DIVALENT CARBON INSERTIONS INTO GROUP IV HYDRIDES AND HALIDES

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ABSTRACT

A summary, dealing in large part with the author's own work, is presented of reactions in which a methylene bridge (CH_2, CHX, CX_2, etc.) is introduced into a Group IV element-to-other element covalent bond

$$(\gt M{-}Y \rightarrow \gt M{-}\overset{|}{\underset{|}{C}}{-}Y).$$

In these reactions M is silicon, germanium, tin or lead; Y can be hydrogen, halogen, carbon, mercury and, in the case of tin, another tin. The reagents which effect such methylenations include diazoalkanes, carbenes and 'carbenoid' organometallics. Emphasis is placed on carbenes generated via phenyl(trihalomethyl)mercury compounds and on diazomethane. The scope and mechanism of these reactions are discussed.

INTRODUCTION

One general procedure for the formation of Group IV element-to-carbon bonds involves reactions in which a carbon atom with two substituents is inserted into a single bond connecting the Group IV atom to an atom of some other element. Such a reaction is indicated schematically in equation 1* and it is *not* meant to have any mechanistic implications. A number of reagents exists which can effect the $R_3MY \rightarrow R_3MCXYZ$ transformation,

$$R_3M{-}Y + X{-}C{-}Z \rightarrow R_3M{-}\overset{X}{\underset{Z}{C}}{-}Y \qquad (1)$$

and it is the purpose of this paper to discuss such reactions. At the outset it should be stressed that a variety of mechanisms is involved in these reactions, and only in a few cases are actual divalent carbon intermediates (i.e. carbenes) involved. To avoid any confusion with actual carbene processes,

* In this paper M will be used to denote a Group IV atom (Si, Ge, Sn, Pb) including or without attached substituents.

we will call the general reaction shown in equation 1 a 'methylenation' reaction, a term which implies nothing concerning mechanism but merely states that the product obtained has in some manner acquired a methylene bridge between the central metal atom and one of its original substituents.

Among the M—Y single bonds which have been methylenated are the following:

Silicon	*Germanium*	*Tin*	*Lead*
Si—H	Ge—H	Sn—H	Pb—H
Si—X	Ge—X	Sn—X	Pb—X
Si—C	Ge—C	Sn—Sn	
Si—Hg	Ge—Hg		

This list undoubtedly will grow within the next few years. In this paper we shall restrict ourselves to such insertions into metal–hydrogen and metal–halogen bonds and discuss such reactions in terms of the various applicable reagents.

METHYLENATIONS WITH DIAZOMETHANE AND SUBSTITUTED DIAZOMETHANES

Diazomethane, whose description in the valence bond picture requires a number of resonance structures (Ia–Id), methylenates both M–hydrogen

$$H_2\overset{-}{C}-\overset{+}{N}=N: \qquad H_2\overset{-}{C}-N=\overset{+}{N}: \qquad H_2C=\overset{+}{N}=\overset{-}{N}: \qquad H_2\overset{+}{C}-N=\overset{-}{N}:$$

Ia Ib Ic Id

and M–halogen bonds[1]:

$$M-X + CH_2N_2 \rightarrow M-CH_2-X + N_2 \quad (2)$$

$$M-H + CH_2N_2 \rightarrow M-CH_3 + N_2 \quad (3)$$

With organosilicon, organogermanium and organotin hydrides, diazomethane itself is reported to react only in the presence of ultra-violet (u.v.) radiation or copper powder[2–5]. This suggests that a carbene (with u.v.) or a carbenoid (with copper)* process is involved, rather than a reaction in which diazomethane reacts directly with the hydride. Some of the less stable diazoalkanes react with organotin hydrides in the absence of catalyst[2] and organolead hydrides appear to react even with diazomethane in ether without needing a catalyst[6]. However, the organolead hydrides in question underwent partial decomposition during these reactions to give the R_4Pb compound, hydrogen and metallic lead, and the latter, formed in a finely divided state, very likely catalysed the decomposition of diazomethane.

* Such a 'carbenoid' process could be pictured as involving interaction of diazomethane with Cu(I) or Cu(II) compounds on the copper surface to give a CH_2—Cu(I or II) complex which then transfers CH_2 to the M—H bond. The important distinction is that free methylene itself is not involved in this process.

Table 1. Methylenations of M^{IV}—H bonds with diazoalkanes

Hydride	*Diazoalkane*	*Product*	*% Yield*	*Ref.*
	Ultra-violet-initiated reactions			
$PhSiH_3$	CH_2N_2 (xs in Et_2O)	$PhMeSiH_2$ $PhMe_2SiH$	70 5	4
Ph_2SiH_2	CH_2N_2 (xs in Et_2O)	$PhMe_2SiH$	50	4
Ph_3SiH	CH_2N_2 (xs in Et_2O)	Ph_3SiMe	<0·1	4
Et_3SiH	CH_2N_2 (xs in Et_2O)	Et_3SiMe	1	4
Me_3SiH	CF_3CHN_2	$CF_3CH_2SiMe_3$ $CF_3CH_2CH_2SiMe_2H$	34 41	4a
Et_3GeH	CH_2N_2 (xs in Et_2O)	Et_3GeMe	9	4
n-Pr_3GeH	CH_2N_2 (xs in Et_2O)	n-Pr_3GeMe	5	4
n-Bu_3GeH	CH_2N_2 (xs in Et_2O)	n-Bu_3GeMe	2	4
Ph_3GeH	CH_2N_2 (xs in Et_2O)	No reaction		4
Ph_2GeH_2	CH_2N_2 (xs in Et_2O)	Ph_2MeGeH Ph_2Me_2Ge	43 5	5
$PhGeH_3$	CH_2N_2 (xs in Et_2O)	$PhMeGeH_2$ $PhMe_2GeH$	59 14	5
Et_3SnH	CH_2N_2 (xs in Et_2O)	Et_3SnMe	75	4
$PhSiH_3$	CH_3CHN_2 (xs in Et_2O)	$PhEtSiH_2$	5	4
$PhSiH_3$	N_2CHCO_2Et (xs in Et_2O)	$PhH_2SiCH_2CO_2Et$	20	4
Ph_2SiH_2	N_2CHCO_2Et (xs in Et_2O)	$Ph_2HSiCH_2CO_2Et$	20	4
	Copper-catalysed reactions			
$PhSiH_3$	CH_2N_2 (xs in Et_2O)	$PhMeSiH_2$	3	4
$PhSiH_3$	CH_3CHN_2 (xs in Et_2O)	$PhEtSiH_2$	5	4
Ph_2GeH_2	CH_2N_2 (xs in Et_2O)	Ph_2MeGeH	25	5
Et_3GeH	$N_2CHCOMe$	Et_3GeCH_2COMe		3
Et_3GeH	$N_2CHCOPh$	Et_3GeCH_2COPh		3
n-Bu_3GeH	N_2CHCO_2Et	n-$Bu_3GeCH_2CO_2Et$		3
Me_3SnH	CH_2N_2 (xs in Et_2O)	Me_4Sn	30	4
n-Pr_3SnH	CH_2N_2 (xs in Et_2O)	n-Pr_3SnMe	100	2
n-Bu_3SnH	CH_2N_2 (xs in Et_2O)	n-Bu_3SnMe	100	2
Et_2SnH_2	CH_2N_2 (xs in Et_2O)	Et_2Me_2Sn		2
n-Pr_3SnH	N_2CHCO_2Et (in benzene*)	n-$Pr_3SnCH_2CO_2Et$		2
n-Bu_3SnH	N_2CHCO_2Et (in benzene*)	n-$Bu_3SnCH_2CO_2Et$		2
n-Bu_3SnH	$N_2CHCOMe$ (in Et_2O; no catalyst)*	n-Bu_3SnCH_2COMe		2
n-Pr_3SnH	$N_2CHCOPh$ (in Et_2O–benzene; no catalyst)*	n-Pr_3SnCH_2COPh		2
n-Bu_3SnH	$N_2CHCOPh$ (in Et_2O–benzene; no catalyst)*	n-Bu_3SnCH_2COPh		2
n-Bu_3SnH	N_2CHCN (in toluene; no catalyst)*	n-Bu_3SnCH_2CN		2
Et_3PbH	CH_2N_2 (in Et_2O at $-80°$)	Et_3PbMe	31	6
Et_2PbH_2	CH_2N_2 (in Et_2O at $-80°$)	Et_2PbMe_2	2	6
Me_3PbH	CH_3CHN_2 (in Et_2O at $-80°$)	Me_3PbEt	11	6
Me_2PbH_2	CH_3CHN_2 (In Et_2O at $-80°$)	Me_2PbEt_2	5	6

* Reaction mixture was heated.

