Halomethylmetal Compounds. XXXIV. The Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Carbon–Hydrogen Bonds. Tetraalkylsilicon and Tetraalkyltin Compounds[1]

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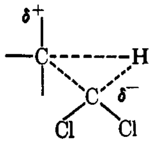
Abstract: Trialkyltin and trialkylsilyl substituents have been found to activate C–H bonds of alkanes in the β position toward insertion of dichlorocarbene. The reaction $Me_3MCH_2CH_2CH_3 + PhHgCCl_2Br \rightarrow Me_3MCH_2CH(CCl_2H)CH_3 + PhHgBr$ (M = Sn and Si) is typical. A consideration of product yields in 36 such reactions and of the results of relative reactivity studies as well as of the related CCl_2 insertions into β C–H bonds of dialkylmercurials (Landgrebe) suggests to us that it is metal–carbon bond hyperconjugation and, to a lesser extent, the +I inductive effect of the alkylmetal substituents which are the important factors involved and that these operate to stabilize transition state I, in which the carbon atom into whose bond to hydrogen CCl_2 insertion is occurring bears a partial positive charge. Thirty new silicon- or tin-containing products of such CCl_2 insertion were prepared and characterized during the course of this study.

Our previous work[1,5] has shown that phenyl(bromodichloromethyl)mercury-derived dichlorocarbene inserts into C–H bonds of alkanes, alkylbenzenes, and aliphatic ethers (eq 1). In favorable cases preparatively

$$PhHgCCl_2Br + -\overset{|}{\underset{|}{C}}H \longrightarrow -\overset{|}{\underset{|}{C}}CCl_2H + PhHgBr \quad (1)$$

useful yields (40–90%) of insertion products were obtained. The available evidence suggested an insertion process involving transition state I, since those substituents on the carbon into whose bond hydrogen



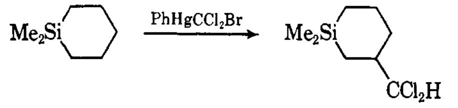
I

insertion was occurring which would be expected to stabilize best a partial positive charge, seemed to promote these reactions.

Our long-standing interest in organofunctional derivatives of the group IV elements led us to investigate the reaction of phenyl(bromodichloromethyl)mercury with tetraalkylsilanes and tetraalkyltin compounds. We had already devoted extensive study to the preparation of dihalomethylsilicon compounds, R_3SiCX_2H, by the reaction of phenyl(trihalomethyl)mercurials with organosilicon hydrides,[6,7] and so the synthesis of silicon compounds in which the dihalomethyl group was situated further out on an alkyl chain attached to silicon seemed worth examining. Also, we had prepared some dihalomethyltin compounds,[8,9] and thus this study was extended to include tetraalkyltins as well.

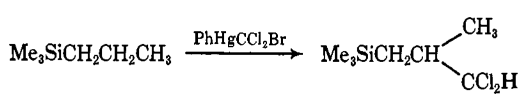
Results and Discussion

Preparative Studies. The reactions for the most part were carried out by heating at reflux a benzene solution of the tetraalkylsilicon or -tin compound (3 molar equiv) and phenyl(bromodichloromethyl)mercury (1 molar equiv) for 2–4 hr. The phenylmercuric bromide which precipitated was filtered and the organic filtrate was distilled or analyzed by gas–liquid partition chromatography (glpc). The initial results[10] were extremely intriguing and are summarized in eq 2–5. With



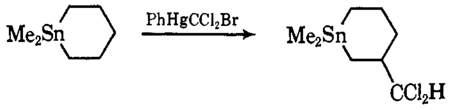
(2)

(68%)



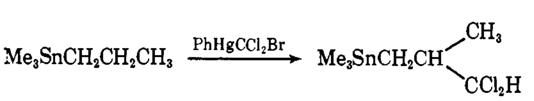
$$Me_3SiCH_2CH_2CH_3 \xrightarrow{PhHgCCl_2Br} Me_3SiCH_2CH(CH_3)(CCl_2H) \quad (3)$$

(15%)



(4)

(50%)



$$Me_3SnCH_2CH_2CH_3 \xrightarrow{PhHgCCl_2Br} Me_3SnCH_2CH(CH_3)(CCl_2H) \quad (5)$$

(70%)

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[1] Part XXXIII: D. Seyferth, V. A. Mai, and M. E. Gordon, *J. Org. Chem.*, in press.

[2] National Science Foundation Predoctoral Fellow, 1964–1966; Union Carbide Fellow, 1966–1967.

[3] Postdoctoral Research Associate, 1967–1968.

[4] Postdoctoral Research Associate, on leave from the Department of Synthetic Chemistry, Faculty of Engineering, Kyôto University, Japan, 1968–1969.

[5] D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, in press.

[6] D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, **7**, 405 (1967).

[7] D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, **90**, 2944 (1968).

[8] D. Seyferth and F. M. Ambrecht, Jr., *J. Organometal. Chem.*, **16**, 249 (1969).

[9] D. Seyferth and R. L. Lambert, in preparation.

[10] D. Seyferth and S. S. Washburne, *J. Organometal. Chem.*, **5**, 389 (1966).

Table I. Reactions of Tetraalkylsilicon and Tetraalkyltin Compounds with Phenyl(bromodichloromethyl)mercury

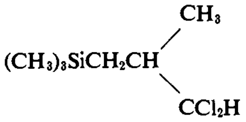
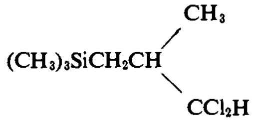
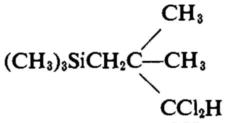
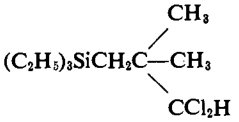
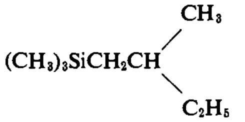
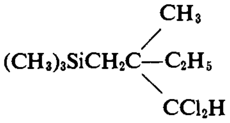
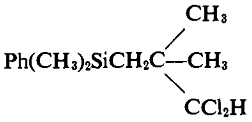
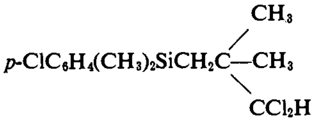
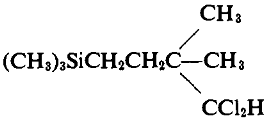
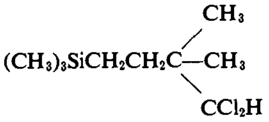
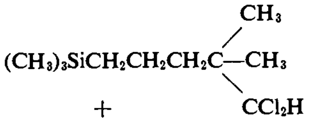
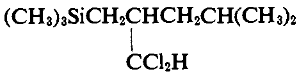
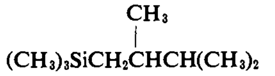
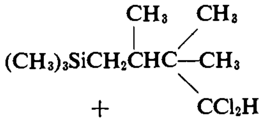
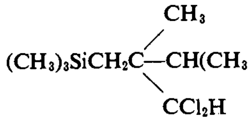
Expt no.	Compound	Solvent	Product	Yield (recovery), %
		Silicon Compounds		
1	$(CH_3)_2Si(C_2H_5)_2$	Benzene	None	
2	$(CH_3)_3SiCH_2CH_2CH_3$	Benzene	 $(CH_3)_3SiCH_2CH(CH_3)CCl_2H$	16
	$(CH_3)_3SiCH_2CH_2CH_3$	None	 $(CH_3)_3SiCH_2CH(CH_3)CCl_2H$	41
3	$(CH_3)_3SiCH_2CH(CH_3)_2$	Benzene	 $(CH_3)_3SiCH_2C(CH_3)(CCl_2H)CH_3$	69, 62
4	$(C_2H_5)_3SiCH_2CH(CH_3)_2$	Benzene	 $(C_2H_5)_3SiCH_2C(CH_3)(CCl_2H)CH_3$	77
5	 $(CH_3)_3SiCH_2CH(CH_3)C_2H_5$	Benzene	 $(CH_3)_3SiCH_2C(CH_3)(CCl_2H)C_2H_5$	52
6	$Ph(CH_3)_2SiCH_2CH(CH_3)_2$	Benzene	 $Ph(CH_3)_2SiCH_2C(CH_3)(CCl_2H)CH_3$	77
7	$p\text{-}ClC_6H_4(CH_3)_2SiCH_2=CH(CH_3)_2$	Benzene	 $p\text{-}ClC_6H_4(CH_3)_2SiCH_2C(CH_3)(CCl_2H)CH_3$	40
8	$Ph_2CH_3SiCH_2CH(CH_3)_2$	Benzene	None	(97)
9	$Ph_3SiCH_2CH(CH_3)_2$	Benzene	None	(99)
10	$(CH_3)_2ClSiCH_2CH(CH_3)_2$	Benzene	None	(96)
11	$CH_3Cl_2SiCH_2CH(CH_3)_2$	Benzene	None	(96)
12	$(CH_3)_3SiCH_2CH_2CH(CH_3)_2$	Benzene	 $(CH_3)_3SiCH_2CH_2C(CH_3)(CCl_2H)CH_3$	13
	$(CH_3)_3SiCH_2CH_2CH(CH_3)_2$	None	 $(CH_3)_3SiCH_2CH_2C(CH_3)(CCl_2H)CH_3$	64
13	$(CH_3)_2ClSiCH_2CH_2CH(CH_3)_2$	None	None	(91)
14	$(CH_3)_3SiCH_2CH_2CH_2CH(CH_3)_2$	None	 $(CH_3)_3SiCH_2CH_2CH_2C(CH_3)(CCl_2H)CH_3$ +	32
			 $(CH_3)_3SiCH_2CH(CCl_2H)CH_2CH(CH_3)_2$	9
15	 $(CH_3)_3SiCH_2CH(CH_3)CH(CH_3)_2$	None	 $(CH_3)_3SiCH_2CH(CH_3)C(CH_3)(CCl_2H)CH_3$ +	27
			 $(CH_3)_3SiCH_2C(CH_3)(CCl_2H)CH(CH_3)_2$	25

