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HALOMETHYL–METAL COMPOUNDS

LVII*. THE INSERTION OF PHENYL(BROMODICHLOROMETHYL)-MERCURY-DERIVED DICHLOROCARBENE INTO C–H BONDS. FURTHER STUDIES OF THE β-METAL ACTIVATED C–H INSERTION REACTION

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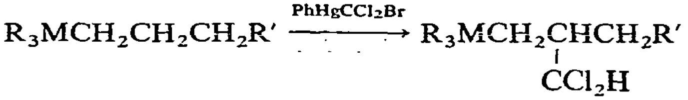
SUMMARY

Phenyl(bromodichloromethyl)mercury-derived dichlorocarbene inserts into the β C–H bonds of $Me_3MCH(CH_3)CH_2CH_3$ and $Me_3MCD(CH_3)CH_2CH_3$ (M = Si and Sn) to give $Me_3MCH(CH_3)CH(CH_3)CCl_2H$ and $Me_3MCD(CH_3)CH(CH_3)$-CCl_2H, respectively. That no rearrangement of deuterium to the β position occurred was suggested by the ^{13}C and ^{1}H NMR spectra of the products. This result is taken to speak against the intervention of sila- and stannacyclopropenium ion intermediates in the insertion process and in favor of stabilization of the transition state of the insertion reaction by metal–carbon bond hyperconjugation (σ–π stabilization, a vertical stabilization process).

INTRODUCTION

In previous papers we have described the insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene into C–H bonds of alkyl derivatives of silicon[2], germanium[3], and tin[2]. The distinguishing feature of these reactions was the great preference for insertion into C–H bonds β with respect to the metal function (eqn. 1). A systematic investigation of such reactions, and, in particular, investigation



$$R_3MCH_2CH_2CH_2R' \xrightarrow{PhHgCCl_2Br} R_3MCH_2\underset{\displaystyle CCl_2H}{\underset{|}{C}}HCH_2R' \qquad (1)$$

of the effect of other substituents on silicon on the insertion of CCl_2 into the β C–H bond of isobutylsilanes and of the effect of the metal on the relative rate of CCl_2 insertion into isobutyl derivatives of these Group IV elements (Sn > Ge > Si) led us to conclude that the activation by the metal occurred by means of transition state stabilization via metal–carbon bond hyperconjugation (σ–π conjugation)[2]. Such

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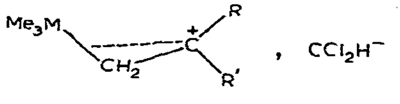
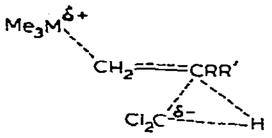
* For Part LVI see ref. 1.

hyperconjugative electron release from the metal–carbon bond to the developing electron-deficient β carbonium center was pictured in its extreme form (I) for the sake of simplicity[2], but complete ionization as shown is by no means a requirement and an alternative picture is shown in II. Landgrebe[4] had reported that similar CCl_2

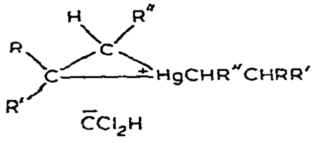


(I)



(II)

insertion can occur into β C–H bonds of dialkylmercury compounds, but had suggested the intermediacy of a bridged species, the mercurinium ion pair, III, in such insertions. Similar bridged intermediates, IV, also could be considered for the Group



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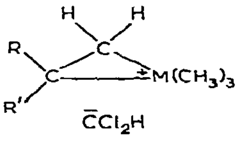
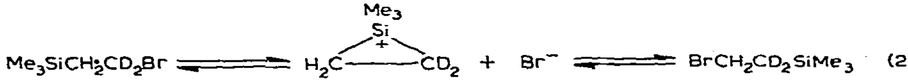


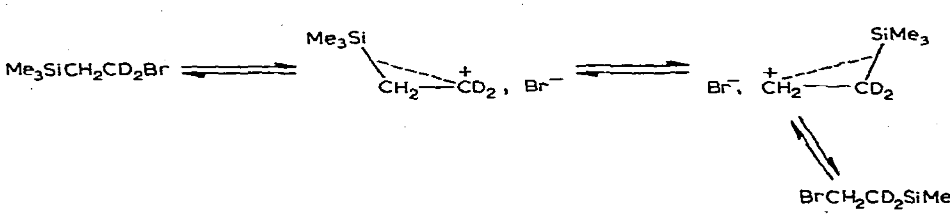
(IV)

IV metal-activated insertion reactions. The bridged mercurinium ion is an intermediate which has been invoked repeatedly in organomercury chemistry[5] and, in fact, has been shown to be detectable by NMR spectroscopy in strongly acidic medium[6]. On the other hand, bridged cations of the type shown in IV did not play a significant role in the mechanisms of Group IV organometallic reactions until recently. The discoveries that solvolysis of $Me_3SiCH_2CD_2Br$ was accompanied by rearrangement to $Me_3SiCD_2CH_2Br$[7] and that reaction of thionyl chloride with $Me_3SiCH_2CD_2OH$ gave a 55/45 mixture of $Me_3SiCH_2CD_2Cl$ and $Me_3SiCD_2CH_2Cl$[8] raised the possibility of silacyclopropenium ion intermediates, *e.g.*, eqn. 2. It was



(2)

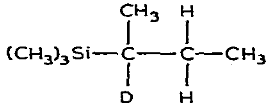
recognized[7,8] that the observed rearrangements could be explained in terms of equilibrating carbonium ions which are stabilized by σ–π conjugation (eqn. 3), and, in fact, the latter alternative appeared to be favored by Jarvie *et al.*[8], while Eaborn and his coworkers[7] favored the bridged intermediate.



