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MECHANISMS OF THE REACTIONS OF CHLOROMETHANES WITH TRIMETHYLSTANNYLSODIUM. SYNTHESIS OF TETRAKIS[TRIMETHYLSTANNYL]METHANE.

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Summary

The reactions of CCl_4, $CHCl_3$, and CH_2Cl_2 with trimethylstannylsodium in tetraglyme have been examined. Tetrakis[trimethylstannyl]methane can be obtained by reaction with CCl_4 in yields of about 40%. Among other products which have been characterized in varying degree are the following: trichloromethyltrimethylstannane, bis[trimethylstannyl]dichloromethane, tris[trimethylstannyl]methane, and hexamethyldistannane. The first step in the reaction leads to the formation of the trichloromethyl anion, and dichlorocarbene has been trapped with 2,3-dimethyl-2-butene. Dichlorobis[trimethylstannyl]methane reacts with Me_3SnNa to form tetrakis[trimethylstannyl]methane in 85% yield. When the reaction was carried out in the presence of <u>t</u>-butyl alcohol the only product formed was bis[trimethylstannyl]methane, indicating carbanionic intermediates. Chloroform yields tetrakis[trimethylstannyl]methane and bis[trimethylstannyl]methane, but no detectable tris[trimethylstannylmethane. Trapping experiemtns with 3-pentanol and 2,3-dimethyl-2-butene indicate the intermediacy of dichloromethyl anion and of dichlorocarbene. Methylene chloride yields bis[trimethylstannyl]methane. No intermediates could be trapped by added alcohol.

<u>Introduction</u>.- As a part of a broad investigation on the scope and mechanisms of the reactions of organostannylalkalis with organic halides[1,2] we have examined the reactions of trimethylstannylsodium with carbon tetrachloride, chloroform, and

methylene chloride. Such a study should add to our understanding of the reactions of the alkali metal derivatives of group IV in general with these same halides. Relevant earlier studies include those on triphenylsilyllithium by Gilman and Aoki;[3] on organogermylalkalis by Smith and Kraus,[4] and of Bulten and Noltes;[5] on trimethylstannylsodium by Kraus and Neal[6] and by Kaesz;[7] and on organoplumbylalkalis by Willemsens and van der Kerk.[8] As will be discussed below, when one goes down the series from silicon to lead, there is neither uniformity in behavior nor a monotonic change. Our mechanistically oriented study provides both substantive and presumptive experimental evidence concerning intermediates in the reactions of trimethylstannylsodium, confirming earlier postulates made with regard to reactions of halomethanes with tripehnylsilyllithium, and adding some new perspectives.

Carbon Tetrachloride.- Trimethylstannylsodium was prepared in tetraglyme [$CH_3O(CH_2CH_2O)_4CH_3$] by stirring metallic sodium with hexamethyldistannane until the latter was completely consumed. Addition to an excess of carbon tetrachloride, followed by gas-liquid chromatography revealed the presence of chloroform (19%), trimethylchlorostannane (33%), hexamethyldistannane (44%), and a minor amount of tetramethylstannane as indicated by their retention times. Extraction of the reaction mixture with petroleum ether, concentration, and dissolution in carbon tetrachloride yielded a solution with pmr signals (in ppm downfield from tetramethylsilane) at δ0.08 due to tetramethylstannane,[7] δ0.11 (unidentified), δ0.22 due to hexamethyldistannane, and δ0.15 due to tetrakis[trimethylstannyl]methane (see below). No signal due to trimethylchlorostannane was observed, suggesting that its presence in the gas chromatogram was due to its formation in the injection port. Support for this was provided by the observation that lowering the injection port temperature caused a decrease in the peak area. Its precursor was probably trichloromethyltrimethylstannane whose presence in a reaction conducted at -40 to -30° was indicated by a pmr signal at δ0.49 ppm a $^2J(^{119}Sn\text{-}H)$ coupling of 59 Hz.[9]