Table I (*Continued*)

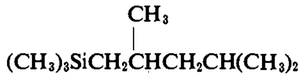
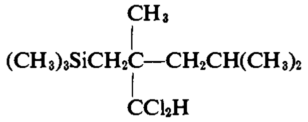
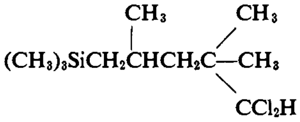
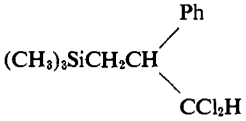
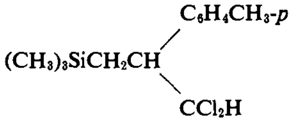
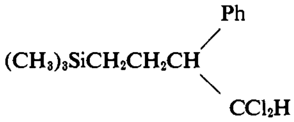
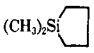
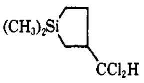
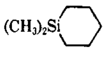
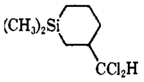
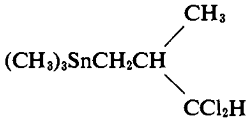
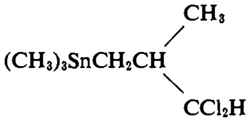
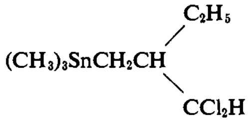
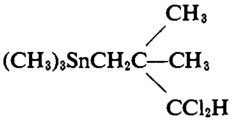
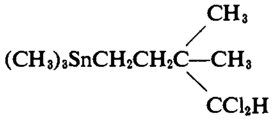
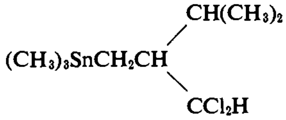
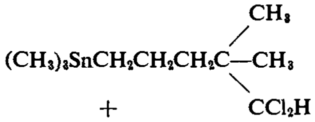
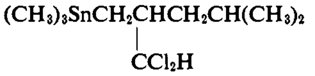
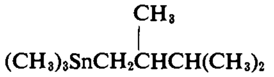
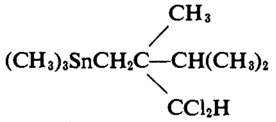
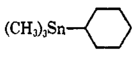
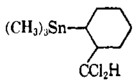
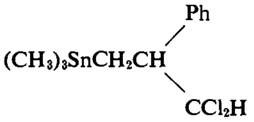
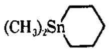
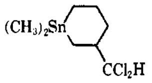
Expt no.	Compound	Solvent	Product	Yield (recovery), %
16	 $(CH_3)_3SiCH_2CH(CH_3)CH_2CH(CH_3)_2$	None	 $(CH_3)_3SiCH_2C(CH_3)(CCl_2H)CH_2CH(CH_3)_2$	42
			+	
				18
17	$(CH_3)_3SiCH_2CH_2C(CH_3)_3$	Benzene	None	(94)
18	$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$	Benzene	$[(CH_3)_3SiCH_2]_2CHCCl_2H$	9
19	$(CH_3)_3SiCH_2CH_2Ph$	Benzene		61
20	$(CH_3)_3SiCH_2CH_2C_6H_4CH_3$-*p*	Benzene		50
21	$(CH_3)_3SiCH_2CH_2CH_2Ph$	Benzene		27
22		Benzene		8
23		Benzene		68, 65
		Tin Compounds		
24	$(CH_3)_4Sn$	Benzene	None	
25	$(CH_3)_3SnCH_2CH_3$	Benzene	None	
26	$(CH_3)_3SnCH_2CH_2CH_2$	Benzene		70
	$(CH_3)_3SnCH_2CH_2CH_3$	None		68
27	$(CH_3)_3SnCH(CH_3)_2$	Benzene	None	
28	$(CH_3)_3SnCH_2CH_2CH_2CH_3$	Benzene		36
29	$(CH_3)_3SnCH_2CH(CH_3)_2$	Benzene		82
30	$(CH_3)_3SnC(CH_3)_3$	Benzene	None	97
31	$(CH_3)_3SnCH_2CH_2CH(CH_3)_2$	None		29 26*
			+	
	$(CH_3)_3SnCH_2CH_2CH(CH_3)_2$	Benzene*		21 23*

Table I (*Continued*)

Expt no.	Compound	Solvent	Product	Yield (recovery), %
32	$(CH_3)_3SnCH_2CH_2CH_2CH(CH_3)_2$	None	 $(CH_3)_3SnCH_2CH_2CH_2C(CH_3)_2CCl_2H$	15
			+  $(CH_3)_3SnCH_2CH(CCl_2H)CH_2CH(CH_3)_2$	54
33	 $(CH_3)_3SnCH_2CH(CH_3)CH(CH_3)_2$	None	 $(CH_3)_3SnCH_2C(CH_3)(CCl_2H)CH(CH_3)_2$ (possibly a trace of the γ insertion product)	74
34		Benzene		34
35	$(CH_3)_3SnCH_2CH_2Ph$	Benzene	 $(CH_3)_3SnCH_2CH(Ph)CCl_2H$	47
36		Benzene		78

tetramethyltin no reaction was observed. In these reactions the dichlorocarbene inserted *exclusively* into a C–H bond β with respect to the silicon or tin atom. Furthermore, in reactions 2, 4, and 5 the yields were astonishingly high and most certainly of synthetic utility. (In contrast, *under these experimental conditions*, CH_2 groups of simple unsubstituted alkanes react only very poorly.[5]) The obvious conclusion is that the group IV atoms both direct and activate the attack by CCl_2. As has been noted in our previous reports,[1,5] high regiospecificity was observed in reactions of $PhHgCCl_2Br$-derived dichlorocarbene with alkylbenzenes (specific insertion into the benzylic position) and with aliphatic ethers (specific insertion into C–H bonds α to the oxygen atom). This regiospecificity, together with other observations, was taken to indicate the involvement of transition state I. Further work with alkylsilicon and alkyltin systems was designed to provide more information concerning the β-metal effect: was it connected with an enhancement of the stability of I *via* some metal-associated electronic factor or was a basically different type of process involved? Table I lists the results obtained with a large number of tetraalkylsilicon and -tin compounds in which the structure of the alkyl group at which CCl_2 insertion takes place was varied widely and in which the other substituents on silicon were varied as well.

Inspection of Table I leads to the following conclusions concerning factors which affect these insertion reactions.[11]

(a) For such β C–H insertion processes the relative reactivity of C–H bonds (holding the Me_3M group constant) is in the order tertiary C–H > secondary C–H; primary C–H unreactive (expt no. 1, 2, 3 and no. 25, 26, 29), which is exactly the reactivity sequence observed in unsubstituted alkanes.[5]

(b) β-Silicon and β-tin activation of CCl_2 insertion into C–H bonds appears to be a general phenomenon, and tin is more effective in this respect than is silicon. Note that the β-insertion reactions in $Me_3SnCH_2CH_2CHMe_2$ (expt 31) and $Me_3SnCH_2CH_2CH_2CHMe_2$ (expt 32) compete strongly with insertion of CCl_2 into the tertiary C–H bonds further out along the chain, but that in the analogous silicon compounds the β-insertion reaction is either not observed at all (expt 12) or only as a minor process (expt 14). When the β C–H bond competing with a tertiary C–H bond further out along the alkyl chain is itself also tertiary, then in the tin case (expt 33) *only* β insertion is observed, while with the analogous silicon compound insertion into both the β and the more remote tertiary C–H bonds occurs (expt 15 and 16).

(c) C–H bonds involving the carbon atom directly linked to the group IV metal are totally inert.

(d) The other substituents on the group IV metal are very important. Electronegative substituents on silicon, for instance, can inhibit completely such insertion, as shown by the complete deactivation of the $\geqslant SiCH_2CHMe_2$ moiety when one or more of the methyl groups of $Me_3SiCH_2CHMe_2$ is replaced by chlorine atoms or when two or all three of the methyl groups are replaced by phenyl groups (expt no. 3, 4, 6, 7, 8, 9, 10, 11).

(e) The β-insertion reaction is subject to steric hindrance (expt 17, possibly no. 18) and conformational factors in cyclic systems may play an important role (expt 22 and 23).