(3)

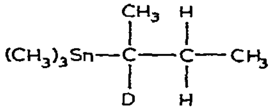
It was of interest to us to determine, if possible, if the β-Group IV metal activated insertion reaction (eqn. 1) involved a vertical stabilization effect[9] (M–C σ bond delocalization without change in bond length or angle) or if bridging metallacyclopropenium ions played a role in this CCl_2 reaction.

The compounds chosen to test these possibilities were V and VI, which were synthesized as shown in eqn. 4.



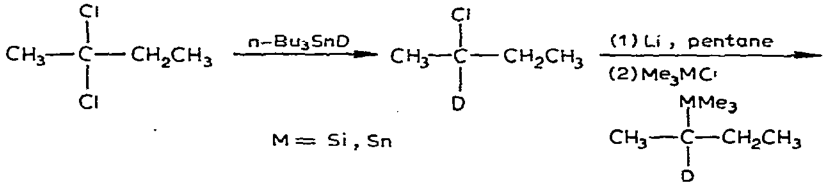
$(CH_3)_3Si-\overset{CH_3}{\underset{D}{C}}-\overset{H}{\underset{H}{C}}-CH_3$

(V)



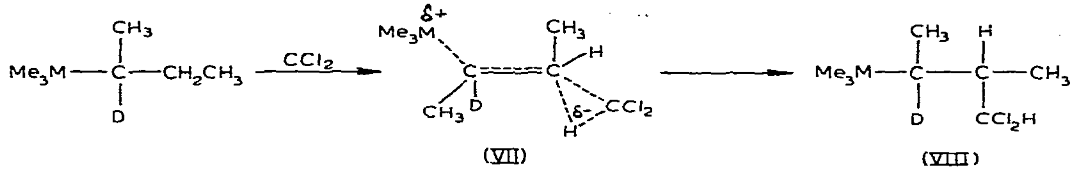
$(CH_3)_3Sn-\overset{CH_3}{\underset{D}{C}}-\overset{H}{\underset{H}{C}}-CH_3$

(VI)



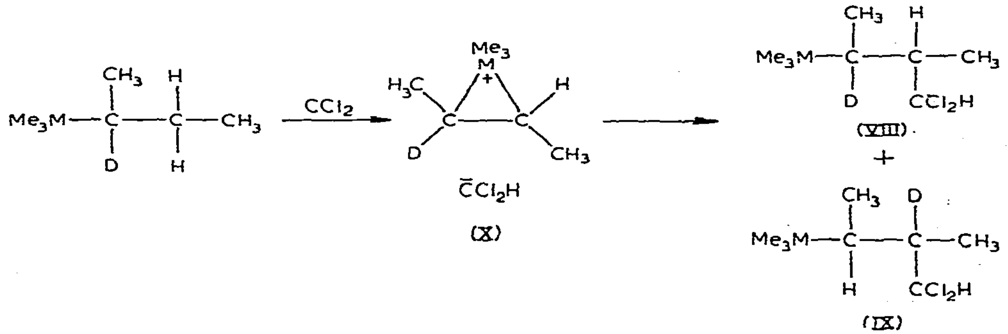
(4)

In the case of a vertical stabilization process, the only product to be expected is VIII (eqn. 5). If, on the other hand, bridging sila- or stannacyclopropenium ions



(5)

are involved, one would expect to find rearranged products (eqn. 6). A mixture of VIII and IX in a ratio close to unity should be formed if the symmetrical cation in X

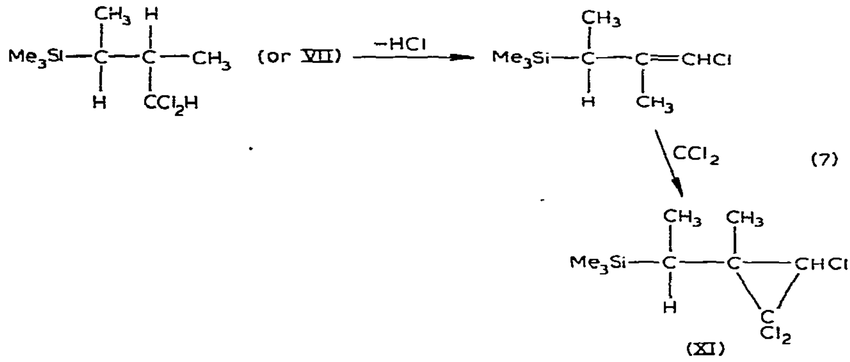


(6)

were indeed involved. The ^1H and ^{13}C NMR spectra of the insertion products should serve to distinguish between these extremes.

