyclopropylgermane, was formed as well. Evidence is presented that the reduction products are in large part formed by way of an organomagnesium intermediate.

Introduction

The preparation and the chemistry of silacyclopropanes (siliranes) have been developed in some detail since we reported the preparation and characterization of the first members of this long-sought class of silacarbocycles in 1972 [1]. The basic preparative procedure involved ring closure by reaction of a 1,3-dihalide with magnesium in tetrahydrofuran (THF), e.g., eq. 1. Prepared in this manner were compounds I, II and III in our initial work [1,2], and subse-

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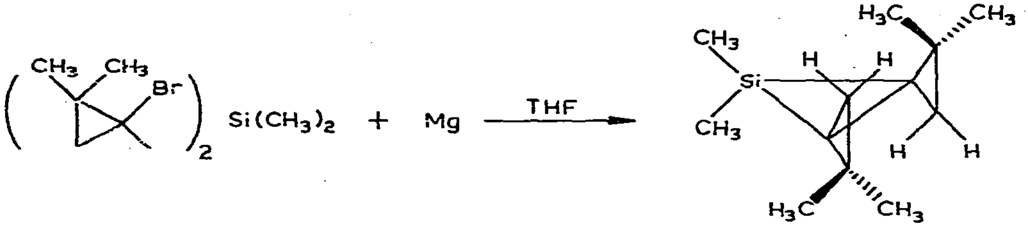
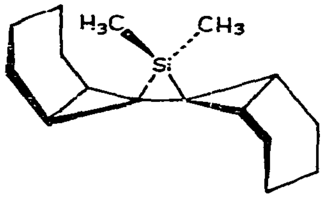
* NATO Postdoctoral Fellow at the Massachusetts Institute of Technology, 1971-1972.

quently this procedure was used in the preparation of hexamethylsilirane [3].



(1)

(I)



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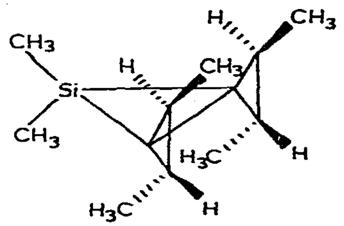
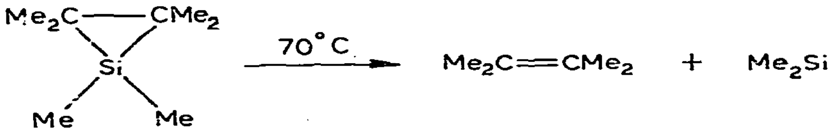


(III)

Later work showed that silacyclopropanes also are accessible by the addition of silylenes, generated either thermally from hexamethylsilirane [4] or photochemically from polysilanes [5], to olefins, e.g., eq. 2, 3.



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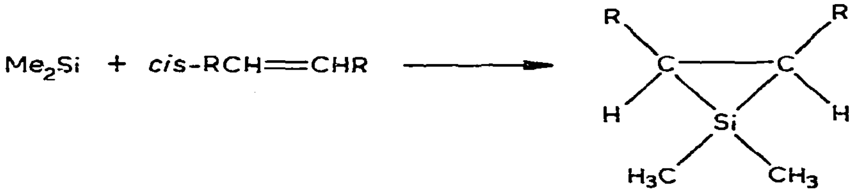


(3)

Noteworthy is the extremely high reactivity of silacyclopropanes: they react exothermally at room temperature with oxygen, water, alcohols, ammonia, many primary and secondary amines, hydrogen sulfide, carboxylic acids, hydrogen halides, and with many other reagents, with cleavage of a ring silicon-carbon bond to give acyclic products [6], and they undergo unusual two-atom insertion reactions with compounds containing C=C, C=O, C=N, and C≡C bonds [7].

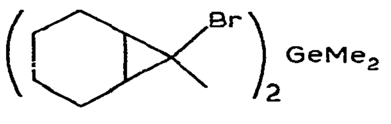
With the existence of silacyclopropanes secured, it became of interest to examine the possibility of preparing analogous germa- and stannacyclopropanes. At the time our work was begun (and this still is the case at the present time), no compounds containing a saturated GeC_2 or SnC_2 ring had been prepared and characterized. Compounds containing an unsaturated GeC_2 ring, germacyclopropenes, had been claimed by Vol'pin and his coworkers as products of the addition of germylenes to diphenylacetylene [8]. However, subsequent work showed that the materials isolated actually were the formal dimers, 1,4-digerma-2,5-cyclohexadienes [9]. (Silacyclopropenes, on the other hand, have been shown in recent studies to be isolable species which are quite stable thermally but highly reactive [10].)

Germacyclopropanes have been cited by Russian workers as possible intermediates in reactions of dichlorogermylene with ethylene and other olefins [11]. More recently, Jones and his coworkers have presented evidence for the formation of 1,1-dimethyl-2-phenylgermacyclopropane as a transient intermediate in a pyrolytic process [12]. On the basis of molecular orbital considerations, there is no reason why germacyclopropanes should not be capable of existence as stable compounds at room temperature [13]. A calculation of the endocyclic C—Ge—C bond angle in a germacyclopropane in which the C—C bond distance is 1.52 Å as found in silirane II [14] and the Ge—C bond distance is 1.94 Å * gives a value of about 46°. This bond angle may be compared with the 49.2° C—Si—C endocyclic angle found in II [14]. Thus germacyclopropanes, like the silacyclopropanes, would be expected to be a highly reactive class of compounds as a result of rather severe ring strain. Nonetheless, one might hope that germacyclopropanes with suitable substituents on the germanium atom and the carbon atoms of the GeC_2 ring would be capable of isolation and study.

