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HALOMETHYL-METAL COMPOUNDS
XLIX*. THE INSERTION OF PHENYL(BROMODICHLOROMETHYL)-MERCURY-DERIVED DICHLOROCARBENE INTO CARBON-HYDROGEN BONDS: TETRAALKYLGERMANES. THERMOLYSIS OF 3-DICHLOROMETHYL-1-METALLACYCLOALKANES

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SUMMARY

Phenyl(bromodichloromethyl)mercury-derived dichlorocarbene was found to insert into βC–H bonds of a number of tetraalkylgermanes: into the n-propyl group of $Et_3GeCH_2CH_2CH_3$, the isobutyl group of $Et_3GeCH_2CHMe_2$, the trimethylene bridges of $Et_3Ge(CH_2)_3GeEt_3$ and 1,1,2,2-tetraethyl-1,2-digermacyclopentane, the tetramethylene bridge of 1,1,2,2-tetraethyl-1,2-digermacyclohexane and the pentamethylene bridge of 1,1-diethyl-1-germacyclohexane. Pyrolysis of these insertion products resulted in γ-elimination of Ge–Cl to give germyl-substituted chlorocyclopropanes, reactions which served well in confirming the structures of the insertion products. For instance, thermolysis of 1,1-diethyl-3-dichloromethyl-1-germacyclohexane gave 1-chloro-2-(γ-diethylchlorogermylpropyl)cyclopropane. The various insertion products were reduced to the chlorine-free methyl derivatives, *e.g.*, $Et_3GeCH_2C(CCl_2H)Me_2$ to $Et_3GeCH_2CMe_3$. A competition between Et_3GeCH_2-$CHMe_2$ and $Et_3SiCH_2CHMe_2$ for a deficiency of $PhHgCCl_2Br$ showed the germane to be 1.35 times more reactive toward this CCl_2 source than the silane. The pyrolysis of 1,1-dimethyl-3-dichloromethyl-1-silacyclopentane and -cyclohexane, as well as of 1,1-dimethyl-3-dichloromethyl-1-stannacyclohexane was also studied.

INTRODUCTION

In an earlier paper of this Series[2], we reported the remarkable β-activation of C–H bonds in tetraalkylsilicon and tetraalkyltin compounds toward CCl_2 insertion reactions. Such reactions were observed with acyclic derivatives [*e.g.*, eqn. (1)], as well as with alicyclic compounds [eqn. (2)]. On the basis of the available evidence, it was concluded that it was metal–carbon bond hyperconjugation and, to a lesser

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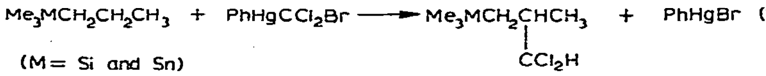
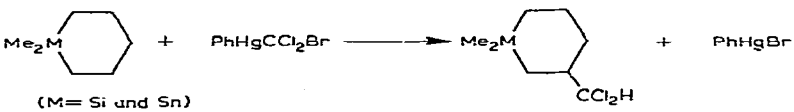
* Part XLVIII, see ref. 1.



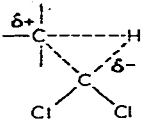
$$Me_3MCH_2CH_2CH_3 + PhHgCCl_2Br \longrightarrow Me_3MCH_2\underset{CCl_2H}{\underset{|}{C}}HCH_3 + PhHgBr \quad (1)$$

(M = Si and Sn)



(2)

extent, the +*I* inductive effect of the Me_3M substituents which were responsible for this β-metal effect. Both effects serve to stabilize the insertion reaction transition state (I)[3] in which the carbon atom into whose bond to hydrogen CCl_2 insertion is occurring bears a partial positive charge.



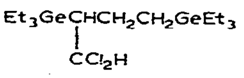
(I)

Since both trialkylsilyl and trialkyltin substituents showed this β-activating effect, it was of interest to examine reactions of some analogous tetraalkylgermanes with phenyl(bromodichloromethyl)mercury.

RESULTS AND DISCUSSION

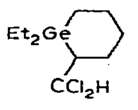
Reactions of three acyclic and three cyclic germanium compounds with phenyl(bromodichloromethyl)mercury were carried out in refluxing benzene solution. In each case CCl_2 insertion occurred very specifically into a βC–H bond. Table 1 summarizes the results and presents supporting analytical data. In the NMR spectrum of each product the resonance due to a CCl_2H group was observed between δ 5.71 and 5.93 ppm. In the case of the reaction product from isobutyltriethylgermane the CCl_2H signal was a singlet at 5.61 ppm, in agreement with the assigned structure, $Et_3GeCH_2C(CCl_2H)Me_2$. The insertion product from triethyl-n-propylgermane was reduced with lithium and tert-butanol in THF. The reduction product was found to be isobutyltriethylgermane, and thus the assigned insertion product structure, Et_3Ge-$CH_2CH(CCl_2H)CH_3$, has firm experimental support.