RESULTS AND DISCUSSION

The reactions with phenyl(bromodichloromethyl)mercury were carried out first using undeuterated sec-butyltrimethyl compounds of silicon and tin, and it was established by this means that the desired β C–H insertion of CCl_2 did indeed take place. The products in each case were obtained as a mixture of diastereomers. The ratio of the diastereomer with the shorter retention time on an Apiezon L GLC column to that with the longer retention time was 1.4/1 in the case of the silicon compound and 1/1.9 for the tin compound. (We shall return to this point later in this discussion). In the sec-butyltrimethylsilane/$PhHgCCl_2Br$ reaction two other higher boiling products were present in comparable yield. One was identified tentatively as XI, and its possible mode of formation is indicated in eqn. 7. The other product remains unidentified. The diastereomeric product mixture from the sec-butylsilane was reduced with tri-n-butyltin hydride to give $Me_3SiCH(CH_3)CH(CH_3)_2$.



(7)

(XI)

These CCl_2 insertions were carried out with the α-deuterated compounds V and VI. In both cases, diastereomeric insertion products were obtained, with the isomer ratios very similar to those obtained with the undeuterated compounds. The product yield obtained with the silicon compound was 15%, with the tin compound it was 53%. Figure 1 shows the CCl_2H resonances in the ^1H NMR spectra of the diastereomeric mixtures formed with the undeuterated and the deuterated sec-butyltrimethylsilane. As can be seen, these spectra are almost superimposable. No deuterium coupling with the proton of the CCl_2H group is detectable in the case of the Me_3Si-$CD(CH_3)CH_2CH_3$-derived product. Figure 2 shows the ^1H NMR spectra (CCl_2H region) for the mixture of diastereomeric insertion products obtained from $Me_3SnCH(CH_3)CH_2CH_3$ and $Me_3SnCD(CH_3)CH_2CH_3$. Here also there is essentially no change in the CCl_2H resonance.

The Fourier transform ^{13}C NMR spectra of the dichlorocarbene insertion products derived from the undeuterated and the deuterated sec-butyltrimethyltins were obtained with a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system*. The spectra shown in Fig. 3 and 4 were obtained from CCl_4 solutions of these insertion products. The solvent lines are not shown. The two lines

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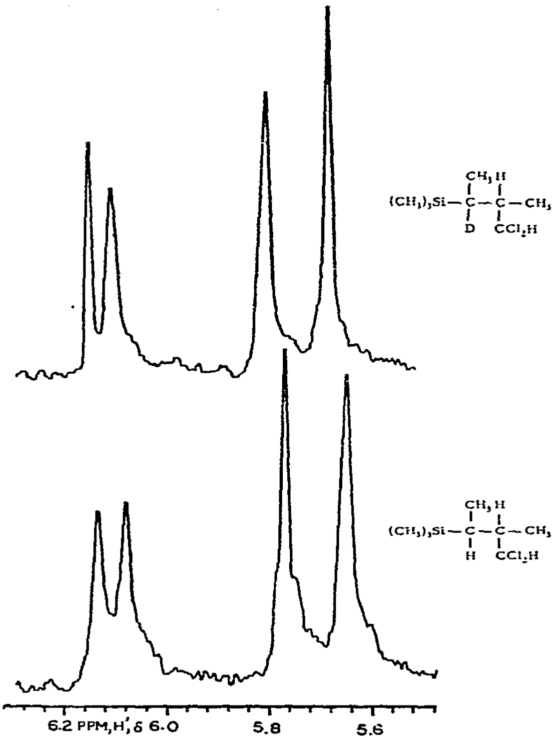
[*] A 1.7 mm capillary containing C_6F_6 was used for field-frequency lock, and the typical pulsing parameters used were a 4K transform size, a 10 kHz sampling frequency and a total of one sec between pulses.



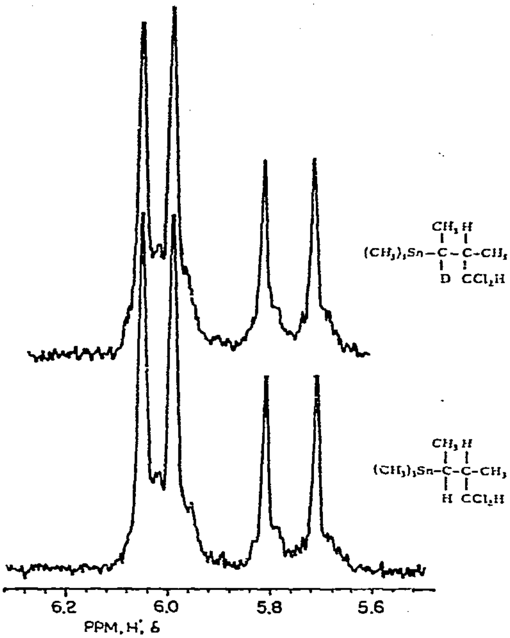


Fig. 1. Comparison of CCl_2H signals in the proton NMR spectra of $Me_3SiCH(CH_3)CH(CH_3)CCl_2H$ and $Me_3SiCD(CH_3)CH(CH_3)CCl_2H$.