We report here concerning studies aimed at the preparation of stable germa- and stannacyclopropanes. These investigations were initiated at the Massachusetts Institute of Technology in 1972 and continued thereafter at the Université Paul Sabatier.

Results

In view of the facility of the magnesium-induced ring closure reaction which was used in the preparation of the first silacyclopropanes (eq. 1) and the high thermal stability of the products, we examined the possibility of preparing the



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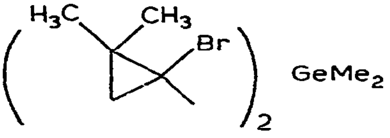

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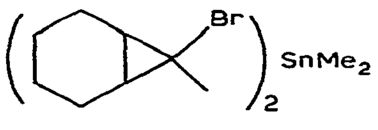

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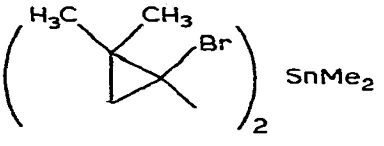

(VII)

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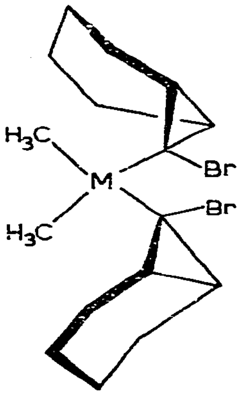
* This is the Ge—C distance in $(CH_3)_3GeH$, according to a microwave study [15].

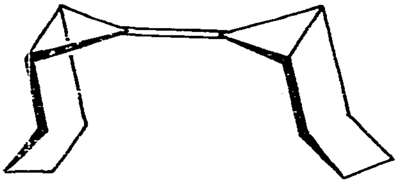
germanium and tin analogs of silacyclopropanes I and II. The preparation of the required 1,3-dibromides, the germanes IV and V and the stannanes VI and VII, has been described in a previous paper [16]. In the case of V and VII the multiplicity of the CH_3—Ge and CH_3—Sn resonances in their proton NMR spectra indicated that a mixture of isomers was present. The ^1H NMR spectra of IV and VI showed only a single methyl resonance, so it was considered likely that only one isomer, VIII, was present in the case of each compound.



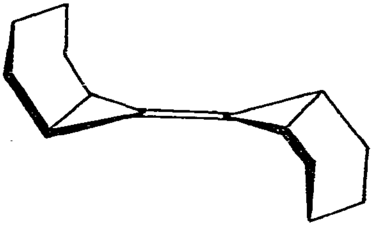
(VIII)

In the first experiment, the action of magnesium (200% excess) on IV in THF medium was examined. The reaction mixture was not hydrolyzed, rather 1,4-dioxane was added to precipitate magnesium bromide as the dioxate. Evaporation of the THF solution left a residue which was found to be unreactive toward air, water and methanol, and which, therefore, did not contain the desired germacyclopropane. Distillation of this residue gave 7,7′-bis(norcaranylidene) in 43% yield. The nonvolatile distillation residue contained the CH_3—Ge moiety (by NMR) and may have been polymeric dimethylgermylene, $(Me_2Ge)_x$. A single isomer, m.p. 77—78° C, of 7,7′-bis(norcaranylidene) was formed. When this reaction was repeated, but with a hydrolytic work-up, the same isomer of 7,7′-bis(norcaranylidene) was isolated in 43% yield.

On the basis of the assignment of Köbrich and Goyert [17], who had prepared both isomers of 7,7′-bis(norcaranylidene) by a carbene route, the isomer with m.p. 77—78° C has the *syn* structure IXa, while the isomer with m.p.



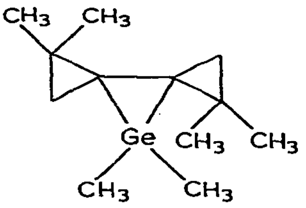
(IXa)



(IXb)

120.5—121.5° C has the *anti* structure IXb. These assignments, however, were based solely on the observed melting points. NMR spectroscopy was of no direct assistance in this structural problem and for this reason a dipole moment study of these isomers was undertaken through the courtesy of Professor P. Mauret (Toulouse). A sample of the isomer with m.p. 122° C was prepared by the method of Moore and Ward [18], so that a comparison could be made. In benzene solution at room temperature the dipole moment of the isomer with m.p. 122° C was found to be 0.31 D greater than that of the isomer with m.p. 77—78° C, and the dipole moment of the latter, depending on the C—C bond increment used, could be essentially zero. Accordingly, the structural assignment of Köbrich and Goyert should be reversed: the isomer with m.p. 77—78°C has the *anti* structure IXb, while the isomer with m.p. 122°C has the *syn* structure IXa. The dipole moment of the latter, although low, would be expected to be larger than that of the *anti* isomer, which should be close to zero [19]. An X-ray crystal structure determination of one or both of these isomers would be desirable in order to secure these structural assignments. We note that in a recent paper Fukuda et al. also have reported that the isomer assignments of Köbrich and Goyert should be reversed [20].