The volatile products of a reaction mixture initially 0.2 M in trimethylstannylsodium, and 0.4 M in t-butyl alcohol and in carbon tetrachloride were found to consist of 89% chloroform, 10% hexamethyldistannane, and 56% trimethylchlorostannane. The formation of the large amount of chloroform indicates that the first step in the reaction is the expected nucleophilic displacement on chlorine (halogen-metal exchange), eq. 1, rather than the improbable displacement on carbon.

$$Me_3SnNa + ClCCl_3 \longrightarrow Me_3SnCl + MaCCl_3 \qquad (1)$$

The trichloromethyl anion then reacts rapidly with the alcohol to form the chloroform, eq. 2. An important conclusion which follows from this observation is that

$$NaCCl_3 + \underline{t}\text{-}C_4H_9OH \longrightarrow HCCl_3 + \underline{t}\text{-}C_4H_9ONa. \qquad (2)$$

trimethylstannylsodium reacts as a nuclophile in attacking chlorine of carbon tetrachloride much faster than it reacts as a base in proton abstraction from <u>t</u>-butyl alcohol, eq. 3.

$$Me_3SnNa + \underline{t}\text{-}C_4H_9OH \longrightarrow Me_3SnH + \underline{t}\text{-}C_4H_9OK \qquad (3)$$

Another consequence of the presence of an effective proton source in the reaction mixture is displayed by the data in Table I. These are the results of a series of experiments which are substantially identical, with the exception that increments of ethanol were present in the carbon tetrachloride solution to which the trimethylstannylsodium was added. The figures in the third column show the expected increase in the percentage of the reacted carbon tetrachloride which appears as chloroform in the product when the amount of added ethanol is increased. A striking observation is that the amount of CCl_4 consumed <u>increases</u> as the amount of ethanol initially present increases. This increase in consumption covers a four-fold range up to the point where the percentage appearing as $CHCl_3$ in the product mixture reaches about 90, which seems to be a maximum value. This is a clearcut demonstration that trimethylstannylsodium reacts more rapidly with species derived from trichloromethyl anion, than it does with CCl_4.

Table I

Effect of Added Ethanol on the Amount of Carbon Tetrachloride Consumed by Reaction with Trimethylstannylsodium and on Yield of Chloroform[a]

mmoles EtOH added	mmoles CCl_4[b] consumed	% $CHCl_3$[c]
0	0.10	38
0.27	0.15	46
0.74	0.20	73
1.28	0.22	78
3.30	0.32	85
5.56	0.37	90
9.23	0.42	86

[a] Initial Me_3SnNa concn: 0.15 M

[b] Initial CCl_4 concn: 0.24 M (1.2 mmoles/5ml rxn solution); solvent: tetraglyme; ambient temperature.

[c] Based on CCl_4 consumed.

When CCl_4 was added to a solution containing four moles of trimethylstannylsodium at room temperature tetrakis[trimethylstannyl]methane, 1, was formed in 18% yield; if the reaction temperature was decreased to -23° the yield increased to 41%. Large amounts of hexamethyldistannane were formed in these reactions. The yield of 1 at ambient temperature could be increased to 44% by adding CCl_4 to a solution containing four moles of trimethylstannylsodium and excess sodium metal. The rationale for this procedure was the expectation that the sodium would react with

$(Me_3Sn)_4C$	$(Me_3)_2SnCl_2$	Me_3SnCCl_3	Me_2SnCH_2
1	2	3	4

hexamethyldistannane, formed from trimethylchlorostannane by eq. 4, to produce additional stannylsodium, eq. 5, which would then be available for further reaction

$$Me_3SnCl + Me_3SnNa \longrightarrow Me_3Sn\text{-}SnMe_3 \qquad (4)$$

$$Me_3Sn\text{-}SnMe_3 + 2\ Na \longrightarrow 2\ Me_3SnNa \qquad (5)$$

with CCl_4 or intermediates.

