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THE PREPARATION OF GROUP IV ORGANOMETALLIC COMPOUNDS CONTAINING *gem*-DIHALOCYCLOPROPYL GROUPS

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The addition of dichlorocarbene to alkenylsilanes has been reported by several research groups during the past five years. Such addition to allylsilanes occurred in moderate yield when the $CHCl_3$ + tert-BuOK system was used as CCl_2 source[1,2], in relatively low yield when dichlorocarbene was produced by sodium trichloroacetate decarboxylation[3], and in good yield when CCl_3SiCl_3 thermolysis was used to generate CCl_2[4]. The success of CCl_2 addition to vinylic silanes was even more reagent-dependent, occurring in only extremely low yield when the $CHCl_3$ + tert-BuOK reagent was used[1,2,5], but in good yield with CCl_2 derived from the thermolysis of phenyl(bromodichloromethyl)mercury in benzene at 80° (ref. 6) or CCl_3SiCl_3 at 250° (ref. 4). As we have pointed out previously[6], the $CHCl_3$ + tert-BuOK reagent is not applicable to the preparation of *gem*-dichlorocyclopropanes from alkenylsilanes containing Si–Cl bonds, but Si–Cl bonds are not affected in CCl_2 addition to alkenylsilanes containing such functionality when phenyl(bromodichloromethyl)mercury is used as CCl_2 source. This concept, the use of a non-basic, non-nucleophilic CCl_2 source, was later extended by others to the application of (trichloromethyl)trichlorosilane in the dichlorocyclopropanation of alkenylchlorosilanes[4]. More recently, we have described several examples of difluorocarbene addition (via the Me_3SnCF_3 + NaI reagent system) to the C=C bonds of allyl and vinyl derivatives of silicon, germanium and tin[7]. Only one example of dichlorocarbene addition to an olefinic organotin compound, that of sodium trichloroacetate-derived CCl_2 to allyltri-n-butyltin in 47% yield, has been reported[8].

Two different studies in these laboratories required the synthesis of the *gem*-dichloro- and *gem*-dibromocyclopropanes from various allylic and vinylic derivatives of carbon, silicon, germanium and tin. We report here concerning their synthesis and properties, as well as concerning the reaction of organosilicon and organotin hydrides to 1,1-dichloro-2-vinylcyclopropane, another potential route to compounds of the type discussed.

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TABLE 1

ORGANOMETALLIC *gem*-DIHALOCYCLOPROPANES

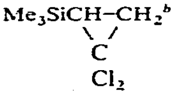
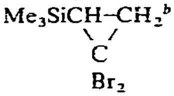
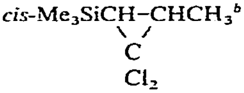
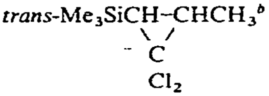
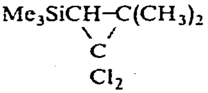
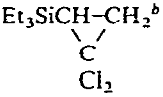
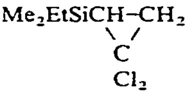
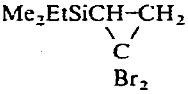
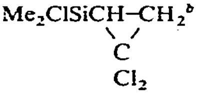
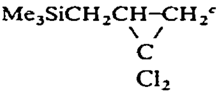
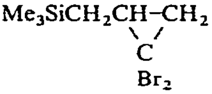
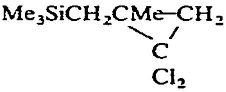
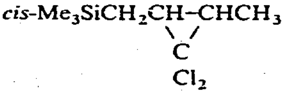
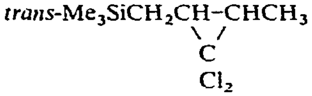
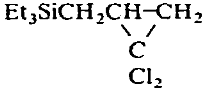
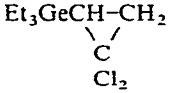
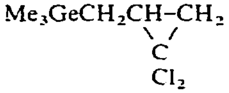
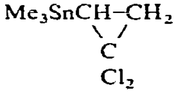
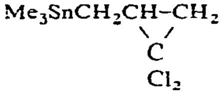
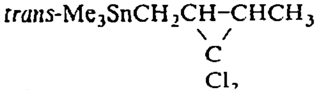
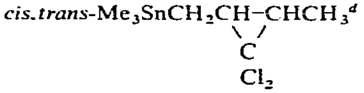
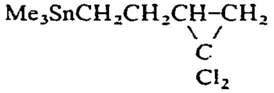
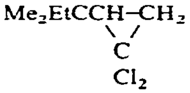
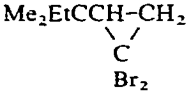
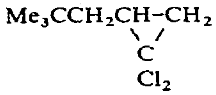
No.	*Compound*	*B.p.* (°*C/mm Hg*)	n_D^{25}	*Yield* (%)	*Procedure*[a]
	Silanes				
1	 $\mathrm{Me_3Si}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH_2}}$[b]	80(50)	1.4558	78	A
2	 $\mathrm{Me_3Si}\underset{\mathrm{C}\atop\mathrm{Br_2}}{\mathrm{CH{-}CH_2}}$[b]	67–68(6.5)	1.5032	57	A
3	 *cis*-$\mathrm{Me_3Si}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH}}\mathrm{CH_3}$[b]	89–90(40)	1.4614	78	A
4	 *trans*-$\mathrm{Me_3Si}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH}}\mathrm{CH_3}$[b]	86.5–88(40)	1.4559	73	A
5	 $\mathrm{Me_3Si}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}C}}\mathrm{(CH_3)_2}$	60–61(6.6)	1.4618	70	A
6	 $\mathrm{Et_3Si}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH_2}}$[b]	54–57(0.8)	1.4735	41	A
7	 $\mathrm{Me_2EtSi}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH_2}}$		1.4623	64	A
8	 $\mathrm{Me_2EtSi}\underset{\mathrm{C}\atop\mathrm{Br_2}}{\mathrm{CH{-}CH_2}}$		1.5133	31	A
9	 $\mathrm{Me_2ClSi}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH_2}}$[b]	68(11)		58	A
10	 $\mathrm{Me_3SiCH_2}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH_2}}$[c]	76–78(20)	1.4555	67 97	B A
11	 $\mathrm{Me_3SiCH_2}\underset{\mathrm{C}\atop\mathrm{Br_2}}{\mathrm{CH{-}CH_2}}$	60(1.8)	1.4989	52	B
12	 $\mathrm{Me_3SiCH_2}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CMe{-}CH_2}}$	60–62(7.0)	1.4632	76	B
13	 *cis*-$\mathrm{Me_3SiCH_2}\underset{\mathrm{C}\atop\mathrm{Cl_2}}{\mathrm{CH{-}CH}}\mathrm{CH_3}$	91–93(20)	1.4606	89	B