Similar reactions of germane V with an excess of magnesium at 35° C in THF or in diethyl ether-medium, with hydrolytic or non-hydrolytic work-up, were studied in some detail. Here also, no evidence for the presence of a stable



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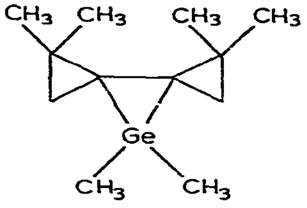
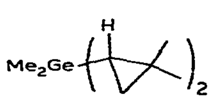
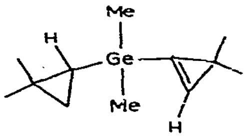


(XI)

TABLE 1

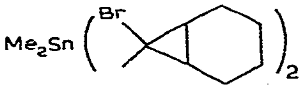
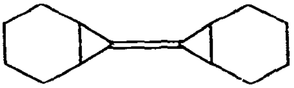
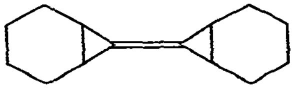
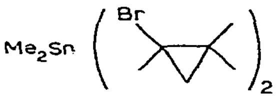
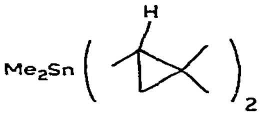
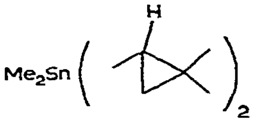
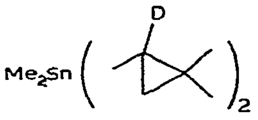
REACTIONS OF DIMETHYLBIS(1-BROMO-2,2-DIMETHYLCYCLOPROPYL)GERMANE WITH MAGNESIUM [a]

Solvent	Hydrolytic work-up	Products (% Yield)	
			
THF	yes	38	—
THF	no	18	—
Et_2O	yes	30	46
Et_2O	no	30	40

[a] Mg in 200% excess, at 35°C for 15 h.

TABLE 2

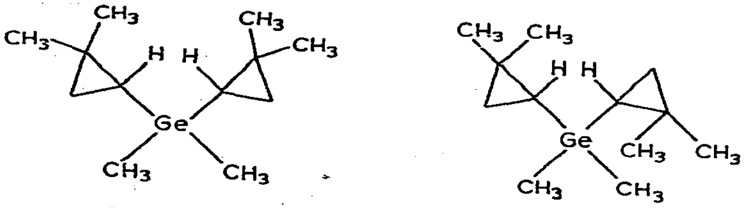
REACTIONS OF DIMETHYL-BIS(α-BROMOCYCLOPROPYL)TIN COMPOUNDS WITH MAGNESIUM IN THF MEDIUM[a]

Tin compound	Work up procedure	Products (% Yield)	
	dioxane, ↓ $MgBr_2$		(25)
	hydrolysis	 $[\mathrm{Me_2Sn}]_x$[b]	(38)
	dioxane, ↓ $MgBr_2$		(19)
	hydrolysis		(36)
	D_2O	 (81% D incorporation)	(57)

[a] 200% Excess of magnesium at 35°C for 15 h. [b] Me_2Sn polymer, ^1H NMR δ 0.63 ppm. Me_2SnCl_2 produced in 19% yield on treatment with $HgCl_2$.

germacyclopropane, X or XI, was obtained. The major products in all reactions were organogermanium compounds containing *gem*-dimethylcyclopropyl and -cyclopropenyl substituents, XII and XIII. The experiments summarized in Table 1 show that the solvent used, THF or diethyl ether, has a marked effect on the product composition. In these experiments there were other minor products. However, these were not conclusively identified.

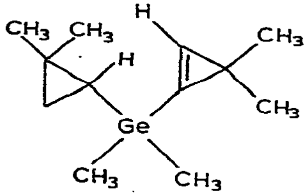
The cyclopropenylgermane XIII, an unexpected and novel product, was identified on the basis of its IR, NMR and mass spectral properties. It appeared to be air-stable, and it was stable to methanol and carbon tetrachloride at room temperature. However, it reacted with methanol at reflux.



(a) meso

(b) dl

(XII)

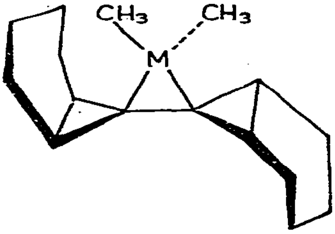


(XIII)

The action of an excess of magnesium at 35°C in THF on the two α-bromocyclopropyltin derivatives VI and VII was studied in similar fashion. The results are given in Table 2. 7,7′-Bis(norcaranylidene) was obtained in the case of VI, but cyclopropenylstannanes (equivalent to XIII) were absent among the products of such reactions of VII. Only reduced cyclopropyl derivatives were obtained, regardless of the type of work-up (hydrolytic or non-hydrolytic). In one experiment, deuterium incorporation into the organotin product was observed when D_2O was added to the reaction mixture upon completion of the VII/Mg reaction.