The results of these studies are summarized in *Table 1*. Noteworthy in these reactions is the lack of reactivity of R_3SiH compounds toward the reagent generated by photolysis of diazomethane (presumably CH_2) and the generally poor reactivity of the Si—H bond in copper-catalysed diazomethane reactions. Still, the reactivity of the Si—H bond toward CH_2 was estimated[4] to be at least 100 times greater than that of the C—H bonds in the diethyl ether solvent used.

In the gas phase, irradiation at 3660 Å of a mixture of SiH_4 and diazomethane gave methylsilane[7], CH_3SiH_3. At high (*ca.* 200 mm) pressures, methylsilane represented about 80 per cent of the observed products and thus under these conditions the insertion of CH_2 into the Si—H bond was by far the most important process occurring. Further gas phase irradiation studies showed that singlet CH_2 inserted into the Si—H bonds of CH_3SiH_3 ($\rightarrow Me_2SiH_2$) 8·9 times faster than into the C—H bonds[8] ($\rightarrow CH_3CH_2SiH_3$). The reaction of trifluoromethylcarbene (via CF_3CHN_2 photolysis) with trimethylsilane in the liquid phase gave both Si--H and C—H insertion products (*Table 1*). The ratio k(Si—H insertion)/k(C—H insertion) was 7·4. Thus the Si—H bond insertion process is one of the fastest methylene reactions known and the Si—H bond is a particularly effective divalent carbon trap.

While we can assume with confidence that methylenations of M—H bonds by diazomethane are carbene or carbenoid processes, the methylenation of M–halogen bonds with diazoalkanes is a completely different type of reaction. This subject has been reviewed and all known examples of reaction 2 up until 1955 have been listed[1]. There has been moderate activity in this area in the intervening years, and this reaction has been used repeatedly to prepare (monohalomethyl)-germanium and -tin compounds for studies of the α-organofunctional chemistry of these elements[9–19]. Typical of such methylenations of Group IV halides are the examples shown below:

$$HSiCl_3 + CH_2N_2 \xrightarrow[-78^\circ]{Et_2O} ClCH_2SiHCl_2 + N_2 \quad (73\%) \tag{4}$$

$$GeCl_4 + CH_2N_2 \xrightarrow[-60^\circ]{Et_2O} ClCH_2GeCl_3 + N_2 \quad (94\%) \tag{5}$$

$$Me_2SnBr_2 + CH_2N_2 \xrightarrow[-5^\circ]{Et_2O} Me_2(CH_2Br)SnBr + N_2 \quad (73\%) \tag{6}$$

$$Et_3PbCl + CH_2N_2 \xrightarrow[10\text{–}15^\circ]{Et_2O,\ Cu\ bronze} Et_3PbCH_2Cl + N_2 \tag{7}$$

In general, organic substitution in the Group IV halides tends to decrease the reactivity of the M—X bond toward diazomethane. Thus it was found that silicon tetrachloride reacts rapidly with diazomethane in ether even at -50° to give $ClCH_2SiCl_3$ in high yield[20, 21]. Further methylenation to $(ClCH_2)_2SiCl_2$ and $(ClCH_2)_3SiCl$ was found to be increasingly difficult and the tetra-insertion product, $(ClCH_2)_4Si$, could not be prepared by this method. Similarly, trialkyl- and triphenyl-chlorosilanes were inert toward diazomethane. A similar reactivity series was found for organogermanium[22] and organotin[23, 24] halides. Thus methylenation of dimethyltin dichloride in ether at $-5°$ with an excess of diazomethane gave (chloromethyl)dimethyltin chloride in high yield, but the reaction did not proceed past this stage. Tri-*n*-butyltin and triphenyltin chlorides did not react with diazomethane. On the other hand, triethyllead chloride did react to give (chloromethyl)triethyllead in high yield.

In these studies the following reactivity sequences could be discerned:

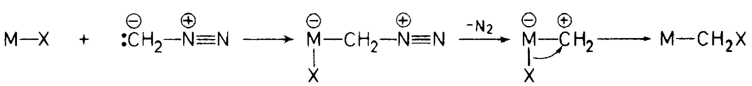
(i) Pb—X > Sn—X > Ge—X > Si—X

(ii) M—I > M—Br > M—Cl (M—F does not react)

(iii) $SiCl_4$ > $ClCH_2SiCl_3$ > CH_3SiCl_3 ~ $(ClCH_2)_2SiCl_2$ > $(CH_3)_2SiCl_2$ (R_3SiCl do not react)

(iv) effect of solvent on rate: diethyl ether > pentane.

All three reactivity sequences and the solvent dependence of the reaction rate are most readily rationalized in terms of a process in which the (organo) metallic halide is undergoing *nucleophilic* attack by diazomethane. Indeed, such a process was proposed by Hellerman and Newman[25], the discoverers of this very generally applicable methylenation of metallic and organometallic halides, and supported by most other workers in this field[1, 24, 26].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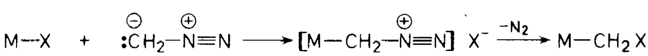
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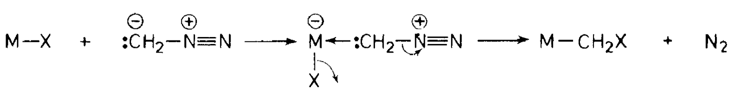
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Either a stepwise process (equation 8 or 9) or a completely concerted process (equation 10) could be envisioned. Yakubovich and Ginsburg[20], on the other hand, in their discussion of the methylenations of silicon halides suggested a free methylene mechanism (equations 11 and 12). A piece of

$$CH_2N_2 \xrightarrow{-N_2} CH_2 \tag{11}$$

$$M{-}X + CH_2 \rightarrow M{-}CH_2X \tag{12}$$

evidence cited in favour of such a process was the finding that the reaction of diazomethane with methyltrichlorosilane, which is quite slow at $-30°$, is accelerated by addition of a catalytic quantity of copper bronze or copper (II) sulphate, agents which supposedly served to increase the rate of diazomethane decomposition. Also, it was noted in the silicon tetrachloride/ diazomethane reaction that above $-15°$ the formation of polymethylene became an important side reaction and that this reaction occurred at room temperature to the total exclusion of Si—Cl methylenation. The view that such reactions, and more specifically, the mercuric halide/diazomethane reaction, proceed via intermediate CH_2 was reiterated recently by other Russian workers[27].

One piece of information which serves as evidence against the intervention of free CH_2 in at least the Si—X-diazomethane reactions is the observation that when $HSiCl_3$ was the reactant, absolutely no Si—H insertion was detected; $ClCH_2SiHCl_2$ was the only product formed[22]. The ready insertion of free CH_2 into the Si—H bond has already been mentioned, and as will be discussed below, dichlorocarbene, while it is very reactive with respect to insertion into the Si—H linkage, is inert toward the Si—Cl bond.