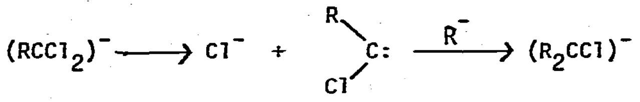
A search for other products and intermediates was conducted by trapping experiments and by careful examination of glpc traces of volatile products, and by pmr examination of reaction product mixtures. The presence of dichlorocarbene was demonstrated by trapping with 2,3-dimethyl-2-butene to form 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, characterized by the expected singlet in its pmr spectrum at δ 1.38 ppm, an ion in its 70 eV mass spectrum at m/e 169 along with other expected ions. Among other products which were characterized with varying degrees of thorouqhness was about 5% of dichlorobis[trimethylstannyl]methane.[2] Its signal in the pmr spectrum appeared at δ 0.29 with $^2J(Sn\text{-}H)$ 54.2 Hz in agreement with the value reported in the literature.[10] About 5% of tris[trimethylstannyl]methane was isolated and characterized by its elemental analysis and its pmr spectrum in which the methyl proton signals were observed at δ 0.09; $^2J(Sn\text{-}H)$, 52.0 Hz. The methine proton signal appeared at δ -0.73; $^2J(Sn\text{-}H)$, 64.4. In addition to chloroform, discussed above, methylene chloride was also observed in small amounts; both were characterized by their gas phase infrared spectra. The presence of <u>3</u> would suggest that the most simple mechanism for the replacement of the halogens of CCl_4 by trimethylstannyl groups as shown in eq. 6 ($R = Me_3Sn$) can occur. This type of mechanism has been shown to be feasible for the stepwise replacement of

$$R^- + ClCCl_3 \longrightarrow RCl + {}^-CCl_3 \longrightarrow R\text{-}CCl_3 + Cl^- \qquad (6)$$

the bromines of CBr_4 by trimethylsilyllithium at -100° by Köbrich and von Nagel.[11] Furthermore, this is the simplest way to account for the isolation of partially plumbylated products in the reactions of triphenylplumbyllithium with CCl_4 in tetrahydrofuran at temperatures below -40°.[8] An alternative scheme, suggested by Gilman and Aoki for the reaction of triphenylsilyllithium with polyhalomethanes,[3] involves formation of carbenes as intermediates by loss of halide ions from the α-halomethylanion intermediates, eq. 7, (R = Ph_3Si).

$$^{-}CCl_3 \longrightarrow Cl^- + :CCl_2 \xrightarrow{R^-} (RCCl_2)^- \xrightarrow{H^+} RCHCl_2 \qquad (7)$$

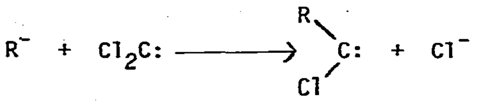
A new carbene and a new anion could be formed via eq. 8; this could lose chloride ion to produce still another carbene.



$$(RCCl_2)^- \longrightarrow Cl^- + \overset{R}{\underset{Cl}{>}}C: \xrightarrow{R^-} (R_2CCl)^- \qquad (8)$$

Trapping of dichlorocarbene in the reaction of trimethylstannylsodium with CCl_4 is consistent with this type of mechanism. However, the coupling mechanism representec by eq. 6 probably does occur. Absence of 3 in products of reactions carried out at ambient temperatures would suggest that it reacts much more rapidly with Me_3SnNa to form $(Me_3SnCCl_2)^-$ than does CCl_4, which is consistent with the data in Table I. This anion can then react with Me_3SnCl to form $(Me_3Sn)_2CCl_2$, small amounts of which were, in fact, isolated. In addition, the formation of methylene chloride can be rationalized only on the assumption of the intermediacy of both trichloromethyl and dichloromethyl anions each of which abstracts a proton, presumably from the solvent. No pathway to methylene chloride which involves a carbene intermediate seems to be available.