TABLE 1 *(continued)*

No.	*Compound*	*B.p. (°C/mm Hg)*	n_D^{25}	*Yield (%)*	*Procedure*[a]
14	 $\textit{trans}\text{-Me}_3\text{SiCH}_2\underbrace{\text{CH-CH}}_{\text{CCl}_2}\text{CH}_3$	87–89(20)	1.4570	82	B
15	 $\text{Et}_3\text{SiCH}_2\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.4735	80	A
	Germanes				
16	 $\text{Et}_3\text{Ge}\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.4868	65	A
17	 $\text{Me}_3\text{GeCH}_2\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.4737	94	A
	Tins				
18	 $\text{Me}_3\text{Sn}\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.5059	55	A
19	 $\text{Me}_3\text{SnCH}_2\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$	57.5–58(1.4)	1.5041	68	B
20	 $\textit{trans}\text{-Me}_3\text{SnCH}_2\underbrace{\text{CH-CH}}_{\text{CCl}_2}\text{CH}_3$	73.5–74(2.2)	1.5018	81	B
21	mixed  $\textit{cis,trans}\text{-Me}_3\text{SnCH}_2\underbrace{\text{CH-CH}}_{\text{CCl}_2}\text{CH}_3$[d]	83–85(4.3)	1.5004	62	B
22	 $\text{Me}_3\text{SnCH}_2\text{CH}_2\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$	81–83(3.1)	1.5004	53	B
	"*Carbanes*"				
23	 $\text{Me}_2\text{EtC}\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.4584	66	A
24	 $\text{Me}_2\text{EtC}\underbrace{\text{CH-CH}_2}_{\text{CBr}_2}$		1.5260	44	A
25	 $\text{Me}_3\text{CCH}_2\underbrace{\text{CH-CH}_2}_{\text{CCl}_2}$		1.4502	99	A

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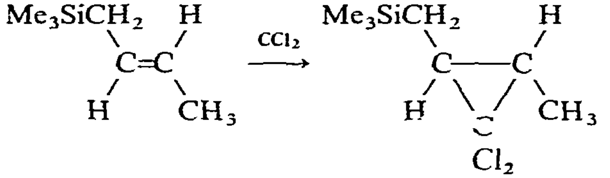
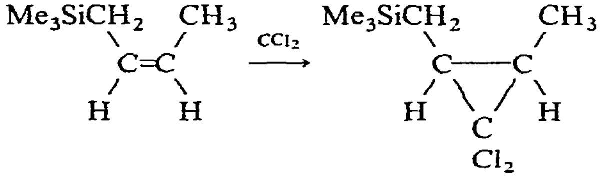
[a] Procedure A: $PhHgCX_2Br$ route; Procedure B: CHX_3 + tert-BuOK reaction. [b] Details in ref. 5. [c] Ref. 1 reports b.p. 79–80° (23 mm), n_D^{25} 1.4558. [d] Starting crotyltrimethyltin 30% *cis*, 70% *trans* isomers.

ALLYL DERIVATIVES

The Komrsová–Farkas variation[9] of the Doering–Hoffmann procedure[10] (addition of potassium tert-butoxide to a haloform/olefin solution in pentane) served well in the preparation of *gem*-dihalocyclopropanes from allylic derivatives of the Group IV elements. The product yields ranged from good (~50%) to excellent (nearly quantitative). The $PhHgCCl_2Br$ route was used in the case of allyltrimethyl- and allyltriethylsilane, allyltrimethylgermane and allyltrimethylmethane; noteworthy are the excellent yields obtained by this procedure (*cf.* Table 1). Of interest were the reactions of *cis*- and *trans*-crotyltrimethylsilane with CCl_2 (via the haloform/base route). In accord with the generally observed stereospecificity of dihalocarbene addition to olefins[6,11–13], each isomer gave a different *gem*-dichlorocyclopropane:





Although the structures of the two isomeric products could not be determined by spectroscopic means, there is no reason to expect these reactions to be an exception to the general rule.

VINYL DERIVATIVES

We have described previously[6] the preparation of 1,1-dichloro- and 1,1-dibromo-2-(trimethylsilyl)cyclopropane, 1,1-dichloro-2-(triethylsilyl)cyclopropane and *cis*- and *trans*-1,1-dichloro-2-methyl-3-(trimethylsilyl)cyclopropane by the $PhHgCX_2Br$ procedure. This method now has been used to good advantage to prepare the *gem*-dichlorocyclopropanes from isobutenyltrimethylsilane, $Me_3SiCH{=}CMe_2$, ethyldimethylvinylsilane and triethylvinylgermane, as well as 1,1-dibromo-2-(ethyldimethylsilyl)cyclopropane. Also of interest is that this procedure could be used to add CCl_2 and CBr_2 in good yield to the highly hindered $Me_2EtCCH{=}CH_2$. Difficulties were encountered in the addition of CCl_2 to trialkylvinyltins by the mercurial procedure. When a benzene solution of triethylvinyltin and phenyl(bromodichloromethyl)-mercury was heated at reflux, an extremely malodorous reaction mixture resulted. Notable also was that the solid which formed originally went into solution again on further heating. These initial observations suggested to us that the phenylmercuric bromide formed reacts with the vinyltin compound as follows:

