Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

HALOMETHYL-METAL COMPOUNDS
XLII*. TRIMETHYLSILYL-SUBSTITUTED HALOMETHYLMERCURY COMPOUNDS AS PRECURSORS FOR TRIMETHYLSILYL-SUBSTITUTED CARBENES

DIETMAR SEYFERTH AND EARLE MARIE HANSON**
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received September 16th, 1970)

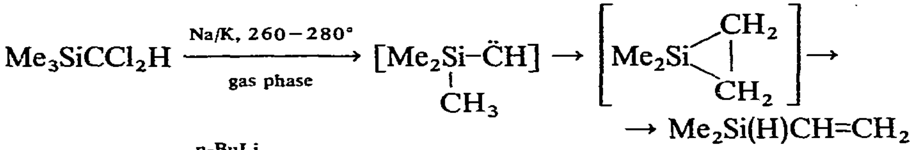
SUMMARY

The silicon-substituted organomercurials $(Me_3SiCCl_2)_2Hg$, $(Me_3SiCBr_2)_2Hg$ and $(Me_3SiCHBr)_2Hg$ have been evaluated as potential divalent carbon transfer agents. $(Me_3SiCCl_2)_2Hg$, in combination with an equimolar quantity of diphenylmercury, was found to react with olefins at ca. 120–130° to give *x*-chloro-*x*-trimethylsilylcyclopropanes in moderate to good yield. Me_3SiCCl_2–Hg bond homolysis, which is a minor side reaction at 120°, became the major process at 220°, and evidence indicates that the trimethylsilyldichloromethyl radicals formed couple and abstract hydrogen and chlorine. $(Me_3SiCBr_2)_2Hg$ reacted with cyclohexene at 95° in the presence of diphenylmercury to give 7-bromo-7-trimethylsilylnorcarane in moderate yield, but $(Me_3SiCHBr)_2Hg$ is too stable, even at 160°, to serve as a divalent carbon transfer agent.

INTRODUCTION

During the course of our studies concerning the use of functional halomethylmercury compounds as reagents for the generation of functional carbenes[1,3,4] we became interested in the possibility of an organomercury route to organosilicon-substituted carbenes.

At the time we began this investigation there were only two examples where a silyl-substituted carbene had been claimed as an intermediate [eqn. (1)[5] and (2)[6]]. In



$$Me_3SiCCl_2H \xrightarrow[\text{gas phase}]{\text{Na/K, 260-280°}} [Me_2\underset{CH_3}{Si}\text{-}\ddot{C}H] \rightarrow \left[Me_2Si\begin{smallmatrix}CH_2\\ |\\ CH_2\end{smallmatrix}\right] \rightarrow Me_2Si(H)CH{=}CH_2 \qquad (1)$$

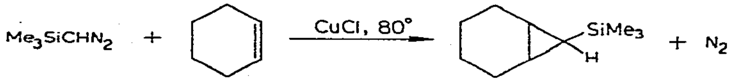
$$Me_3SiCH_2Cl \xrightarrow{\text{n-BuLi}} [Me_3SiCHClLi] \rightarrow [MeSi\ddot{C}H] \rightarrow Me_3SiCH{=}CHSiMe_3 + \text{other products} \qquad (2)$$

---

* For part XLI see ref. 1; for preliminary communication see ref. 2.

** National Institutes of Health Predoctoral Fellow, 1965–1969.

both cases the evidence for the intermediacy of Me_3SiCH was circumstantial at best, and when reaction (2) was carried out in the presence of cyclohexene, no 7-trimethylsilylnorcarane was detected[6]. While the present investigation was in progress, Connally and Urry [7,8] reported on the generation of silyl-substituted carbenes (or carbenoids) by the action of metallic sodium on trialkyl(chloromethyl)silanes and several groups prepared silyl-substituted diazoalkanes[9–13], reagents which were shown to be useful precursors for silyl-substituted carbenes[10,11], *e.g.*:



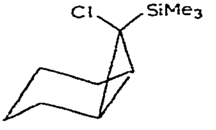
(3)

In the present paper we describe the use of $(Me_3SiCCl_2)_2Hg$[14], $(Me_3SiCBr_2)_2Hg$[15] and $(Me_3SiCHBr)_2Hg$[15] as sources of the Me_3SiCCl, Me_3SiCBr and Me_3SiCH reagents, respectively.

