HALOMETHYL–METAL COMPOUNDS
XXIX*. REACTIONS OF MONOHALOMETHYL–MERCURY COMPOUNDS WITH ORGANOSILICON HYDRIDES: A NEW PREPARATION OF METHYLSILICON COMPOUNDS
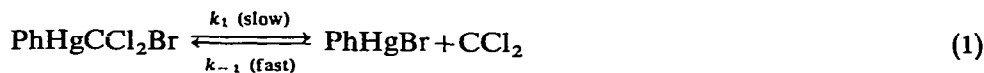
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SUMMARY

The reactions of the halomethyl–mercury reagents $Hg(CH_2Br)_2$, ICH_2HgI/Ph_2Hg and $Hg(CH_2Br)_2/Ph_2Hg$ with a number of organosilicon hydrides [Et_3SiH, Ph_3SiH, Ph_2SiH_2, $ViPh_2SiH$, Me_2PhSiH, $Me_2(ZC_6H_4)SiH$ ($Z = p$-Cl, p-F, m-CF_3 and p-CH_3)] resulted in CH_2 insertion into the Si–H bonds to give methylsilanes. A similar reaction with triethylgermane gave triethylmethylgermane. Although the mechanism of this new methylenation reaction is not known, a free methylene process seems to be excluded and it is likely that a direct reaction between the halomethyl–mercury reagent and the hydride is involved. A Hammett study of the reaction of $Hg(CH_2Br)_2$ with substituted phenyldimethylsilanes showed a good correlation between $\log k_{rel}$ and σ°, giving a ρ value of -1.31 ± 0.04. A competition study established that triethylsilane is *ca.* 12 times more reactive toward bis(bromomethyl)-mercury than is 3-ethyl-2-pentene.

INTRODUCTION

The insertion of divalent carbon species into the Si–H bond is by now a well-known reaction (Chart 1). In the case of the reaction of phenyl(bromodichloromethyl)-mercury with triethylsilane, the operation of a mechanism involving the insertion of free dichlorocarbene into the Si–H bond was indicated [eqns. (1) and (2)][9]. Carbene mechanisms also are very likely for the reactions of organosilicon hydrides with sodium

$$PhHgCCl_2Br \underset{k_{-1} \text{ (fast)}}{\overset{k_1 \text{ (slow)}}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (1)$$

$$CCl_2 + Et_3SiH \xrightarrow{k_2 \text{ (fast)}} Et_3SiCCl_2H \qquad (2)$$

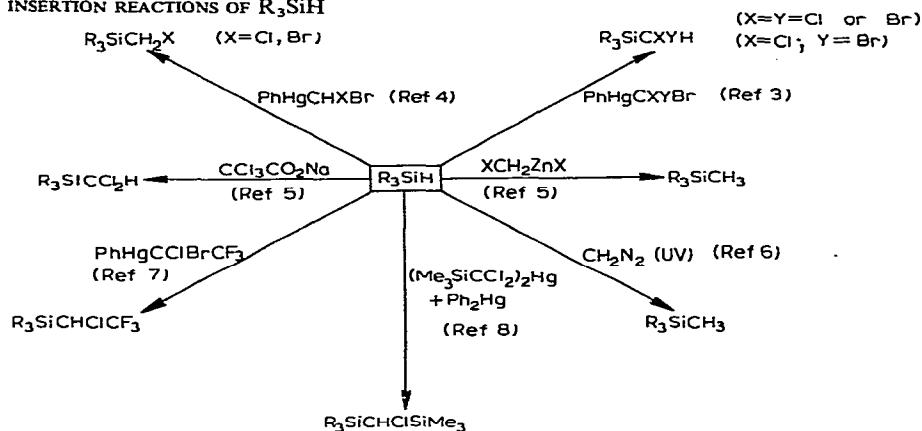trichloroacetate, the other phenylmercury compounds shown in Chart 1 (with the possible exception of PhHgCHXBr compounds) and diazomethane (with UV

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* For Part XXVIII see ref. 1; preliminary communication: ref. 2.
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CHART 1

INSERTION REACTIONS OF R_3SiH

$$R_3SiCH_2X \quad (X=Cl, Br) \qquad\qquad R_3SiCXYH \quad \begin{array}{l}(X=Y=Cl \text{ or } Br)\\(X=Cl; Y=Br)\end{array}$$

PhHgCHXBr (Ref 4)   PhHgCXYBr (Ref 3)

$$R_3SiCCl_2H \xleftarrow{\substack{CCl_3CO_2Na\\(Ref\ 5)}} \boxed{R_3SiH} \xrightarrow{\substack{XCH_2ZnX\\(Ref\ 5)}} R_3SiCH_3$$

PhHgCClBrCF$_3$ CH_2N_2 (UV) (Ref 6)
(Ref 7)