For the other four products, (III), (IV), (V) and (VI), the evidence in favor of the structures shown is chemical in nature. All four insertion products were stable thermally to well above 100°. The compounds (III), (IV) and (V) could be isolated by gas chromatography, (III) at 170°, (IV) at 180°, and (V) at 190°. This stability speaks *against* CCl_2 insertion into αC–H bonds of the starting germanes to give (VII)–(X),

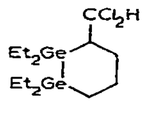


$$Et_3Ge\underset{CCl_2H}{\underset{|}{C}}HCH_2CH_2GeEt_3$$

(VII)



(VIII)



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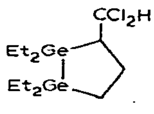
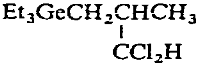
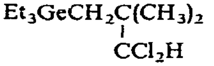
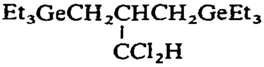
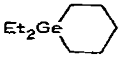
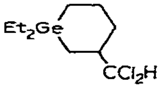
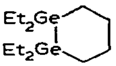
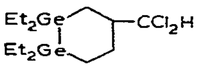
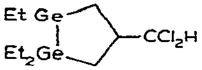


(X)

TABLE 1

CCl_2 INSERTION PRODUCTS FROM TETRAALKYLGERMANES

Starting compound	Insertion product		n_D^{25}	$\delta(CCl_2H)$ (ppm)	Analysis found (calcd.) (%)		
	Structure	Yield (%)			C	H	Cl
$Et_3GeCH_2CH_2CH_3$	(I)  $Et_3GeCH_2\underset{CCl_2H}{\underset{\mid}{C}}HCH_3$	41	1.4845	5.76 d J 3.2 Hz	41.92 (42.02)	7.66 (7.76)	24.87 (24.81)
$Et_3GeCH_2CH(CH_3)_2$	(II)  $Et_3GeCH_2\underset{CCl_2H}{\underset{\mid}{C}}(CH_3)_2$	91	1.4837	5.61 s	44.05 (44.07)	8.14 (8.07)	24.16 (23.65)
$Et_3GeCH_2CH_2CH_2GeEt_3$	(III)  $Et_3GeCH_2\underset{CCl_2H}{\underset{\mid}{C}}HCH_2GeEt_3$	61	1.4951	5.93 d J 2.4 Hz	42.94 (43.23)	8.01 (8.16)	15.88 (15.95)
	(IV) 	71	1.5025	5.71 d J 3.0 Hz	42.23 (42.32)	7.23 (7.10)	25.19 (24.99)
	(V) 	85	1.5290	5.85 d J 2.8 Hz	38.97 (38.99)	7.06 (7.05)	17.49 (17.71)
	(VI) 	64		5.88 d J 4.0 Hz	[a]		

[a] Not isolated in analytical purity.

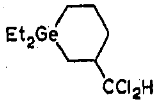
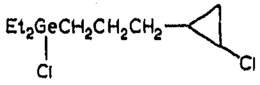
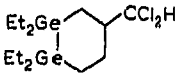
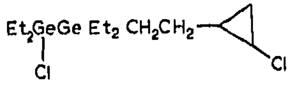
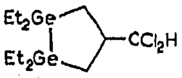
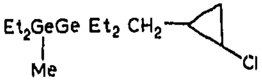
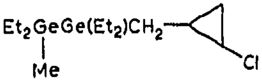
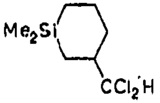
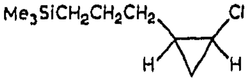
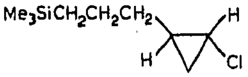
respectively. These are β-chloroalkylgermanes and as such would be expected to undergo facile β-elimination of Ge–Cl[4]. In addition to this negative evidence, more positive indication of the structures of (IV), (V) and (VI) was provided by their high temperature thermolysis. All three cyclic β-insertion products, (IV), (V) and (VI) (Table 1) are γ-chloroalkylgermanes. They would be expected to be much more stable than the isomeric β-chloroalkylgermanes with respect to Ge–Cl elimination, but, nevertheless, such eliminations should be realizable under more drastic temperature conditions. Accordingly, (IV), (V) and (VI) were pyrolyzed, (IV) and (V) as the neat liquids at 200°, (VI) in the presence of zinc chloride at 145°. The first three entries in Table 2 summarize the results of these experiments. The formation of the observed chlorocyclopropane derivatives is exactly what would be expected if (IV), (V) and (VI) were the βC–H insertion products indicated and had undergone γ-elimination of Ge–Cl. If the insertion products were (VIII), (IX) and (X), then formation of vinyl chloride derivatives would have occurred. In the case of the germacyclohexane, insertion of CCl_2 into a γC–H bond would have given a product whose thermolysis, if at all realizable in the form of Ge–Cl elimination, would be expected to be a chlorocyclobutane derivative. The scheme below illustrates these alternatives for the case of 1,1-diethyl-1-germacyclohexane. The sum total of our evidence thus is very strongly in favor of the structures shown in Table 1.