Fig. 2. Comparison of the CCl_2H signals in the proton NMR spectra of $Me_3SnCH(CH_3)CH(CH_3)CCl_2H$ and $Me_3SnCD(CH_3)CH(CH_3)CCl_2H$.

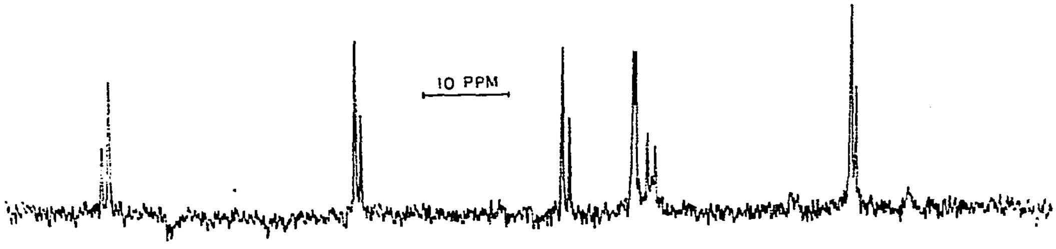


Fig. 3. ^{13}C NMR Spectrum of $Me_3SnCH(CH_3)CH(CH_3)CCl_2H$.

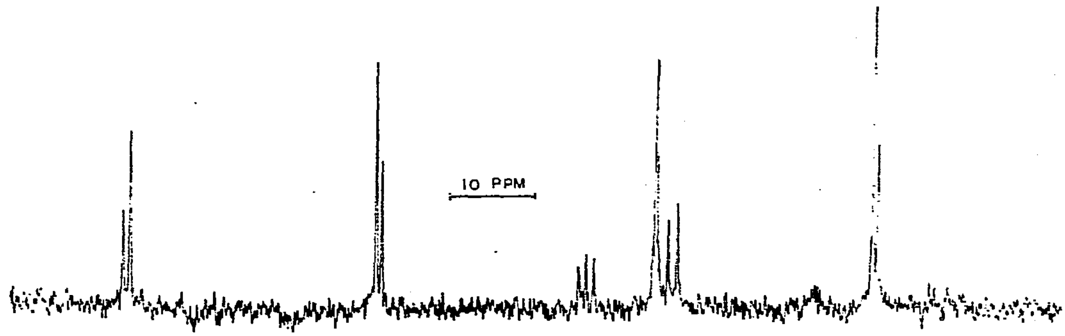


Fig. 4. ^{13}C NMR Spectrum of $Me_3SnCD(CH_3)CH(CH_3)CCl_2H$.

TABLE 1

^{13}C CHEMICAL SHIFTS OF THE ORGANOTIN COMPOUNDS OF THIS STUDY (ppm relative to TMS)

$Me_3SnCH(CH_3)CH(CH_3)CCl_2H$	$Me_3SnCD(CH_3)CH(CH_3)CCl_2H$	$Me_3SnCH(CH_3)CH_2CH_3$	$Me_3SnCD(CH_3)CH_2CH_3$
78.52	78.49	28.67	28.37
77.70	77.68	22.35	22.55
48.82	48.76	17.76	21.71
48.16	48.07	13.94	20.87
24.30	24.81	−11.74	17.48
23.53	23.95		13.76
	23.04		−11.84
15.95	15.82		
15.73	15.78		
14.36	14.34		
13.43	13.26		
−9.52	−9.56		
−10.12	−10.14		

for each of the six main resonance groups are attributed to the presence of two pairs of diastereomers. By comparisons of the line intensities between the two spectra, it is estimated that at least 93% of the deuterium present in the $Me_3SnCD(CH_3)CH_2CH_3$-derived product is located in only one position. The identification of this position as being the secondary carbon adjacent to the tin atom was made by comparisons with the ^{13}C NMR spectra of $Me_3SnCH(CH_3)CH_2CH_3$ and $Me_3SnCD(CH_3)CH_2CH_3$. Table 1 contains the chemical shifts* of $Me_3SnCH(CH_3)CH(CH_3)CCl_2H$ and $Me_3SnCD(CH_3)CH(CH_3)CCl_2H$ relative to TMS, and are accurate to ±0.05 ppm.

On the basis of these results, we may conclude that very little if any rearrangement to give the β-deuterated compound IX occurred during CCl_2 insertion into $Me_3SiCD(CH_3)CH_2CH_3$ and $Me_3SnCD(CH_3)CH_2CH_3$. This observation excludes the intervention of metallacyclopropenium intermediates of type X and speaks in favor of a vertical stabilization process (eqn. 5). This result should not be generalized to the organomercury examples of Landgrebe[4], but it does suggest that the intermediate proposed, III, should not be accepted without critical scrutiny and, preferably, experimental verification.