Discussion

The reactions of both the 7-bromonorcaran-7-yl-germanium and the -tin derivatives (IV and VI) with magnesium must have proceeded with ring closure to give, in analogy with the silicon case, the expected metallacyclopropanes XIVa and XIVb, respectively. These, however, in contrast to the analogous silacyclopropane, II, were not stable under the reaction conditions. Their decomposition apparently involved, in part, extrusion of dimethylgermylene and dimethylstannylene, respectively, with formation of the 7,7′-bis(norcaranylidene). The isolation of the latter shows that C—C bond formation, i.e., ring closure, to give XIVa and XIVb had occurred, at least to an extent indicated by the observed olefin yields. While the silicon analog II is very stable thermally and does not decompose in this manner, the rather less stable hexamethylsilirane, as mentioned in the Introduction, does decompose with extrusion of dimethylsilylene and formation of tetramethylethylene. During the course of the decomposition of XIVa and XIVb the dimethylgermylene and dimethyl-



(XIV a, M = Ge ;
XIV b, M = Sn)

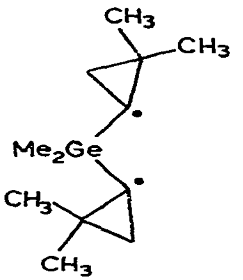
stannylene formed polymerize in known fashion. In the case of the tin compound, the Me_2Sn polymer was converted to dimethyltin dichloride by reaction with mercuric chloride.

In reactions of the type carried out in this study, i.e., of the dibromo compounds IV—VII with magnesium, it is important to show that the products finally isolated have been formed during the course of the reaction, not during work-up of the reaction mixture. Such seems to be the case. Although 7,7′-bis(norcaranylidene) could have been formed by decomposition of the germacyclopropane XIVa during the work-up after the reaction of IV with magnesium had been carried out, this olefin was obtained in such reactions which were worked up with and without initial hydrolysis. Hydrolytic work-up should have opened the ring of germacyclopropane XIVa to give 7-dimethylhydroxygermyl-7,7′-bis(norcaranyl). In the reaction carried out with nonhydrolytic work-up, the product, before final distillation, was found to be unreactive towards air, water and methanol. In the case of the analogous silacyclopropane II, extreme sensitivity toward these reagents characterizes its reactivity. Similar observations were made in reactions aimed at the synthesis of the stannacyclopropane XIVb. 7,7-Bis(norcaranylidene) was the product isolated both in reactions with hydrolytic and non-hydrolytic work-up.

The stereochemistry assigned to the 7,7′-bis(norcaranylidene) isolated in these experiments on the basis of dipole moment measurements is the *anti*-structure IXb. According to spectroscopic evidence, the 1,3-dibromo precursor of silacyclopropane II was the isomer with structure VIII (M = Si) [16]. The stereochemistry of the ring closure product was secured by a single crystal X-ray diffraction study of II [14]. The 7,7′-bis(norcaranylidene) obtained in the present experiments was allowed to react with dimethylsilylene (from hexamethylsilirane thermolysis) and a silirane was formed. This product was not isolated, rather was treated with methanol to give a 7-methoxydimethylsilyl-7,7′-bis(norcaranyl) which was identical with that obtained in the methanolysis of II [2]. (The silacyclopropane isomeric with II had been prepared, and this isomer reacted with methanol to give a methoxysilane which was spectroscopically distinctly different from the methoxysilane obtained from II) [2]. Thus the germa- and stannacyclopropanes which must have been formed in the IV/Mg and VI/Mg reactions decompose to give a 7,7′-bis(norcaranylidene) isomer which reacts with dimethylsilylene to give a silacyclopropane with structure II. In view of our observation that dimethylsilylene (from hexamethylsilirane) reacts with the *cis*- and *trans*-isomers of 1-propenyltrimethylsilane with retention of geometric configuration [22], this result is consistent with our conclusion that the 7,7′-bis(norcaranylidene) formed in the present experiments is the *anti* isomer IXb.

In contrast to what was observed with IV and VI, the results obtained in reactions of V and VII with magnesium gave no clear-cut evidence for ring closure as a major process.

The major products of the V/Mg reactions listed in Table 1 are suggestive of the intervention of radical intermediates, i.e., XV and, possibly, of organomagnesium intermediates, i.e., XVI. Hydrogen atom abstraction by XV from the solvent or hydrolysis of XVI both would give the observed dimethylbis(2,2-dimethylcyclopropyl)germane (XII), while hydrogen atom transfer processes, i.e., radical disproportionation, involving XV would result in formation of XIII. In an attempt to shed further light on this matter, a reaction of V with magnesium (500% excess) was carried out in THF at 40° C. Subsequently, dimethyl sulfate was added to the reaction mixture in order to trap any organomagnesium intermediates present. The products formed in this experiment included the methylated species XVII (56%) and XVIII (19%), in addition to the reduced product XII (13%). This result suggests that in THF organomagnesium species are formed in the reaction of V with magnesium. The formation of the main product, XII, on hydrolytic work-up thus is readily explained. Its formation in reactions with non-hydrolytic work-up (in lower yield) may be explained in terms of hydrogen abstraction from solvent during distillation of the reaction mixture. In diethyl ether solution radicals of type XV obviously must be formed: the (2,2-dimethylcyclopropyl)(3,3-dimethylcycloprop-1-enyl)germane is best explained in terms of the disproportionation of XV. These suggestions concerning possible mechanisms are, however, speculation. Clarification of this complicated chemistry would require more detailed experimental study.