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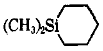
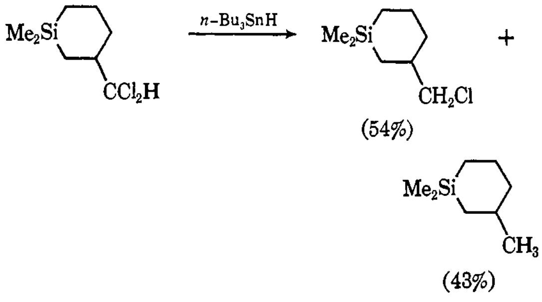
(11) We make the assumption that the yields of products are an approximate measure of the relative reactivity of the reacting C–H bond toward dichlorocarbene. In support of this, we note that the products appear to be stable to the reaction conditions and to the conditions used in their isolation and analysis.

Table II. Competition Experiments

Expt no.	S_1 (mmol)	S_2 (mmol)	$PhHgCCl_2Br$, mmol	Product from S_1, % yield	Product from S_2, % yield	Av $k_{rel} = k_{S_1}/k_{S_2}$ (per reactive C–H bond)
1	$(CH_3)_3SnCH_2CH_2CH_3$ (15.0, 15.1)	$(CH_3)_3SiCH_2CH_2CH_3$ (30.03, 24.18)	5.0, 5.0[a]	62.62, 62.00	11.83, 9.74	10.43
2	$(CH_3)_3SnCH_2CH(CH_3)_2$ (12.0, 12.0)	$(CH_3)_3SiCH_2CH(CH_3)_2$ (24.02, 16.0)	4.0, 4.0[a]	59.2, 68.0	19.7, 15.8	5.88
3	$(CH_3)_3SiCH_2CH(CH_3)_2$ (12.05, 12.02)	$(CH_3)_2CHCH_2CH_2CH_2CH_3$ (24.06, 35.14)	4.01, 4.01[a]	58.2, 54.0	18.4, 25.2	6.29
4	$(CH_3)_2CHCH_2CH_2CH_2CH_3$ (12.03)	$(CH_3)_3SiCH_2CH_2CH_3$ (24.24)	4.0[a]	23.6	35.5	0.37
5	$(CH_3)_3SiCH_2CH(CH_3)_2$ (9.96)	 (9.97)	3.0[b]	31.3	29	2.16
6	$(CH_3)_3SiCH_2CH(CH_3)_2$ (9.99)	$(CH_3)_3SiCH_2CH_2Ph$ (10.0)	3.0[b]	38	34	2.24
7	$(CH_3)_3SiCH_2CH_2Ph$ (9.85)	CH_3CH_2Ph (9.87)	3.0[b]	50.0	8.0	6.25
8	$(CH_3)_3SiCH_2CH_2C_6H_4CH_3$-*p* (9.99)	$(CH_3)_3SiCH_2CH_2Ph$ (9.99)	3.0[b]	34.0	19.4	1.80

[a] No solvent. [b] Benzene solvent.

(f) As a more general observation, the yields in many of the examples in Table I are good (40–50%) to excellent (>75%), and thus these reactions could well find useful preparative application. In cases where the yields are low when the reaction is carried out in benzene solution, substantially improved yields could be realized in the absence of solvent (expt 2, 12). These insertion products can be reduced to the monochloromethyl and to the methyl derivatives (*e.g.*, eq 6) and the insertion products themselves, or their derived monochlorides, should have some interesting chemistry in their own right.



(6)

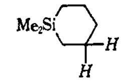
Relative Reactivity Studies. To provide more information concerning the nature of the β-metal effect in these reactions, a series of competition studies was carried out in which a mixture of two CCl_2-reactive compounds (S_1 and S_2) was allowed to compete for a deficiency of $PhHgCCl_2Br$, the $S_1 + S_2$/mercurial ratio used being sufficiently large so that the Doering–Henderson procedure for computing k_{rel} values[12] was applicable.

From the relative reactivity studies summarized in Table II the following observations and conclusions emerged.

(a) Even the more reactive of the metal-activated C–H bonds are quite unreactive when compared with a "standard" C=C bond. Thus when 30 mmol each of cyclohexene and 1,1-dimethylsilacyclohexane were allowed to compete for 10 mmol of phenyl(bromodichloromethyl)mercury (in 20 ml of benzene at 80° for 3 hr), the products obtained were 7,7-dichloronorcarane (80% yield) and 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane (0.93% yield). In this connection, we have noted previously the low reactivity of C–H bonds, compared with that of olefinic double bonds.[5]

(b) In order to achieve more meaningful comparisons, some of the relative rate constants in Table II were recalculated in terms of k_{rel} (2-methylhexane) = 1.0 and these k_{rel} values are given in Table III. These relative rate constants express in quantitative terms what already has been gleaned from the results shown in Table I. The activating effect of a β Me_3Sn substituent is much greater than that of a β Me_3Si group. When the C–H bond is a secondary one, this reactivity ratio, *k*(Sn)/*k*(Si), is 10.4. However, when insertion into the much more reactive tertiary C–H bonds is involved, the difference between Me_3Sn and Me_3Si activation is diminished [*k*(Sn)/*k*(Si) = 5.9].

Table III. Relative Rate Constants for Dichlorocarbene Insertion into C–H Bonds

Bond in compound	Type of bond	k_{rel}[a]
$Me_3SnCH_2C\mathit{H}Me_2$	β Sn, tertiary	37
$Me_3SiCH_2C\mathit{H}Me_2$	β Si, tertiary	6.3
$Me_3SnCH_2C\mathit{H}_2CH_3$	β Sn, secondary	3.8
	β (ring) Si, secondary	2.9
$Me_3SiCH_2C\mathit{H}_2Ph$	β Si, α Ph, secondary	2.8
$CH_3(CH_2)_3C\mathit{H}Me_2$	simple, tertiary	1.0
$PhC\mathit{H}_2CH_3$	α Ph, secondary	0.45
$Me_3SiCH_2CH_2CH_3$	β Si, secondary	0.37

[a] Relative reactivity per C–H bond in position indicated.

(c) The extra activation of an α phenyl group[5] is readily apparent ($Me_3SiCH_2CH_2CH_3$ *vs.* $Me_3SiCH_2CH_2Ph$), and a *para*-methyl substituent on such a phenyl group provides an extra measure of activation. Conversely, the enhancement of the reactivity of a C–H bond α to a phenyl group by a β Me_3Si substituent also is demonstrated ($Me_3SiCH_2CH_2Ph$ *vs.* CH_3CH_2Ph).

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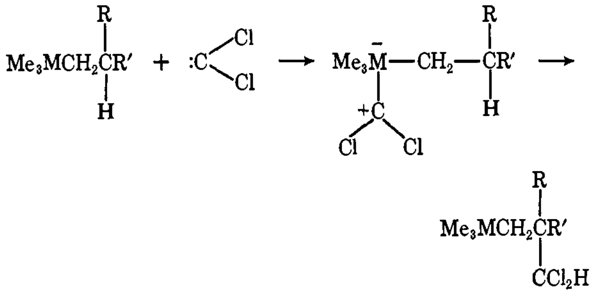
[12] W. von E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, 80, 5274 (1958).

(d) Noteworthy is the enhanced reactivity of C–H bonds β to silicon when the silicon atom is part of a six-membered carbocyclic ring system (a conformational effect?).

The Nature of the Activation of C–H Bonds toward Dichlorocarbene Insertion by Group IV Substituents in the β Position. As the discussion has shown, the effect of R_3Si and R_3Sn substituents is to amplify other activating effects already present. On the basis of these results one can develop a plausible explanation of the β-metal activation effect reported here.

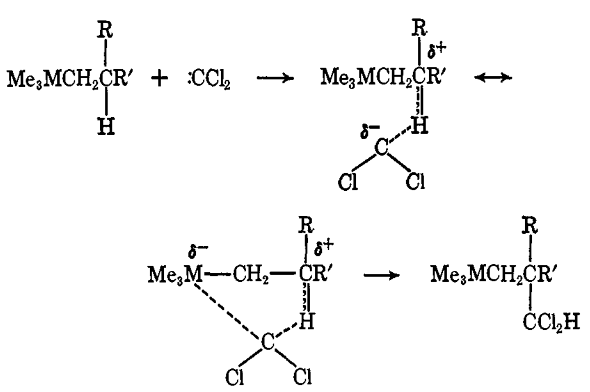
The electronic effects of R_3M (M = Si, Ge, Sn, Pb) groups which have been recognized to be operative in R_3M-substituted compounds are (1) the +I electron-releasing effect, caused by the low electronegativity of silicon and its congenors,[13] (2) effects resulting from participation of vacant M d orbitals in the bonding in the ground state or in the transition state,[13] and (3) electron-releasing hyperconjugation from the R_3M–carbon bond.[14] Based on these effects, four different possibilities for group IV metal β activation of CCl_2 insertion into C–H linkages can be discussed.