Although strict comparisons cannot be made due to differences in reaction parameters, some further observations made by others might be added here. Trimethylplumbylsodium reacts with CBr_4 in liquid ammonia to give tetrakis[trimethylplumbyl] methane in unspecified yield; however, CCl_4 yields none of this product under the same conditions.[8] Triethylgermylpotassium in hexamethylphosphoramide yields no products resulting from displacement of halogen from carbon when allowed to react with CBr_4, CCl_3, or $CHCl_3$.[12] These differences are not difficult to understand: in order to replace all four chlorines of CCl_4 by organometallic groups a minimum of eight steps is required in a sequence of two-step substitutions as in eq. 6; and eight steps are also required for the carbene sequence if one-step nucleophilic displacements on carbenes, eq. 9, are excluded. The overall course of the



$$R^- + Cl_2C: \longrightarrow \begin{matrix} R \\ \quad C: \\ Cl \end{matrix} + Cl^- \qquad (9)$$

reaction in any specific case will depend on the rates of the several reactions which will depend, in turn, on the structural parameters of the reactants and on the nature of the reaction environment. The clean stepwise substitutions with triphenylplumbyllithium may be due to high electrophilic reactivity of Ph_3PbCl toward anions, as in the second step of eq. 6, for example.

It was of interest to ascertain whether either of the last two replacements of chlorine by trimethylstannyl groups in the formation of <u>1</u> might occur by a simple SN2 reaction. The following reaction, eq.10,, was carried out under the conditions used in the experiments described above with the result that <u>1</u> was obtained in 85% yield. When <u>t</u>-butyl alcohol was present in the initial reaction

$$(Me_3Sn)_2SnCCl_2 \quad + \quad 2\ Me_3SnNa \longrightarrow \underset{\underline{1}}{(Me_3Sn)_4C} \qquad (10)$$

mixture with the dichloride compound <u>1</u> could not be detected in the reaction product mixture. Instead $(Me_3Sn)_2CH_2$ was isolated. Thus it may be concluded that both of the chlorines are replaced by the two-step substitution mechanism, eq. 6, or by the carbene-stannyl anion addition-substitution mechanism, eq. 9. An SN2 sequence is clearly ruled out.

<u>Chloroform</u>.- The reaction of chloroform with trimethylstannylsodium in liquid ammonia has been reported to form bis[trimethylstannyl]methane, <u>4</u>, as the only substitution product.[7] Its formation was rationalized according to eq. 11, followed

$$Me_3SnNa + CHCl_3 \longrightarrow Me_3SnCl + NaCHCl_2 \xrightarrow{NH_3} NaNH_2 + CH_2Cl_2 \qquad (11)$$

by reaction of the methylene chloride with two moles of Me_3SnNa to form the product observed. It was of interest to ascertain whether the result would be the same in a solvent such as tetraglyme which is a much weaker acid than ammonia. When chloroform was added to an excess of Me_3SnNa in this solvent the only products isolated, in addition to the ubiquitous hexamethyldistannane, were 10% of 1 and 55% of 4. When the reaction was conducted in the presence of 2,3-dimethyl-2-butene the only carbene trapping product detected was 1,1,dichloro-2,2,3,3-tetramethylbutane in 9% yield. The formation of this product suggest an initial step involving proton abstraction from chloroform to form trichloromethyl anions, which loses chloride to form dichlorocarbene. On the other hand, when the reaction was carried out in the presence of 3-pentanol at ambient temperature substantial amounts of methylene chloride were formed, indicating initial sodium-chlorine exchange,

Table II

Effect of Added 3-Pentalol on the Formation of Methylene Chloride from Reaction of Trimethylstannylsodium with Chloroform[a]

3-pentanol added (mmoles)	mmoles $CHCl_3$ consumed	% yield of CH_2Cl_2[b]
0	0.34	37
.089	.33	35
.30	.34	62
.68	.30	95
.97	.35	89

[a] 2.5 ml tetraglyme as solvent; 0.59 mmoles Me_3SnNa and ca. 0.60 mmoles $CHCl_3$ used.