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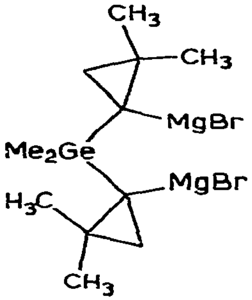

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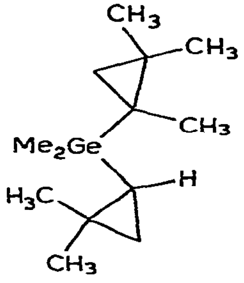

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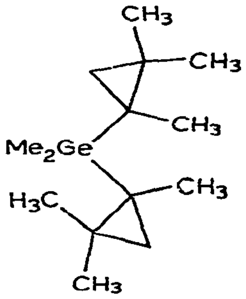

(XVIII)

Similar reactions of tin compound VII with magnesium in THF gave dimethylbis(2,2-dimethylcyclopropyl)tin as the organotin product. Such a reaction which was followed by treatment of the reaction mixture with D_2O resulted in formation of this tin compound as well, but it was found to be 81% monodeuterated. Organomagnesium intermediates thus are implicated in these reactions as well. However, no products which could be directly or indirectly related to a ring closure process, i.e., the formation of a stannacyclopropane, were isolated.

It must be emphasized that in all the reactions which we report here the material balances were not good. If di-Grignard and diradical intermediates are indeed involved, one might expect to have formation of non-volatile products of higher molecular weight and even polymeric material. In any case, it is clear that the chemistry which is developed when these germanium- and tin-containing 1,3-dibromides react with magnesium is quite complex and still poorly understood. Since the prime objective of this work, the isolation and characterization of stable germa- and stannacyclopropanes, was not realized, we have chosen not to pursue these matters further. However, we have investigated the chemistry of the cyclopropenylgermane XIII and will report concerning these studies in a subsequent paper [21].

The formation of 7,7'-bis(norcaranylidene) in the reactions of IV and VI with magnesium has been interpreted in terms of dimethylgermylene and dimethylstannylene extrusion from the initially formed germa- and stannacyclopropanes, XIVa and XIVb. That the stannacyclopropane ring is not stable under our reaction conditions is not too surprising. The larger covalent radius of the tin atom (1.40 Å) results in a tin—carbon bond which is considerably longer than the Si—C bond (2.17 vs. 1.95 Å), and thus considerably more strain is present in the hypothetical SnC_2 ring. (Assuming C—C and Sn—C distances of 1.52 and 2.15 Å, respectively, we calculate an internal C—Sn—C bond angle of 41.3° in the stannacyclopropane ring). On the other hand, the germanium atom is not much larger than the silicon atom (1.22 Å covalent radius, vs. 1.18 Å for silicon). As mentioned in the introduction, the internal C—Ge—C angle in a germacyclopropane was calculated as 46°, only 3° smaller than the internal C—Si—C angle in II. In view of these considerations, we feel that it is likely that with other substituents on the ring atoms, and, perhaps, under milder conditions, more direct evidence for the formation of the saturated GeC_2 ring can be obtained, and, perhaps, such a species will be capable of isolation.

Experimental

General comments.

All reactions were carried out under an atmosphere of dry nitrogen in glassware which had been flamed out in a stream of nitrogen. Rigorously dried solvents were used. Air- or moisture-sensitive reagents and solutions were transferred by syringe or cannula.

Infrared spectra were measured using a Perkin—Elmer 337 or 457A infrared spectrophotometer, ^1H NMR spectra using Varian A60 or T60 spectrometers. Chemicals shifts are given in δ units, ppm downfield from internal tetramethylsilane. Tetramethylsilane or chloroform were used as internal standards. ^{13}C NMR spectra were obtained using a Bruker HFX-90 Spectrometer interfaced with a Digilab FTS/NMR-3 computer. Mass spectra were recorded using a Hitachi/Perkin—Elmer RMU-6D mass spectrometer (ionizing voltage 70 eV). Analyses of reaction mixtures, isolation of samples of products and yield determinations (internal standard method) were effected by gas chromatography.

The preparation of the 1,3-dibromides used in this study, compounds IV, V, VI and VII, has been described in a previous paper [16].

The action of magnesium on dimethylbis(7-anti-bromobicyclo[4.1.0]hept-7-yl)-germane

A 200 ml three-necked, round-bottomed flask equipped with a reflux condenser topped with a nitrogen inlet tube, a pressure-equalizing addition funnel and a magnetic stir-bar was charged with 1.22 g (0.05 g atom) of magnesium powder. The flask and contents were flame-dried under nitrogen, allowed to cool while maintaining the stream of nitrogen, and then the magnesium was covered with 10 ml of freshly distilled tetrahydrofuran (THF). Subsequently, a solution of 6.76 g (0.015 mol) of the germane in 50 ml of THF was charged into the addition funnel. To initiate the reaction, 0.5 ml of this solution and 100 μl of 1,2-dibromoethane were added to the magnesium. After the reaction had been initiated (temperature rise to 35° C), the remainder of the germane solution was added dropwise with stirring, under nitrogen during the course of 2 h. The resulting brown reaction mixture was stirred at room temperature overnight. Subsequently, 50 ml of 1,4-dioxane was added to precipitate magnesium salts. These were centrifuged. Extraction of the yellow-brown solid with THF was followed by concentration of the THF solutions at reduced pressure to leave 3.60 g of a yellow residue which appeared to be unreactive toward air, water and methanol. Distillation of this residue (85—110° C/0.45 mmHg) gave 1.2 g (43% yield) of white crystalline solid. Recrystallization from methanol gave material with m.p. 77—78° C. (Found: C, 88.61; H, 10.58. $C_{14}H_{20}$ calcd.: C, 89.29; H, 10.71%.) The spectral properties of this product were in agreement with those in the literature for 7,7′-bis(norcaranylidene) of m.p. 77.5—78.5° C (presumed *syn* isomer IXa [17]). Further distillation to 120° C at 0.45 mmHg gave 0.6 g of yellow oil and a residue which was insoluble in organic solvents.