(a) Dichlorocarbene attacks at the metal atom as a nucleophilic reagent, giving the "reverse ylide" II, from which CCl_2 transfer to the accessible β C–H bond occurs. This possibility was suggested in our first report of preliminary results concerning such insertion processes.[10]



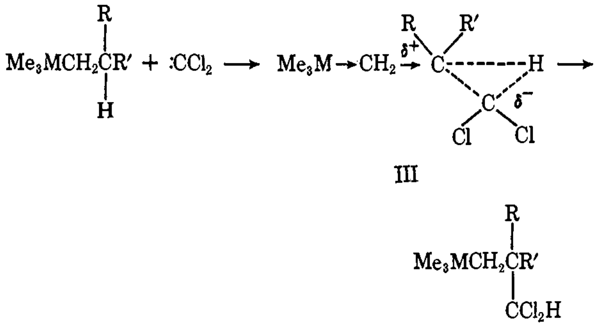
(7)

(b) Dichlorocarbene attacks at the β C–H bond as an electrophilic reagent and this mode of attack, in which negative charge is built up on the carbene carbon atom, is facilitated by interaction of the filled carbene carbon orbital with the vacant metal d orbitals (eq 8).



(8)

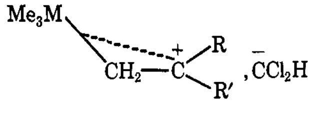
(c) Dichlorocarbene attacks as an electrophile at the C–H bond whose hydrogen is the most hydridic in nature, *i.e.*, whose carbon atom could best stabilize a partial positive charge. The effect of the Me_3M substituent is solely one of inductive release of electron density, an effect which would assist in the stabilization of the δ^+ charge on the carbon atom. The d orbitals would not be involved.



III

(9)

(d) The attack of dichlorocarbene occurs as in (c), but the activating effect of the Me_3M substituent results from stabilization of the transition state by hyperconjugative electron release from the Si–C or Sn–C bond to the developing electron-deficient carbon atom. This is shown in IV in terms of the extreme ion pair structure for the sake of simplicity.



IV

The results of the experiments shown in Table I allow one to rule out the first two possibilities. In (a) and (b) it is the Lewis acid properties of the Me_3M group which are of decisive importance. A partial negative charge is built up on the metal atom either in an intermediate (such as II) or in the transition state, and one would expect electronegative substituents on silicon to facilitate the observed β insertion process. The reverse is true as the following series show: $Me_3SiCH_2CHMe_2$ (62% β insertion), $Me_2PhSiCH_2CHMe_2$ (77% β insertion), $MePh_2SiCH_2CHMe_2$ (no β insertion), $Ph_3SiCH_2CHMe_2$ (no β insertion), $Et_3SiCH_2CHMe_2$ (77% β insertion), and $Me_3SiCH_2CHMe_2$ (62% β insertion), $Me_2ClSiCH_2CHMe_2$ (no β insertion), $MeCl_2SiCH_2CHMe_2$ (no β insertion). The results obtained in the first series might be explained in terms of the steric effects of the phenyl substituents on silicon, but the effect of the chlorine-for-methyl substitution can only be electronic in origin. One may note that the Lewis acidity of silicon decreases in the methylchlorosilane series as chlorine substitution decreases and methyl substitution increases.[13] Silicon tetrachloride is the strongest Lewis acid in the series; tetramethylsilane has no Lewis acid properties at all.

Thus possibilities (c) and (d) remain. Both operate in the same direction and at first sight their relative importance seems unassessible. All the observations made during the course of this investigation can be explained very readily in terms of the inductive effects of the silicon and tin substituents. The observed greater effect of tin as compared with that of silicon is in line with such an explanation. Eaborn and his coworkers have shown in several studies that the +I electron-releasing properties of the Me_3MCH_2 increase as M is

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[13] (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, Chapter 3; (b) E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 1.

[14] (a) C. Eaborn, *J. Chem. Soc.*, 4858 (1956); (b) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometal. Chem.*, 20, 49 (1969).

changed from silicon to germanium to tin.[15] Furthermore, the two reactivity series above are those to be expected if inductive effects played the greatest part in these insertion reactions.

Noteworthy throughout this study was the total absence of CCl_2 insertion into C–H bonds α to the silicon and tin atoms. Such α insertion would give $R_3MCH(CCl_2H)R'$ compounds in which the chlorine substituent is in β position with respect to the metal. Such systems often are unstable with respect to thermal or acid or base-catalyzed β elimination of R_3MCl, and many examples of β elimination from $R_3SiCH_2CH_2X$ compounds have been reported.[16] Since none of the expected products of CCl_2 insertion into α C–H bonds were isolated, a careful search was made in a few cases for the expected products of their β elimination, *e.g.*, R_3SiCl and $R'CH{=}CHCl$ in the general case noted above. Such products, however, were absent and thus we conclude α insertion does not occur at all or at the most as only a very minor side reaction. If the discussion were restricted to the present cases involving trimethylsilyl- and trimethyltin substituents, this observation would be most readily understandable in terms of steric hindrance to CCl_2 attack at α H by the three other substituents (usually methyl groups) on the silicon and tin atoms. That such insertion processes are subject to steric hindrance had been shown by the example of $Me_3SiCH_2CH_2CMe_3$ where no β insertion was observed. However, similar insertion reactions of dichlorocarbene (generated *via* CCl_3CO_2Et + NaOMe) into β C–H bonds of dialkylmercury compounds have been reported recently.[17] For example, the product mixture obtained from diisobutylmercury contained 91% *i*-$BuHgCH_2C(CCl_2H)Me_2$ and 9% *i*-$BuHgCCl_2CH_2CHMe_2$. In the case of diisoamylmercury, $Hg(CH_2CH_2CHMe_2)_2$, CCl_2 insertion occurred *exclusively* at the β position. Insertion into the α C–H bonds of dialkylmercurials would not be expected to be a sterically hindered process, yet in no case was insertion into an α C—H bond observed. Little is known concerning the inductive effect of alkylmercury substituents, but in any case, one would not expect the "β-metal effect" of RHg groups to be so much more pronounced than that of the Me_3Sn group (as indicated by the results obtained with the isoamylmercury and -tin compounds).

We suggest that the "β metal effect" on CCl_2 insertion into alkyl groups attached to silicon, tin and mercury is best understood in terms of transition state stabilization through metal–carbon bond hyperconjugation, as in IV. On this basis the relative β activating effects, RHg > Me_3Sn > Me_3Si, can be rationalized: release of M–C bonding electron density to an electron deficient center in the β position should be the easiest for the weakest metal–carbon bond. Quantitative statements concerning the relative importance of M–C hyperconjugation and the +I inductive effect cannot be made, but we suggest that the former is of greater importance in the reaction in question.[18,18a]

Irrespective of the importance of M–C hyperconjugation of the +I effect, these insertion reactions might possibly involve an ion pair intermediate (*i.e.*, $Me_3MCH_2{}^+CRR', {}^-CCl_2H$ (VI)), rather than proceeding in a concerted fashion. We have no evidence for or against such a possibility, but if a species such as VI is involved, it must be present as a tight ion pair since in the treatment of $Me_3SiCH_2CDMe_2$ with phenyl(bromodichloromethyl)mercury in dichloromethane medium the product is essentially pure $Me_3SiCH_2C(CCl_2D)Me_2$. Had the CCl_2D^- ion been kinetically free, exchange with the CH_2Cl_2 solvent would have been expected to give some CCl_2H^-, hence a significant amount of substitution of protium for deuterium in the product.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen or dry argon. Gas–liquid partition chromatography was used extensively in the analysis of reaction mixtures and for the isolation of products. F & M Model 700, 720, and 5754 gas chromatographs were used with 0.25-in. o.d. aluminum or stainless steel columns. The column packing used most was General Electric Co. SE-30 silicone rubber gum on Chromosorb P or W, but other packings (Dow Corning DC fluids, General Electric Co. XF-1150, Carbowax 20M on Chromosorb P or W) were used as well. Yields were determined by the internal standard procedure. Nmr spectra were obtained using Varian Associates A60 or T60 nmr spectrometers. Unless otherwise noted, these spectra were determined using solutions of the compounds in carbon tetrachloride; nmr resonances are given in δ units (parts per million downfield from internal TMS). In many cases chloroform was used as the experimental internal standard. Nmr spectra of methyltin compounds all showed spin-spin coupling, $J_{^{117}Sn-^{1}H}$ and $J_{^{119}Sn-^{1}H}$, of 51–55 Hz and these will not be given in the individual spectra cited. Infrared spectra were obtained using Perkin-Elmer Model 337 and 237 spectrophotometers. Thin layer chromatography was used to monitor the organomercurial reactions as described previously.[19] Phenyl(bromodichloromethyl)mercury was prepared in benzene medium[19] in the early stages of this work, later by the improved procedure in which THF is used as solvent.[20]

Preparation of Starting Materials. When the tin and silicon compounds were already described in the literature, the recommended procedure, usually the Grignard reaction, was used to prepare them from the commercially available trimethylchlorosilane and trimethyltin chloride. The physical constants and the spectra

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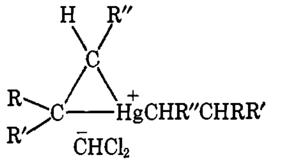
[15] (a) R. W. Bott, C. Eaborn, K. C. Pande, and T. W. Swaddle, *J. Chem. Soc.*, 1217 (1962); (b) R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, **2**, 154 (1964); (c) R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Organometal. Chem.*, **5**, 233 (1966); (d) C. Eaborn, A. R. Thompson, and D. R. M. Walton, *ibid.*, **17**, 149 (1969).