$(Me_3SiCCl_2)_2Hg$
$+Ph_2Hg$

$R_3SiCHClCF_3$ (Ref 8) R_3SiCH_3
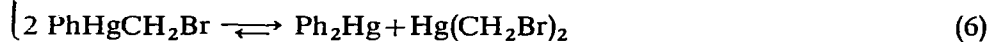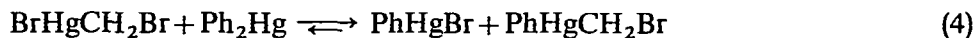
$R_3SiCHClSiMe_3$

irradiation). A direct reaction of the organometallic reagent with the silane is the most likely mechanism for the XCH_2ZnX/R_3SiH reaction. The discovery that monohalomethyl–mercury compounds [$Hg(CH_2Br)_2$ and ICH_2HgI] react with olefins in benzene solution at 80° to give cyclopropanes[10], i.e., that they also are divalent carbon transfer agents, prompted the study of the reactions of these monohalomethyl–mercury compounds with organosilicon hydrides which is the subject of the present paper.
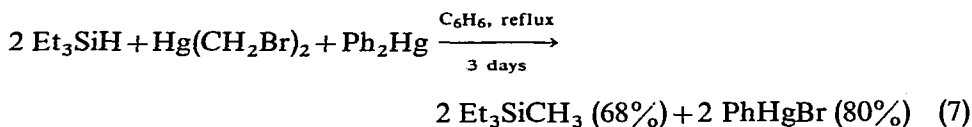
RESULTS AND DISCUSSION

The reaction of bis(bromomethyl)mercury with triethylsilane in refluxing benzene solution for 20 h gave the methylenation product, triethylmethylsilane, in 89% yield, based on eqn. (3). (Bromomethyl)mercuric bromide was formed in 96%
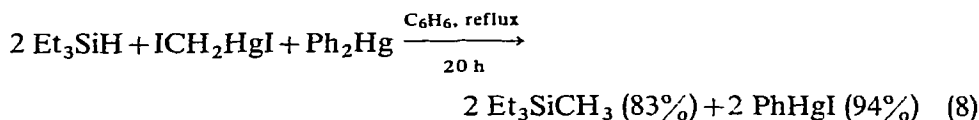
$$Et_3SiH + Hg(CH_2Br)_2 \rightarrow Et_3SiCH_3 + BrHgCH_2Br \qquad (3)$$
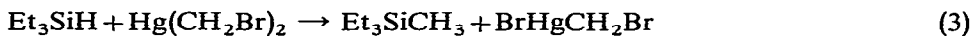
yield. We had shown previously[10] that the utilization of both CH_2 groups of bis-(bromomethyl)mercury was possible when the $(BrCH_2)_2Hg$/olefin reaction was carried out in the presence of one molar equivalent of diphenylmercury, and subsequent work[11] showed that this "activation" of the otherwise inert $BrCH_2HgBr$ is due to re-formation of the reactive $Hg(CH_2Br)_2$ by the reactions shown in eqns. (4)–(6). Accordingly, the triethylsilane/$Hg(CH_2Br)_2$ reaction was carried out in the

$$BrHgCH_2Br + Ph_2Hg \rightleftharpoons PhHgBr + PhHgCH_2Br \qquad (4)$$

$$\left\{ \begin{array}{l} PhHgCH_2Br + BrHgCH_2Br \rightleftharpoons PhHgBr + Hg(CH_2Br)_2 \qquad (5) \\[6pt] \text{or} \\[6pt] 2\ PhHgCH_2Br \rightleftharpoons Ph_2Hg + Hg(CH_2Br)_2 \qquad (6) \end{array} \right.$$

presence of one equivalent of diphenylmercury. The result obtained is shown in eqn. (7).

$$2\ Et_3SiH + Hg(CH_2Br)_2 + Ph_2Hg \xrightarrow[\text{3 days}]{C_6H_6,\ reflux}$$

$$2\ Et_3SiCH_3\ (68\%) + 2\ PhHgBr\ (80\%) \quad (7)$$

The $Hg(CH_2Br)_2$ methylenation reagent is prepared by the reaction of diazomethane with mercuric bromide. This reaction gives excellent yields of this product but has the disadvantage of requiring the preparation and use of a reagent that is both toxic and potentially explosive and that normally is not handled in large quantities for these reasons. (Iodomethyl)mercuric iodide, on the other hand, can be prepared by reaction of methylene iodide with metallic mercury[12] and thus is a somewhat more practical methylenation reagent. It also can be "activated" by addition of one equivalent of diphenylmercury[10], and the ICH_2HgI/Ph_2Hg reagent was found to methylenate triethylsilane in high yield; eqn. (8).

$$2\ Et_3SiH + ICH_2HgI + Ph_2Hg \xrightarrow[\text{20 h}]{\text{C}_6\text{H}_6, \text{ reflux}}$$

$$2\ Et_3SiCH_3\ (83\%) + 2\ PhHgI\ (94\%) \quad (8)$$

The potential utility of the halomethyl–mercury reagents in methylsilane synthesis having been established by these reactions with triethylsilane, it was of interest to investigate their general applicability. To this end, reactions of the $Hg(CH_2Br)_2/Ph_2Hg$ system in benzene at reflux were carried out with triphenylsilane, diphenylsilane, vinyldiphenylsilane and triethylgermane. The progress of the organosilicon hydride experiments was monitored by following the disappearance of the Si–H stretching frequency at *ca.* $2140\ cm^{-1}$ of the starting hydride in the reaction mixture. These experiments are summarized in Table 1. Noteworthy is the retarding effect of