[b] Based on $CHCl_3$ consumed.

analogous to eq. 1. Data are shown in Table II. Three points concerning the data are pertinent. First, significant amounts (37%) of methylene chloride are formed in the absence of added alcohol. Second, up to about 89% of the chloroform consumed can be trapped as methylene chloride. Third, in contrast to the results obtained with CCl_4, the amount of $CHCl_3$ consumed is independent of the amount of alcohol initially present. Since about 0.34 mmoles of $CHCl_3$ is consumed by 0.59 mmoles of Me_3SnNa to form mostly $NaCHCl_2$ and Me_3SnCl, the latter must consume the remaining Me_3SnNa, eq. 4, and this reaction must be faster than the reaction of Me_3SnNa with $CHCl_3$. The observation that 37% of methylene chloride is formed in the absence of alcohol means that $NaCHCl_2$ abstracts protons from the reaction medium with high efficiency. When sufficient excess Me_3SnNa is present the CH_2Cl_2 can react to form the major reaction product, <u>4</u>. The remainder of the $NaCHCl_2$ forms chlorocarbene, which goes on to form other products as yet uncharacterized, but does not react efficiently enough with 2,3-dimethyl-2-butene to be trapped as a cyclopropane. The reaction of $CHCl_3$ with Me_3SnNa can be summarized, on the basis of the data now available, by eqs. 12a and 12b.

$$\mathrm{Me_3SnNa} + \mathrm{CHCl_3} \longrightarrow \begin{cases} \underset{\text{(minor)}}{\mathrm{Me_3SnH}} + \mathrm{NaCCl_3} \rightarrow\!\!\rightarrow\!\!\rightarrow \underline{1} & \text{(12a)} \\ \underset{\text{(major)}}{\mathrm{Me_3SnCl}} + \mathrm{NaCHCl_2} \rightarrow\!\!\rightarrow\!\!\rightarrow \underline{4} & \text{(12b)} \end{cases}$$

<u>Methylene Chloride</u>.- Kraus and Neal[6] have reported that trimethylstanylsodium and methylene chloride react "quantitatively" in liquid ammonia to yield bis[trimethylstannyl]methane. When methylene chloride was added to a two-fold excess of trimethylstannylsodium in tetraglyme and the reaction product mixture examined by qunatitative glpc a 37% yield of bis[trimethylstannyl]methane and a significant amount of hexamethyldistannane were found to be present. In an attempt to monitor the possible formation of carbene intermediates the reaction was conducted in the presence of 2,3-dimethyl-2-butene (two moles per mole of CH_2Cl_2). Careful exam-

ination of the product mixture revealed a 42% yield of bis[trimethylstannyl]methan and no products which could be construed by the glpc retention times as the expected tetramethylcyclopropane or its monochloro derivative.

In order to determine whether $CHCl_2^-$ was formed as an intermediate in the reaction, experiments were conducted using 3-pentanol as a trap. Results are presented in Table III. The experiments were identical except for the variation in the amounts of alcohol added. It can be seen that, in contrast to the results with CCl_4 and $CHCl_3$, the effect of the added alcohol is to decrease the consumption of CH_2Cl_2 by about 20% in the range of concentrations studies. This may well be due to the intrusion of a reaction between Me_3SnNa and the alcohol, analogous to eq. 3. Thus less of the Me_3SnNa is available for reaction with CH_2Cl_2, indicating that this compound reacts more slowly with CH_2Cl_2 than with $CHCl_3$ and CCl_4, as expected. Further indication that the anticipated anion is not formed was the observation that no CH_3Cl could be detected in the reaction product mixture despite careful search. These failures to trap intermediates would suggest that

Table III

Effect of Added 3-Pentanol on the Consumption of Methylene Chloride on Its Reaction with Trimethylstannylsodium[a]

3-Pentanol mmoles	CH_2Cl_2 reacted mmoles
0	0.216
0.086	0.203
0.30	0.190
0 .53	0 .197
0.96	0 .172

[a] Ambient temp. in tetraglyme; initial amounts (mmoles in 1.14 ml solution): CH_2Cl_2, 0.51; Me_3SnNa, 0.59.

the reaction involves simple nucleophilic substitution on carbon as the mechanism for the formation of $[Me_3Sn]_2CH_2$, but such a conclusion must be considered tentative in the absence of direct evidence.