$$PhHgBr + Et_3SnCH{=}CH_2 \rightarrow Et_3SnBr + PhHgCH{=}CH_2$$

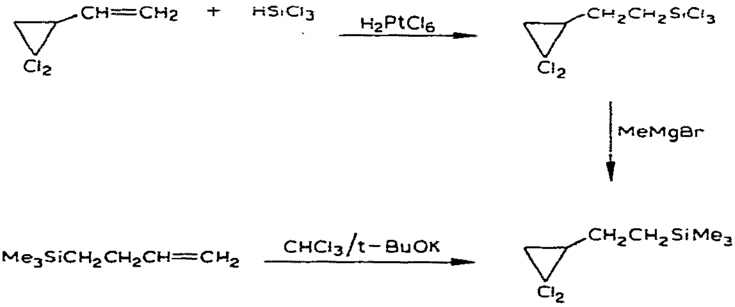
$$2\ PhHgCH{=}CH_2 \rightarrow Ph_2Hg + (CH_2{=}CH)_2Hg$$

In support of this suggestion we cite the following. The cleavage of vinyl groups from tin by mercuric halides is a known reaction[14], as is the disproportionation of unsymmetrical diorganomercurials. Examination of the reaction mixture from the $PhHgCCl_2Br + Et_3SnCH{=}CH_2$ reaction showed the presence of triethyltin halide (precipitation as Et_3SnF with KF solution) and of diphenylmercury (thin layer chromatography), and the intensely vile odor observed is characteristic of divinylmercury*. These difficulties were in part circumvented by minimizing the time of contact between the vinyltin compound and phenylmercuric bromide: the vinyltrimethyltin was added dropwise to a stirred solution of $PhHgCCl_2Br$ maintained at about 80°. With this variation in procedure, an 88% yield of phenylmercuric bromide was obtained. The filtrate, according to its vile odor, contained some divinylmercury, but a 55% yield of 1,1-dichloro-2-(trimethyltin)cyclopropane was realized.

Data concerning the organometallic *gem*-dihalocyclopropanes prepared are listed in Table 1.

ADDITION OF TRICHLOROSILANE AND TRIALKYLTIN HYDRIDES TO 1,1-DICHLORO-2-VINYLCYCLOPROPANE

1,1-Dichloro-2-vinylcyclopropane is easily accessible by CCl_2 addition to 1,3-butadiene[6,15], and thus, in principle, silicon and tin hydride addition to this olefin represents an alternate route to the *gem*-dichlorocyclopropanes prepared from 3-butenylsilicon and tin derivatives. We have found chloroplatinic acid-catalyzed addition of trichlorosilane to occur in good yield, and methylation of the product gave 1,1-dichloro-2-[β-(trimethylsilyl)ethyl]cyclopropane, which was identical in all respects with the product of CCl_2 addition to 3-butenyltrimethylsilane[1]:



This was as expected in view of the coordination mechanism demonstrated for H_2PtCl_6-catalyzed Si–H addition to olefins[16]. In the case of organotin hydrides, whose predominant mode of reaction involves homolysis of the Sn–H bond[17], a firm prediction of the reaction course could not be made. A simple C=C bond addition of trimethyltin hydride to give 1,1-dichloro-2-[β-(trimethyltin)ethyl]cyclopropane would be anticipated if a polar mechanism were operative, but a radical route would be expected to be accompanied by opening of the cyclopropane ring, since this was found

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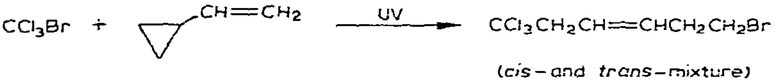
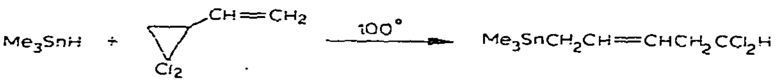
* An odor which will be remembered and recognized again by anyone who has ever encountered it before. The toxicity of this volatile organomercury compound also should be mentioned.

to occur in the radical-initiated addition of polyhalomethanes[18,19] and thiols[20] to vinylcyclopropanes and in the radical polymerization of 1,1-dichloro-2-vinylcyclopropane[21] and vinylcyclopropane[22], *e.g.*:

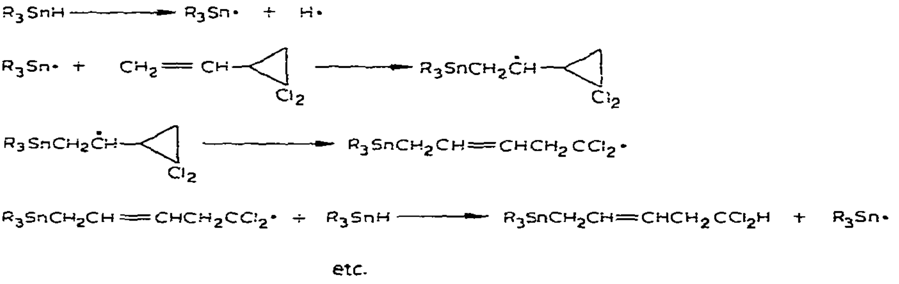


When equimolar quantities of trimethyltin hydride and 1,1-dichloro-2-vinylcyclopropane were heated at 100° in a sealed tube for 40 h, one major product was produced in 35% yield. Its NMR and IR spectra showed it to be $Me_3SnCH_2CH=CHCH_2CCl_2H$, presumably predominantly the *trans* isomer.