In conclusion, we return to the question of the formation of diastereomers in these reactions and their identity. We recall that in the sec-butyltrimethylsilane-derived diastereomeric product mixture and in that derived from the analogous tin compound the diastereomer ratio appeared to reverse on going from the silicon to the tin compound. GLC retention times provided the basis for this statement, but the NMR spectra of the insertion products also seemed to indicate such a reversal.

case of the $Me_3SiCH(CH_3)CH(CH_3)CCl_2H$ diastereomer pair, the major isomer had $J(H\text{–}C\text{–}CCl_2H) = 6.8$ Hz, while this coupling in the less abundant isomer

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* These shifts were calculated from the shifts relative to the CCl_4 solvent by use of the equation $\delta(TMS) = \delta(CCl_4) + 95.99$, where $\delta(TMS)$ and $\delta(CCl_4)$ are the chemical shifts relative to TMS and CCl_4, respectively. The value of 95.99 used was obtained from the spectrum of 10% TMS in CCl_4, and no corrections for any solvent effects were made.

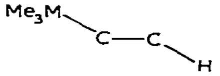
TABLE 2

CONFORMATIONAL ENERGIES OF sec-BUTYLTRIMETHYLSILANE AND sec-BUTYLTRIMETHYLTIN AS OBTAINED FROM FORCE FIELD CALCULATIONS[10] (in kcal/mol)

M	*(A)*		*(B)*		*(C)*	
	Si	*Sn*	*Si*	*Sn*	*Si*	*Sn*
E(stretch)	0.66	0.77	0.79	0.82	0.76	0.81
E(bend)	1.65	1.54	2.63	1.70	1.97	2.12
E(torsional)	0.48	0.29	0.81	0.44	0.95	0.51
E(nonbonded)	−4.96	−2.66	−5.43	−3.56	−5.42	−3.53
E(total)	−2.17	−0.07	−1.20	−0.61	−1.74	−0.09
Conformer population						
at 25°	59.4%	22.2%	11.7%	55.0%	28.9%	22.8%
at 80°	55.8%	23.8%	14.0%	51.6%	30.2%	24.5%

was 4.0 Hz. In contrast, in the $Me_3SnCH(CH_3)CH(CH_3)CCl_2H$ diastereomer pair, the major isomer had the smaller $J(H{-}C{-}CCl_2H)$, 3.6 Hz, *vs.* 5.8 Hz for the less abundant isomer*. An explanation for these observations was provided by some calculations very kindly carried out by Professor R. J. Ouellette[10]. Calculation of the total strain energies of the rotational isomers** of sec-butyltrimethyl-silane and -tin (as the sum of bending, stretching, torsional and nonbonding contributions) provided information concerning the conformer populations of these molecules at 25°. These are given in Table 2.

We assume that conformers B and C with the *trans* arrangement XII which



(XII)

would maximize σ–π overlap as CCl_2 insertion into the C–H bond occurs[9], are the ones which lead to product and that conformer A is relatively unreactive toward CCl_2 insertion. It is interesting to note that for the silicon and tin compounds the relative stabilities of conformers B and C are reversed. For the tin compound it is B which is more stable and for the silane it is C. If one assumes that the activation energies for CCl_2 insertion into the *trans-β* C–H bonds of B and C are equal or nearly so, then one would expect the product *erythro/threo* ratios to reflect the starting material B/C ratios as shown in Scheme 1. Since the preferred diastereomer produced in CCl_2 insertion into the sec-butylsilane is different from the preferred diastereomer obtained from sec-butyltrimethyltin, it would appear that this expectation has merit. This leads us to assign the *threo* configuration to the major organosilicon diastereomer and the *erythro* configuration to the major organotin diastereomer. We note that at 80° the B/C ratio for the sec-butyltin compound is 2.1; this is to be compared to the

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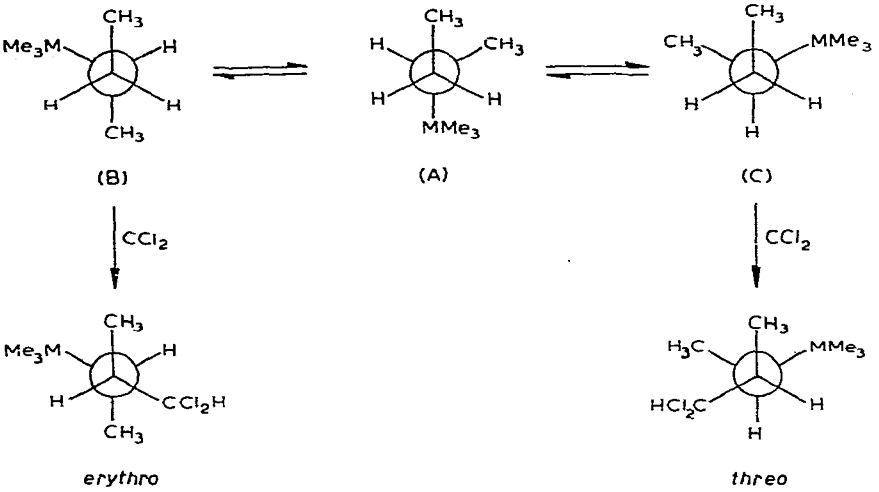
* We assume that the products with the smaller $J(H{-}C{-}CCl_2H)$ in the silicon and tin compounds represent the same diastereomers, *i.e.*, that these two compounds do not differ from one another structurally, and that the same is true for the silicon- and tin-containing diastereomers with the higher $J(H{-}C{-}CCl_2H)$.