If a nucleophilic displacement mechanism (equations 8, 9 or 10) was operative, one would expect that in a series of substituted $ZC_6H_4MX_3$ compounds, the rate of the methylenation reaction would be strongly accelerated (with respect to Z = H) when Z is an electron-attracting substituent and retarded if Z is an electron-donating substituent. On the other hand, if free CH_2 were involved as an intermediate, one might expect to find these substituent effects reversed, since most carbenes in general (including CH_2 in the singlet state) have the characteristics of electrophilic reagents[28]. Accordingly, in order to obtain more information concerning the nature of the reaction occurring between diazomethane and Group IV halides and thus about the nature of the methylenation reagent itself, we recently determined[29], by means of competition reactions, the relative rates of the reactions of a number of *para*-substituted aryltrichlorogermanes (p-$ZC_6H_4GeCl_3$; Z = H, Cl, F, Me, MeO) with diazomethane in diethyl ether at −78°; see equation 13. *Table 2* lists the relative rate constants

$$p\text{-}ZC_6H_4GeCl_3 + CH_2N_2 \xrightarrow[\text{(no catalyst)}]{Et_2O;\ -78°} p\text{-}ZC_6H_4(CH_2Cl)GeCl_2 + N_2 \quad (13)$$

Table 2. Relative rate constants for methylenation of substituted aryltrichlorogermanes, p-$ZC_6H_4GeCl_3$

Z	Cl	F	H	CH_3	CH_3O
$k_{rel.}$ (±5%)	9·76	5·37	2·24	1·29	1·00
σ^0	0·27	0·17	0	−0·15	−0·16

which were determined. It is immediately clear that the electron-withdrawing substituents enhance the rate of the methylenation reaction, while those which supply electron density have a rate-retarding effect. A satisfactory linear correlation of $k_{rel.}$ with Taft's σ° substituent constants was found; this is shown in *Figure 1*. The trend shown in *Figure 1* is consistent with an S_N2 process with a transition state in which a higher electron density is localized on the reaction centre than in the ground state, or in terms of a concerted process, a transition state in which bond-making is more developed than bond-breaking.

The findings summarized in *Table 2* and *Figure 1* can be rationalized very nicely in terms of nucleophilic attack of diazomethane (as a carbon nucleophile) at the germanium atom, but they cannot be readily reconciled with the absence of nucleophilic character in free CH_2 generated by pyrolysis, photolysis or the catalysed decomposition of diazomethane.

Other observations made during our study spoke against a free CH_2 mechanism for CH_2 insertion into the Ge—Cl bond. *If* such a process did indeed occur, in a two-step fashion (equations 11 and 12), then from a kinetic point of view, there would be three possibilities: reaction 11 is fast, reaction 12 is slow; or reaction 11 is slow, reaction 12 is fast; or perhaps both reactions occur at comparable rates. For all three possibilities, under

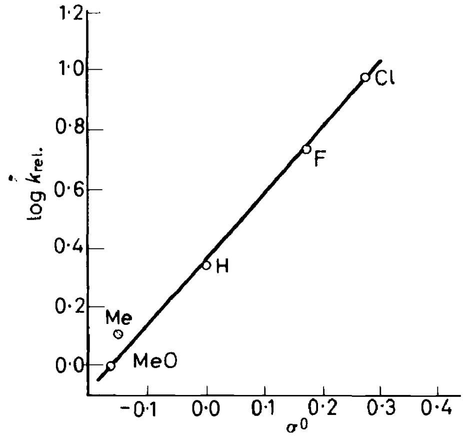
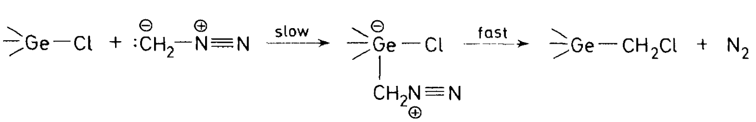


Figure 1. Relative reactivities of *p*-$ZC_6H_4GeCl_3$ toward diazomethane (in ether at $-78°$) versus σ^0.

comparable conditions of temperature and reagent concentrations, the rate of decomposition of diazomethane should be independent of the aryltrichlorogermane used. This, however, is not so. When 0·1 mmole of diazomethane in ether was added to 0·35 mmole of *p*-chlorophenyltrichlorogermane at $-78°$, a reaction time of about 30 min was required to discharge the yellow colour of the diazomethane, while a reaction time of about 240 min was necessary in an identical experiment carried out with *p*-$CH_3OC_6H_4GeCl_3$. In contradiction to the first and third possibilities, an ethereal diazomethane solution of comparable concentration decomposes very slowly in the absence of added aryltrichlorogermane under these reaction conditions. Clearly, the rate of diazomethane consumption depends on the aryltrichlorogermane used, and we were thus led to the conclusion that a direct reaction between the diazomethane and aryltrichlorogermane is involved in the methylenation of the Ge—Cl bond (equation 14 or 15).



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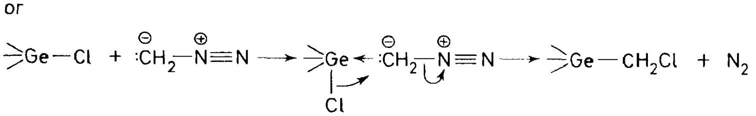
or



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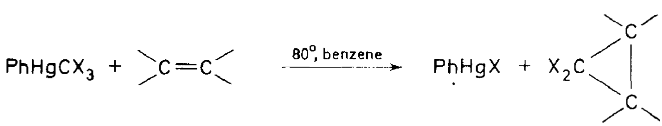
In such methylenations of silicon and germanium halides with diazomethane, it had been customary in preparative reactions to add copper powder or copper bronze to the reaction mixture, since it had been claimed that these substances promoted the desired reactions, especially those in which more than one methylene group was to be introduced[20, 24]. We investigated briefly the copper catalysis of the aryltrichlorogermane/diazomethane reaction. In experiments in which 0·36 mmole of p-$CH_3OC_6H_4GeCl_3$ and 0·1 mmole of diazomethane in 3·5 ml of ether at $-78°$ were allowed to react, once in the absence of a catalyst, once in the presence of 0·03 g of copper powder, the times required for discharge of the diazomethane colour were 240 and 210 min, respectively. The effect of copper powder, if real, is not very significant. If a process such as that shown in equation 14 obtains, it is difficult to understand a catalytic effect of copper powder. In a concerted process (equation 15), however, copper catalysis might be understood in terms of providing a surface for adsorption of the incipient nitrogen molecule. The values of $k(PhGeCl_3)/(p\text{-}MeOC_6H_4GeCl_3)$ in the $ArGeCl_3$/diazomethane reaction in the absence of a catalyst and in the presence of catalytic amounts of copper powder were 2·26 and 2·13, respectively, i.e. identical within experimental error. This suggests to us that the reaction mechanism does not change in the presence of added copper powder.

METHYLENATIONS WITH HALOMETHYL–MERCURY COMPOUNDS

During the past seven years, a study of the chemistry of halomethylmercury compounds has been very actively pursued at the Massachusetts Institute of Technology. The observation that the phenyl(trihalomethyl)mercury compounds $PhHgCCl_3$ and $PhHgCBr_3$ would transfer CCl_2 and CBr_2, respectively, to the C═C bond of olefins at 80° to give the respective dihalocyclopropanes in very high yield was communicated[30] by us in 1962.