None of the simple C=C addition product appeared to have been formed. An authentic sample of the latter, prepared by reaction of 3-butenyltrimethyltin and dichlorocarbene derived from the $CHCl_3$+tert-BuOK reaction, was available for comparison. Two additional minor products were formed in the Me_3SnH + 1,1-dichloro-2-vinylcyclopropane reaction: trimethyltin chloride and 1-chloro-2-vinylcyclopropane (3.5% yield). The latter was present as a mixture of *cis* and *trans* isomers, but no structural assignments were made. The reduction of *gem*-dichlorocyclopropanes to monochlorocyclopropanes by tri-n-butyltin hydride is a known reaction[23], so the formation of this minor product finds ready explanation. The ring-opened addition product was obtained in *ca.* 6% yield when the trimethyltin hydride + 1,1-dichloro-2-vinylcyclopropane reaction was carried out in the presence of azobisisobutyronitrile at 45° for 96 h. The same mode of reaction was observed when a mixture of tri-n-butyltin hydride and 1,1-dichloro-2-vinylcyclopropane in a quartz flask was irradiated with a UV lamp for 38 h. The product, which was formed in 16% yield, had NMR and IR spectra indicative of the $n\text{-}Bu_3SnCH_2CH=CHCH_2CCl_2H$ structure, but an analytically pure sample of this high-boiling compound was not obtained. Again, a small amount of reduction to 1-chloro-2-vinylcyclopropane occurred.

It is clear from these results that the trialkyltin hydride + 1,1-dichloro-2-vinylcyclopropane reactions as carried out in this study proceed by a free radical mechanism of the type shown below.



etc.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Analyses were performed by Dr. S. M. Nagy, M.I.T. Microchemical Laboratory, and by the Galbraith Laboratories, Knoxville, Tenn. IR spectra were recorded on a Perkin–Elmer Infracord 337 grating spectrophotometer and NMR spectra were obtained using a Varian Associates A 60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal tetramethylsilane. Gas–liquid partition chromatography (GLPC) was performed with MIT isothermal units (25% Dow Corning 710 Silicone Oil, General Electric Co. SE-30 Silicone Rubber Gum or General Electric Co. XF-1150 Silicone Fluid on Chromosorb P) or with an F&M Model 700 gas chromatograph.

Preparation of starting materials

Phenyl(trihalomethyl)mercury compounds were prepared as described in a previous publication[24]. The allyl derivatives of silicon, germanium and tin were prepared by reaction of allyllithium[25] with the respective R_3MCl compound, $Me_3SiCH_2CMe{=}CH_2$ via methallyllithium[25]. The reaction of isobutenyllithium with trimethylchlorosilane served in the preparation of $Me_3SiCH{=}CMe_2$[26]. The reaction of ethylmagnesium bromide in ether with dimethylvinylchlorosilane gave $Me_2EtSiCH{=}CH_2$. Vinyllithium[27] was used in the preparation of triethylvinylgermane and trimethylvinyltin. These are all known compounds, and their properties (b.p., n_D^t, IR spectra) agreed with those reported in the literature.

The carbon derivatives, $Me_3CCH_2CH{=}CH_2$ and $Me_2EtCCH{=}CH_2$, were purchased from Chemical Samples, Inc., Columbus, Ohio.

Preparation of crotyl derivatives

(*a*) *Crotyltriphenyltin.* Triphenyltinsodium was prepared from 0.2 mole of triphenyltin chloride and 0.4 g-atom of sodium in liquid ammonia by the method of Chambers and Scherer[28]. To the resulting pale yellow slurry (at −78°) was added a solution of 0.22 mole of crotyl chloride (Aldrich Chemical Co.) in 25 ml of petroleum ether. The ammonia was allowed to evaporate overnight and the solid residue was diluted with 200 ml of petroleum ether and hydrolyzed with an excess of saturated ammonium chloride solution. The organic layer was dried, filtered and evaporated to give 68.8 g of pale yellow solid. Solution in hot ligroin followed by slow cooling to −10° gave 38.6 g of white solid with m.p. 56.5–57.5° and a second crop of 15.3 g, m.p. 54–56°; the total yield was 65%. An analytical sample, recrystallized from ethanol, had m.p. 57–59°. Calcd. for $C_{22}H_{12}Sn$: C, 65.23; H, 5.48; found: C, 65.20; H, 5.51.

(*b*) *Crotyltrimethylsilane.* In a two liter, three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, mechanical stirrer and 500 ml dropping funnel was placed 93.0 g (0.23 mole) of crotyltriphenyltin and 400 ml of diethyl ether. The dropping funnel was charged with 255 ml of 0.91 *N* phenyllithium in ether (0.232 mole), which then was added to the stirred crotyltriphenyltin solution. A precipitate of tetraphenyltin and a clear yellow solution of crotyllithium resulted. To this mixture then was added dropwise 25.0 g (0.23 mole) of trimethylchlorosilane (Dow Corning Corp.). The reaction mixture was heated at reflux for 10 h, hydrolyzed with 50 ml of water and filtered to remove tetraphenyltin (97.0 g, 98%). The dried organic layer was distilled using a Widmer column to give 23.4 g (80%) of crotyltrimethylsilane, b.p. 110–115°, n_D^{25} 1.4192; lit.[29] b.p. 113°, n_D^{20} 1.4195, for an unspecified isomeric mixture.

The distilled crotyltrimethylsilane was analyzed by GLPC (XF-1150 column isothermally at 71°, 10 psi helium). Two isomers with retention times of 6.0 and 7.5 min were present in a ratio of 61 : 39. GLPC analysis was also performed using a column packed with 20% by weight of a 15% $AgNO_3$ solution in tetraethylene glycol on Chromosorb P at 32° with 20 psi helium. Under these conditions the retention time was 7.5 min for the first isomer and 12.6 min for the second to be eluted. The ratio of the peak areas was approximately 3 : 2. According to Muhs and Weiss[30], the *cis* isomer of an olefin has a longer retention time than the *trans* isomer on a silver nitrate column.