TABLE 1

METHYLSILANES PREPARED BY REACTION OF SILANES WITH BIS(BROMOMETHYL)MERCURY/DIPHENYLMERCURY

Silane	(mmoles)	mMoles of $(BrCH_2)_2Hg$	Reaction time (days)	Yield of PhHgBr (%)	Product	Yield[a] (%)
Et_3SiH	20	10	3	80	Et_3SiMe	68
Ph_3SiH	20	10	12	87	Ph_3SiMe	80[b]
Et_3GeH	17	8.5	[c]	43	Et_3GeMe	40
					Et_3GeBr	9
					$(Et_3Ge)_2O$	20
Ph_2SiH_2	20	20	16	91	Ph_2SiMe_2	83
					$Ph_2Si(Me)H$	7
$Ph_2Si(CH=CH_2)H$	20	10	13	90	$Ph_2Si(CH=CH_2)Me$	83

[a] GLPC yield, unless otherwise noted. [b] Isolated yield. [c] 4.5 h.

phenyl substitution on silicon on the rate of the methylenation reaction. Good yields of methyltriphenylsilane and dimethyldiphenylsilane could be realized by methylenation of triphenyl- and diphenylsilane, but very long reaction times were required. The case of vinyldiphenylsilane is of interest since it has a C=C bond, which, in principle, should react with the methylenation reagent, as well as a reactive Si–H linkage. However, reaction occurs exclusively at the Si–H bond and no cyclopropylsilicon compound was formed. A similar observation was made with vinyldiphenylsilane

when it was allowed to react with phenyl(bromodichloromethyl)mercury: only $Ph_2(CH_2=CH)SiCCl_2H$ was produced[3].

The reaction of triethylgermane with the $Hg(CH_2Br)_2/Ph_2Hg$ reagent was complicated by the reactivity of the Ge–H bond toward phenylmercuric bromide, a complication previously encountered in the $Et_3GeH/PhHgCBr_2H$ reaction[4]. This reaction, which produces triethylbromogermane, metallic mercury and diphenyl-mercury, serves to reduce the yield of the triethylmethylgermane.
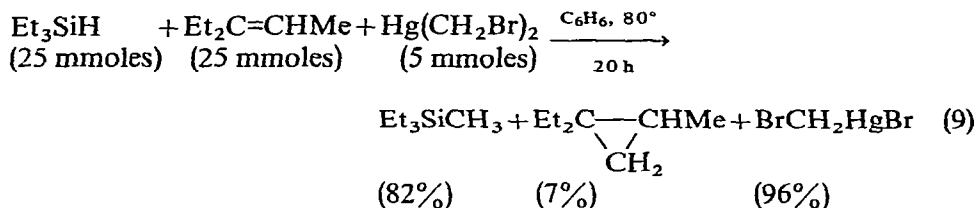
In another series of experiments, five substituted aryldimethylsilanes were treated with a four-fold excess of bis(bromomethyl)mercury in benzene at 80° until the respective silane had been consumed. The yields of substituted aryltrimethyl-silanes were excellent (86–98%), but the reaction times required to obtain these yields varied considerably with the substituent on the aryl group (Table 2).

TABLE 2

PREPARATION OF $ZC_6H_4SiMe_3$ COMPOUNDS BY REACTION OF $ZC_6H_4SiMe_2H$ WITH $Hg(CH_2Br)_2$

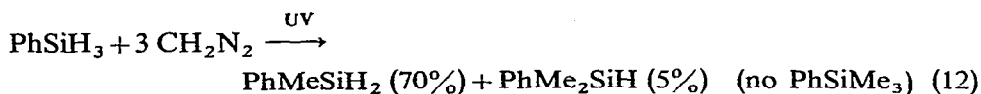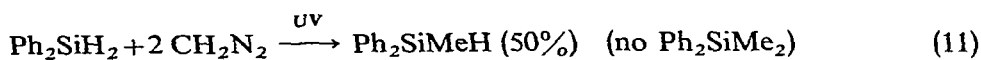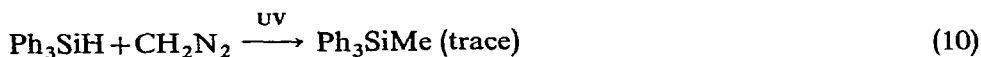| Z in $ZC_6H_4SiMe_2H$	Yield of $ZC_6H_4SiMe_3$ (%)	Reaction time required (days)
H	93	7
m-CF$_3$	92	31
p-F	98	20
p-Cl	91	20
p-CH$_3$	86	9