** For details and other applications of such calculations see ref. 11 and 12.

SCHEME 1



erythro/threo ratio of 1.9 for the sec-butyltrimethyltin-derived CCl_2 insertion product. For the organosilicon compound the agreement is not so good. The C/B ratio for sec-butyltrimethylsilane is 2.1_5 at 80°; the *threo/erythro* ratio in its CCl_2 insertion product was 1.4.

EXPERIMENTAL

General comments. All reactions were carried out under an atmosphere of dry nitrogen in flame-dried glassware. The standard reaction apparatus consisted of a three-necked, round-bottom flask of appropriate size equipped with a stirrer (magnetic or overhead), a reflux condenser topped with a nitrogen inlet tube, a thermometer (if needed) and a pressure-equalizing addition funnel (if needed). Infrared spectra were obtained using a Perkin–Elmer 257 or 457A grating infrared spectrophotometer, proton NMR spectra, using a Varian Associates T60 spectrometer. Proton chemical shifts are reported in δ units, ppm downfield from TMS; chloroform was used as the internal standard (δ 7.27 ppm) in the case of the silicon and tin compounds. Gas–liquid chromatography (GLC) was used extensively in this work in the analysis of reaction mixtures, determination of yields and isolation of samples of products for characterization. Commercial F&M 700, 720 and 5754 gas chromatographs were used. The internal standard procedure was used in yield determinations. Falling drop analyses for deuterium were carried out by J. Nemeth, Urbana, Illinois.

Preparation of the sec-butyltrimethyl compounds of silicon and tin

(*a*) *Silicon.* A solution of sec-butyllithium was prepared from 14.4 g (2.1 g-atom) of lithium dispersion (50% in Amsco, from Foote Mineral Co.) and 92.5 g (1.0 mol) of sec-butyl chloride in 350 ml of pentane. To the light yellow filtered reagent solution was added dropwise 46.7 g (0.43 mol) of trimethylchlorosilane in 100 ml of THF. The reaction mixture was heated at reflux for 2 h and then was trap-to-trap distilled at reduced pressure to give 360 ml of distillate. Careful fractional distillation gave 29.6 g (53%) of the silane, b.p. 115–115.5°. A minor impurity could not be separated by distillation, and the samples required for this project were purified by preparative GLC (MIT isothermal unit, 6 ft. × $\frac{5}{8}$ in. 20% Apiezon L column at 85°). The product obtained had n_D^{25} 1.4067; lit.[13] n_D^{25} 1.4064, b.p. 114°. NMR (CCl_4): δ 0.01 (s, 9), 0.60 (m, 1), 0.90 (m, 6) and 1.35 ppm (m, 2).

(*b*). *Tin.* The tin compound was prepared from sec-butyllithium (from 0.75 g-atom of lithium dispersion and 0.25 mol of sec-butyl chloride in pentane) and 0.19 mol of trimethyltin chloride in ether (4 h at reflux). Hydrolysis was followed by distillation of the dried organic layer to give (15 cm packed column) 19.6 g (47%) of the tin compound, b.p. 146–148°, n_D^{25} 1.4591; lit.[14] b.p. 146–148°, n_D^{20} 1.4630. GLC analysis showed this material to be pure. NMR ($CDCl_3$): δ 0.11 (s, 9) 0.78 (m, 1), 0.98 (m, 3), 1.24 (m, 3) and 1.57 ppm (m, 2).

Preparation of deuterated compounds V and VI

(*a*) *Preparation of* 2-*chlorobutane*-2-d_1. A mixture of 175.0 g (0.6 mol) of tri-n-butyltin deuteride (prepared by the procedure of Lahournère and Valade[15] in 83% yield) and 75.0 g (0.59 mol) of 2,2-dichlorobutane (Chemical Samples Co.) was stirred under nitrogen and slowly warmed to 55° and maintained at this temperature for 16 h. Trap-to-trap distillation of the reaction mixture in vacuo at 25° afforded 52.7 g (97%) of clear distillate, which GLC indicated to contain only neglible amounts of impurities. NMR (CCl_4): $CH_3CHClCH_2CH_3$: δ 1.22 (t, $J = 8.0$ Hz, 3), 1.69 (d, $J = 6.8$ Hz, 3), 1.85 (quintet, $J = 6.0$ Hz, 2) and 4.07 ppm (sextet, $J = 6.8$ Hz, 1); CH_3CDCl-CH_2CH_3 as prepared above: δ 1.03 (t, $J = 6.0$ Hz, 3), 1.49 (t, $J = 0.5$ Hz, 3), 1.67 ppm (q, $J = 6.5$ Hz, 2). There were no resonances in the region of δ 4 ppm.