Tetrakis[trimethylstannyl]methane, 1.- This compound has the high melting point and relative ease of sublimation characteristic of molecules of high symmetry. Yet it can be readily crystallized from acetone and methylene chloride. The ^{13}C chemical shift of the central carbon atom is -35.7 ppm and that of the methyl carbons -13.7 ppm relative to internal tetramethylsilane.[13] In bis[trimethylstannyl] methane, IV, the methylene carbon signal appears at -24.8 ppm, and the methyl carbons at -17.9. These observations are consistent with substantial shielding effects on tin atoms bound to carbon. The values of $^{1}J(^{119}Sn-^{13}C)$ for 1 and 4 are 319 and 329.5 Hz, respectively; and they also show a three-bond couplings Sn-C-Sn-C of 11.1 and 10.0 Hz, respectively.

The reaction of 1 with bromine does not follow a simple course. When one equivalent of bromine was added to 1 at temperatures ranging from -12° to 26° the pmr spectrum of the reaction mixture showed only minor variations. Eight signals were observed in the region expected for protons bound to tin (0.09 to 1.13 ppm), and a strong signal at 2.61 ppm attributable to methyl bromide was also present. The weak signal at 0.09 ppm was attributed to tris[trimethylstannyl]bromide, and one at 0.71 ppm was assigned to trimethylbromostannane indicating some cleavage of the bond between the central carbon and tin. The strong signal due to trimethylbromostannane and others at 1.04 ppm $^{2}J(^{119}Sn-H)$ 61.5 Hz and at 1.13 ppm, ^{2}J ca. 62 Hz indicate that methyl-tin cleavage predominates.

EXPERIMENTAL

Proton nmr spectra were obtained with a Varian Associates A60-A or Ha-100 spectrometers. Carbon-13 spectra were obtained with the latter interfaced to a Digilab FTS-3 pulse and data system. Spectra were 8 K or 16 K Fourier transformed recorded at bandwidths of 2000 Hz. Coupling constants involving tin are given for ^{119}Sn, i.e., ^2J = $^2J(^{119}Sn\text{-}H)$, or for the center of unresolved signals due to ^{117}Sn and ^{119}Sn when the couplings are small. Infrared spectra were recorded with a Beckman IR-10 instrument. Most of the gas chromatograms were obtained with a column of 10% Apiezon L on Chromosorb W, 60-80 mesh, 6 ft by 1/8 in. All reactions involving hexamethyldistannane or trimethylstannylsodium were conducted under an atmosphere of dry nitrogen.

Approximately 0.2 M solutions of trimethylstannylsodium were prepared in tetraglyme, distilled from sodium, by stirring hexamethyldistannane with a threefold excess of metallic sodium peices for about 20 hr.

Bis[trimethylstannyl]dichloromethane was prepared by the reaction of hexamethyldistannane with dibromocarbene[10] generated from phenyl(bromodichloromethyl) mercury.[14]

Preparation of Tetrakis[trimethylstannyl]methane, 1.- (a) To a solution of 0.90 g (5.9 mmole) of CCl_4 in 5 ml tetraglyme at -23° was added slowly 65 ml of a 0.36 M solution of trimethylstannylsodium (23.4 mmole) in tetraglyme at the same temperature. Reaction occurred immediately as indicated by formation of a milky gray suspension. This was allowed to warm to room temperature, treated with 100 ml each of petroleum ether and water, and the two layers separated. The organic layer was treated with iodine until the color persisted, extracted with water again, dried over $MgSO_4$ concentrated and filtered, providing a solid and ca. 1 ml of filtrate.*