A competition experiment showed that the Si–H bond is much more reactive than the C=C bond toward bis(bromomethyl)mercury; eqn. (9) gives the results obtained. It may be noted that 3-ethyl-2-pentene is *ca.* four times more reactive toward

$$Et_3SiH \quad + Et_2C=CHMe + Hg(CH_2Br)_2 \xrightarrow[20\,h]{C_6H_6,\ 80°}$$
$$(25\ mmoles) \quad (25\ mmoles) \quad (5\ mmoles)$$

$$Et_3SiCH_3 + Et_2C\!\!\!\overset{\diagdown\diagup}{\underset{CH_2}{\quad}}\!\!\!CHMe + BrCH_2HgBr \quad (9)$$
$$(82\%) \qquad (7\%) \qquad\qquad (96\%)$$

this organomercury reagent than is cyclohexene, and thus it would appear that the Si–H bond of triethylsilane is more reactive toward $Hg(CH_2Br)_2$ than is the C=C bond of the most reactive olefin.
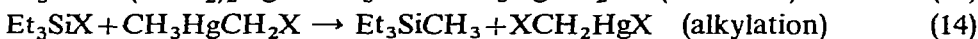
The mechanism of the transfer of CH_2 from a halomethyl–mercurial to the Si–H bond is not known with certainty, but it very likely does not involve a free CH_2 intermediate. The evidence supporting this statement is indirect, a kinetic study having not yet been carried out. We note, however, that bis(bromomethyl)mercury 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[10,11]. Very noteworthy also is the marked difference between the reactions of Si–H compounds with halomethyl–mercurials and with di-

azomethane under photolysis conditions[6]. As mentioned above, the mercury reagents convert triethylsilane to triethylmethylsilane in high yield. On the other hand, diazomethane irradiation in the presence of triethylsilane gave triethylmethylsilane in but 1% yield. Other reactions with diazomethane reported were those shown in the eqns. below.

$$\text{Ph}_3\text{SiH} + \text{CH}_2\text{N}_2 \xrightarrow{\text{UV}} \text{Ph}_3\text{SiMe (trace)} \tag{10}$$

$$\text{Ph}_2\text{SiH}_2 + 2\,\text{CH}_2\text{N}_2 \xrightarrow{\text{UV}} \text{Ph}_2\text{SiMeH (50\%)} \quad \text{(no Ph}_2\text{SiMe}_2\text{)} \tag{11}$$

$$\text{PhSiH}_3 + 3\,\text{CH}_2\text{N}_2 \xrightarrow{\text{UV}}$$
$$\text{PhMeSiH}_2 \ (70\%) + \text{PhMe}_2\text{SiH} \ (5\%) \quad \text{(no PhSiMe}_3\text{)} \tag{12}$$

Thus *tri*organosilanes appear to be virtually inert to diazomethane under conditions which should serve to generate free CH_2.

Other reaction pathways were considered. Silicon hydrides are mild reducing agents and alkylmercury compounds are known to be mild alkylating agents. Thus the reactions of halomethyl–mercury reagents with organosilicon hydrides could in principle proceed by the path illustrated with eqns. (13) and (14). Such a reduction-alkylation sequence, if it were to occur, should be especially favorable in the case of $\text{X} = \text{I}$. However, an independent experiment established that CH_3HgI does not react with triethyliodosilane in refluxing benzene (39 h reaction time), and, in any case, the alkylation of R_3SiX compounds by alkylmercurials would not be expected to occur under such mild conditions.
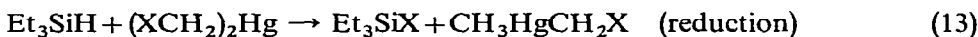
$$\text{Et}_3\text{SiH} + (\text{XCH}_2)_2\text{Hg} \rightarrow \text{Et}_3\text{SiX} + \text{CH}_3\text{HgCH}_2\text{X} \quad \text{(reduction)} \tag{13}$$

$$\text{Et}_3\text{SiX} + \text{CH}_3\text{HgCH}_2\text{X} \rightarrow \text{Et}_3\text{SiCH}_3 + \text{XCH}_2\text{HgX} \quad \text{(alkylation)} \tag{14}$$

A Hammett study of the reaction of phenyl(bromodichloromethyl)mercury with substituted aryldimethylsilanes showed a good correlation of log k_{rel} vs. σ, giving $\rho = -0.632$[9]. As mentioned earlier, the $\text{R}_3\text{SiH}/\text{PhHgCCl}_2\text{Br}$ reaction is known to involve free CCl_2 as an intermediate, and so a comparison of the reactions of substituted aryldimethylsilanes with bis(bromomethyl)mercury with the reactions of the same silanes with phenyl(bromodichloromethyl)mercury in terms of their characteristic ρ values would be quite worthwhile. A comparison by this means of the selectivity of the two organomercury reagents might provide information concerning the mechanism of the halomethyl–mercurial/organosilicon hydride reaction.

The intended plan for this Hammett study called for a series of competition experiments under conditions similar to those used in our previous study[9]. However, in experiments with *p*-tolyldimethylsilane it was found that this silane was not sufficiently stable under the reaction conditions for the long reaction times required; some cleavage of the *p*-tolyl group from silicon appeared to occur. 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: 0.6 M mercurial reagent concentration, 0.2 M silane concentration, a temperature of $80.2 \pm 0.1°$. 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 3 days, and,

in another set of experiments, dimethylphenylsilane, p-chlorophenyldimethylsilane, p-fluorophenyldimethylsilane and m-trifluoromethylphenyldimethylsilane for 4 days. If one assumes that the CH_2 insertion reaction mechanism is the same for each of the silanes used, then the yield of the respective aryltrimethylsilane after a given length of time is a measure of the rate of reaction. The various yields (*i.e.*, rates) can then be related to the yield of phenyltrimethylsilane by the relationship:

$$\frac{\% \text{ Yield } p\text{-ZC}_6\text{H}_4\text{SiMe}_3}{\% \text{ Yield PhSiMe}_3} = \frac{k_{\text{ZC}_6\text{H}_4\text{SiMe}_2\text{H}}}{k_{\text{PhSiMe}_2\text{H}}}$$