(*b*) *α-Deuterio-sec-butyltrimethylsilane.* This compound was prepared using the procedure applied to the preparation of the undeuterated compound using 0.5 mol of 2-chlorobutane-2-d_1, 1.5 g-atom of lithium dispersion and 0.375 mol of trimethylchlorosilane. Samples of the pure product were isolated by GLC, n_D^{25} 1.4064. (Found: atom % excess of D, 5.58: $C_7H_{17}DSi$ calcd.: 5.56). NMR ($CDCl_3$): δ 0.04 (s, 9), 0.98–1.17 (m, 6) and 1.17–1.64 ppm (m, 2).

(*c*) *α-Deuterio-sec-butyltrimethyltin.* The reaction of 0.1 mol of 2-chlorobutane-2-d_1 and 0.32 g-atom of lithium dispersion in pentane served to prepare the lithium reagent which was treated with 0.08 mol of trimethyltin chloride. Fractional distillation after hydrolytic work-up gave 8.5 g (48%) of the title compound, b.p. 102.5–103° (190 mm), n_D^{25} 1.4576. (Found: atom % excess of D, 5.57; $C_7H_{17}DSn$ calcd.: 5.56). NMR ($CDCl_3$): δ 0.07 (s, 9), 0.93 (t, $J = 6.2$ Hz, 3), 1.15 (t, $J = 10$ Hz, 3) and 1.42–1.78 (m, 2).

Reaction of sec-butyltrimethyltin with phenyl(bromodichloromethyl)mercury

A mixture of 9.65 g (43.6 mmol) of the tin compound and 6.60 g (15.0 mmol) of phenyl(bromodichloromethyl)mercury[16] was stirred under nitrogen at 80–85° for 4 h. The reaction mixture was allowed to cool to room temperature, diluted with 15 ml of pentane and filtered to remove 5.04 g (94%) of PhHgBr. The filtrate was concentrated at reduced pressure and the residue was trap-to-trap distilled at 0.1 mm and room temperature to remove unconverted sec-butyltrimethyltin and then at 60° to distil the product as a water-white liquid (2.25 g). GLC analysis of the distillate (20% SE-30 at 125°) indicated a purity of better than 98%, for a yield of 50%. The product had n_D^{25} 1.5046. (Found: C, 31.48; H, 5.94; Cl, 23.33. $C_8H_{18}Cl_2Sn$ calcd.:

C, 31.62; H, 5.97; Cl, 23.34). NMR ($CDCl_3$): δ 0.09 (s, 9), 1.05 (m, 3), 1.18 (d, $J=8$ Hz, 3), 1.29–1.75 (m, 1), 1.98–2.35 (m, 1), 5.78 (d, $J=5.8$ Hz, 0.33H) and 6.04 ppm (d, $J=3.6$ Hz, 0.67H). The two CCl_2H doublets in 2/1 ratio indicate the presence of diastereomers in that ratio.

The same reaction carried out between α-deuterio-sec-butyltrimethyltin (21.6 mmol) and $PhHgCCl_2Br$ (7.5 mmol) gave the insertion product in 53% yield, n_D^{25} 1.5054. (Found: C, 31.61; H(D), 6.02; Cl, 23.30; atom % excess D, 5.56. $C_8H_{17}DCl_2Sn$ calcd.: C, 31.53; H(D), 6.25; Cl, 23.26; atom % excess D, 5.56). NMR ($CDCl_3$): δ 0.09 (s, 9), 0.99–1.26 (m, 6), 2.15–2.47 (m, 1), 5.78 (d, $J=6.3$ Hz, 0.345H) and 6.03 ppm (d, $J=3.6$ Hz, 0.655H).

Reaction of sec-butyltrimethylsilane with phenyl(bromodichloromethyl)mercury

The sec-butyltrimethylsilane/$PhHgCCl_2Br$ reaction was carried out using 75.9 mmol of the silane and 27.2 mmol of the mercurial. The yield of PhHgBr was 95%. The insertion product was obtained in 17% yield. It was collected by GLC (20% SE-30 at 125°). (Found: C, 45.11; H, 8.49; Cl, 33.38. $C_8H_{18}Cl_2Si$ calcd.: C, 45.06; H, 8.51; Cl, 33.26). GLC and the NMR spectrum indicated the presence of two diastereomers. NMR ($CDCl_3$): δ 0.09 and 0.11 (2 peaks, 9), 0.92–1.30 (m, 7), 2.01–2.54 (m, 1), 5.74 (d, $J=6.8$ Hz, 0.6H) and 6.14 ppm (d, $J=4.0$ Hz, 0.4H).