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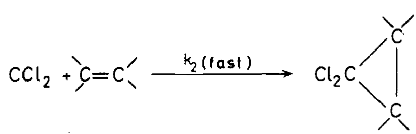
Subsequent work showed phenyl(bromodichloromethyl)mercury to be far superior as a CCl_2 precursor[31] and a broad study of $PhHgCX_3$/olefin reactions was undertaken[31]. Later studies established that the $PhHgCX_3$/olefin reaction proceeded via a free carbene mechanism[32–34]; equations 17 and 18.

$$PhHgCCl_2Br \underset{k_1\ (fast)}{\overset{k_1\ (slow)}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (17)$$



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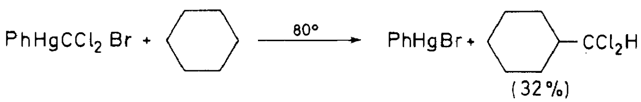
The discovery that dichlorocarbene generated via $PhHgCCl_2Br$ will insert into C—H bonds[35] (e.g. equations 19 and 20) prompted us to investigate the possibility of dihalocarbene insertion into Si—H, Ge—H and Sn—H

$$PhHgCCl_2Br + PhCHMe_2 \xrightarrow{80°} PhHgBr + \underset{(58\%)}{PhCMe_2CCl_2H} \qquad (19)$$



(20)

bonds. It was found that organosilicon and organogermanium hydrides react rapidly with mercurials of type $PhHgCCl_nBr_{3-n}$ (n = 0 to 2) to give dihalomethyl derivatives of these elements, generally in high yield (equation 21)[35,36]. The results of these studies are listed in *Table 3*.

$$PhHgCYZBr + \text{—M—H} \xrightarrow{80°,\ \text{benzene}} PhHgBr + \text{—M—CYZH} \qquad (21)$$

(Z = Cl and/or Br)

As new mercurial reagents were developed in these Laboratories, their reactions with silicon and germanium hydrides were studied. *Table 4* lists the results of these experiments.

Table 3. (Dihalomethyl)-silicon and -germanium compounds: yields

Hydride	*Mercurial*	*Product*	*Yield* (%)	*Ref.*
$(C_6H_5)_3SiH$	$PhHgCCl_2Br$	$(C_6H_5)_3SiCCl_2H$	90	36
$(C_2H_5)_3SiH$	$PhHgCCl_2Br$	$(C_2H_5)_3SiCCl_2H$	79	36
$(C_6H_5)_2SiH_2$	$PhHgCCl_2Br$	$(C_6H_5)_2HSiCCl_2H$	77	36
$(C_6H_5)_2SiH_2$	$PhHgCCl_2Br$	$(C_6H_5)_2Si(CCl_2H)_2$	72	36
$(C_6H_5)_2(CH_2{=}CH)SiH$	$PhHgCCl_2Br$	$(C_6H_5)_2(CH_2{=}CH)SiCCl_2H$	82	36
$C_6H_5Me_2SiH$	$PhHgCCl_2Br$	$C_6H_5Me_2SiCCl_2H$	High*	37
m-$CF_3C_6H_4Me_2SiH$	$PhHgCCl_2Br$	m-$CF_3C_6H_4Me_2SiCCl_2H$	High	37
p-$FC_6H_4Me_2SiH$	$PhHgCCl_2Br$	p-$FC_6H_4Me_2SiCCl_2H$	High	37
p-$ClC_6H_4Me_2SiH$	$PhHgCCl_2Br$	p-$ClC_6H_4Me_2SiCCl_2H$	High	37
p-$Me_3SiCH_2C_6H_4Me_2SiH$	$PhHgCCl_2Br$	p-$Me_3SiCH_2C_6H_4Me_2SiCCl_2H$	High	37
$(C_6H_5)_3SiH$	$PhHgCBr_3$	$(C_6H_5)_3SiCBr_2H$	65	36
$(C_2H_5)_3SiH$	$PhHgCBr_3$	$(C_2H_5)_3SiCBr_2H$	65	36
$(C_6H_5)_3GeH$	$PhHgCCl_2Br$	$(C_6H_5)_3GeCCl_2H$	88	36
$(C_2H_5)_3GeH$	$PhHgCCl_2Br$	$(C_2H_5)_3GeCCl_2H$	83	36
$(C_6H_5)_3SiH$	$PhHgCClBr_2$	$(C_6H_5)_3SiCClBrH$	86	38
$(C_2H_5)_3SiH$	$PhHgCClBr_2$	$(C_2H_5)_3SiCClBrH$	81	38

* 'high' denotes 85 to 95 per cent.

It is clear from the data in *Tables 3* and *4* that halomethylmercury compounds serve well in the methylenation of organosilicon and organogermanium hydrides. Although it will be shown later that the Sn—H bond

Table 4. Halomethylmercurial/Group IV hydride reactions

Hydride	*Mercurial*	*Reaction temperature C°*	*Reaction time*	*Product (% yield)*	*Ref.*
Et_3SiH	$PhHgCCl_2F$	80	48 h	$Et_3SiCClFH$ (83)	39
Et_3SiH	$(Me_3SiCCl_2)_2Hg + Ph_2Hg$	126	3d	$Et_3SiCHClSiMe_3$ (42) $Et_3SiCH_2SiMe_3$ (7)	40
Et_3SiH	$PhHgCClBrCF_3$	140		$Et_3SiCHClCF_3$ (51) $Et_3SiCHBrCF_3$ (4)	41
Et_3SiH	$PhHgCBr_2H$	130	34·5 h	Et_3SiCH_2Br (61)	42
Et_3SiH	$PhHgCBr_2H$	109	27 h	Et_3SiCH_2Br (72)	42
Et_3SiH	$PhHgCClBrH$	130	142 h	Et_3SiCH_2Cl (72) Et_3SiCH_2Br (7)	42
n-Bu_3SiH	$PhHgCBr_2H$	130	23·5 h	n-Bu_3SiCH_2Br (80)	42
n-Bu_3SiH	$PhHgCClBrH$	130	144 h	n-Bu_3SiCH_2Cl (76) n-Bu_3SiCH_2Br (3)	42
Et_2SiH_2	$PhHgCBr_2H$	130	36 h	Et_2HSiCH_2Br (42) $Et_2Si(CH_2Br)_2$(2)	42
n-$BuSiH_3$	$PhHgCBr_2H$	130	36 h	n-BuH_2SiCH_2Br (28) n-$BuHSi(CH_2Br)_2$ (3)	42
Ph_3SiH	$PhHgCBr_2H$	130	20 h	Ph_3SiCH_2Br (4)	42
Et_3GeH	$PhHgCBr_2H$	130	66 h	Et_3GeCH_2Br (28)	42
Et_3SiH	$Hg(CH_2Br)_2$	80	20 h	Et_3SiCH_3 (89)	43
Et_3SiH	$Hg(CH_2Br)_2 + Ph_2Hg$	80	3 d	Et_3SiCH_3 (68)	43
Et_3SiH	$ICH_2HgI + Ph_2Hg$	80	20 h	Et_3SiCH_3 (83)	43
Ph_3SiH	$Hg(CH_2Br)_2 + Ph_2Hg$	80	12 d	Ph_3SiMe (80)	43
Ph_2ViSiH	$Hg(CH_2Br)_2 + Ph_2Hg$	80	13 d	$Ph_2ViSiMe$ (83)	43
Ph_2SiH_2	$Hg(CH_2Br)_2 + Ph_2Hg$	80	16 d	Ph_2Me_2Si (83) Ph_2MeSiH (7)	43
Et_3GeH	$Hg(CH_2Br)_2 + Ph_2Hg$	80	4·5 h	Et_3GeMe (40)	43
$C_6H_5Me_2SiH$	$Hg(CH_2Br)_2$	80	7 d	$C_6H_5Me_3Si$ (93)	43
m-$CF_3C_6H_4Me_2SiH$	$Hg(CH_2Br)_2$	80	31 d	m-$CF_3C_6H_4Me_3Si$ (92)	43
p-$FC_6H_4Me_2SiH$	$Hg(CH_2Br)_2$	80	20 d	p-$FC_6H_4Me_3Si$ (98)	43
p-$ClC_6H_4Me_2SiH$	$Hg(CH_2Br)_2$	80	20 d	p-$ClC_6H_4Me_3Si$ (91)	43
p-$CH_3C_6H_4Me_2SiH$	$Hg(CH_2Br)_2$	80	9 d	p-$CH_3C_6H_4Me_3Si$ (86)	43

is reactive toward dichlorocarbene, a carbene source other than a halomethylmercurial must be used. The most reactive and hence most useful mercurials are those which permit elimination of phenylmercuric bromide in the carbene extrusion process, and their C—Br bonds are very reactive toward organotin hydrides. Thus, tri-*n*-butyltin hydride will react rapidly with $PhHgCCl_2Br$ even below room temperature, but the reaction involved is a radical-chain reduction of the C—Br bonds (equation 22)[36]. Carbene extrusion from the mercurial cannot compete with this process.