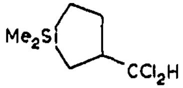
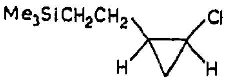
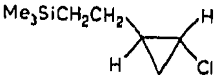
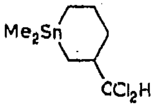
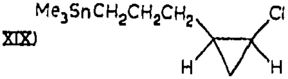
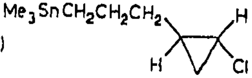
In the case of the CCl_2 insertion product of the digermacyclopentane, pyrolysis gave not only (XXI), but also 1,2-dichloro-1,1,2,2-tetraethyldigermane. The latter,

(continued on p. 376)

TABLE 2

THERMOLYSIS OF 3-DICHLOROMETHYL-1-METALLACYCLOALKANES

3-Dichloromethyl-1-metallacycloalkane	Thermolysis product (or methylated thermolysis product)	Cyclopropane NMR δ(CHCl) (ppm)	n_D^{25}	Analysis found (calcd.) (%)[a]		
				C	H	Cl
	(XI)  (mixture of *cis* and *trans* isomers)	3.21 sextet J_{trans} 4.0 J_{cis} 7.0 Hz	1.4902	42.29 (42.32)	7.33 (7.10)	24.63 (24.99)
	(XII)  (mixture of *cis* and *trans* isomers)	3.22 sextet J_{trans} 4.0 J_{cis} 7.0 and 7.5 Hz	1.5259	38.84 (38.99)	7.13 (7.05)	17.75 (17.71)
	(XIII)  (mixture of *cis* and *trans* isomers)	3.18 m[b]		36.87 (37.29)	6.66 (6.78)	18.05 (18.35)
	(XIV)  (5.7 : 1 mixture of *cis* and *trans* isomes)	3.02 m[b]	1.5127[b]			9.81 (9.69)
	(XV)  (3.2 parts)	2.91 sextet J_{cis} 7.0 J_{trans} 4.0 Hz	1.4478			
	(XVI)  (1 part)	2.47 m	1.4438			

	(XVII)  (1.5 parts)	2.92 sextet J_{cis} 7.0 J_{trans} 4.0 Hz	1.4463	54.71 (54.41)	9.76 (9.70)	19.76 (20.06)
	(XVIII)  (1 part)	2.46 m	1.4432			
	(XIX)  (3.4 parts)	3.12 sextet J_{cis} 7.0 and 7.1 J_{trans} 4.0 Hz	1.4914	38.64 (38.41)	6.96 (6.81)	12.40 (12.61)
	(XX)  (1 part)	2.76 m	1.4878			

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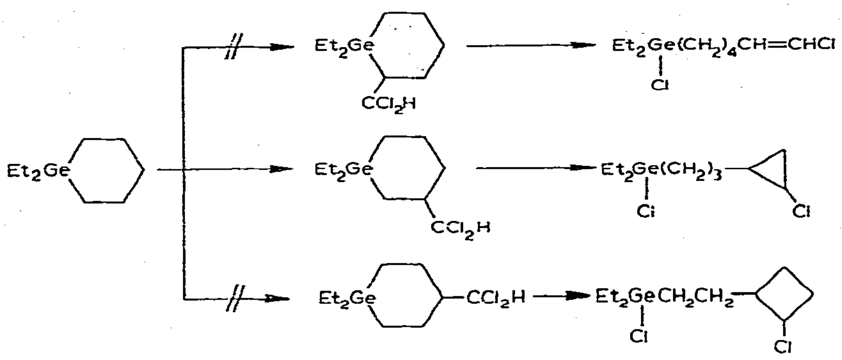
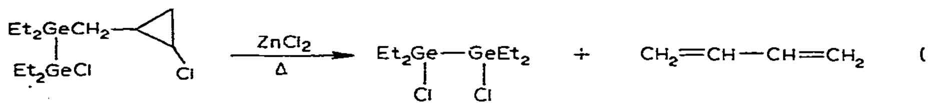
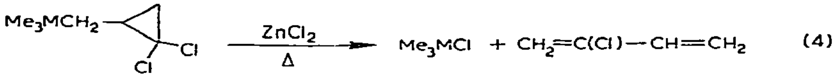
[a] Analytical values for a mixture of both isomers. [b] Combined isomers. [c] Authentic samples prepared.



no doubt, was derived from (XIII) as shown in eqn. (3), in a process analogous to the thermolysis of dichlorocyclopropylcarbinyl derivatives of silicon and tin which we studied previously [eqn. (4)][5].