Another reaction was carried out in the same manner using 1.22 g (0.05 g atom) of magnesium and 7.33 g (0.016 mol) of the germane. In this case the reaction mixture was hydrolyzed by the slow addition of 50 ml of saturated aqueous ammonium chloride. The resulting mixture was extracted with 50 ml of hexane. Concentration at reduced pressure left a yellow-brown oil. Distillation (85—110° C at 0.35 mmHg) gave an oil (1.45 g, 43%) which crystallized on being cooled and was identified as 7,7′-bis(norcaranylidene), presumed isomer IXa, m.p. 77° C. Further distillation up to 120° C/0.35 mmHg gave an oil whose ^{1}H NMR spectrum (δ 0.51 ppm) indicated the presence of a CH_3—Ge compound.

The yields of 7,7′-bis(norcaranylidene) were variable. For instance, in one reaction in which the THF solution after dioxane precipitation of magnesium bromide was treated with chloromethyl methyl ether to trap dimethylgermylene, distillation gave 7,7′-bis(norcaranylidene) in 73% yield.

Dipole moment measurements in benzene solution at 25° C of the 7,7′-bis(norcaranylidene) product of this reaction and of the other bis(norcaranylidene) isomer of m.p. 120—121° C (prepared by the method of Moore and Ward [18]) were carried out by Professor P. Mauret and Dr. J.P. Fayet et the Laboratoire de Chimie Organique Structurale of the Université Paul Sabatier, Toulouse. An average of six runs each using solutions of weight fraction 0.001—0.002 gave the following results: isomer with m.p. 77—78° C, μ 0.29 D; isomer with m.p. 120—121° C, μ 0.60 D. These values assume the classical increment for C—C bonds in the calculation of $RM_D = 59.33$ ($\alpha = 0.065$; $\beta = -0.098$; $P_{2\infty} = 61.01$ for the former and $\alpha = 0.254$; $\beta = -0.114$; $P_{2\infty} = 66.81$ for the latter). If we assume that RM_D is known to ±1, then the dipole moment of the m.p. 77—78° C isomer should be zero. The difference in the dipole moments of the two isomers being 0.31, we conclude that the isomer with m.p. 77—78° C has the *anti* structure IXb.

The action of magnesium on dimethylbis(1-bromo-2,2-dimethylcyclopropyl)germane

(a) In tetrahydrofuran medium. A solution of 3.67 g (9.2 mmol) of the title germane in 35 ml of THF was added over the course of 2 h, under nitrogen with stirring, to 0.25 g (10 mg atom) of magnesium. Gentle heating was required to maintain the reaction. Stirring was continued for 15 h, at which time the magnesium had been consumed. The magnesium salts were precipitated by addition of 20 ml of dry dioxane, the reaction mixture was centrifuged and the THF solution was decanted. Trap-to-trap distillation at 0.005 mmHg gave a distillate which was concentrated at 45 mmHg to leave 2.53 g of liquid. GLC analysis (4 ft. UCW 98 at 110° C) showed the presence of a major component and small amounts of two other components of higher retention time. The main product was collected by GLC (6 ft. DC200 at 150° C); its yield, determined by GLC, was 18% based on the starting germane. (Found: C, 59.76; H, 9.79. $C_{12}H_{24}Ge$ calcd.: 59.82; H, 10.04%). On the basis of this analysis and its NMR and mass spectra it was identified as dimethylbis(2,2-dimethylcyclopropyl)germane (XII, n_D^{25} 1.4642). Two isomers, XIIa and XIIb, appeared to be present. NMR (CCl_4): δ 0.10 (s, CH_3—Ge, assigned to XIIb), 0.15 and 0.16 (s, CH_3—Ge, assigned to XIIa; XIIa/XIIb = 40/60), 1.08 and 1.13 (s, CH_3—C). The cyclopropyl protons appeared as a complex multiplet centered at δ 0.16 ppm.

The mass spectrum showed, among others, fragment ions with *m/e* 225 ($M^+ - CH_3$), 171 ($M^+ - C_3H_3Me_2$), 103 (Me_2GeH^+, parent ion) and 87 ($MeGe^+$).

In a similar experiment, 5.03 g (12.5 mmol) of the title germane in 40 ml of THF was added over 2 h to 1.0 g (41 mg atom) of magnesium in 5 ml of THF. Gentle heating and addition of a small amount of 1,2-dibromoethane was necessary to initiate the reaction. The resulting reaction mixture was stirred for 4 h and then was hydrolyzed by careful addition of 50 ml of saturated NH_4Cl solution. The hydrolyzed reaction mixture was extracted with diethyl ether and the organic phase was dried over anhydrous Na_2SO_4. Removal of the solvents was followed by distillation of the residue at 0.5 mmHg into a trap at −78° C. GLC analysis showed that one major and one minor component were present. Vacuum distillation of this product mixture gave dimethylbis(2,2-dimethylcyclopropyl)germane (XII, 1.16 g, 38%), b.p. 112—113°C at 45 mmHg. The minor component, which was higher boiling, was not identified.