Table 3 lists the relative rate constants which these experiments provided. Possible correlations of the log k_{rel} values of Table 3 with σ, σ^+ and σ° were examined. The correlation with σ° was by far the best (Fig. 1) and a rho value of -1.31 ± 0.04 was computed. Thus it would appear that the polar effects exerted by the substituents on

TABLE 3

RELATIVE RATE CONSTANTS OF CH_2 INSERTION INTO THE Si–H BOND OF $ZC_6H_4SiMe_2H$

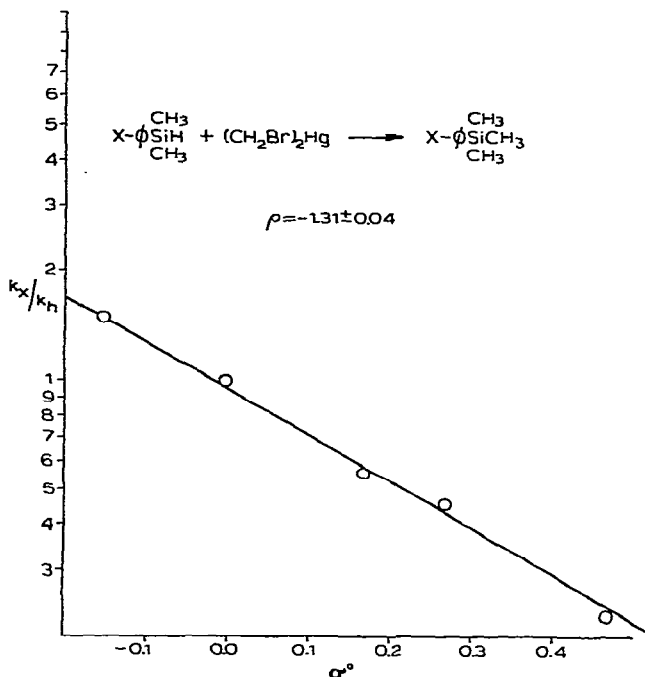| Z	$k_{\text{ZC}_6\text{H}_4\text{SiMe}_2\text{H}}/k_{\text{PhSiMe}_2\text{H}}$
p-CH$_3$	1.52
H	1.00
p-F	0.562
p-Cl	0.462
m-CF$_3$	0.230

Fig. 1.

the reaction center which are transmitted by induction are the important ones in the reaction studied. The calculated ρ value is approximately two times more negative than the ρ value obtained for the reaction of PhHgCCl$_2$Br-derived CCl$_2$ with substituted aryldimethylsilanes; this indicates a transition state which is more polar. It further indicates that the methylene 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 CCl$_2$, these experiments also would speak against a free CH$_2$ intermediate in these Si–H insertions. Further speculation about the exact nature of the transition state cannot be made at this time because of the limited amount of other information. The facts that bis(bromomethyl)mercury is stable at $80°$ in the absence of CH$_2$ acceptors such as organosilicon hydrides and olefins and that the reaction times at $80°$ required to achieve good yields of methylsilanes vary so widely as a function of the substitutents on silicon in R$_3$SiH compounds suggest that a direct reaction between the organomercury reagent and the organosilicon hydride is taking place. The Hammett study has shown that the reagent which attacks at the Si–H bond is an electrophilic species. A kinetic study is required to more fully define what this electrophilic species is.

Since the methyl Grignard reagents and methyllithium reagents serve well in the preparation of methylsilicon compounds, the latter reacting even with the Si–H bond, the halomethyl–mercury procedure for the synthesis of methylsilanes described in the present paper is expected to find little, if any, practical application. A possible application would be in the synthesis of specifically deuterated methylsilicon compounds, by reactions of halomethylmercurials with organosilicon deuterides, or of XCD$_2$Hg compounds with organosilicon hydrides or deuterides. In this way SiCH$_2$D, SiCHD$_2$ and SiCD$_3$ compounds could be prepared.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Gas–liquid partition chromatographic (GLPC) analyses were carried out using MIT isothermal units with glass columns (3 m × 12 mm o.d.) packed with 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb P unless otherwise noted. Helium at 15 psi was used as carrier gas. Yields were determined by the internal standard method. IR spectra were recorded with a Perkin–Elmer Infracord Model 337 IR spectrophotometer. Triethyl-, triphenyl-, diphenyl- and vinyldiphenylsilane were purchased from commercial sources. Dimethylphenylsilane was prepared by LiAlH$_4$ reduction of dimethylphenylchlorosilane, the remaining dimethylarylsilanes by reaction of the appropriate Grignard reagent with dimethylchlorosilane, Me$_2$Si-HCl. The IR, NMR and mass spectra of these silanes are recorded in the Ph.D. thesis of R.D. (M.I.T., 1967). The refractive indices and spectral properties of the known silanes agreed well with literature data. All were available in 99 + % purity. Triethylgermane was prepared by the reduction of triethylbromogermane with lithium aluminum hydride in 66% yield; n_D^{25} 1.4311 (lit.[13] n_D^{20} 1.4330). The benzene used as solvent was distilled from calcium hydride or from sodium wire. (Iodomethyl)mercuric iodide was prepared by the method of Blanchard *et al.*[12], diphenylmercury by the reaction of phenylmagnesium bromide with mercuric chloride in THF.