[16] Reference 13a, pp 133–137.

[17] (a) J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, **88**, 3545 (1966); (b) J. A. Landgrebe and D. E. Thurman, *ibid.*, **91**, 1759 (1969).

[18] Landgrebe[17] has suggested the intermediacy of a mercurinium ion pair, V, in CCl_2 insertion into β C–H bonds of dialkylmercurials. A pathway to V proceeding by way of nucleophilic attack by dichlorocarbene at mercury was discussed but was not considered an essential feature of the proposed mechanism. Mercurinium ions such as V appear to play an important role in some areas of organomercury chemistry, and thus the postulation of V as an intermediate in the β C–H insertion reaction does not introduce any fundamentally new concept. In contrast, organosilicon or organotin analogs of the mercurinium ion have not been discussed seriously in organosilicon and organotin reaction mechanisms. We see no need, on the basis of the available evidence, to introduce such intermediates into our reaction scheme.



V

[18a] NOTE ADDED IN PROOF. The recent paper by W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970), provides further evidence for the occurrence of metal–carbon bond hyperconjugation (σ–π conjugation) in organometallic systems, including compounds of silicon, tin, and mercury.

[19] D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

[20] D. Seyferth and R. L. Lambert, Jr., *ibid.*, **16**, 21 (1969).

Table IV. Products of CCl_2 Insertion into Tetraorganosilicon and Tetraorganotin Compounds

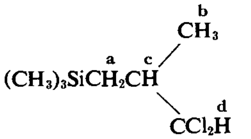
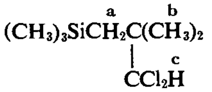
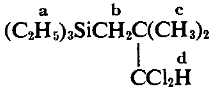
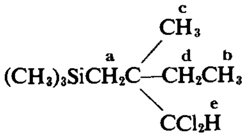
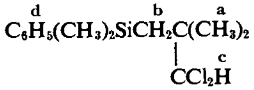
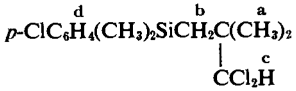
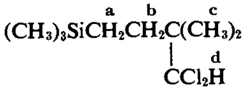
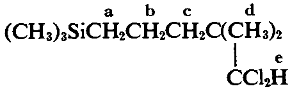
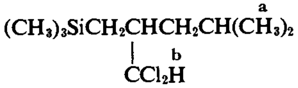
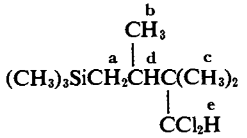
Compound	$n^{25}D$	Calcd, %			Found, %			Nmr spectrum (in δ units)
		C	H	Cl	C	H	Cl	
					Silicon Compounds			
	1.4561	42.09	8.16	35.41	42.21	8.10	35.60	a, 0.57–0.93 (unsym t, AB pattern); b, 1.14 (d), J = 7.5 Hz; c, 1.95–2.50 (m); d, 5.71 (d), J = 3.5 Hz
 $(CH_3)_3Si\overset{a}{CH_2}\underset{\substack{\vert \\ \overset{c}{CCl_2H}}}{C}\overset{b}{(CH_3)_2}$	1.4622	45.02	8.59	33.84	45.06	8.51	33.26	a, 0.89 (s); b, 1.13 (s); c, 5.46 (s)
 $(\overset{a}{C_2H_5})_3Si\overset{b}{CH_2}\underset{\substack{\vert \\ \overset{d}{CCl_2H}}}{C}\overset{c}{(CH_3)_2}$	1.4782	51.97	9.62	Si 11.00	51.74	9.47	11.01	a + b, 0.5–1.1 (m); c, 1.15 (s); d, 5.47 (s)
	1.4682	47.65	9.17	31.35	47.57	8.87	31.21	a + b, 0.68–0.95 (m); c, 1.05 (s); d, 1.42 (q), J = 6.5 Hz; e, 5.55 (s)
 $\overset{d}{C_6H_5}(CH_3)_2Si\overset{b}{CH_2}\underset{\substack{\vert \\ \overset{c}{CCl_2H}}}{C}\overset{a}{(CH_3)_2}$	1.5258	56.69	7.21	Si 10.20	56.71	7.32	10.21	a, 1.12 (s); b, 1.26 (s); c, 5.5 (s); d, 7.35 (s)
 $p\text{-}Cl\overset{d}{C_6H_4}(CH_3)_2Si\overset{b}{CH_2}\underset{\substack{\vert \\ \overset{c}{CCl_2H}}}{C}\overset{a}{(CH_3)_2}$	1.5310	50.18	6.17	34.61	50.41	6.18	34.34	a 1.00 (s), b 1.11 (s), c 5.40 (s), d 7.28 (q)
 $(CH_3)_3Si\overset{a}{CH_2}\overset{b}{CH_2}\underset{\substack{\vert \\ \overset{d}{CCl_2H}}}{C}\overset{c}{(CH_3)_2}$	1.4552	47.85	9.14		47.57	8.87		a 0.47 (m), b 1.3–1.6 (m), c 1.06 (s), d 5.66 (s)
 $(CH_3)_3Si\overset{a}{CH_2}\overset{b}{CH_2}\overset{c}{CH_2}\underset{\substack{\vert \\ \overset{e}{CCl_2H}}}{C}\overset{d}{(CH_3)_2}$	1.4570	49.54	9.04	29.59	49.78	9.19	29.39	a 0.55 (m), b + c 1.45 (m), d 1.11 (s), e 5.63 (s)
 $(CH_3)_3SiCH_2\underset{\substack{\vert \\ \overset{b}{CCl_2H}}}{CH}CH_2CH\overset{a}{(CH_3)_2}$	1.4543	49.88	9.09		49.78	9.19		a 0.92 and 0.97 (d), J = 6.0 Hz, b 5.89 (d), J = 3 Hz
 $(CH_3)_3Si\overset{a}{CH_2}\overset{\substack{\overset{b}{CH_3} \\ \vert}}{\underset{\substack{\vert \\ \overset{e}{CCl_2H}}}{\overset{d}{CH}}}\overset{c}{C(CH_3)_2}$	1.4674	49.67	8.98	29.85	49.78	9.19	29.39	a 0.3–0.6 (m), b 0.90 (d), J = 6.8 Hz, c 1.02 and 1.04 (d), J = 6.8 Hz, d 1.94 (m), e 5.83 (s)

Table IV (*Continued*)

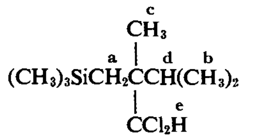
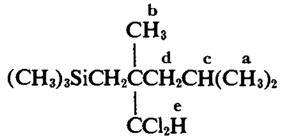
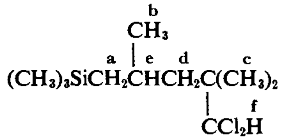
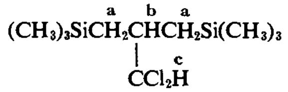
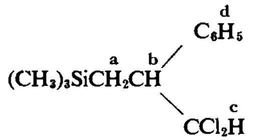
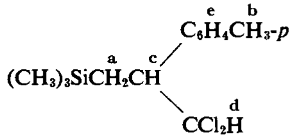
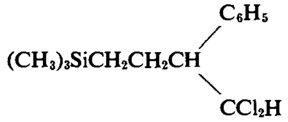
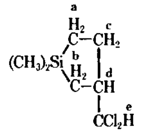
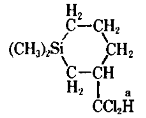
Compound	$n^{25}D$	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl	Nmr spectrum (in δ units)
 $(CH_3)_3SiCH_2\overset{CH_3}{\underset{CCl_2H}{C}}CH(CH_3)_2$	1.4746	49.97	9.07	29.74	49.78	9.19	29.39	a 0.92 (s), b 0.95 and 0.98 (d), *J* = 7 Hz, c 1.12 (s), d 2.05 (m), e 5.77 (s)
 $(CH_3)_3SiCH_2\overset{CH_3}{\underset{CCl_2H}{C}}CH_2CH(CH_3)_2$		51.42	9.14	27.26	51.75	9.48	27.77	a 0.98 (d), *J* = 5.6 Hz, b 1.18 (s), c + d 1.56 (m), e 5.77 (s)
		(Mixture with $(CH_3)_3SiCH_2CHMeCH_2C(CCl_2H)Me_2$)						
 $(CH_3)_3SiCH_2\overset{CH_3}{CH}CH_2\underset{CCl_2H}{C}(CH_3)_2$		(Analyzed as mixture with $Me_3SiCH_2C(CH_3)(CCl_2H)CH_2CHMe_2$)						a 1.1–1.3 (m), b 1.01 (d), *J* = 6.0 Hz, c 1.13 (s), d + e 1.55 (m), f 5.60 (s)
 $(CH_3)_3SiCH_2\underset{CCl_2H}{CH}CH_2Si(CH_3)_3$	1.4585	44.11	8.97	26.33	44.28	8.86	26.20	a 0.84 (m), b 2.31 (m), c, 5.83 (d), *J* = 2.5 Hz
 $(CH_3)_3SiCH_2CH(C_6H_5)(CCl_2H)$	1.5168	55.04	7.06	26.87	55.15	6.94	27.14	a 1.42 (m), b 3.36 (quintet), *J* = 5 Hz, c 5.80 (d), *J* = 5 Hz, d 7.14 (s)
 $(CH_3)_3SiCH_2CH(C_6H_4CH_3\text{-}p)(CCl_2H)$	1.5114	57.08	7.48	26.07	56.71	7.32	25.76	a 1.56 (s, broadened), b 2.58 (s), c 3.41 (m), d 5.95 (d), *J* = 4 Hz, e 7.48 (s)
 $(CH_3)_3SiCH_2CH_2CH(C_6H_5)(CCl_2H)$	1.5123	56.32	7.26	25.66	56.71	7.32	25.76	a 0.75 (t), *J* = 8.5 Hz, b 2.0 (m), c 3.22 (m), d 5.85 (d), *J* = 5 Hz, e 7.35 (s)
	1.4819	42.31	7.04	36.12	42.63	7.16	35.96	a + b 0.65–1.45 (m), c + d 1.50–2.75 (m), e 5.92 (d), *J* = 5 Hz
	1.4878 (bp 81–82° (6 mm))	45.51	7.52	33.24	45.49	7.64	33.56	a 5.71 (d), *J* = 3.5 Hz, ring protons, 0.3–2.1 (m)