(b) In diethyl ether medium. A 100 ml, three-necked flask equipped with a reflux condenser, a pressure-equalizing dropping funnel, a nitrogen inlet tube and a magnetic stirring bar was charged with 0.108 g (4.5 mg atom) of magnesium. A solution of 1.632 g (4 mmol) of the title germane in 300 ml of dry diethyl ether was added dropwise during the course of 30 min. The reaction was initiated with a small quantity of 1,2-dibromoethane. The reaction mixture

was stirred until the magnesium was consumed and then was treated with 50 ml of saturated NH_4Cl solution. Extraction with diethyl ether was followed by separation and drying of the organic phase over anhydrous Na_2SO_4. Evaporation of the solvents left a yellow liquid residue which was trap-to-trap distilled at 0.35 mmHg into a receiver at —78° C. GLC analysis of the distillate showed the presence of two major products. The product of higher retention time (UCW 98 at 110° C) was identified as dimethylbis(2,2-dimethylcyclopropyl)germane (30% yield). The other product was identified as dimethyl-3,3-dimethylcyclopropenyl-2,2-dimethylcyclopropylgermane (XIII, 46% yield), n_D^{25} 1.4765). (Found: C, 60.28; H, 9.29. $C_{12}H_{22}Ge$ calcd.: C, 60.33; H, 9.28%). ^1H NMR (C_6D_6, TMS): δ 0.33 (s, 6H, Me_2Ge), 1.08 (two closely spaced s, each 3H, $C—CH_3$), 1.26 (s, 6H, $C—CH_3$), 7.75 ppm (m, 1H, =CH). The latter signal is at rather low field, but δ (=CH) of cyclopropene is 7.01 ppm, of 3-methylcyclopropene 7.2 ppm and of 3,3-dimethylcyclopropene 7.00 ppm [23]. ^{13}C NMR (proton-decoupled) (C_6D_6, C_6H_6), δ_C —1.30, 15.10, 18.66, 24.05, 28.58, 29.56 and 136.1 ppm. The 136.1 ppm resonance is near the 125—130 ppm region reported for the resonances of unsubstituted unsaturated carbon atoms in methyl-substituted cyclopropenes [24]. There should be nine carbon atom signals, but three of the carbon atoms in XIII are quaternary.

The infrared spectrum of XIII showed a strong band at 1663 cm^{-1}; ν(C=C) of cyclopropene, 3-methylcyclopropene and 3,3-dimethylcyclopropene are 1641, 1638 and 1632 cm^{-1}, respectively [23]. Compound XIII appeared to be air-stable. It also was stable to methanol and carbon tetrachloride at room temperature, but it reacted with methanol at reflux.

(c) In THF medium; dimethyl sulfate quench. The V/Mg reaction was carried out as in (a) using 1.0 g (41 mg atom) of magnesium, 3.075 g (7.7 mmol) of V and 40 ml of THF. Upon completion of the addition the reaction mixture was stirred under nitrogen at room temperature for 15 h. Subsequently, 1.17 g (9.3 mmol) of dimethyl sulfate in 10 ml of THF was added slowly. A mildly exothermic reaction resulted. The reaction mixture was stirred for 15 h, hydrolyzed with dilute sulfuric acid and extracted with pentane. The organic phase was dried over anhydrous Na_2SO_4 and evaporated at reduced pressure to leave a yellow liquid residue. Trap-to-trap distillation (120° C at 0.05 mmHg) into a receiver at —78° C gave 1.65 g of liquid distillate. Analysis by GLC (UCW at 135° C) showed the presence of three components. These were isolated by GLC (DC 200 at 150° C) and identified as follows: (i) Dimethylbis(2,2-dimethylcyclopropyl)germane, 13% yield. (ii) Dimethyl(2,2-dimethylcyclopropyl)(1,2,2-trimethylcyclopropyl)germane (XVII) 56% yield. (Found: C, 60.92; H, 10.14; $C_{13}H_{26}Ge$ calcd.: C, 61.24; H, 10.28%). ^1H NMR (CCl_4), three singlets centered at 0.1 ppm ($CH_3—Ge$) and three singlets centered at 1.14 ppm ($CH_3—C$). This is in agreement with the presence of a mixture of isomers, as in the case of XII. The mass spectrum showed fragment ions corresponding to $Me_2GeC_3Me_2H_3^+$ (*m/e* 171) and $Me_2GeC_3Me_3H_2^+$ (*m/e* 185). (iii) Dimethylbis(1,2,2-trimethylcyclopropyl)germane (XVIII) 19% yield. (Found: C, 62.21; H, 10.43. $C_{14}H_{28}Ge$ calcd.: C, 62.51; H, 10.49%). ^1H NMR (CCl_4): three singlets centered at 0.13 ppm ($CH_3—Ge$) and two broad peaks centered at 1.1 ppm ($C—CH_3$): δ (CH_2) an AB system, ν_A 0.43 ppm, ν_B 0.15 ppm, J(AB) 4 Hz. Here also, a mixture of isomers must be present. The mass spectrum showed a principal fragment ion corresponding to $Me_2GeC_3Me_3H_2^+$ (*m/e* 185).