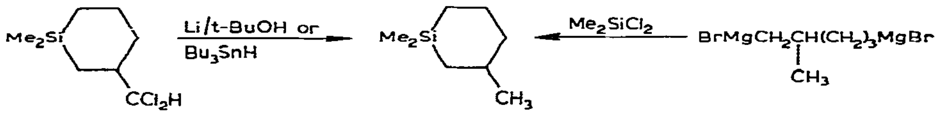
(XIII) (3)



(4)

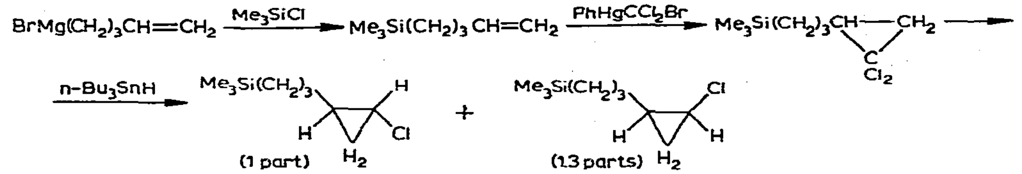
(M=Si, Sn)

The successful application of the thermolysis of (IV), (V) and (VI) to the determination of their structure led us to extend this procedure to the CCl_2 insertion products of 1,1-dimethyl-1-silacyclopentane, 1,1-dimethyl-1-silacyclohexane and 1,1-dimethyl-1-stannacyclohexane. The reactions of these metallacycloalkanes with phenyl(bromodichloromethyl)mercury had been carried out previously[2] [eqn. (2)], but only in the case of the silacyclohexane reaction product had the structure been proven as shown in eqn. (5). Accordingly, these insertion reactions were repeated and the products were heated (the silicon compounds in the presence of zinc chloride) until thermal decomposition occurred. The decomposition products, which were methylated for easier handling, are shown in Table 2, and their formation confirms the structures which we reported earlier[2]. In all three cases the formation of chlorocyclopropanes is compatible only with insertion into C–H bonds β with respect to the Group IV atom. Complete confirmation of the structure of the methylated pyrolysis product derived from 1,1-dimethyl-3-dichloromethyl-1-silacyclohexane was provided by its independent synthesis as shown in the scheme on the top of next page.



(5)

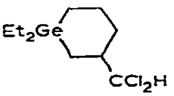
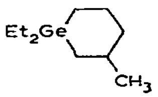
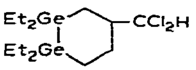
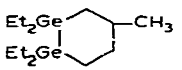
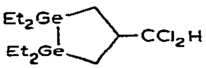
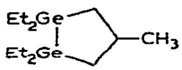
The thermolysis of CCl_2 insertion products into βC–H bonds of metallacycloalkanes thus represents a novel synthesis of metal-substituted cyclopropanes. In view of the high yields with which such insertions occur in some cases (ref. 2 and this work),



this insertion-thermolysis sequence may find useful application in synthesis. As might be expected from a consideration of metal–carbon bond energies, the order of reactivity with respect to M–Cl elimination in this general class of compounds decreases as the metal is changed from tin to germanium to silicon.

TABLE 3

REDUCTION PRODUCTS

Starting compound	Reduction product		n_D^{25}	Analysis found (calcd.) (%)	
	Structure	Yield (%)		C	H
$Et_3GeCH_2\underset{\underset{CCl_2H}{\mid}}{C}HCH_3$	$Et_3GeCH_2CH(CH_3)_2$	67	1.4470[a]		
$Et_3GeCH_2\underset{\underset{CCl_2H}{\mid}}{C}(CH_3)_2$	$Et_3GeCH_2C(CH_3)_3$	34	1.4526	57.34 (57.21)	11.23 (11.35)
$(Et_3GeCH_2)_2CHCCl_2H$	$(Et_3GeCH_2)_2CHCH_3$	25	1.4782	51.42 (51.15)	10.00 (10.18)
		68	1.4694	56.09 (55.89)	10.57 (10.30)
			1.5080	46.87 (47.09)	9.07 (9.12)
			1.5071	45.69 (45.38)	8.81 (8.89)

[a] Isobutyltriethylgermane starting material used had n_D^{25} 1.4469 and identical NMR and IR spectra.

The reduction of $Et_3GeCH_2CH(CCl_2H)CH_3$ has been noted already. The other insertion products also were reduced, (II), (III) and (IV) with lithium and tert-butanol in THF, (V) and (VI) with tri-n-butyltin hydride. The reduction products are given in Table 3.

The reaction of 1,1,2,2-tetraethyldigermacyclopentane with phenyl(bromodichloromethyl)mercury is of special interest since it was not clear where CCl_2 attack might be expected to occur. βC–H insertion was one possibility, but attack at the Ge–Ge bond to give 1,1,3,3-tetraethyl-2,2-dichloro-1,3-digermacyclohexane (XXI) was an alternate possibility*. It may be recalled that our previous work has shown

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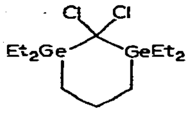
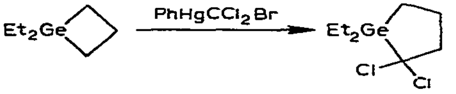
* In this connection note our previously reported[6] insertion of dihalocarbenes into the Sn–Sn bond of several hexaorganoditin compounds.