Table IV (*Continued*)

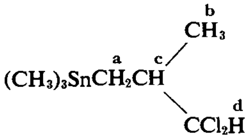
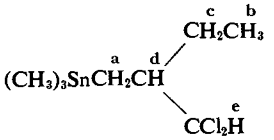
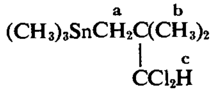
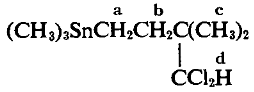
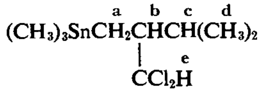
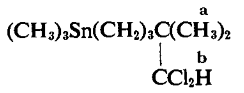
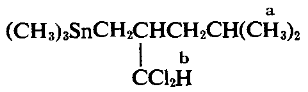
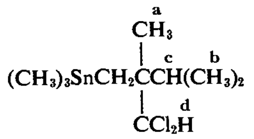
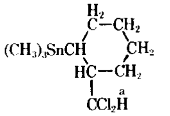
Compound	$n^{25}D$	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl	Nmr spectrum (in δ units)
Tin Compounds								
 $(CH_3)_3Sn\overset{a}{C}H_2\overset{c}{C}H(\overset{b}{C}H_3)\overset{d}{C}Cl_2H$	1.5005	29.29	5.45	24.64	29.01	5.57	24.47	a 0.5–1.55 (m), b 1.13 (d), *J* = 7 Hz, c 1.9–2.8 (m), d 5.59 (d), *J* = 4 Hz
 $(CH_3)_3Sn\overset{a}{C}H_2\overset{d}{C}H(\overset{c}{C}H_2\overset{b}{C}H_3)\overset{e}{C}Cl_2H$	1.5044	31.81	6.18	23.49	31.62	5.97	23.33	a 0.91 (s, broadened), b 1.00 (t), *J* = 5 Hz, c 1.40 (q), *J* = 6 Hz, further split, d 2.01 (m), e 5.74 (d), *J* = 4 Hz
 $(CH_3)_3Sn\overset{a}{C}H_2C(\overset{b}{C}H_3)_2\overset{c}{C}Cl_2H$	1.5017	31.69	5.78	22.87	31.62	5.97	23.33	a + b 1.15 (s, broadened), c 5.60 (s)
 $(CH_3)_3Sn\overset{a}{C}H_2\overset{b}{C}H_2C(\overset{c}{C}H_3)_2\overset{d}{C}Cl_2H$	1.4959	35.28	6.35		35.41	6.31		a 0.65 (m), b 1.68 (m), c 1.09 (s), d 5.72 (s)
		(Mixture with $Me_3SnCH_2CH(CCl_2H)CHMe_2$)						
 $(CH_3)_3Sn\overset{a}{C}H_2\overset{b}{C}H(\overset{e}{C}Cl_2H)\overset{c}{C}H(\overset{d}{C}H_3)_2$	1.4979	(Analysis of a mixture with $Me_3SnCH_2CH_2C(CH_3)_2(CCl_2H)$)						a 0.63 (m), b + c 1.9 (m), d 0.96 (d), *J* = 6.0 Hz, e 5.95 (d), *J* = 3.0 Hz
 $(CH_3)_3Sn(CH_2)_3C(\overset{a}{C}H_3)_2\overset{b}{C}Cl_2H$		(Analysis of a mixture with $Me_3SnCH_2CH(CCl_2H)CH_2CHMe_2$)						a 1.09 (s), b, 5.53 (s)
 $(CH_3)_3SnCH_2CH(\overset{b}{C}Cl_2H)CH_2CH(\overset{a}{C}H_3)_2$	1.4901	35.84	6.73	20.86	36.19	6.68	21.36	a 0.95 (d), *J* = 6.0 Hz, further splitting, *J* = 1.8 Hz, b 5.83 (d), *J* = 2.5 Hz
		(Mixture with $Me_3Sn(CH_2)_3C(CCl_2H)Me_2$)						
 $(CH_3)_3SnCH_2C(\overset{a}{C}H_3)(\overset{d}{C}Cl_2H)\overset{c}{C}H(\overset{b}{C}H_3)_2$	1.5054	36.60	6.71	21.58	36.19	6.68	21.36	a 1.10 (s), b 0.95 and 0.97 (d), *J* = 7.2 Hz, c 2.06 (m), d 5.80 (s)
	1.5291	36.34	6.21	21.88	36.41	6.11	21.50	a 5.73 (d), *J* = 2.2 Hz, ring protons, 1.1–2.7 (m)

Table IV (*Continued*)

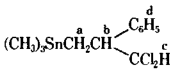
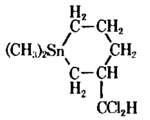
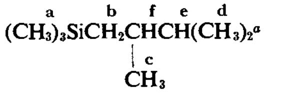
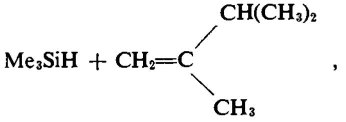
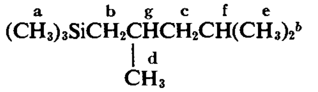
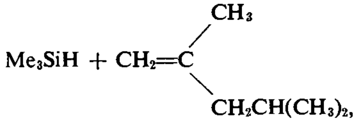
Compound	n^{25}D	Calcd, %			Found, %			Nmr spectrum (in δ units)
		C	H	Cl	C	H	Cl	
	1.5484	41.23	4.86	20.99	40.95	5.15	20.76	a 1.22–1.66 (ABq), Δ_{AB} = 26 Hz, J_{AB} = 10 Hz, b 3.4 (m), c 5.88 (d), J = 6 Hz, d 7.31 (s)
	1.5278 bp 112–114° (3.5 mm)	31.68	5.30		31.83	5.34		

Table V. Starting Materials. New Compounds

Compound	Procedure, % yield	Bp, °C (mm)	n^{25}D	Calcd, %			Found, %		
				C	H	Other	C	H	Other
$(C_6H_5)_2CH_3SiCH_2CH(CH_3)_2$	Grignard, 75%	127.5–128.5 (1.6)	1.5483	79.79	8.82	Si 11.47	80.24	8.72	11.04
$C_6H_5(CH_3)_2SiCH_2CH(CH_3)_2$	Grignard, 75%	84–86 (6)	1.4892	75.19	10.50	Si 14.50	74.90	10.48	14.61
p-$ClC_6H_4(CH_3)_2SiCH_2CH(CH_3)_2$	Grignard	Glpc isolation	1.4949	63.44	8.40	Cl 15.94	63.54	8.44	15.63
$(CH_3)_2ClSiCH_2CH(CH_3)_2$	Grignard, 26%	131–133	1.4187	47.78	10.09	Cl 23.36	47.81	10.03	23.52
$CH_3Cl_2SiCH_2CH(CH_3)_2$	Grignard, 21%	143–145	1.4295	35.05	7.05	Cl 41.41	35.09	7.07	41.43
$(CH_3)_3SiCH_2CH_2CH_2CH(CH_3)_2$	$Me_3SiH + CH_2{=}CHCH_2CH(CH_3)_2$, sealed tube, H_2PtCl_6 in i-PrOH catalyst, 80°, 8.6 hr, 76%	36.5–36.8 (10)	1.4104	68.04	13.76		68.26	14.00	
$(CH_3)_3SiCH_2CH_2C(CH_3)_3$	Grignard, 56%	143–145	1.4098	68.51	14.01	Si 17.60	68.26	14.00	17.74
 $\overset{a}{(CH_3)_3}Si\overset{b}{CH_2}\underset{\lvert\,c \atop CH_3}{\overset{f}{CH}}\overset{e}{CH}(\overset{d}{CH_3})_2{}^a$	 sealed tube, H_2PtCl_6 in i-PrOH catalyst, 80° 16 hr, 82%	40.7–41.0 (12)	1.4178	68.39	13.91		68.26	14.00	
 $\overset{a}{(CH_3)_3}Si\overset{b}{CH_2}\underset{\lvert\,d \atop CH_3}{\overset{g}{CH}}\overset{c}{CH_2}\overset{f}{CH}(\overset{e}{CH_3})_2{}^b$	 sealed tube, H_2PtCl_6 in i-PrOH catalyst, 115°, 19 hr, 39%	61.5–62 (16)	1.4168	70.08	14.04		69.67	14.03	
$(CH_3)_3SiCH_2CH_2C_6H_4CH_3$-$p$	Grignard, 79%	95–97 (6)	1.4859	74.92	10.34		74.92	10.48	
$(CH_3)_3SnCH_2CH_2CH(CH_3)_2$	Grignard, 86%	79–80 (32) 52.0–52.3 (12)	1.4545	41.13	8.58	Sn 50.65	40.90	8.58	50.52
$(CH_3)_3SnCH_2CH_2CH_2CH(CH_3)_2$	$Me_3SnH + CH_2{=}CHCH_2CH(CH_3)_2$, uv, 134 hr, 91%	76–77 (15)	1.4559	43.23	9.03		43.42	8.92	
$(CH_3)_3SnCH_2CH_2C_6H_5$	Grignard, 65%	95–96 (5)	1.5270	49.30	6.61		49.12	6.74	