The action of magnesium on dimethylbis(7-anti-bromobicyclo[4.1.0]hept-7-yl)tin

A 100 ml, three-necked, round-bottomed flask was charged with 1.0 g (41 mg atom) of magnesium powder and flame-dried under nitrogen. The magnesium was covered with 10 ml of THF and then 6.0 g (12.1 mmol) of the title tin compound in 50 ml of THF was added dropwise with stirring over the course of 2 h. The resulting brown solution was stirred at room temperature overnight. Precipitation of magnesium salts with dioxane was followed by centrifugation, washing of the solid phase and concentration of the solution at reduced pressure. The yellow residue was treated with 50 ml of methanol. After evaporation of the methanol, the residue was taken up in pentane and distilled at reduced pressure to give 0.56 g (25%) of a product which formed colorless crystals on cooling. Recrystallization from methanol gave material with m.p. 77° C, 7,7′-bis(norcaranylidene) (IXb). The distillation residue was treated with 3.3 g (12 mmol) of mercuric chloride. After extraction with pentane, 0.50 g (19%) of dimethyltin dichloride was isolated.

In another experiment, 3.70 g (7.5 mmol) of the tin compound in 50 ml of THF was added to 0.6 g (25 mg atom) of magnesium over a period of 5 h. After the reaction mixture had been stirred at room temperature overnight it was hydrolyzed by addition of 100 ml of saturated aqueous ammonium chloride solution. Extraction of the reaction mixture with pentane followed by evaporation of the extracts left a yellow oil. Distillation of the latter gave 0.53 g (38%) of a semi-liquid material, boiling range 85—110° C at 0.08 mmHg. Recrystallization from methanol gave 7,7′-bis(norcaranylidene), m.p. 77—78° C. The crystallization residue was shown by NMR to contain principally additional 7,7′-bis(norcaranylidene) and a minor amount of a methyltin compound (δ 0.63 ppm, with tin satellites).

The action of magnesium on dimethylbis(1-bromo-2,2-dimethylcyclopropyl)tin

To 1.0 g (41 mg atom) of magnesium was added dropwise over the course of 2 h (under nitrogen) a solution of 5.26 g (11.8 mmol) of the title tin compound in 50 ml of THF. The resulting brown solution was stirred at room temperature for 15 h and then was hydrolyzed with 100 ml of saturated NH_4Cl solution. Extraction with pentane and evaporation of the extracts left a yellow liquid residue. This was trap-to-trap distilled at 0.05 mmHg into a receiver at —78° C. GLC examination of the distillate (10% UCW 98 at 120° C) showed the pressence of two minor components and one major product. Fractional distillation of the trap-to-trap distillate gave 1.23 g of liquid, b.p. 117—119° C at 35 mmHg, n_D^{25} 1.4831, which contained one of the minor products in addition to the major product. The latter could be isolated by preparative GLC, n_D^{25} 1.4826. (Found: C, 49.63; H, 8.34. $C_{12}H_{24}Sn$ calcd.: C, 50.21; H, 8.42%). ^1H NMR (CCl_4, TMS): singlets at δ 0.02, 0.03 and 0.06 ppm (Me_2Sn), singlets at δ 1.09 and 1.16 ppm (Me_2C) and a multiplet centered between 0.72 and —0.44 ppm (cyclopropyl protons). The NMR spectrum suggests that two isomers, the dimethyltin analogs of XIIa and XIIb, are present. The isomer ratio, obtained by integration of the Me_2C signals, is 40/60.

The mass spectrum of the isomer mixture showed inter alia the molecular ion (*m/e* 288), $[M-CH_3]^+$ (*m/e* 273), $[M-C_5H_9]^+$ (*m/e* 219), $[Me_2SnH]^+$ (*m/e* 151) and $[MeSn]^+$ (*m/e* 135).

A similar reaction carried out with 1.91 g (4.3 mmol) of the tin compound and 0.31 g (13 mg atom) of magnesium in 15 ml of THF was quenched with D_2O (6 ml). Extraction with pentane, evaporation of the extracts and trap-to-trap distillation gave a distillate which was examined by GLC (10% UCW 98 at 108°C). The major product was dimethylbis(2,2-dimethylcyclopropyl)tin-d_x (57% yield). Fractional distillation gave 0.61 g (49%) of this product, b.p. 88—89°C at 13 mmHg, n_D^{25} 1.4928. (Found: C, 49.64; H(D), 8.45. $C_{12}H_{22}D_2Sn$ calcd.: C, 49.87; H, 7.69; D, 1.39%). Percent deuteration (by mass spectrometry): 80.5. ^1H NMR (CCl_4, TMS): singlets at δ —0.05, —0.04 and 0 ppm, with tin satellites (Me_2Sn), singlets at δ 1.03 and 1.09 ppm (Me_2C) and an AB multiplet, J_{AB} 3 Hz (CH_2). For the dideuterated species, the mass spectrum showed the molecular ion (m/e 290), $[M - CH_3]^+$ (m/e 275), $[M - C_5H_8D]^+$ (m/e 220), $[Me_2SnH]^+$ (m/e 151) and $[MeSn]^+$ (m/e 135).

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