The two diastereomers could be separated by GLC using a 15 ft. 20% Apiezon L column at 135°. In order of increasing GLC retention time they were present in 1.4/1 molar ratio. The first diastereomer had n_D^{25} 1.4666. NMR (microtube, neat): δ 0.11 (s, 9), 0.99–1.26 (m, 7), 1.96 (m, 1) and 6.06 ppm (d, $J=4.0$ Hz). The second diastereomer to be eluted had n_D^{25} 1.4666. NMR (microtube, neat): δ 0.09 (s, 9), 0.90–1.17 (m, 7), 2.30 (m, 1) and 5.68 ppm (d, $J=6.8$ Hz, 1).

Two higher boiling products also were present. The first of these (*i.e.*, the one of lower GLC retention time) remains unidentified, although a composition of $C_9H_{17}Cl_3Si$ is indicated. (Found: C, 41.60; H, 6.58; Cl, 40.57. Calcd.: C, 41.62; H, 6.59; Cl, 40.95). NMR ($CDCl_3$): δ 0.35 (s, 9), 1.01 (t, $J=7.0$ Hz, 3), 1.41 (s, 3) and 1.68 ppm (m, 2). IR (neat): 2975 m, 2954 w, 2907 w, 2897 w(sh), 1458 w, 1254 s, 1052 w, 925 m(sh), 909 s, 845 s, 810 m, 767 w, and 759 w cm^{-1}. The compound 1,1,2-trichloro-3-methyl-3-ethyl-2-trimethylsilylcyclopropane is a possibility, but no easy route to this structure seems available.

The second product was assigned the structure XI on the basis of its NMR and IR spectra. (Found: C, 41.67; H, 6.58; Cl, 40.81. $C_9H_{17}Cl_3Si$ calcd.: C, 41.62; H, 6.59; Cl, 40.95). NMR ($CDCl_3$): δ 0.18, 0.21 (2 peaks, 9), 1.03–1.53 (m, 6), 1.88 (m, 1) and 3.23 ppm (s, 1). IR (neat): 2992 m, 2912 w, 2892 w, 1456 w, 1401 w, 1392 w, 1255 s, 1214 w, 1151 m, 1124 w, 1051 w, 998 w, 931 w, 886 s(sh), 844 s, 779 w, 758 w and 718 w cm^{-1}.

In another such reaction between 12.37 mmol of sec-butyltrimethylsilane and 4.66 mmol of $PhHgCCl_2Br$, the yields of the simple insertion product, the unidentified product and the product assigned structure XI were determined by GLC to be 8.5, 12 and 21%, respectively. This ratio, however, was variable, and in other reactions these products were formed in a molar ratio of 1.0/0.7/0.95.

The insertion product was formed in 15% yield when 38.1 mmol of $Me_3SiCD(CH_3)CH_2CH_3$ and 14.1 mmol of $PhHgCCl_2Br$ were heated at 80–85° for 4 h. A 1.37/1 mixture (in order of increasing GLC retention time on an Apiezon L column) of diastereomers was present. The mixture of isomers, n_D^{25} 1.4662, was characterized. (Found: C, 44.70; H(D), 8.38; Cl, 33.47. $C_8H_{17}DCl_2Si$ calcd.: C, 44.87; H(D), 8.94; Cl, 33.12%.) A deuterium analysis established the presence of 5.53 atom % excess D (*vs.* 5.56). NMR ($CDCl_3$): δ 0.07, 0.09 (2 peaks, 9), 0.92–1.25 (m, 6), 2.22 (m, 1), 5.67 (d, $J=7.0$ Hz, 0.7H) and 6.17 ppm (d, $J=3.6$ Hz, 0.3H).

Reduction of $Me_3SiCH(CH_3)CH(CH_3)CCl_2H$ to $Me_3SiCH(CH_3)CH(CH_3)_2$

A mixture of 220.3 mg (1.04 mmol) of the sec-butyltrimethylsilane CCl_2 insertion product, 2.12 g (7.30 mmol) of tri-n-butyltin hydride and 30 mg of azobisisobutyronitrile was stirred and heated at 80° under nitrogen for 24 h. Trap-to-trap distillation at 7 mm (room temperature) gave a colorless distillate which GLC analysis (6 ft. 20% Apiezon L at 100°) showed that the reduction product had been formed in 61% yield. A sample was isolated by GLC, n_D^{25} 1.4187. (Found: C, 66.74; H, 14.01. $C_8H_{20}Si$ calcd.: C, 66.55; H, 13.97). NMR ($CDCl_3$): δ 0.05 (s, 9), 0.72–1.10 (complex m, 10) and 1.80 ppm (m, 1). IR (neat): 2965 s, 2880 m, 2840 w, 1465 w, 1370 w, 1251 s, 858 s, 837 s, 745 m, and 688 m cm^{-1}. Examination of this product by GLC using Carbowax 20M, Lac 728 and DC-200 columns established that this was a single compound.

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