The identity of the first isomer to be eluted from the silver nitrate column with the first to be eluted from the XF-1150 column was established by a comparison of their IR spectra. The first isomer to be eluted had ν(C=C) at 1655 (w) cm^{-1}, the second had ν(C=C) at 1645 (m) cm^{-1}. Bellamy[31] states that the C=C stretching frequency generally is less intense and occurs at higher frequency for the *trans* isomer of a pair of isomeric olefins. On the basis of elution times from the silver nitrate column and the IR data, the more abundant isomer and the first to be eluted is *trans*-crotyltrimethylsilane and the second is the *cis* isomer. Both isomers were isolated by GLPC and characterized:

trans-Crotyltrimethylsilane, n_D^{25} 1.4159. IR (carbon tetrachloride): 3010(s), 2960(s), 2948(sh), 2925(sh), 2885(m), 2855(m), 2730(w), 1925(w), 1655(w), 1525(w), 1450(m), 1440(m), 1400(m), 1375(sh), 1310(w), 1257(s), 1165(s), 1072(m), 1050(m), 970(s), 912(m), 855(s), 695(m) cm^{-1}. NMR (in CCl_4): singlet at 0.11 (9 H), doublet at 1.26 (*J* 5 cps) (2 H), doublet at 1.55 (*J* 4 cps) (3 H) and an overlapping pattern between 5.0 and 5.4 ppm (2 H).

cis-Crotyltrimethylsilane, n_D^{25} 1.4208. IR (in CCl_4): 3010(s), 2960(s), 2920(m), 2890(w), 2860(sh), 2810(sh), 2750(sh), 1925(w), 1645(m), 1525(w), 1440(sh), 1415(m), 1395(m), 1360(m), 1290(sh), 1266(sh), 1255(s), 1158(s), 1062(w), 1037(w), 995(s), 908(m), 855(s), 719(s), 701(s), 659(s), 590(m) cm^{-1}. NMR (in CCl_4): singlet at 0.05 (9 H), an overlapping pattern of three broadened single peaks between 1.2 and 1.9 (5 H) and a complex multiplet centered at about 5.36 ppm (2 H).

A portion of the mixture of *cis*- and *trans*-crotyltrimethylsilane also was separated by careful fractional distillation under nitrogen through a Nester–Faust annular Teflon spinning band column of approximately 150 theoretical plates using a 100 : 1 reflux ratio. The course of the distillation was monitored by GLPC. In this manner 2.70 g of *trans* isomer, b.p. 109–110° (762 mm) and 0.70 g of the *cis* isomer, b.p. 112° (762 mm) was obtained.

(*c*) *Crotyltrimethyltin*. A mixture of *cis*- and *trans*-crotyltrimethyltin was prepared following the procedure of Kuivila and Verdone[32]. Trimethyltinsodium was prepared from 0.615 mole of trimethyltin bromide and 1.23 g-atom of sodium in liquid ammonia by the method of Kraus and Greer[33]. To this reagent solution (at −78°) was added dropwise 0.615 mole of crotyl chloride. The reaction mixture was diluted with 200 ml of dry pentane, the ammonia was allowed to evaporate overnight and the residue was hydrolyzed with saturated ammonium chloride solution. The dried organic layer was distilled to give 106.3 g (79%) of crotyltrimethyltin, b.p.

148–154°.

Analysis of the product by GLPC (XF 1150, 91°, 15 psi helium) showed it to contain two components with retention times of 8.6 and 10.8 min, with an area ratio of 3 : 1, respectively.

The IR spectrum (in CCl_4) of the isomer to be eluted first showed bands at: 3010(s), 2980(s), 2960(sh), 2920(s), 2885(sh), 2855(m), 2730(w), 1745(w), 1690(w), 1655(m), 1545(w), 1455(m), 1440(m), 1410(sh), 1375(w), 1310(m), 1260(w), 1195(m), 1162(m), 1105(m), 1072(m), 1040(m), 967(s), 905(m), 525(s) cm^{-1}. Its NMR spectrum (in CCl_4) showed a singlet at 0.06 (9 H), a sharp singlet at 1.52 overlapping with a somewhat broadened singlet at 1.62 (total of 5 H) and a complex pattern of at least nine lines centered at about 5.21 ppm (2 H). The expected splitting due to the ^{117}Sn and ^{119}Sn isotopes also was present. These data are in agreement with those reported by Verdone[32] for the *trans* isomer.

The IR spectrum of the second isomer showed absorption at: 3015(s), 2975(s), 2960(sh), 2915(s), 2860(sh), 2740(w), 1710(w), 1690(w), 1640(s), 1540(w), 1440(w), 1420(sh), 1390(s), 1360(s), 1260(m), 1205(sh), 1195(m), 1162(m), 1097(m), 996(m), 965(sh), 895(w), 815(m), 563(sh), 522(s) cm^{-1}. The NMR spectrum consisted of a singlet at 0.06 with $^{117,119}Sn$ satellites (9 H), two partially overlapping doublets showing further fine splitting centered at 1.52 (J 6 cps) and at 1.68 (J 10 cps) (total of 5 H) and a complex pattern of at least 12 lines between 5.0 and 5.6 ppm (2 H). These spectra are in agreement with those reported[32] for the *cis* isomer.

The isomers of crotyltrimethyltin also were separated by fractional distillation through a Nester–Faust annular Teflon spinning band column at a 100 : 1 reflux ratio into nitrogen-filled glass ampoules fitted with no-air stoppers, the distillation being monitored by GLPC. A total of 20.6 g of *trans*-crotyltrimethyltin, b.p. 147–148° (761 mm), n_D^{25} 1.4762, containing less than 5% of the *cis* isomer and 6.7 g of *cis*-crotyltrimethyltin, b.p. 150–151° (761 mm), n_D^{25} 1.4824, was obtained.