$$PhHgCCl_2Br + n\text{-}Bu_3SnH \rightarrow PhHgCCl_2H + n\text{-}Bu_3SnBr \qquad (22)$$

The question of the mechanisms of these preparatively useful methylenation reactions was of some interest. In our studies concerning the reactions of phenyl(bromodichloromethyl)mercury[32-34] and of bis(bromomethyl)mercury[44] we had found, as mentioned above, that the former converted olefins to gem-dichlorocyclopropanes via intermediate dichlorocarbene, but with the second reagent, it was found that the olefin to cyclopropane conversion proceeded via a direct reaction between $Hg(CH_2Br)_2$ and the olefin, in which free CH_2 was not an intermediate.

We have devoted most of our efforts to obtaining a better understanding of the $PhHgCCl_2Br$/organosilicon hydride reaction. At the outset it was by no means certain that this reaction also was a process involving free CCl_2 as a primary intermediate as shown in equation 17. It may be noted, for instance, that CCl_2 transfer from phenyl(bromodichloromethyl)mercury to more strongly nucleophilic substrates such as tertiary phosphines[45] and tertiary amines[46] has all the characteristics of a process in which the nucleophile attacks at mercury to displace the trihalomethyl anion which subsequently gives the dihalocarbene. Even though the $PhHgCX_3$/organosilicon hydride reactions more closely resembled the $PhHgCX_3$/olefin reactions than those of these mercurials with phosphines and amines, a closer examination of the $PhHgCCl_2Br$/organosilicon hydride reaction was undertaken to define the operative mechanism if at all possible. A kinetic study and a Hammett study carried out at the M.I.T. and a study of the stereochemistry of this reaction by L. H. Sommer and co-workers at the University of California at Davis[47] gave results which could most readily be rationalized in terms of a free dichlorocarbene process (equation 17 followed by equation 23—in the case of triethysilane).

$$Et_3SiH + CCl_2 \xrightarrow{k'_2} Et_3SiCCl_2H \qquad (23)$$

Variable concentration competition experiments, in which mixtures of triethylsilane and cyclohexane were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury, were carried out first, and it was found[36] that the rate constant ratio at 80° for the CCl_2 reactions occurring, $k(Et_3SiH)/k$(cyclohexene), was 0·8. This ratio was independent of the initial (Et_3SiH)/(cyclohexene) concentration ratio, being 0·805 when this concentration ratio was one; 0·800 when it was a half; 0·796 when it was two. This indicated that the kinetic order of triethylsilane in its reaction with the mercurial is the same as the kinetic order of cyclohexene in its reaction with $PhHgCCl_2Br$. Thus a free carbene mechanism for the $PhHgCCl_2Br/Et_3SiH$

reaction seemed likely. However, independent confirmation by means of a kinetic study was sought.

The rate of the $PhHgCCl_2Br/Et_3SiH$ reaction was measured in benzene solution at 39·0° by determining[37] by means of gas–liquid partition chromatography the rate of formation of the product, Et_3SiCCl_2H. The results of these experiments are shown in *Table 5*. As can be seen, doubling the

Table 5. The Et_3SiH–$PhHgCCl_2Br$ reaction: kinetic runs at 39·0° in benzene solution

Run	$[Et_3SiH]$*	$[PhHgCCl_2Br]$*	$dx/dt \times 10^5$†
1	0·20	0·099	8·6
2	0·10	0·099	8·2
3	0·20	0·20	17·8

* Initial concentration in moles/litre.
† In moles/litre minute.

initial triethylsilane concentration has no effect on the reaction rate. On the other hand, when the mercurial concentration was doubled, the reaction rate was increased by a factor of about two. Of significance also is the fact that the rate of formation of Et_3SiCCl_2H at 39·0° in benzene solution is, within experimental error, the same as the rate of formation of 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane from the $Me_2C{=}CMeEt/PhHgCCl_2Br$ reaction and of 9,9-dichlorobicyclo [4.1.0] nonane from the cyclooctene/$PhHgCCl_2Br$ reaction ($8{\cdot}8 \times 10^{-5}$ mol/l min) at the same reagent concentrations[33]. The results of our $PhHgCCl_2Br$/olefin reaction study suggested that this was the limiting rate, i.e. the one for which the applicable rate expression for the reaction sequence 17–18 (equation 24) simplified to equation 25.

$$\frac{dx}{dt} = \frac{k_1(PhHgCCl_2Br)}{1 + \dfrac{k_{-1}(PhHgBr)}{k_2(\text{olefin})}} \tag{24}$$

$$dx/dt = k_1(PhHgCCl_2Br) \tag{25}$$

These findings, that the $PhHgCCl_2Br/Et_3SiH$ reaction is approximately first order in mercurial and approximately zero order in the silane and that the observed rate is equal to that found previously for olefin/mercurial reactions at comparable reagent concentrations suggested that the mechanism defined by the reaction sequence 17–23 is indeed operative.

Our further interest centred on the nature of the Et_3SiH/CCl_2 reaction (equation 23). Sommer *et al.*[47] reported that the reaction of phenyl(bromodichloromethyl)mercury with optically active α-naphthylphenylmethylsilane produced optically active α-naphthylphenylmethyl(dichloromethyl)silane with retention of configuration. This is the result one would expect for the insertion of free CCl_2 into the Si—H bond. At the M.I.T. we carried out a study[37] of the relative reactivities of a series of substituted aryldimethylsilanes toward $PhHgCCl_2Br$. The reactions of such silanes, $ZC_6H_4SiMe_2H$

(Z = H, *m*-CF_3, *p*-F, *p*-Cl and *p*-CH_3), with this mercurial all gave the expected $ZC_6H_4SiMe_2CCl_2H$ compounds in high yield. In the competition study, a mixture of two aryldimethylsilanes and $PhHgCCl_2Br$ in 5:5;1 ratio in benzene solution was stirred and heated at 79° ± 1° for two hours. Gas chromatography served to determine the yields of the two aryldimethyl (dichloromethyl)silanes formed, and from these the relative rate constants could be calculated. The results are presented in *Table 6*. The necessary control experiments were carried out.