Preparation of bis(bromomethyl)mercury

Diazomethane was prepared by the method of Moore and Reed[14] from 71.4 g (0.2 mole) of N,N'-dimethyl-N,N'-dinitrosoterephthalamide (du Pont EXR-101). The diazomethane solution was dried over 50 g of KOH pellets for 3 h, with occasional stirring. This solution then was decanted slowly into a 2 l flask containing a magnetically stirred suspension of 45.0 g (0.125 mole) of mercuric bromide (Mallinckrodt, analytical reagent) in 300 ml of dry diethyl ether. Initial addition caused precipitation of a dense, white solid, (bromomethyl)mercuric bromide, but further addition resulted in solution of all solids. The yellow solution was stirred for 30 min. The excess diazomethane was destroyed by distillation into a flask containing 20 ml of glacial acetic acid in 20 ml of diethyl ether. The remaining diethyl ether was removed, leaving a white solid. The latter was dissolved in 100 ml of chloroform and hexane was added slowly to the resulting solution at ambient temperature until cloudiness persisted in the mixture (*ca.* 30 ml). At this point a drop of colorless liquid settled to the bottom of the flask. Upon standing, this liquid crystallized and more solid formed. Recrystallization afforded an analytical sample of bis(bromomethyl)mercury, m.p. 43–44.5° (lit.[15] m.p. 42–43°), The yield of material of m.p. 41–42° was 34.8 g (72%). It must be noted that rapid removal of excess diazomethane is essential; this reduces substantially the formation of polymethylene, thus facilitating the purification of the product. (Found: C, 6.34; H, 1.04; Br, 41.11; Hg, 51.62. $C_2H_4Br_2Hg$ calcd.: C, 6.18; H, 1.04; Br, 41.14; Hg, 51.64%.) NMR (in CCl_4, Varian A60): δ 3.18 s ppm. IR (in CCl_4): 2950 w, 1385 w, 1110 m, 702 m cm^{-1}.

Reaction of triethylsilane with the ICH_2HgI/Ph_2Hg reagent

A 100 ml, three-necked flask equipped with reflux condenser, nitrogen inlet tube and magnetic stirring assembly was charged with 9.36 g (20 mmoles) of (iodomethyl)mercuric iodide (m.p. 115–118°), 7.09 g (20 mmoles) of diphenylmercury, 11.6 g (100 mmoles) of triethylsilane (Peninsular ChemResearch, Inc., redistilled) and 40 ml of dry benzene under nitrogen. The reaction mixture was stirred and heated at reflux for 20.5 h. Filtration gave 15.13 g of phenylmercuric iodide, m.p. 270–273° (m.p. of pure material, 273–274°), a yield of 93.5%. GLPC analysis of the filtrate after high vacuum trap-to-trap distillation showed that triethylmethylsilane was present in 83% yield (ethylbenzene internal standard). A sample of this product isolated by preparative GLPC had n_D^{20} 1.4151 (lit.[16] n_D^{20} 1.4156). Its IR spectrum was in excellent agreement with that published for this compound by Westermark[16].

Reaction of triethylsilane with bis(bromomethyl)mercury

A solution of 1.94 g (5 mmoles) of bis(bromomethyl)mercury and 5.81 g (50 mmoles) of triethylsilane in 15 ml of dry benzene under nitrogen was stirred at reflux. GLPC analysis of the reaction mixture (at 90°) showed that a single product had been formed, the yield of which did not increase significantly beyond a reaction time of 20 h. Trap-to-trap distillation at 0.3 mm (pot temperature to 50°) of the reaction mixture left a white solid. The latter was washed with cold benzene to give 1.80 g (96% yield) of $BrCH_2HgBr$, m.p. 119–123° (lit.[15] m.p. 124.5–125.5°). GLPC analysis of the distillate showed that triethylmethylsilane had been formed in 89% yield. NMR (in CCl_4): δ −0.04 (3H, CH_3) s; 0.2–1.3 (15H, Et_3Si) m ppm.

Reactions of the $Hg(CH_2Br)_2/Ph_2Hg$ reagent with organosilicon hydrides

Since in many cases of preparative interest it would not be desirable or practical to use the organosilicon hydride in large excess, these reactions were carried out with a stoichiometry of one Hg–CH₂Br group for one Si–H bond.

(*a*). *Triethylsilane*. A mixture of 10 mmoles of each organomercury compound and 20 mmoles of the silane in 13 ml of benzene to which 15.0 mmoles of ethylbenzene (GLPC internal standard) had been added was stirred at reflux under nitrogen. The progress of the reaction was monitored by GLPC. After 3 h, the Et₃SiMe yield was 11%, after 9 h, 26%, after 22 h, 44%, after 44 h, 59% and after 70 h, 68%. The reaction mixture was heated for another 21 h (91 h total). Filtration gave 5.69 g (80%) of phenyl-mercuric bromide, m.p. 279–282°. The filtrate was trap-to-trap distilled at 0.2 mm. Analysis by GLPC of the distillate showed the triethylmethylsilane yield to be 69%.