3-*Butenyltrimethyltin*

The Grignard reagent was prepared in 120 ml of diethyl ether from 0.4 g-atom of magnesium turnings and 0.4 mole of 4-bromo-1-butene and to this was added dropwise an ethereal solution of 0.2 mole of trimethyltin bromide. The reaction mixture was heated at reflux for 12 h and subsequently was hydrolyzed with saturated ammonium chloride solution. Distillation of the organic layer gave 33.9 g (77.5%) of 3-butenyltrimethyltin, b.p. 146–148°, n_D^{25} 1.4688. (Found: C, 38.36; H, 7.31. $C_7H_{16}Sn$ calcd.: C, 38.41; H, 7.37%.)

The IR spectrum (liquid film) of the product showed bands at 3080(m), 2980(s), 2930(sh), 2900(s), 2840(sh), 1820(w), 1700(w), 1640(m), 1440(m), 1415(sh), 1310(w), 1290(sh), 1255(w), 1195(m), 1135(w), 1048(w), 997(m), 915(s), 890(sh), 880(sh), 768(s), 740(sh), 715(sh) cm^{-1}. Its NMR (in CCl_4) is consistent with the structure shown:

$$\underset{a}{(CH_3)_3}Sn{-}\underset{b}{CH_2}{-}\underset{c}{CH_2}{-}\underset{d}{CH}{=}\underset{e}{CH_2}$$

Protons "a": singlet at 0.09 ppm with $^{117,119}Sn$ satellites; protons "b": triplet at 0.92 ppm (J 8 cps); protons "c": quartet showing further fine splitting at 2.30 ppm ($J \sim 7$ cps); proton "d": complex, multiline pattern at 5.5–6.1 ppm; protons "e": complex pattern between 4.6–5.2 ppm.

TABLE 2

ANALYTICAL DATA: % FOUND (% CALCD.)

Compound No.[a]	*Carbon*	*Hydrogen*	*Halogen*
5	45.65 (45.49)	7.64 (7.66)	33.36 (33.30)
7	42.67 (42.64)	7.25 (7.16)	35.25 (35.97)
8			56.44 (55.87)
11	29.17 (29.39)	4.76 (4.93)	55.81 (55.87)
12	45.62 (45.49)	7.76 (7.64)	
13, 14 mixture	45.68 (45.49)	7.52 (7.64)	
15	50.08 (50.19)	8.56 (8.43)	29.53 (29.64)
16	40.14 (40.07)	6.82 (6.73)	26.59 (26.29)
17	34.76 (34.79)	6.09 (5.84)	29.11 (29.27)
18	26.17 (26.32)	4.48 (4.43)	
19	29.45 (29.21)	4.92 (4.90)	24.40 (24.62)
21	31.84 (31.83)	5.42 (5.34)	23.37 (23.52)
22	31.83 (31.83)	5.48 (5.34)	23.37 (23.52)
23	53.36 (53.05)	7.84 (7.79)	38.97 (39.16)
24	35.41 (35.58)	5.20 (5.22)	59.25 (59.20)
25	53.20 (53.05)	7.92 (7.79)	38.80 (39.16)

[a] For formula equivalents see Table 1.

*Preparation of gem-dihalocyclopropyl derivatives**

(*a*) *By the Doering–Hoffman route.* The preparation of 1,1-dichloro-2-[(trimethyltin)methyl]cyclopropane is described as an example of the procedure used.

A solution of 1.25 moles of chloroform and 0.118 mole of allyltrimethyltin in 300 ml of petroleum ether was prepared in a three-necked flask equipped with a mechanical stirrer and nitrogen inlet tube and a rubber connecting tube which led to a flask containing the tert-BuOK monosolvate prepared from 0.50 g-atom of potassium[34]. The solution was cooled to −30° and the butoxide was added in small portions to the stirred olefin/chloroform solution (under nitrogen). Upon completion of the addition, the reaction mixture was warmed to room temperature and poured into an equal volume of water. The volatiles were removed from the dried organic layer at reduced pressure and the residue was distilled using a Vigreux column to give 22.9 g (68 %) of product, b.p. 57.5–58.0° (1.4 mm).

(*b*) *By the mercurial route.* A solution of 0.155 mole of phenyl(bromodichloromethyl)mercury in 125 ml of benzene was prepared in a 300 ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly. A solution of 0.155 mole of isobutenyltrimethylsilane was added and the reaction mixture was stirred at 60° overnight. Filtration gave 53.8 g (96 %) of phenylmercuric bromide, m.p. 276–278°. The solvent was removed by distillation and the residue purified by a trap-to-trap distillation at 25 mm (pot temperature to 90°). Redistillation using a Vigreux column gave 22.8 g (70 %) of 1,1-dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane, b.p. 60–61° (6.6 mm).

In other preparations the reaction mixture was heated at reflux for 3–4 h. In

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* Analytical data for all the new compounds prepared in this study are given in Table 2. IR and/or NMR spectra were recorded for all compounds and were in agreement with the structures indicated. Spectral data are recorded in the Ph.D. theses (M.I.T., 1967) of T.F.J. and H.D.

those reactions carried out on a 5 mmole scale the product yield was determined by GLPC, usually using the F&M Model 700 gas chromatograph with a 60–250° (10° per min) temperature program; the column packing was 20% SE-30 on Chromosorb W. Samples for analyses, refractive index and spectral measurements were obtained via preparative GLPC.