Table 6. Relative rate constants for insertion of $PhHgCCl_2Br$-derived CCl_2 into the Si—H bond of $XC_6H_4SiMe_2H$

Z	σ	$\frac{k(XC_6H_4SiMe_2H)}{k(PhSiMe_2H)}$ (av)
p-CH_3	−0·17	1·25
H	0·00	1·00
p-F	0·06	0·883
p-Cl	0·23	0·733
m-CF_3	0·47	0·482

Table 6 shows clearly that an electron-donating substituent increases the relative rate constant of insertion. *Figure 2*, a plot of log $k_{rel.}$ versus σ, shows that the values obtained fit the Hammett equation quite well. The slope of the line obtained gave a ρ value of −0·632 ± 0·032. Electrophilic attack by dichlorocarbene on the silane seems indicated. The value of ρ is small and this suggests that the transition state is not highly charged. In comparison,

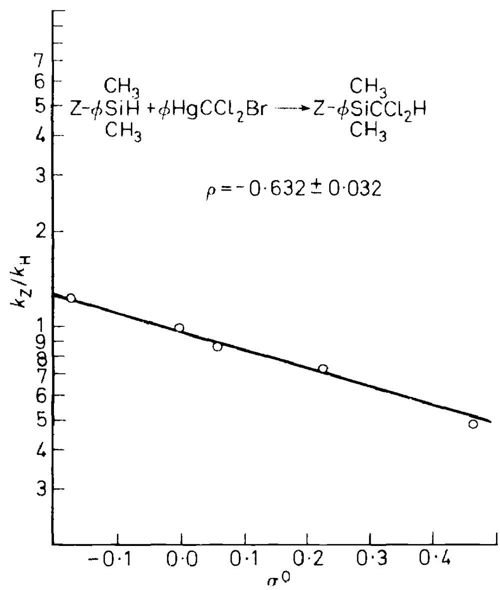
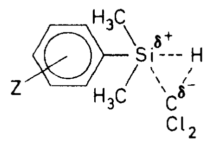


Figure 2.

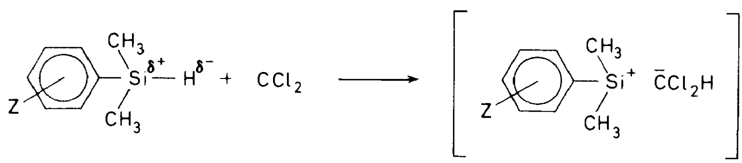
$\rho^* = -4.2$ for the $R_3Si{-}H + Cl_2 \rightarrow R_3SiCl + HCl$ reaction, which presumably involves the attack of chlorine as an electrophilic reagent[48]. Another competition study showed triethylgermane to be 4·5 times more reactive than triethylsilane toward $PhHgCCl_2Br$-derived dichlorocarbene[36].

The available information concerning the $PhHgCCl_2Br$/organosilicon hydride reaction suggested to us three possible mechanisms for the R_3SiH/CCl_2 reaction: (a) insertion of CCl_2 into Si—H bond via the but slightly polar transition state I; (b) hydride abstraction by the CCl_2 followed by collapse of the resulting tight ion pair (II); (c) radical abstraction of a hydro-

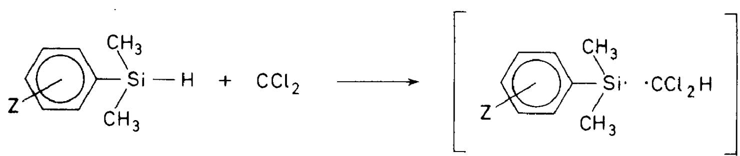


I

gen atom followed by a rapid radical coupling step within the solvent cage (III). Since the rate-determining step of this process is the generation of CCl_2



II

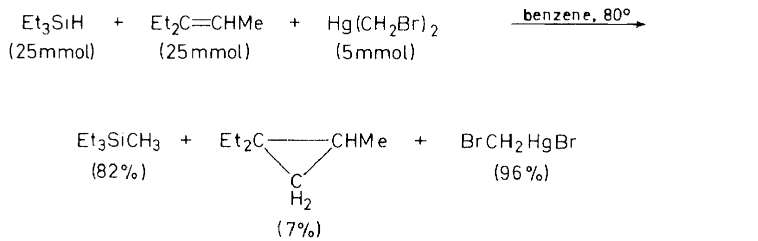


III

from $PhHgCCl_2Br$, any of these three possibilities must occur very rapidly and kinetic experiments cannot distinguish between them. As noted, the $R_3SiH/PhHgCCl_2Br$ reactions proceed virtually quantitatively without formation of byproducts; this, as well as the complete absence of prior reports of any radical-type behaviour of CCl_2, leads us to remove from further consideration the process involving III. The process involving ion pair II cannot be excluded out of hand in view of the well-recognized electrophilic character of dichlorocarbene and the $Si^{\delta+}{-}H^{\delta-}$ polarization of the Si—H bond. We can, however, exclude a process in which the ion partners of II are ever free by the observation that Et_3SiD reacted with phenyl(bromodichloromethyl)mercury in benzene, and more significantly, in methylene chloride solution, to give *only* Et_3SiCCl_2D. If the CCl_2D^- anion had been involved as an intermediate free in solution, exchange with the methylene chloride solvent should have produced some CCl_2H^- and thus a mixture of Et_3SiCCl_2D and Et_3SiCCl_2H would have been formed. When all is considered, we prefer to describe the R_3SiH/CCl_2 reaction in terms of transition state I.

The mechanism of the transfer of CH_2 from a monohalomethylmercury compound [$Hg(CH_2Br)_2$ and ICH_2HgI, alone or in combination with diphenylmercury] to the Si—H bond is not yet known with certainty, but most likely it does not involve a free carbene intermediate. The evidence supporting this is indirect, a kinetic study having not yet been carried out. We noted, however, that bis(bromomethyl)mercury is quite stable at 80° in the absence of a substrate to which it could transfer CH_2 and that all available evidence speaks against the operation of a free CH_2 mechanism in the $Hg(CH_2Br)_2$/olefin reaction[44]. Very noteworthy also is the marked difference between the reactions of organosilicon hydrides with halomethylmercurials and with diazomethane under photolysis conditions: as has been mentioned, the methylenation of R_3SiH compounds, which proceeds in high yield with $Hg(CH_2Br)_2$, gives only minimal yields when diazomethane is the CH_2 source[4]. Some sort of a direct, bimolecular process might thus be envisioned for the $R_3SiH/Hg(CH_2Br)_2$ reaction.

A competition experiment showed that the Si—H bond is much more reactive than the C=C linkage toward bis(bromomethyl)mercury; equation 26 gives the results obtained. It may be noted that 3-ethyl-2-pentene is



(26)

approximately four times more reactive toward this organomercury reagent than is cyclohexene, and thus it would appear that the Si—H bond of triethylsilane is more reactive towards bis(bromomethyl)mercury than is the C=C bond of the most reactive olefin examined thus far.