(XXI)

that single bonds which normally are not reactive toward $PhHgCCl_2Br$ (*e.g.*, Si–C, Ge–C) can undergo insertion of mercurial-derived CCl_2 when they are part of a strained cyclic system. Thus we may compare the reactions of the first four germanes in Table 1 with phenyl(bromodichloromethyl)mercury with the major reaction observed in the case of 1,1-diethyl-1-germacyclobutane [eqn. (6)][7], *i.e.*, CCl_2 insertion



into the Ge–C bond. The Ge_2C_3 ring of the digermacyclopentane also appears to be quite strained, and its Ge–Ge bond is much more reactive than the Ge–Ge bonds of unstrained digermanes[8]. Had CCl_2 insertion into the Ge–Ge bond of the 1,2-digermacyclopentane occurred, then the product to be expected, (XXI), would be an α-chloroalkylgermane which should be stable thermally. This product was not detected in our GLC analysis of the reaction mixture, and the only reaction which appeared to have occurred was CCl_2 insertion into a βC–H bond to give (VI).

In view of this qualitative similarity between the reactions of tetraalkyl derivatives of tin, germanium and silicon with phenyl(bromodichloromethyl)mercury-derived dichlorocarbene, it was of interest to obtain some more quantitative data concerning relative reactivities. A competition experiment in which four molar equivalents each of isobutyltriethylgermane and isobutyltriethylsilane were allowed to compete for one molar equivalent of $PhHgCCl_2Br$ gave the germanium-containing and the silicon-containing products in yields of 54% and 40%, respectively. Thus the relative reactivity toward C–H insertion, $k(\text{Ge})/k(\text{Si})$, is 1.35. The corresponding relative rate constant $k(\text{Sn})/k(\text{Si})$, obtained in a similar competition for CCl_2 between $Me_3SnCH_2CHMe_2$ and $Me_3SiCH_2CHMe_2$, was 5.9[2]. The relative effectiveness of Group IV substituents in the activation of βC–H bonds toward CCl_2 insertion then is Sn > Ge > Si. Such a reactivity sequence is quite compatible with the explanation for the β-metal activation which we have suggested[2].

EXPERIMENTAL

Starting Materials

Phenyl(bromodichloromethyl)mercury was prepared by our THF procedure[9]. The organogermanes which have been described previously are: 1,1-diethyl-1-germacyclohexane[10], 1,1,2,2-tetraethyl-1,2-digermacyclo-pentane and -hexane[8], 1,3-bis(triethylgermyl)propane[11], triethyl-n-propylgermane[12]. Isobutyltriethylgermane, b.p. 88° (24 mm), n_D^{20} 1.4493, d_4^{20} 0.9744, was prepared in nearly quantitative yield by the reaction of isobutylmagnesium bromide in diethyl ether with Et_3GeBr. (Found: C, 55.64; H, 11.26. $C_{10}H_{24}Ge$ calcd.: C, 55.37; H, 11.15).

Reaction of tetraalkylgermanes with phenyl(bromodichloromethyl)mercury

A 25 ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, thermometer and a magnetic stirring assembly was charged with 2.64 g (6.0 mmol) of the mercury reagent and 10.0 mmol of the germane, together with 4 ml of dry benzene. The reaction mixture was stirred and heated at reflux (81–83°) under an atmosphere of dry nitrogen. The phenylmercuric bromide which crystallized out during this time was filtered (yields were 90–95%) and the filtrate was trap-to-trap distilled at 0.01 mm into a receiver at −78°. The distillate was examined by gas-liquid chromatography (GLC). Samples for characterization and analysis were isolated by GLC and the product yields were determined by GLC using the internal standard procedure. An F&M Model 720 gas chromatograph was used. For compounds (I) and (II) a 6 ft × 0.25 in., 20% Dow Corning DC 200 on Chromosorb W column (at 180–185°) served well, but compounds (III), (IV) and (V) were not stable to those GLC conditions. It was found that these three products could be estimated and isolated using GLC when a 4 ft. × 0.25 in. column containing 5% UC W98 on Chromosorb W was used (170–190°). The products obtained are listed in Table 1.

In the case of 1,1,2,2-tetraethyl-1,2-digermacyclopentane, the CCl_2 insertion product was not stable to the GLC conditions used, and our experiments are described in more detail.

Phenyl(bromodichloromethyl)mercury (2.21 g, 5.0 mmol) and 1,1,2,2-tetraethyl-1,2-digermacyclopentane (1.50 g, 4.95 mmol) in benzene (3 ml) were sealed under argon in a 15 ml flask and stirred at room temperature for 12 days. (A room temperature reaction was carried out in order to minimize attack by the phenylmercuric bromide formed on the Ge–Ge bond of the starting material.) The gray solid, m.p. 250–258°, 1.5 g, which formed during this period was filtered and the colorless filtrate was examined by GLC (4 ft. × 0.25 in., 10% UC W98 at 175°). The presence of a high-boiling product, starting material and some low boiling materials was apparent. Attempted isolation of the product by GLC was not successful, the decomposition which occurred during GLC giving impure material. All low-boiling components and starting germane were removed from the filtrate by distillation (to 80° at 0.03 mm). The NMR spectrum of the residue showed a doublet (J 4.0 Hz) at δ 4.88 ppm, a signal indicative of the presence of the C–H insertion product. The thermolysis and the reduction of the crude insertion product will be described in the appropriate sections. Another experiment, however, provided evidence in favor of structure (VI).