(*b*). *Triphenylsilane*. A solution of 10 mmoles of Hg(CH₂Br)₂, 10 mmoles of diphenylmercury and 20 mmoles of triphenylsilane (Peninsular ChemResearch) in 15 ml of benzene was stirred at reflux under nitrogen. The progress of the reaction was monitored by observation of the Si–H absorption at 2130 cm⁻¹ in the IR spectrum of the reaction mixture. After 12 days of reaction, the intensity of the Si–H absorption did not diminish further. Filtration of the reaction mixture gave 6.22 g of PhHgBr. The filtrate was concentrated to an oil and this was washed with heptane to extract the product. Evaporation of the heptane extracts left 4.62 g of crude methyltriphenyl-silane, m.p. 50–57°. Recrystallization from methanol gave 4.40 g (80%), m.p. 65–67° (undepressed mixture m.p. with authentic material prepared by reaction of methyl-lithium with triphenylsilane; lit.[17] m.p. 65–67°). The IR spectrum of this product agreed well with that published by Kanazashi and Takakusa[17]. NMR (in CCl₄): δ 0.8 (3H, CH₃) s; 7.1–7.7 ppm (15H, Ph₃Si).

(*c*). *Diphenylsilane*. A mixture of 20 mmoles each of Hg(CH₂Br)₂, diphenyl-mercury and diphenylsilane (Peninsular ChemResearch, Inc.) in 20 ml of dry benzene under nitrogen was stirred at reflux. After a reaction time of 16 days the Si–H absorp-tion intensity at 2140 cm⁻¹ did not diminish. Filtration gave 12.92 g (91%) of PhHgBr. Trap-to-trap distillation of the filtrate at 0.3 mm (pot temperature to 100°) and GLPC analysis of the distillate (F&M Model 5754, 10% LAC on Chromosorb W at 150°, methyl benzoate internal standard) showed that dimethyldiphenylsilane (83% yield) and methyldiphenylsilane (7%) were present. Samples were isolated by preparative GLPC.

MePh₂SiH, n_D^{25} 1.5670 (lit.[18] n_D^{20} 1.5694); ν(Si–H) 2125 cm⁻¹ (lit.[19] 2124 cm⁻¹).

Me₂SiPh₂, n_D^{25} 1.5606 (lit.[20] n_D^{25} 1.5607). (Found: C, 78.93; H, 7.63. C₁₄H₁₆Si calcd.: C, 79.18; H, 7.59%.) The IR spectrum was in excellent agreement with that described for this compound by Kanazashi and Takakusa[17].

(*d*). *Vinyldiphenylsilane*. A mixture of 10 mmoles each of Hg(CH₂Br)₂ and diphenylmercury and 20 mmoles of the silane in 10 ml of benzene was stirred at reflux under nitrogen. The intensity of the Si–H absorption at 2130 cm⁻¹ remained constant after a reaction time of 13 days. Filtration of the reaction mixture gave phenylmercuric bromide in 90% yield. Trap-to-trap distillation of the filtrate at 0.3 mm (pot temperature to 100°) was followed by GLPC analysis [same conditions as in (*c*)] of the distillate (diphenylmethane internal standard). It was found that methyl-diphenylvinylsilane was present in 83% yield. (Found: C, 80.05; H, 7.12. C₁₅H₁₆Si calcd.: C, 80.29; H, 7.19%.) The n_D^{25} was 1.5693 (lit.[21] n_D^{20} 1.5716). The IR spectrum

was in excellent agreement with that reported for this compound by Chumaevskii[22].

Reaction of the $Hg(CH_2Br)_2/Ph_2Hg$ reagent with triethylgermane.

A mixture of 8.5 mmoles each of $Hg(CH_2Br)_2$ and diphenylmercury and 17.0 mmoles of triethylgermane in 15 ml of dry benzene was stirred at reflux under nitrogen. The progress of the reaction was monitored by GLPC. After 4.5 h almost all of the germane had been consumed. Filtration of the reaction mixture gave 2.62 g (43%) of phenylmercuric bromide. The filtrate was trap-to-trap distilled at 0.25 mm (pot temperature to 90°), leaving 3.17 g of pale yellow oil which solidified on cooling. This material appeared to decompose on attempted recrystallization from ethanol and only metallic mercury (0.43 g) and phenylmercuric bromide (1.89 g, 31%) could be isolated.

The distillate was analyzed by GLPC (20% SE-30 at 117°, n-nonane internal standard) and found to contain triethylmethylgermane (40% yield), triethylbromo-germane ($\sim$9%) and hexaethyldigermoxane ($\sim$20%). The respective retention times were in the ratio 1/1.8/3.1.

Et_3GeMe, n_D^{25} 1.4307 (lit.[23] n_D^{20} 1.4328). Its IR spectrum was in excellent agreement with that published for this compound previously[23].

Et_3GeBr, n_D^{25} 1.4850 (lit.[24] n_D^{20} 1.4881). The IR spectrum checked well with that published by Cross and Glockling[25].