A Hammett study similar to that carried out with substituted aryldimethylsilanes for phenyl(bromodichloromethyl)mercury[37] could not be applied to the reaction of these silanes with bis(bromomethyl)mercury[43]. In experiments with *p*-tolyldimethylsilane it was found that this silane was not stable to the reaction conditions; some cleavage of the *p*-tolyl group occurred during the rather long reaction times required. Accordingly, the conditions chosen were those of a 'one-point' kinetic run. An excess of bis (bromomethyl)mercury and each substituted aryldimethylsilane were allowed to react, all under the same rigorously defined conditions: 0·6M mercurial reagent concentration; 0·2M silane concentration; 80·2° ± 0·1°. Because of the large reactivity span of the silanes studied, reaction times of the same length could not be used for all. *p*-Tolyldimethylsilane and dimethylphenylsilane were allowed to react for three days and, in another set of experiments, dimethylphenylsilane, *p*-chlorophenyldimethylsilane, *p*-fluorophenyldimethylsilane and *m*-trifluoromethylphenyldimethylsilane for four days. If one assumes that the CH_2 insertion mechanism is the same for each of the silanes used, then the yield of the respective aryltrimethylsilane after a given length of time under these standard conditions is a measure of the rate of reaction. The various yields (i.e. rates) can then be related to the yield of phenyltrimethylsilanes and relative rate constants can be calculated. The values of these, obtained in this manner, were: *p*-tolyldimethylsilane, 1·52; phenyldimethylsilane, 1·00 (reference compound); *p*-fluorophenyldimethylsilane, 0·562; *p*-chlorophenyldimethylsilane, 0·462; *m*-trifluoromethylphenyldimethylsilane, 0·230. Possible correlations of the log $k_{rel.}$ values with σ, σ^+, and σ^0 were examined. The best correlation by far was that with σ^0 (*Figure 3*) and a ρ value of $-1·31 \pm 0·04$ was computed. Thus it would appear that the polar effects exerted by the substituents on the reaction centre which are transmitted by induction are the more important ones in the reaction studied. The computed ρ value is approximately twice as negative as the ρ-value obtained for the reaction of $PhHgCCl_2Br$-derived dichlorocarbene with substituted aryldimethylsilanes; this indicates a transition state which is more polar. It further indicates that the CH_2 transfer reagent is a more selective species than the dichlorocarbene derived from phenyl(bromodichloromethyl)mercury. Since all available evidence suggests that free CH_2 is much less selective than is CCl_2, these experiments also would speak against a free CH_2 intermediate in these Si—H methylenations. Further speculation about the exact nature of the transition state cannot be made at the present time because of the limited amount of other information.

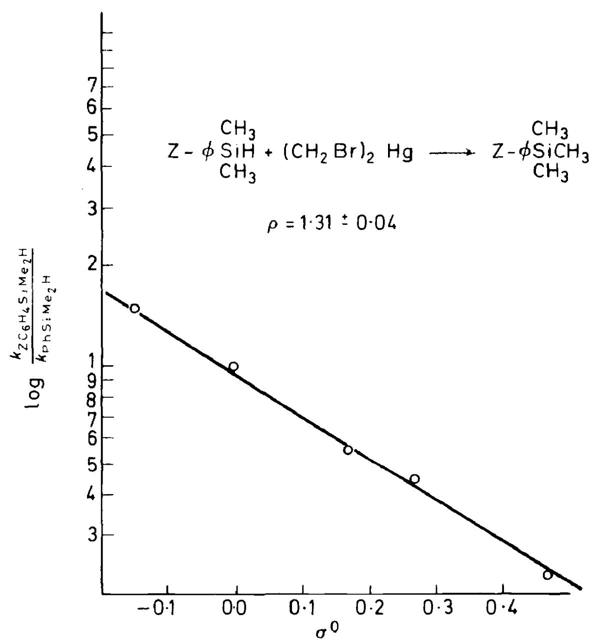


Figure 3.

Thus far we know nothing concerning the mechanism of the reaction between phenyl(dihalomethyl)mercurials and organosilicon and organogermanium hydrides which produces monohalomethyl derivatives of these elements[42].

Regardless of the mechanisms involved, it is the reactions of phenyl(trihalomethyl)mercurials with organosilicon and organogermanium hydrides which enjoy the greatest preparative utility. Monohalomethyl-silanes and -germanes are more readily prepared by other routes, including the simply effected, high yield monoreduction of R_3MCBr_2H and $R_3MCClBrH$ compounds (M = Si and Ge) with tri-*n*-butyltin hydride to give R_3MCH_2Br and R_3MCH_2Cl, respectively[49]. The reaction conditions required for the $PhHgCX_2H$/Group IV hydride reactions simply are too impractical, involving long reaction times at relatively high temperatures (cf. *Table 4*). Furthermore, high product yields are obtained only with trialkylsilanes. With trialkylgermanes, the reaction of as yet unconverted R_3GeH with phenylmercuric bromide (equation 27) causes severe problems.

$$R_3GeH + PhHgBr \rightarrow R_3GeBr + \tfrac{1}{2}Ph_2Hg + \tfrac{1}{2}Hg \qquad (27)$$

Methylsilanes are more easily prepared by reactions of active methylating reagents with halosilanes than by methylenation processes. However, the $Hg(CH_2X)_2$/organosilicon hydride reaction may enjoy unique applicability in the preparation of specifically deuterated methylsilanes.

The reactions of organosilicon and organogermanium hydrides with halomethylmercurials may find their most valuable use in the synthesis of novel organofunctional silicon and germanium compounds. In this connection the reactions of triethylsilane with $PhHgCClBrCF_3$ (ref. 41) and with $(Me_3SiCCl_2)_2Hg/Ph_2Hg$[40] are to be noted, as is our current active research programme directed toward the synthesis of new halomethylmercury compounds.

The transfer of mercurial-derived dihalocarbenes into Group IV–halogen bonds has been less successful and, in fact, the positive results which were obtained are rather ambiguous. In our Laboratories we found Me_3SiCl, Et_3SiCl and Et_2SiCl_2 to be inert toward CCl_2 generated from phenyl(bromodichloromethyl)mercury under the usual conditions, and Benkeser and Smith[50] observed no CCl_2 transfer reaction between silicon tetrachloride and $PhHgCCl_3$. The finding that dihalocarbenes were capable of inserting into the mercury–halogen linkage[51] suggested to us that such reactions, if they were to be found at all with Group IV halides, would occur with the heavier Group IV elements. Such insertion does indeed occur with organotin halides[52]. The thermolysis of phenyl(bromodichloromethyl)mercury in the presence of a 50 per cent excess of trimethyltin bromide in refluxing benzene gave trimethyl(bromodichloromethyl)tin in 63 per cent yield (equation 28). However, this product could have been formed by two different routes:

$$Me_3SnBr + PhHgCCl_2Br \rightarrow PhHgBr + Me_3SnCCl_2Br \qquad (28)$$

CCl_2 insertion into the Sn—Br bond or substituent exchange between mercury and tin. In order to obtain more information concerning this question, the analogous reaction of $PhHgCCl_2Br$ with trimethyltin *chloride* was examined. In this case, the insertion process would give trimethyl(trichloromethyl)tin (in the absence of complicating halogen exchange reactions) and the substituent exchange process should give trimethyl(bromodichloromethyl)tin. When this reaction was carried out, the total product yield was only 16 per cent, probably as a result of the lesser reactivity of the Sn—Cl bond, and a 1·5/1 mixture of Me_3SnCCl_3 and Me_3SnCCl_2Br was obtained. A possible explanation of this result, the formation of Me_3SnBr by reaction of phenylmercuric bromide and trimethyltin chloride, was excluded by experiment. From these results it would appear that trimethyl(bromodichloromethyl)tin could have been formed by both routes in the $PhHgCCl_2Br$/Me_3SnBr reaction.

METHYLENATIONS WITH HALOMETHYL–ZINC COMPOUNDS

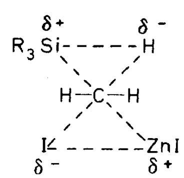
Halomethylzinc compounds of type XCH_2ZnX and $Zn(CH_2X)_2$ transfer CH_2 to olefins to give cyclopropanes. The available evidence strongly suggests that a direct reaction between the zinc reagent and the olefin is occurring[53–58]. The fact that those methylenation reagents which generally converted olefins to cyclopropanes also inserted the divalent carbon moiety into the Si—H bond led us to examine reactions of these zinc reagents with organosilicon hydrides.