Two hundred mg of the crude reaction product was diluted with 0.5 ml of hexane and treated with bromine until its color was no longer discharged. This mixture was treated with an excess of ethereal methyllithium and then hydrolyzed with saturated ammonium chloride solution. The dried organic layer was concentrated at reduced pressure to 0.3 ml and analyzed by GLC (conditions as above). Two major components were present:

$(Et_2MeGeCH_2)_2CHCCl_2H$. (Found: C, 40.19; H, 7.71; Cl, 16.77. $C_{14}H_{32}Cl_2Ge_2$ calcd.: C, 40.36; H, 7.75; Cl, 17.03%.) NMR (neat): δ 0.25 (s, 6, Ge–Me), 1.07 (m, 24, Ge–Et), 2.35 (m, 1, HCCCl$_2$H) and 5.86 ppm (d, J 2.5 Hz, 1, CCl_2H).

$(Et_2MeGeCH_2)_2C{=}CHCl$ *(tentative)*. (Found: C, 43.50; H, 8.13. $C_{14}H_{31}ClGe_2$ calcd.: C, 44.24; H, 8.22%.) NMR (neat): δ 0.50 (s, 3, Ge–Me), 0.60 (s, 3, Ge–Me), 1.00 (m, 20), 1.62 (s, 2), 1.80 (s, 2) and 5.42 ppm (s, 1). The infrared spectrum (liquid film) showed absorption characteristic of an olefinic C–H at 3080 cm^{-1}. This product is the formal dehydrochlorination product of the compound immediately above and its formation in the presence of an excess of methyllithium is not surprising.

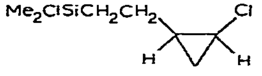
In another $PhHgCCl_2Br$/digermacyclopentane reaction carried out on a 1.75 mmol scale (12 days at room temperature), the crude product was obtained by concentration of the filtrate in 64% yield.

The NMR spectra of the insertion products were recorded using a Varian Associates A60 or T60 NMR spectrometer; no solvent was used. Chemical shifts are given in δ units, ppm downfield from internal TMS. The chemical shifts due to the CCl_2H substituents are given in Table 1. Infrared spectra were recorded for all products using a Perkin–Elmer 237B or 337 infrared spectrophotometer; ethyl groups were indicated by bands in the 1462–1449, 1428–1414, 1377–1368, 1235–1209, 1029–1005, 971–949 and 727–673 cm^{-1} regions.

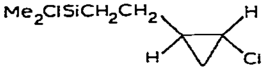
Thermolysis of 3-*dichloromethyl*-1-*metallacycloalkanes*

(*a*). 1,1-*Dimethyl*-3-*dichloromethyl*-1-*silacyclohexane*. The silane (0.60 g, 2.84 mmol) and 20 mg of zinc chloride (dried in vacuum at 115° for 4 h) were sealed in an NMR tube and heated at 170° for 30 min. The resulting black reaction mixture was added to an excess of ethereal methyllithium (3 ml of 5% MeLi solution) and the mixture was stirred at room temperature under nitrogen for 2 h and hydrolyzed with saturated ammonium chloride solution. The ether was distilled from the dried organic layer and the residue was examined by GLC (Table 2). A 6 ft × 0,25 in., 20% DC 200 column at 180° served in the isolation of the isomers formed.

(*b*). 1,1-*Dimethyl*-3-*dichloromethyl*-1-*silacyclopentane*. The silane (150 mg, 0.85 mmol) and 3 mg of anhydrous zinc chloride were heated at 135° for 1 h in a sealed NMR tube. The NMR spectrum of the reaction mixture indicated the presence of both cyclopropane isomers, (XXII) and (XXIII), the former (*cis*) showing the CHCl resonance at δ 3.00 ppm with J_{cis} 7.0 and J_{trans} 4.0 Hz. The *trans* isomer (XXIII) showed CHCl as a quintet at δ 2.55 ppm with J_{cis} and J_{trans} 3.1 Hz.



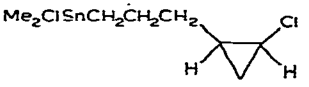
(XXII)



(XXIII)

The reaction mixture was treated with methyllithium as described in the experiment above and the products were isolated by GLC (6 ft × 0.25 in., 20% Carbowax 20M at 95°. The infrared spectra of both isomers (neat liquid) showed absorption due to cyclopropane C–H bonds, (XVII) at 3080, 3060 and 3002; (XVIII) at 3080, 3050 and 3002 cm^{-1}.