$Et_3GeOGeEt_3$, n_D^{25} 1.4588 (lit.[26] n_D^{20} 1.4612). IR (liq. film): 2950 s, 2930 (sh), 2905 s, 2870 s, 2825 w, 2730 w, 1460 m, 1430 m, 1380 w, 1235 w, 1020 s, 1005 (sh), 965 m, 855 m, 700 s, 670 (sh), 575 s,cm^{-1}.

Reactions of bis(bromomethyl)mercury with substituted phenyldimethylsilanes

The same procedure was used in all cases. A dry 50 ml, one-necked flask equipped with a magnetic stirring assembly and a reflux condenser topped with a nitrogen inlet tube was charged with 1 mmole of the silane, 4 mmoles of the mercurial and 5 ml of benzene. The mixture was stirred at $80.2\pm0.1°$ under nitrogen until the silane had been consumed. The product yield was determined by GLPC (F&M gas chromatograph, 4 ft × ¼ in 20% UCW 98 silicone rubber on Chromosorb W, 40–170°, chlorobenzene internal standard). The conversions listed in Table 2 were carried out. Authentic samples of the $ZC_6H_4SiMe_3$ compounds thus produced were prepared by reaction of the appropriate aryl Grignard reagent with trimethylchlorosilane. The physical and spectroscopic properties of these Grignard reaction-derived aryltri-methylsilanes in all cases agreed well with data given in the literature (*cf.* Ph. D. Thesis of R.D., M.I.T., 1967).

Competition of triethylsilane and 3-ethyl-2-pentene for a deficiency of bis(bromomethyl)-mercury

A mixture of 5 mmoles of the mercurial, 25 mmoles of the silane and 25 mmoles of the olefin (Eastman White Label, freshly distilled from $LiAlH_4$) in 15 ml of benzene was stirred at reflux under nitrogen for 20 h. Trap-to-trap distillation at 0.3 mm (pot temperature to 50°) left 1.80 g (96%) of $BrCH_2HgBr$, m.p. 118–122°. Ethylbenzene (4.0 mmoles) was added to the distillate as an internal standard; GLPC analysis showed that triethylmethylsilane (82% yield) and 1,1-diethyl-2-methylcyclopropane (7%) were present. A repetition of this experiment gave triethylmethylsilane in 66% yield, the cyclopropane in 6% yield.

An authentic sample of 1,1-diethyl-2-methylcyclopropane, n_D^{25} 1.4127, n_D^{30} 1.4159, was prepared by the Simmons–Smith procedure[27]. (Found: C, 85.19; H, 14.74. C_8H_{16} calcd.: C, 85.62; H, 14.38%.) It may be noted that 1,1-diethyl-2-methyl-cyclopropane can be prepared in 68% yield by the reaction of bis(bromomethyl)-mercury with 3-ethyl-2-pentene in benzene at 80° for 15 h[11].

"One-point" kinetic experiments

A typical experiment is described. Into a dry 5 ml volumetric flask was charged 0.1360 g (0.998 mmole) of dimethylphenylsilane and 1.1655 g (3.000 mmoles) of bis-(bromomethyl)mercury. The flask was filled to volume with dry benzene. Four ml of the resulting solution was transferred into a dry 50 ml flask equipped with a magnetic stirring unit and a reflux condenser topped with a nitrogen inlet tube. The solution was stirred for 4 days at $80.2 \pm 0.1°$. GLPC yield determination (6 ft $\times \frac{1}{4}$ in UCW 98 silicone rubber on Chromosorb W, 40–160°, chlorobenzene internal standard; F&M gas chromatograph) showed that trimethylphenylsilane was present in 74.2% yield. A duplicate experiment gave this silane in 75.4% yield.

Table 4 summarizes the results. Control experiments established that the products were stable to the reaction conditions. All apparatus used was washed with 5% sulfuric acid, rinsed with acetone and dried at 140°.

The average yields were converted to relative rate constants, $k_{rel} = k_Z/k_H$, as indicated in the discussion. The log k_{rel} values than were plotted vs. the appropriate σ, σ^+ and $\sigma°$ values for the substituents as compiled by Barlin and Perrin[28]. The slopes of the lines (i.e., the rho values) were calculated using a least squares program on an IBM 1620 Computer. Use of $\sigma°$ values gave the best correlation, $\rho = -1.31 \pm 0.04$; σ gave $\rho = -1.27 \pm 0.16$ and σ^+ gave $\rho = -0.958 \pm 0.228$.

TABLE 4

"ONE-POINT" KINETIC EXPERIMENTS. $Hg(CH_2Br)_2 + ZC_6H_4SiMe_2H$

Silane	Reaction time (days)	Yield of $ZC_6H_4SiMe_3$ (%)
$C_6H_5SiMe_2H$	4	74.2 (75.4)
	3	61.4 (59.8)
p-$FC_6H_4SiMe_2H$	4	42.9 (41.4)
m-$CF_3C_6H_4SiMe_2H$	4	17.1 (17.4)
p-$ClC_6H_4SiMe_2H$	4	34.4 (34.0)
p-$CH_3C_6H_4SiMe_2H$	3	93.5 (90.5)

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