The solid was recrystallized from cyclohexane and methylene chloride 1/1 to provide 1.63 g (41%) of I. Pmr: δ 0.13 ppm; ^2J = 51 in CH_2Cl_2; ^{13}Cmr: $\delta\ \underline{C}H_3 = -3.58$ ppm; $^1J(^{119}Sn\text{-}^{13}C) = 318$ Hz; $^3J(^{119}Sn\text{-}^{13}C) = 11.5$ Hz in CH_2Cl_2; $\delta\ \underline{CSN_4}$ -35.7 ppm in $CDCl_3$, with $Cr(acac)_3$ to enhance relaxation. IR (cm^{-1}): 502(m), 620(s), 725(s),

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* This treatment removes hexamethyldistannane by cleaving it into trimethyliodostannane, which is water soluble.

788(s), 1180(m), 1198(m), 2912(s), 2982(s). Anal. Found: C, 23.26, H, 5.49, $C_{13}H_{36}Sn_4$ Calcd: C, 23.40; H, 5.44.

b) To 150 ml of tetraglyme were added 4.91 g (15.0 mmole) hexamethyldistannane and 1.21 g (51.2 mmole) Na with stirring at ambient temperature. Over a period of five hr 1.146 g (7.49 mmol) CCl_4 were added during which a precipitate appeared. Then, a few more drops were added to consume any remaining trimethylstannylsodium. The reaction mixture was filtered and the precipitate recrystallized from a mixture of acetone and methylene chloride yielding 2.11 g (44%) of 1.

Reaction of Trimethylstannylsodium with Excess Carbon Tetrachloride.- To a solution of 52.5 g CCl_4 in 100 ml of tetraglyme at -20° were added 200 ml of 0.43 M Me_3SnNa in the same solvent, with stirring. The mixture was allowed to warm to room temperature, treated with 100 ml of petroleum ether and washed with water. The organic layer was dried ($MgSO_4$) concentrated to a small volume and taken up in CCl_4, followed by glpc analysis. The major products isolated by glpc were hexamethyldistannane (δ 0.22 ppm; ^2J, 47.5 Hz); chloroform (IR identical with authentic sample); I; tris[trimethylstannyl]methane {δ 0.09 ppm (CH_3); ^2J, 52.0 Hz; δ -0.73 (CH) {relative areas 23:1}; Anal. Found: C, 25.17, 25.81; H, 5.59, 5.77. Calc for $C_{10}H_{28}Sn_3$: C, 23.81; H, 5.59); and bis[trimethylstannyl] dichloromethane (δ 0.29 ppm; ^3J, 54.5 Hz).[9]

In another experiment, carried out at -40 to -30°, the product was examined by pmr which revealed, in addition to signals due to the above compounds, a moderately strong one at δ 0.49 ppm, ^2J, 59 Hz, corresponding to the values expected for trichloromethyltrimethylstannane.[9]

Reaction of Trimethylstannylsodium with Dichlorobis[trimethylstannyl]methane.-

To 0.478 g (1.13 mmoles) of dichlorobis[trimethylstannyl]methane (ca. 90% pure) in 2.3 ml of tetraglyme was added, with stirring, 2.6 mmoles of Me_3SnNa in 3 ml of tetraglyme. After standing for four days the reaction mixture was hydrolyzed with water, extracted with methylene chloride, and the extract concentrated.

Glpc analysis revealed the formation of 85% of 1, along with hexamethyldistannane and small amounts of unreacted dichloride, and bis[trimethylstannyl]methane.

Reaction of Trimethylstannylsodium with Dichlorobis[trimethylstannyl]methane in the Presence of t-Butyl Alcohol.- To 0.491 g (1.36 mmole) of dichlorobis[trimethylstannyl]methane and 0.222 g t-butyl alcohol in 1.3 ml of tetraglyme was added 2.6 mmoles of trimethylstannylsodium in 3 ml of tetraglyme. Work-up and glpc analysis as above showed the presence of hexamethyldistannane, 4, and some unreacted starting dichloride. No detectable amount of 1 was present.