[a] Nmr a 0.01 (s); b 0.36–0.58 (m); c 0.79 (d), J = 6.0 Hz, d 0.82 (d), J = 6.0 Hz; e + f 1.19–1.66 (m). [b] Nmr a 0.03 (s); b 0.5 (m), c 1.1 (d); d 0.88 (d), J = 6.4 Hz; e 0.86 (d), J = 6.0 Hz, f + g 2.65 (m).

of these compounds agreed well with those reported in the literature. Those compounds which are new are tabulated in Table V, together with their physical constants and analytical data. Standard methods which do not require detailed description served in their preparation.

Reactions of Tetraorganosilicon and Tetraorganotin Compounds with Phenyl(bromodichloromethyl)mercury. The following general procedure was used. A mixture of 4.40 g (10 mmol) of phenyl(bromodichloromethyl)mercury and 30 mmol of the appropriate tetraorganosilane or tetraorganotin in 15 ml of dry, freshly distilled benzene was charged into a 50-ml three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, a thermometer, and a magnetic stirring unit. The flask then was immersed into an oil bath preheated to 90° and the reaction temperature was maintained at *ca.* 80° (refluxing benzene). The mercurial usually dissolved within 1–2 min and phenylmercuric bromide began to precipitate within 5 min. The mixture was stirred at reflux for 3 hr, then was cooled and filtered from phenylmercuric bromide. Yields of the latter usually were above 90% and the material was of good purity (mp 276–284°) and could be recycled to starting material preparation. The clear filtrate then was trap-to-trap distilled at 0.02–0.1 mm into a receiver cooled to −78°, using an infrared lamp to assist in driving over the less volatile components. The resulting distillate, usually collected in two fractions (1, mostly solvent and starting silicon or tin compound; 2, mostly product with some starting silicon or tin compound) subsequently was analyzed by glpc and samples of pure products were isolated by fractional distillation or preparative glpc.

As has been noted in the Discussion, it was found that in the case of reactions which gave only low product yields when benzene was was used as solvent it was advantageous to carry out the reactions in the absence of any solvent. The yields then were substantially higher (*cf.* examples in Table I).

In quite a few of these reactions with tetraorganosilanes tetrachloroethylene and, in a very few cases, hexachlorocyclopropane, were present as by-products. These are the products of the thermal decomposition of phenyl(bromodichloromethyl)mercury in the absence of a CCl_2 trap[21] and usually are found as by-products when the substrate is only poorly reactive toward dichlorocarbene.

The yields of insertion products obtained in these reactions are listed in Table I. Physical properties, nmr spectra, and elemental analyses of the insertion products are given in Table IV. The infrared spectra of all products were determined but are not given here since they were unexceptional; it was the nmr spectra which were indicative of the structure of each product.

The products listed in Table IV all were liquids with pleasant camphoraceous odors. They were quite stable to moisture and air and could be stored at room temperature for many months without undergoing decomposition. The products from β-phenylethyltrimethyltin and 1,1-dimethyl-1-stannacyclohexane were the least stable, tending to deposit white solids on standing and often developing characteristic R_3Sn-like odors.

3-Dichloromethyl-1,1-dimethyl-1-silacyclohexane. Proof of Structure. (a) Reduction with Sodium in Liquid Ammonia. A solution of sodium (550 mg, 24 mg-atom) in 10 ml of liquid ammonia was prepared under nitrogen in a 50-ml three-necked flask at −78°. A solution of 480 mg (2.2 mmol) of 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane in 1.5 ml of dry hexane was added during 5 min. The reaction mixture was stirred for 30 min and then was warmed slowly to room temperature to remove the ammonia. Addition of solid ammonium chloride destroyed the blue color and left a pasty residue. This was treated with 5 ml of hexane and enough water to give a two-phase system. The organic layer was washed with water, 2% H_2SO_4 and saturated sodium bicarbonate solution, dried, and concentrated at reduced pressure to *ca.* 1 ml of clear, colorless liquid. Glpc analysis (SE-30 at 120°) showed the presence of hexane and four other components, one of which constituted over 90% of the total. Samples of the major product were collected by glpc and identified as 1,1,3-trimethyl-1-silacyclohexane, $n^{25}D$ 1.4340, by comparison of its properties with those of an authentic sample (see below). The infrared spectrum showed the following absorptions (in CCl_4): 2955 s, 2910 s, 2860 s, 1455 m, 1435 m, 1405 w, 1370 w, 1330 w, 1250 s, 1202 m, 1170 m, 1090 w, 1050 w, 1032 w, 1008 m, 935 m, 898 m, 872 m, 850–830 s, 720 w, 703 w, 673 s and 592 w cm^{-1}. The mass spectrum showed a molecular ion at *m/e* 142 (4% of base peak) and other strong peaks at *m/e* 127 (86%), 99 (100%), 85 (66%), 73 (57%), 59 (71%), 43 (45%), and 28 (20%). The base peak at *m/e* 99 ($C_5H_{11}Si^+$) must be either $[Me_2SiC(CH_3){=}CH_2]^+$ or $[Me_2SiCH{=}CHCH_3]^+$. Such a fragment could not be easily formed from the alternative structure 1,1,4-trimethyl-1-silacyclohexane.

Anal. Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.75. Found: C, 67.33; H, 12.69.

(b) Reduction with Tri-*n*-butyltin Hydride. Into a 10-ml flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring unit was placed 1.06 g (5.0 mmol) of 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane, bp 60.5–61.0° (0.6 mm), $n^{25}D$ 1.4884, and 2.91 g (10.0 mmol) of tri-*n*-butyltin hydride. The mixture was stirred under nitrogen at 130° for 6.5 hr. The reaction mixture then was distilled using a 4-in. Vigreux column. The following fractions were collected (oil bath temperatures are given): (a) 40° (0.5 mm), 0.362 g; (b) 60° (0.5 mm), 0.267 g; (c) 70° (0.5 mm), 0.108 g; (d) 85° (0.5 mm), 0.050 g. Fractions c and d were practically pure (by glpc) 3-chloromethyl-1,1-dimethyl-1-silacyclohexane. Fraction a contained 1,1,3-trimethyl-1-silacyclohexane and the chloromethyl compound in 80:20 ratio, fraction b in 6:94 ratio. On this basis, the yields of the 3-methyl and 3-chloromethyl compounds were 43 and 54%, respectively.

Pure 3-chloromethyl-1,1-dimethyl-1-silacyclohexane was characterized: bp 33.5–34.0° (0.5 mm); $n^{25}D$ 1.4714; nmr (in CCl_4) 0.04 and 0.07 (3 H each, Me_2Si, s), 3.30 (2 H, CH_2Cl, d, J = 6.0 Hz), 0.25–2.20 (ring protons).

Anal. Calcd for $C_8H_{17}ClSi$: C, 54.36; H, 9.69; Cl, 20.06. Found: C, 54.58; H, 9.67; Cl, 19.40.

A sample of 1,1,3-trimethyl-1-silacyclohexane was collected by glpc: nmr (in CCl_4) δ 0.02 and 0.06 (3 H each, Me_2Si, s), 0.97 (3 H, CH_3C, d, J = 5.6 Hz), 0.2–2.2 ppm (ring protons); infrared spectrum as above.