Preparation of 1,1*-dichloro-2-(trimethyltin)cyclopropane*

A solution of 3.3 mmoles of $PhHgCCl_2Br$ in 40 ml of dry benzene in a 100 ml three-necked flask equipped with a 15 ml dropping funnel, reflux condenser and a magnetic stirring assembly was heated to 80° under nitrogen and then 3.0 mmoles of vinyltrimethyltin was added dropwise to the stirred solution over a 30 min period. The reaction mixture was heated an additional h at 80°. Filtration gave 10.34 g (88%) of phenylmercuric bromide. The filtrate had the vile odor characteristic of divinylmercury and was handled with due precautions. The benzene was removed by distillation at atmospheric pressure and the residue was distilled at 0.3 mm into a trap at −78° (pot temperature to 80°), giving 6.73 g of faintly yellow liquid with a very disagreeable odor. The distillate was analyzed by GLPC (MIT isothermal, 20% SE-30 on Chromosorb P, 152° and 20 psi helium). The major component (55% yield) was identified as 1,1-dichloro-2-(trimethyltin)cyclopropane by analysis and spectral data.

Its NMR spectrum (in CCl_4) showed a sharp singlet at 0.20 ppm with $^{117,119}Sn$ satellite peaks (9 H) and a well resolved twelve-line pattern from 0.72 to 1.80 ppm (total of 3 H) which agrees well with the ABX spectrum reported for the analogous silicon compound[35]. The IR spectrum of the product showed bands at 3070(w), 2980(m), 2960(sh), 2920(m), 1435(m), 1260(s), 1195(w), 1125(s), 1070(s), 1010(sh), 968(m), 895(m), 870(w), 848(m), 775(s), 732(s), 700(sh) cm^{-1}.

Reaction of trichlorosilane with 1,1*-dichloro-2-vinylcyclopropane*

To a 100 ml three-necked flask equipped with reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was added 0.13 mole of trichlorosilane, 0.125 mole of 1,1-dichloro-2-vinylcyclopropane[6,15] and 0.5 ml of 0.1 *M* $H_2PtCl_6 \cdot 6\,H_2O$ in isopropyl alcohol. An exothermic reaction commenced which required external cooling. After the initial reaction had subsided, the reaction mixture was heated for 1 h at 60°. Distillation gave 21.8 g (64%) of liquid, b.p. 68–70° (1.5 mm), the infrared spectrum of which showed no absorption due to a C=C linkage. The product, assumed to be 1,1-dichloro-2-[β-(trichlorosilyl)ethyl]cyclopropane was not characterized and was converted to the trimethylsilyl derivative by treatment with a 10% excess of ethereal methylmagnesium bromide. The resulting liquid, b.p. 67–70° (5.5 mm), n_D^{25} 1.4537 (lit.[1] n_D^{25} 1.4543), obtained in 78% yield, had an IR spectrum in agreement with the data given by Jakoubková, Horák and Chvalovský[36] for 1,1-dichloro-2-[β-(trimethylsilyl)ethyl]cyclopropane. No absorption due to a C=C bond was apparent, nor did the NMR spectrum of the product show any absorption due to olefinic protons.

Reaction of trimethyltin hydride with 1,1*-dichloro-2-vinylcyclopropane*

A heavy-walled Pyrex tube containing 0.147 mole each of trimethyltin hydride and 1,1-dichloro-2-vinylcyclopropane was sealed under nitrogen and heated, with shaking, for 40 h at 100°. The reaction mixture was distilled at reduced pressure. A fraction collected at 64–66° (0.7 mm) (15.4 g, 35 % yield) was identified as 1,1-dichloro-5-(trimethyltin)-3-pentene, n_D^{25} 1.5131. (Found: C, 32.18; H, 5.25; Cl, 23.74; Sn, 39.22. $C_8H_{16}Cl_2Sn$ calcd.: C, 31.79; H, 5.29; Cl, 23.51; Sn, 39.40%.) Its NMR spectrum (CCl_4) was consistent with the structure shown:

$$\underset{a}{Me_3Sn}-\underset{b}{CH_2}-\underset{c}{CH}=\underset{d}{CH}-\underset{e}{CH_2}-\underset{f}{CCl_2H}$$

Protons "a": singlet at 0.1 ppm with ^{117,119}Sn satellites; protons "b": doublet at 1.71 ppm (*J* 8 cps); protons "e": triplet at 2.76 ppm (*J* 6.5 cps); proton "f": triplet at 5.60 (*J* 6.5 cps); protons "c" and "d": multiplet, 5.2–5.8 ppm. The infrared spectrum of the product showed strong absorption due to the C=C bond at 1650 cm^{-1} and an intense band at 965 cm^{-1} indicative of the presence of a *trans* –CH=CH– system.

The lower boiling fraction was examined by GLPC (20 % SE-30 on Chromosorb P, 100°) and found to contain the two isomers of 1-chloro-2-vinylcyclopropane (3.5 % yield, 7 : 3 ratio in order of increasing retention time) and unconverted 1,1-dichloro-2-vinylcyclopropane (47 %). The 1-chloro-2-vinylcyclopropane isomers were identified by comparison of their GLPC retention times and their IR spectra with those of authentic material prepared in low yield by the addition of CHCl (via BuLi + CH_2Cl_2) to 1,3-butadiene[37].

Reaction of tri-n-butyltin hydride with 1,1-dichloro-2-vinylcyclopropane

A mixture of 19 g (0.065 mole) of tri-n-butyltin hydride and 13 g (0.095 mole) of 1,1-dichloro-2-vinylcyclopropane in a quartz flask under an atmosphere of dry nitrogen was stirred and irradiated for 38 h with a Hanovia Lamp Div. Cat. No. 30600 100 Watt ultraviolet source. Distillation of the reaction mixture gave 4.5 g (16 %) of crude $Bu_3SnCH_2CH=CH-CH_2CCl_2H$, b.p. 108–110° (0.1 mm), n_D^{25} 1.4999. (Found: C, 48.92; H, 8.26. $C_{17}H_{34}Cl_2Sn$ calcd.: C, 47.66; H, 7.94 %.) Its NMR spectrum showed the triplet due to the CCl_2H group at 5.58 ppm (*J* 6.5 cps), the olefinic protons as a multiplet from 5.2–5.8 ppm, a triplet at 2.76 (CH_2CCl_2) and a doublet at 1.71 ppm ($SnCH_2$), as well as resonance due to the butyl groups, and the IR spectrum showed strong bands at 1650 and 965 cm^{-1}; thus the $Bu_3SnCH_2CH=CHCH_2CCl_2H$ structure is confirmed.