Reaction of Trimethylstannylsodium with Methylene Chloride.- To a solution of 0.974 g (11.1 mmole) of CH_2Cl_2 in 10 ml of tetraglyme was added 23 mmoles of Me_3SnNa in 64 ml of tetraglyme. After standing overnight the reaction mixture was treated in the same way as that from the reaction with CCl_4 and the product isolated by preparative glpc yielding 1.98 g (37%) of 4. Pmr in CCl_4: δ -0.02 ppm, ^2J, 53.4 Hz (CH_3), δ -0.3 ppm, ^2J, 60.2 Hz (CH_2); cmr: δ -17.9, ^1J, 329.5 Hz ($\underline{C}H_3$); δ -24.8 ppm, ^1J, 271 ($\underline{C}H_2$), $^3J(\underline{C}H_3\text{-Sn-C-Sn})$, 10.0 Hz. Il (KBr):470(w), 509(m), 527(s), 569(w), 611(s), 734(m), 769(s), 959(w), 1193(w), 2907(s), 2976(s).

Reaction of Trimethylstannylsodium with Chloroform.- To a solution of 8.3 mmole of Me_3SnNa in 30 ml of tetraglyme was slowly added 0.696 g (5.8 mmole) of $CHCl_3$ in 5 ml of tetraglyme. After the reaction was complete 50 ml of CH_2Cl_2 was added and the resultant solution washed with four 50-ml portions of water. Concentration of the organic layer, followed by quantitative glpc analysis indicated the formation of 10% of 1 and 55% of bis[trimethylstannyl]methane based on Me_3SnNa used. The products were characterized by glpc retention times and pmr spectra.

Carbene Trapping Experiments with 2,3-Dimethyl-2-butene.- a) To a solution of 0.869 g (5.7 mmoles) of CCl_4 and 1.57 g (21.2 mmoles) of 2,3-dimethyl-2-butene in 10 ml of tetraglyme was added 6.0 ml of tetraglyme containing 4.56 mmoles of

Me_3SnNa with stirring. Work-up as in above-described reactions followed by glpc analysis and isolation yielded 1,1-dichloro-2,2,3,3-tetramethylcyclopropane characterized by a proton singlet in the pmr at δ 1.38 ppm and M-1 peaks with m/e 169 and 167 among others expected in the mass spectrum.

b) A similar experiment involving the use of 0.816 g (6.8 mmole) of $CHCl_3$, 1.29 g (17 mmoles) of 2,3-dimethyl-2-butene and 3.4 mmoles of Me_3SnNa in a total of 15 ml tetraglyme yielded 9% of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane. Bis(trimethylstannyl)methane, hexamethyldistannane, and CH_2Cl_2 were also present in the reaction product mixture, but no component with the expected retention time of the adduct of chlorocarbene to 2,3-dimethyl-2-butene was observed.

c) In another experiment 0.731 g (8.6 mmoles) of CH_2Cl_2, 1.29 g (17 mmoles) of 2,3-dimethyl-2-butene, and 3.4 mmoles of Me_3SnNa in 15 ml of tetraglyme were allowed to react. Glpc analysis of the reaction product revealed a 42% yield of bis(trimethylstannyl)methane based on Me_3SnNa used, hexamethyldistannane, but no products with retention times corresponding to those expected for the addition of carbene or chlorocarbene to the olefin.

Trapping of Anionic Intermediates with Alcohols.- The procedure was similar for each of the halomethanes. That for CCl_4 is described. To each of a series of vials was added 1.16 mmoles of CCl_4 and 4 ml of tetraglyme. Amounts of ethanol ranging from 0.25 to 20 mmoles were added to individual vials, and one was used as a blank. To each was added in turn 1.0 ml of a 0.76 M solution of Me_3SnNa in tetraglyme containing dodecane as internal standard with stirring. The reaction mixtures were then analyzed for remaining CCl_4 and $CHCl_3$ formed. The procedures were similar for $CHCl_3$ and CH_2Cl_2 except that 3-pentanol was used as the alcohol for analytical convenience.

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