(*c*). 1,1-*Dimethyl*-3-*dichloromethyl*-1-*stannacyclohexane*. This tin compound (0.50 g, 1.78 mmol) was sealed in an NMR tube and heated at 180° for 2 h. The reaction's progress was monitored by NMR and found to proceed cleanly an quantitatively. GLC (20% DC 200, 160°) failed to resolve the isomeric cyclopropane products and the NMR spectrum of the reaction product showed a sextet due to the CHCl proton of the *cis* isomer (XXIV) at δ 3.45 ppm, with J_{cis} 7.0 and J_{trans} 4.0 Hz. The reaction product was treated with methyllithium as described above, and the *cis* and *trans* isomers (XIX) and (XX) were isolated by GLC (20% DC 200, 160°) (*cf.* Table 2). The infrared spectra of both isomers showed cyclopropyl hydrogen absorption at 3080 and 3050 cm^{-1}. The Me_3Sn resonance in the NMR spectrum of (XIX) occurred at δ 0.17 ppm, with $J(^{117}Sn-^{1}H)$ 48 and $J(^{119}Sn-^{1}H)$ 52 Hz. This resonance in the


(XXIV)

NMR spectrum of (XX) was found at 0.16 ppm with identical Sn–H coupling constants.

(*d*). 1,1-*Diethyl-3-dichloromethyl-1-germacyclohexane*. The germane (100 mg, 0.35 mmol) was sealed in a capillary tube and heated at 200° for 2 h. The only major product was found to be (XI) (Table 2), by GLC (4 ft × 0.25 in., 10% UC W-98 at 145°). The infrared spectrum of the product showed cyclopropyl C–H absorption at 3080, 3050 and 3002 cm^{-1}. Although in the NMR spectrum the CHCl resonance of only the *cis* isomer was recognizable, the *trans* isomer also very likely was present in small amount.

(*e*). 1,1,2,2-*Tetraethyl-4-dichloromethyl-1,2-digermacyclohexane*. The germane (150 mg, 0.37 mmol) was heated in a capillary tube at 200° for 2 h. The only major product present was (XII). Absorptions due to the cyclopropyl group at 3080, 3050 and 3002 cm^{-1} occurred in the infrared spectrum of the product.

(*f*). 1,1,2,2-*Tetraethyl-4-dichloromethyl-1,2-digermacyclopentane*. The crude germane (250 mg, 0.65 mmol) and 3 mg of anhydrous zinc chloride were heated in a sealed NMR tube at 145° for 20 min. GLC analysis of the resulting clear yellow solution (4 ft × 0.25 in., 10% UC W-98, 175°) showed the presence of two major products, (XIII) and *sym*-dichlorotetraethyldigermane. The NMR spectrum of the former showed multiplets centered at δ 0.45, 2.00 and 3.18 ppm and singlets at δ 1.20 and 1.28 ppm, and its infrared spectrum showed cyclopropyl hydrogen bands at 3080, 3050 and 3002 cm^{-1}. *Sym*-dichlorotetraethyldigermane was isolated by GLC. (Found: C, 28.98; H, 6.08; Cl, 20.88. $C_8H_{20}Cl_2Ge$ calcd.: C, 28.91; H, 6.07; Cl, 21.33%.) Its NMR spectrum (neat) showed a multiplet at δ 1.37 ppm and its infrared spectrum (liquid film) showed bands at 2975 s, 2940 m, 2820 m, 2790 m, 1465 m, 1430 m, 1385 m, 1230 m, 1025 s, 970 m and 710 vs cm^{-1}.

The reaction mixture was distilled (to 80° at 0.05 mm) to remove low boiling components and the residue was treated with 0.5 ml of 5.3% methyllithium in diethyl ether. After hydrolysis of the mixture, the products (XIV) were isolated from the organic phase by GLC (4 ft × 0.25 in., UC W-98, 155°). The *cis/trans* ratio was 5.7 by GLC, but the isomers were not separated. The isomer mixture obtained had n_D^{25} 1.5127, and its NMR spectrum (neat) showed multiplets centered at δ 1.08, 2.62 and 3.02 ppm and a singlet at 0.22. Its infrared spectrum (liquid film) showed bands at 3080, 3050 and 3002 cm^{-1} due to cyclopropyl hydrogens.

Preparation of authentic 1-chloro-2-(γ-trimethylsilylpropyl)cyclopropane

5-Trimethylsilyl-1-pentene, $Me_3SiCH_2CH_2CH_2CH{=}CH_2$, was prepared by the standard Grignard procedure via the Grignard reagent from $CH_2{=}CH(CH_2)_3$-MgBr. The pure product had b.p. 135–136° and n_D^{25} 1.4267. (Found: C, 67.35; H, 12.88. $C_8H_{18}Si$ calcd.: C, 67.50; H, 12.75%.) The C=C stretching frequency in the infrared spectrum (neat) was found at 1640 cm^{-1}. This olefin (1.70 g, 12.0 mmol), phenyl(bromodichloromethyl)mercury (4.41 g, 10 mmol) and 6 ml of dry benzene were heated under nitrogen at reflux for 3 h. Filtration to remove PhHgBr was followed by distillation of the filtrate to remove solvent and unconverted olefin. Vacuum distillation then gave 1,1-dichloro-2-(γ-trimethylsilylpropyl)cyclopropane, b.p. 70° (0.8 mm), n_D^{25} 1.4563, in 92% yield (2.03 g). (Found: C, 48.06; H, 8.00; Cl, 31.45. $C_9H_{18}Cl_2Si$ calcd.: C, 47.99; H, 8.05; Cl, 31.48%.)