(c) Preparation of Authentic 1,1,3-Trimethyl-1-silacyclohexane by the Grignard Procedure. The Grignard reagent prepared from 9.76 g (40 mmol) of 1,5-dibromo-2-methylpentane[22] and 0.96 g (40 mg-atom) of magnesium in 10 ml of diethyl ether was added to 3.40 g (20 mmol) of silicon tetrachloride in 10 ml of ether. The mixture was stirred for 2 hr, kept at room temperature for another 64 hr, and then was treated with 90 mmol of methylmagnesium bromide in ether. Hydrolysis with saturated ammonium chloride was followed by concentration of the dried organic layer to 1 g of yellow oil. This was shown to contain 1,1,3-trimethyl-1-silacyclohexane as the major (80%) component. Samples were isolated by glpc, $n^{25}D$ 1.4345. The infrared and mass spectra were identical with those of the product obtained in (a).

Standard Procedure for Competition Reactions. A mixture of *ca.* 10 mmol each of the two substrates was weighed into a small bottle or vial on a Mettler balance. This mixture, 1.32 g (3 mmol) of $PhHgCCl_2Br$ and 4 ml of dry benzene, was stirred and heated at 80 ± 1° for 3–4 hr. After filtration from the phenylmercuric bromide which had been formed, an internal standard was added to the filtrate. Direct analysis of the filtrate by glpc followed. The raw area data, determined by planimeter tracings, was corrected using previously determined response factors for the two insertion products in question and yields of these products were calculated. The relative rate constant then was calculated by the method of Doering and Henderson.[12] Conclusive identification of the products was ensured by comparison of their glpc retention times and ir spectra with those of authentic samples. Duplicate runs were carried out and agreement was good. In some cases no benzene solvent was used.

Reaction of Phenyl(bromodichloromethyl)mercury with 2-Deuterioisobutyltrimethylsilane. (a) Preparation of $(CH_3)_2CDCH_2Br$. Anhydrous DBr was prepared by reaction of deuterium oxide (>99%) and phosphorus tribromide. The crude product was purified by trap-to-trap distillation under vacuum.

Gaseous deuterium bromide (19.3 g, 0.236 mol) and isobutylene (13.5 g, 0.236 mol) were expanded into an evacuated 12.5-l. bulb fitted with an ultraviolet light insert. Uv irradiation of the mixture resulted in a rapid photochemical reaction which was essentially complete in 10–15 min. The progress of the reaction was followed by the decrease in pressure on a mercury manometer. The liquid product was washed from the reaction bulb and fractionated to give the desired product: 25.4 g (82%); bp 90–91°; $n^{20}D$ 1.4341 (lit.[23] for the undeuterated isobutyl bromide, bp 90.5–91°, $n^{20}D$

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1.4348). Glpc (General Electric Co. XF 1150) showed the presence of a single component with the same retention time as Me_2CHCH_2Br: nmr (in CCl_4) δ 1.08 (s, 6 H, Me_2C), 3.23 ppm (s, 2 H, CH_2Br), as expected for Me_2CDCH_2Br; ir (neat) 2972 s, 2940 s, 2879 m, 2154 w (ν_{C-D}), 1470 s, 1439 m, 1390 m, 1374 m, 1323 w, 1295 w, 1256 s, 1244 s, 1238 sh, 1208 m, 1157 w, 1133 w, 1108 w, 974 w, 934 m, 970 m, 809 m, 798 w, and 651 s cm^{-1}.

(b) Preparation of $Me_3SiCH_2CDMe_2$. The Grignard reagent was prepared from 15.6 g (0.113 mol) of Me_2CDCH_2Br and 5.40 g (0.225 g-atom) of magnesium turnings in diethyl ether. Trimethylchlorosilane (11.9 g, 0.225 mol) in ether was added and the reaction mixture was stirred and heated at reflux for 72 hr. Hydrolysis with saturated ammonium chloride solution was followed by distillation of the dried organic layer to give 10.2 g (71%) of the product, bp 106–108°, $n^{25}D$ 1.3994. The bp of $Me_2CHCH_2SiMe_3$ prepared in this study was 106.5–108° and the $n^{25}D$ was 1.3988. The glpc retention time of the product on an XF-1150 column was identical with that of the undeuterated material; nmr (in CCl_4) -0.07 (s, 9 H, Me_3Si), 0.48 (s with further minor splitting, 2 H, CH_2Si), 0.88 (s, with further minor splitting, 6 H, Me_2C). The more complex patterns presumably are a consequence of preferred conformations. The infrared spectrum showed C–D bands at 2161 and 2135 cm^{-1}.

A deuterium analysis by the falling drop method (J. Nemeth) showed 5.40 atom % excess deuterium, equivalent to 97% replacement of one hydrogen by deuterium. Assuming that isotopic rearrangement has not occurred during the Grignard reaction, it appears reasonable to conclude that the deuterium is located almost exclusively in the β position, *i.e.*, the product is $Me_3SiCH_2CDMe_2$.

(c) The Insertion Reaction. The reaction with $PhHgCCl_2Br$ was carried out in the usual manner with 30 mmol of the silane and 10 mmol of the mercurial. The product was obtained in 36% yield, $n^{25}D$ 1.4631. The glpc retention time was identical with that of $Me_3SiCH_2C(CCl_2H)Me_2$.

Deuterium analysis by the falling drop method showed 5.35 atom % excess deuterium in the product, equivalent to 96% replacement of one hydrogen by deuterium: nmr (in CCl_4) δ 0.03 (s, 9 H, Me_3Si), 0.88 (s, 2 H, $SiCH_2$), 1.10 ppm (s, 6 H, Me_2C). A high amplitude scan revealed a very weak signal at 5.45 ppm, the position of the CCl_2H proton in the undeuterated product; ir (neat) 2960 s (broad), 2905 s, 2886 sh, 2809 sh, 2220 w (ν_{C-D}), 1940 w, 1855 w, 1555 w, 1478 m, 1469 m, 1425 m, 1391 m, 1375 m, 1296 m, 1258 s, 1228 m, 1205 w, 1155 w, 1096 w, 1085 w, 1015 m, 980 m, 967 m, 919 m, 849 s, 785 s, 769 s, 743 m, 709 m, and 697 m cm^{-1}.

In a similar experiment the unconverted starting silane was recovered and analyzed for deuterium. It was found to contain 5.47 atom % excess deuterium, equivalent to 99% replacement of one hydrogen by deuterium.

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Radiation-Induced Cationic Chain Formation of Ether from Isopropyl Alcohol Vapor[1]

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Abstract: During the γ radiolysis of isopropyl alcohol vapor at temperatures above 250°, diisopropyl ether is produced by a cationic chain mechanism. The mechanism is zero order with respect to alcohol pressure and has an activation energy of 40 ± 1 kcal/mol independent of pressure over the range studied (100–2000 Torr). The ether yield decreases with increasing dose and is not dependent on the surface:volume ratio of the reaction vessel. At 350°, 100 Torr and 2.9×10^{17} eV/g, G(ether) = 1000; the G value is inversely proportional to the alcohol pressure. The addition of about 10 mol % of the following additives decreased the ether yield by amounts in the following increasing order: water < propylene < sulfur hexafluoride < acetone < ammonia. The proton affinities of the additives increase in the same order. The chain propagation reactions appear to be $(ProH)_mH^+ \rightarrow Pr_2O \cdot H^+ \cdot (OH_2)$ $(Pr_2OH_{m-2}$ (4_m), $Pr_2O \cdot H^+ \cdot (OH_2)(PrOH)_{m-2} + 2PrOH \rightarrow Pr_2O + H_2O + (PrOH)_mH^+$ (5_m). The presence of a foreign (nonalcohol) molecule in the "clustered" ion apparently inhibits reaction 4_m. The addition of >10% propylene to the alcohol sensitizes ether formation, presumably by way of the exothermic reaction $C_3H_6^+ + PrOH \rightarrow C_3H_5 + PrOH_2^+$ (eq 9).

A cationic chain reaction that forms diethyl ether from ethanol during vapor phase radiolysis at elevated temperatures has recently been discovered.[2] We have extended the study of this type of reaction by investigating the formation of diisopropyl ether during the radiolysis of isopropyl alcohol vapor at temperatures between 125 and 406°.

Experimental Section

Materials. "Chromatoquality" isopropyl alcohol from Matheson Coleman and Bell was purified by adding 3 g of dinitrophenylhydrazine and 1 ml of concentrated sulfuric acid to 2 l. of the alcohol and refluxing the solution in a stream of dry nitrogen for 3 hr. The isopropyl alcohol was then fractionally distilled and the middle fraction was collected. Although this treatment decreased the small amounts of aldehydes and ketones in the alcohol, it formed a substantial amount of ether. As the study of the radiation-induced formation of ether was the objective of this investigation, the ether had to be removed from the alcohol before irradiation. This was done by fractional distillation of the previously treated alcohol in a spinning band column, with a reflux ratio of 20:1. The middle fraction of the distillate contained $<2 \times 10^{-6}$ M ether. This isopropyl alcohol was then degassed and stored under vacuum in a Pyrex reservoir.

Ammonia (Canadian Industries Ltd.), propylene (Phillips Research Grade), sulfur hexafluoride (Matheson Co.) and acetone (Shawinigan, Reagent) were degassed and stored under vacuum in Pyrex vessels.

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(1) This work received financial assistance from the National Research Council of Canada.

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