Iodomethylzinc iodide as well as bromomethylzinc bromide react with triethylsilane to give triethylmethylsilane in good yield (equation 29)[59].

$$Et_3SiH + XCH_2ZnX \xrightarrow{Et_2O} \underset{\substack{(64\%, X = I)\\(55\%, X = Br)}}{Et_3SiMe} + ZnX_2 \qquad (29)$$

The reactivity of trialkylsilanes toward halomethylzinc halide was compared with that of olefins. When five molar equivalents each of tri-*n*-butylsilane and cyclohexene were allowed to compete for the iodomethylzinc iodide prepared from one molar equivalent of methylene iodide, tri-*n*-butylmethylsilane and norcarane were formed in yields of 51·5 and 2·3 per cent, respectively. In view of the rather narrow spread of relative reactivities of olefins toward iodomethylzinc iodide[54], trialkylsilanes appear to be much more reactive toward the zinc reagent than the most reactive olefins. It will be recalled that the same observation was made for bis(bromomethyl)mercury.

The mechanism of the insertion process is not known. A mechanism involving free CH_2 is very improbable in view of the work of Simmons *et al.* on ICH_2ZnI/olefin reactions[53–55], and we suggest a direct transfer process via transition state IV as the most reasonable possibility. However, in view



IV

of the known reactivity of organozinc compounds as alkylating agents and the examples of C–halogen reductions by organosilicon hydrides already in the literature, reaction sequences 30–31 and 32–33 also had to be considered. Both of these possibilities, of which the first is the more plausible,

$$\begin{cases} Et_3SiH + ICH_2ZnI \rightarrow Et_3SiI + CH_3ZnI & (30) \\ Et_3SiI + CH_3ZnI \rightarrow Et_3SiCH_3 + ZnI_2 & (31) \end{cases}$$

$$\begin{cases} Et_3SiH + ICH_2ZnI \rightarrow Et_3SiCH_2I + HZnI & (32) \\ Et_3SiCH_2I + HZnI \rightarrow Et_3SiCH_3 + ZnI_2 & (33) \end{cases}$$

were excluded by an experiment in which an equimolar mixture of Et_3SiD and n-Bu_3SiH was allowed to react with iodomethylzinc iodide. If either of these reaction pathways (30–31 or 32–33) was operative, then deuterium scrambling would be expected and a mixture of Et_3SiCH_2D, Et_3SiCH_3, n-Bu_3SiCH_2D and n-Bu_3SiCH_3 should have been obtained. The observed result[60] was the formation of *only* Et_3SiCH_2D and n-Bu_3SiCH_3. Thus a direct process seems indicated.

Iodomethylzinc iodide and bromomethylzinc bromide also react with organotin and organolead halides, as illustrated in the equations below[61]. However, we feel certain that in these reactions we are not dealing with a

$$XCH_2ZnX + Me_3SnCl \xrightarrow{THF} Me_3SnCH_2X + ZnXCl \qquad (34)$$
$$(86\%, X = I)$$
$$(84\%, X = Br)$$

$$2\,ICH_2ZnI + Me_2SnCl_2 \xrightarrow{THF} Me_2Sn(CH_2I)_2 + 2\,ZnICl \qquad (35)$$
$$(56\%)$$

$$ICH_2ZnI + Ph_3PbCl \xrightarrow{THF} Ph_3PbCH_2I + ZnICl \qquad (36)$$
$$(33\%)$$

methylenation process, but rather with a halomethylation of the organometallic halide in which the zinc reagent is reacting as an alkylating agent. It may be noted that the useful monohalomethylmercury compounds can be prepared by this organozinc route.

METHYLENATIONS VIA SODIUM TRICHLOROACETATE

The successful insertion of $PhHgCCl_2Br$-derived dichlorocarbene into the Si—H bond led us to investigate other CCl_2 generators in this application. Consideration was given to sodium trichloroacetate, which releases dichlorocarbene on heating in aprotic medium (DME or diglyme) via the sequence[62]

$$CCl_3CO_2Na \rightarrow CCl_3^-Na^+ \rightarrow CCl_2 + NaCl$$

Our studies showed that this reagent can indeed by used to insert CCl_2 into the Si—H bond of triethylsilane[59]. However, the yield of triethyl(dichloromethyl)silane obtained was only 32 per cent, considerably lower than the yield of this product from the $PhHgCCl_2Br/Et_3SiH$ reaction. Chinese workers have reported[63] similar insertion of sodium trichloroacetate-derived dichlorocarbene into the Sn–H bond (equation 37). With triethyltin

$$n\text{-}Bu_3SnH + CCl_3CO_2Na \xrightarrow{DME} \underset{(45\%)}{n\text{-}Bu_3SnCCl_2H} + NaCl + CO_2 \quad (37)$$

hydride a 55 per cent yield of product was obtained. The same authors have claimed the insertion of CCl_2 as generated by this reagent into the Sn—Cl bond of tri-*n*-butyltin chloride[64]. However, this conclusion concerning mechanism is open to question in view of our finding[65] that trimethyltin trichloroacetate functions as a CCl_2 transfer agent via the pathway shown below (equation 38). Thus the formation of $n\text{-}Bu_3SnCCl_3$ in the reaction

$$CCl_3CO_2SnMe_3 \xrightarrow{-CO_2} CCl_3SnMe_3 \rightarrow CCl_2 + Me_3SnCl \quad (38)$$

reported by T'seng *et al.* very likely proceeds by way of decarboxylation of tri-*n*-butyltin trichloroacetate.

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Note added in proof

In the year which has elapsed since this manuscript was submitted, more papers in this area have been published. They are described briefly below so that this review will be up-to-date.

(1) Insertion of CBr_2 (via $PhHgCBr_3$) into Si—H bond of 1-naphthylphenylmethylsilane; of CBr_2 (via $PhHgCBr_3$ and t-BuOK · t-BuOH + $CHBr_3$) into the Ge—H bond of Ph_3GeH; of CBr_2 (via $PhHgCBr_3$) into Ge—H bond of 1-naphthylphenylmethylgermane.

A. G. Brook, J. M. Duff and D. G. Anderson, *Canad. J. Chem.* **48**, 561 (1970).

(2) Insertion of $Me_2C{=}C{:}$ and $\genfrac{}{}{0pt}{}{Me_3C}{Me}\!>\!C{=}C{:}$ into the Si-H bond of Et_3SiH to give $\genfrac{}{}{0pt}{}{Me}{Me}\!>\!C{=}C\!<\!\genfrac{}{}{0pt}{}{SiEt_3}{H}$ and $\genfrac{}{}{0pt}{}{Me_3C}{Me}\!>\!C{=}C\!<\!\genfrac{}{}{0pt}{}{SiEt_3}{H}$, respectively.

M. S. Newman and C. D. Beard, *J. Am. Chem. Soc.* **92**, 4309 (1970).

M. S. Newman and T. B. Patrick, *J. Am. Chem. Soc.* **92**, 4312 (1970).

(3) Production of chemically activated Me_4Si by insertion of singlet CH_2 into the Si—H bond of Me_3SiH.

W. L. Hase and J. W. Simons, *J. Chem. Phys.* **52**, 4004 (1970).

(4) Insertion of PhCCl (via phenylchlorodiazirine) into the Sn—H bond of n-Bu_3SnH.

A. Padwa and D. Eastman, *J. Org. Chem.* **34**, 2728 (1969).

(5) Insertion of HCF_2CF (via $HCF_2CF_2SiF_3$) into Si—H and Si—Cl bonds.

R. N. Haszeldine, A. E. Tipping and R.O'B. Watts, *J. Chem. Soc. D*, 1364 (1969).

(6) Insertion of CF_2 (via Me_3SnCF_3 pyrolysis) into the Sn—H bond of Me_3SnH to give Me_3SnCF_2H.

W. R. Cullen, J. R. Sams and M. C. Waldman, *Inorg. Chem.* **9**, 1682 (1970).

(7) Insertion of $(CF_3)_2C$ [via $(CF_3)_2(CN_2)$] into the Sn—H bond of Me_3SnH.

W. R. Cullen and M. C. Waldman, *Canad. J. Chem.* **48**, 1885 (1970).