This dichlorocyclopropane (0.50 g, 2.22 mmol) was reduced to the monochlorocyclopropane with 0.65 g (2.23 mmol) of tri-n-butyltin hydride in the presence of 3 mg of azobisisobutyronitrile at 80° for 5 h. The reaction mixture was distilled at 90° (6 mm) to give a mixture of the *cis*- and *trans*-1-chloro-2-(γ-trimethylsilylpropyl)cyclopropanes. Tri-n-butyltin chloride was left as a residue. The pure *cis* and *trans* isomers were isolated by GLC (6 ft × 0.25 in., 20% DC 200, 130°). The *cis*/*trans* ratio was 1.30.

(*a*). *cis*-$Me_3Si(CH_2)_3(C_3H_4Cl)$ (XV): n_D^{25} 1.4478. NMR (neat): δ 2.91 (1, sextet, J_{trans} 4.0, J_{cis} 7.0 Hz), 1.55–0.70 (9, m) and 0.10 ppm (9, s). Infrared spectrum (neat liquid): 3075 w, 3048, 3002 w, 2950 s, 2920 s, 2860 (sh), 1440 m, 1410 w, 1290 m, 1280 m, 1250 s, 1180 m, 1035 m, 1015 m, 950 w, 900 (sh), 870 vs, 840 vs, 760 m, 700 m, 660 m, cm^{-1}

(*b*). *trans*-$Me_3Si(CH_2)_3(C_3H_4Cl)$ (XVI): n_D^{25} 1.4438. NMR (neat): δ 2.47 (1, m), 1.23–0.20 (9, m) and 0.10 ppm (9, s). Infrared spectrum (neat liquid): 2076 w, 3045 w, 3002 w, 2950 s, 2920 s, 2870 (sh), 1440 m, 1410 w, 1380 w, 1340 w, 1290 (sh), 1250 vs, 1185 w, 1170 w, 1100 w, 1035 m, 1020 w, 998 w, 935 w, 915 w, 870 vs, 840 vs, 760 m, 750 m, 700 m, 690 m, cm^{-1}. A mixture of the two isomers was analyzed. (Found: C, 56.78; H, 10.00; Cl, 18.54. $C_9H_{19}ClSi$ calcd.: C, 56.65; H, 10.04; Cl, 18.58%.)

Reduction of insertion products

(*a*). *With lithium and tert-butanol in tetrahydrofuran.* The following serves as an example of the procedure used. To a solution of 0.380 g (1.34 mmol) of $Et_3GeCH_2CH(CCl_2H)CH_3$ in 5.7 ml of benzene was added 0.50 g of lithium dispersion, 5 ml of tert-butanol and 5 ml of THF. The reaction was initiated by heating briefly to 80°. A vigorous, exothermic reaction commenced; after it had subsided, the reaction mixture was heated at 70° for 4 h. A trap-to-trap distillation at 0.05 mm served to separate the volatiles. GLC examination of the distillate (20% DC 200 on Chromosorb W, 120°) showed that isobutyltriethylgermane was present in 67% yield. Samples for characterization were isolated by GLC; IR and NMR spectra and refractive index (n_D^{25} 1.4469) were obtained.

An alternative work-up involved filtration, distillation of low boilers, solution of the residue in ether and washing the ether solution with water. After evaporation of the ether, the product was isolated by GLC.

(*b*). *With tri-n-butyltin hydride.* Compound (V) (75 mg), tri-n-butyltin hydride (180 mg) and 2 mg of azobisisobutyronitrile catalyst were sealed in an ampoule and heated at 90° for 24 h. The reduced product was isolated from the reaction mixture by GLC (20% ethylene glycol sebacate, 185°).

The crude product obtained in 64% yield by the room temperature reaction of 1.75 mmol each of $PhHgCCl_2Br$ and 1,1,2,2-tetraethyl-1,2-digermacyclopentane was heated with 0.56 g (1.93 mmol) of tri-n-butyltin hydride and 3 mg of azobisisobutyronitrile at 80° for 3 h. GLC (same conditions as above) served to isolate pure samples of the reduced product which was present in 38% yield (by GLC).

The infrared and NMR spectra of the reduced products were unexceptional.

Competition of isobutyltriethylgermane and isobutyltriethylsilane for phenyl(bromodichloromethyl)mercury

The mercurial (46 mg, 0.104 mmol), the germane (86 mg, 0.40 mmol), the silane (68 mg, 0.40 mmol) and 0.3 ml of benzene were stirred and heated under nitrogen in a preheated (80±2°) oil bath for 3 h. The internal standard (11.4 mg of 1,1-dimethyl-3-dichloromethyl-1-silacyclohexane) was added and the reaction mixture was filtered. GLC analysis (5% UC W98, 150°) of the filtrate showed the yields of $Et_3GeCH_2C(CCl_2H)Me_2$ and $Et_3SiCH_2C(CCl_2H)Me_2$[2] to be 54% and 40%, respectively.

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