GLPC analysis of the lower boiling fractions showed that the 1-chloro-2-vinylcyclopropane isomers (46 : 54 ratio in order of increasing retention time) had been formed in 2.5 % yield.

1,1-Dichloro-5-(tri-n-butyltin)-3-pentene was produced in 16.5 % yield when 0.1 mole each of the tin hydride and 1,1-dichloro-2-vinylcyclopropane were heated at 60° for 24 h in the presence of 0.33 g of azobisisobutyronitrile.

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SUMMARY

Seventeen new *gem*-dihalocyclopropyl-substituted derivatives of carbon, silicon, germanium and tin have been prepared by the Doering–Hoffmann or the phenyl(trihalomethyl)mercurial procedures from allylic and vinylic compounds of these elements. The reaction of vinyltrimethyltin with phenyl(bromodichloromethyl)-mercury (to give 2,2-dichlorocyclopropyltrimethyltin) was complicated by a side reaction in which the phenylmercuric bromide formed cleaved the vinyl group from tin. The H_2PtCl_6-catalyzed addition trichlorosilane to 1,1-dichloro-2-vinylcyclopropane gave the expected 1,1-dichloro-2-(β-trichlorosilylethyl)cyclopropane, but thermal addition of trimethyltin hydride to this olefin apparently proceeded via a radical chain mechanism to give the ring-opened product. $Me_3SnCH_2CH{=}CHCH_2$-CCl_2H.

REFERENCES

1 J. Cudlín and V. Chvalovský. *Collection Czech. Chem. Commun.*, 27 (1962) 1658.
2 J. Cudlín and V. Chvalovský, *Collection Czech. Chem., Commun.*, 28 (1963) 3088.
3 C.-L. Tseng, J.-H. Cho and C.-W. Liu, *Hua Hsueh Hsueh Pao*, 30 (1964) 360; *Chem. Abstr.*, 62 (1964) 584.
4 R. Müller and W. Müller, *Chem. Ber.*, 98 (1965) 2916.
5 J. Cudlín, J. Schraml and V. Chvalovský, *Collection Czech. Chem. Commun.*, 29 (1964) 1476.
6 D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber and S. R. Dowd, *J. Am. Chem. Soc.*, 87 (1965) 4259.
7 D. Seyferth, H. Dertouzos, R. Suzuki and J. Y.-P. Mui, *J. Org. Chem.*, 32 (1967) in press.
8 C.-L. Tseng, J.-H. Cho and S.-C. Ma, *K'o Hsueh T'ung Pao*, 17 (1966) 77; *Chem. Abstr.*, 66 (1967) 2755.
9 H. Komrsová and J. Farkas, *Collection Czech. Chem. Commun.*, 25 (1960) 1977.
10 W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, 76 (1954) 6162.
11 W. von E. Doering and P. La Flamme, *J. Am. Chem. Soc.*, 78 (1956) 5447.
12 P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, 78 (1956) 3409.
13 R. A. Mitsch, *J. Am. Chem. Soc.*, 87 (1965) 758.
14 D. Seyferth, *J. Org. Chem.*, 22 (1957) 478.
15 R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, 79 (1957) 2542.
16 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 87 (1965) 16.
17 H. G. Kuivila, *Advan. Organometal. Chem.*, 1 (1964) 47.
18 E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, 28 (1963) 3442.
19 E. R. Huyser and L. R. Munson, *J. Org. Chem.*, 30 (1965) 1436.
20 I. S. Lishanskii, A. M. Guliev, A. G. Zak, O. S. Fomina and A. S. Khachaturov, *Dokl. Akad. Nauk SSSR*, 170 (1966) 1084.
21 T. Takahashi, I. Yamashita and T. Miyakawa, *Bull. Chem. Soc. Japan*, 37 (1964) 131.
22 T. Takahashi and I. Yamashita, *Polymer Letters*, 3 (1965) 251.
23 D. Seyferth, H. Yamazaki and D. L. Alleston, *J. Org. Chem.*, 28 (1963) 703.
24 D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, 4 (1965) 127.
25 D. Seyferth and M. A. Weiner, *J. Org. Chem.*, 26 (1961) 4797.
26 A. D. Petrov and G. I. Nikishin, *Dokl. Akad. Nauk SSSR*, 93 (1953) 1049.
27 D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, 83 (1961) 3583.
28 R. F. Chambers and D. C. Scherer, *J. Am. Chem. Soc.*, 48 (1926) 1054.
29 V. F. Mironov and N. G. Maksimova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1962) 1303.
30 M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, 84 (1962) 4697.
31 L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 2nd ed., 1958, pp. 35–39.
32 H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, (1964) 119; J. A. Verdone, Ph.D. Thesis, Univ. of New Hampshire, 1963.
33 C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, 44 (1922) 2629.

34 A. J. SPEZIALE AND K. W. RATTS, *J. Am. Chem. Soc.*, 84 (1962) 854.
35 K. L. WILLIAMSON, C. A. LANFORD AND C. R. NICHOLSON, *J. Am. Chem. Soc.*, 86 (1964) 762.
36 M. JAKOUBKOVÁ, M. HORÁK AND V. CHVALOVSKÝ, *Collection Czech. Chem. Commun.*, 31 (1966) 979.
37 A. F. PLATE AND O. A. SHCHERBAKOVA, *Neftekhimiya*, 3 (1963) 276; *Chem. Abstr.*, 59 (1963) 8613.