RESULTS AND DISCUSSION

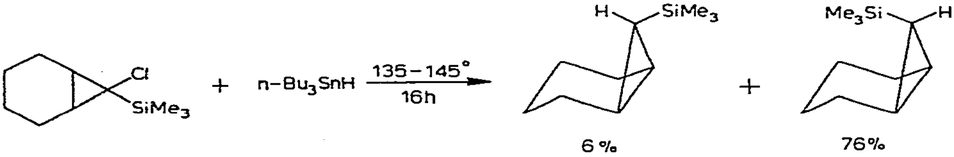
Bis(trimethylsilyldichlormethyl)mercury

When a solution of bis(trimethylsilyldichloromethyl)mercury in cyclohexene was heated at reflux for 7 days, no volatile products were formed and a quantitative recovery of starting material was obtained. The thermal decomposition of this mercury compound to give trimethylsilylchlorocarbene was realized when a mixture of $(Me_3SiCCl_2)_2Hg$ and a tenfold excess of cyclohexene in bromobenzene solution was heated at reflux (120°) for 6 days. Metallic mercury and Me_3SiCCl_2HgCl were among the solid products, and the volatile products included Me_3SiCCl_2H (35%), 7-chloro-7-trimethylsilylnorcarane (24%) and bis(3-cyclohexenyl)methane (4%). It appears that the 7-chloro-7-trimethylsilylnorcarane was obtained in the form of a single isomer and it is probable (but not certain) that it is the less sterically hindered one in which the trimethylsilyl group is *anti* with respect to the tetramethylene bridge (I).



(I)

Further proof of identity was given by the reduction of the 7-chloro-7-trimethylsilylnorcarane with tri-n-butyltin hydride[16] to give a mixture of *anti*-7-trimethylsilylnorcarane (6% yield) and the *syn* isomer (76% yield) [eqn. (4)]. The latter two products are known and their structures have been assigned[9]. The ratio of *syn*/*anti*-7-trimethylsilylnorcarane gives no indication of which isomer of 7-chloro-7-trimethylsilylnorcarane we are dealing with since organotin hydride reductions are known to



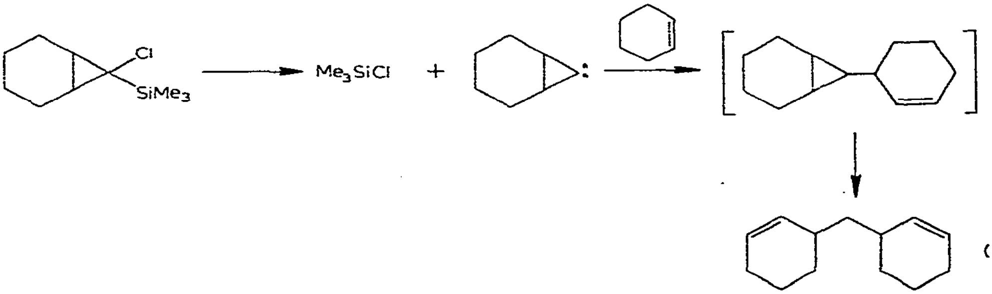
(4)

proceed via a radical chain mechanism and in most cases do not occur with retention of configuration[17].

The trimethyl(dichloromethyl)silane probably was formed by the homolytic cleavage of the C–Hg bond in either the starting material or in trimethylsilyldichloromethylmercuric chloride followed by hydrogen atom abstraction by the resulting trimethylsilyldichloromethyl radical. The presence of metallic mercury is in line with such an explanation.

Bis(3-cyclohexenyl)methane (position of unsaturation uncertain) was identified by comparison of its IR and NMR spectra with those of an authentic sample to which this structure had been assigned[18]. This product probably resulted from decomposition of 7-chloro-7-trimethylsilylnorcarane as shown in eqn. (5)[18].

The isolation of trimethylsilyldichloromethylmercuric chloride in this reaction of bis(trimethylsilyldichloromethyl)mercury suggests that the second trimethylsilyldichloromethyl group is "inert" with respect to Me_3SiCCl. To allow utilization of the second Me_3SiCCl_2 group, one molar equivalent of diphenylmercury was added to such $(Me_3SiCCl_2)_2Hg$ reactions. Thus treatment of a 1/1 bis(trimethylsilyldichloromethyl)mercury/diphenylmercury mixture with a fivefold excess of cyclohexene in n-decane solution at 118° for 10 days gave trimethyl(dichloromethyl)silane (16%), 7-chloro-7-trimethylsilylnorcarane (62%, based on both Me_3SiCCl_2 groups), bis(3-cyclohexenyl)methane (3%) and phenylmercuric chloride (82%) [eqn. (6)]. Similarly,



(5)

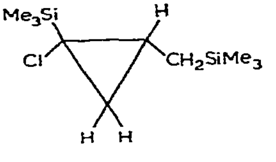
(6)

a 1/1 Me_3SiCCl_2HgCl/Ph_2Hg mixture reacted with cyclohexene in bromobenzene solution (123°, 9 days) to give the expected norcarane (46%), as well as phenylmercuric chloride (74%), trimethyl(dichloromethyl)silane (14%) and several minor products. The effect of the added diphenylmercury in these reactions no doubt is due to the known facile substituent exchange which occurs in organomercury systems. Such an exchange [eqn. (7) and (8)] could generate $PhHgCCl_2SiMe_3$, a possibly active reagent, and $(Me_3SiCCl_2)_2Hg$ whose reactivity already has been demonstrated. The "activating" effect of diphenylmercury on nonreactive halomethylmercury systems had been discovered earlier in the case of bromomethylmercuric bromide, and there the formation of $Hg(CH_2Br)_2$ in the $Ph_2Hg+BrCH_2HgBr$ reaction could be demonstrated[19].

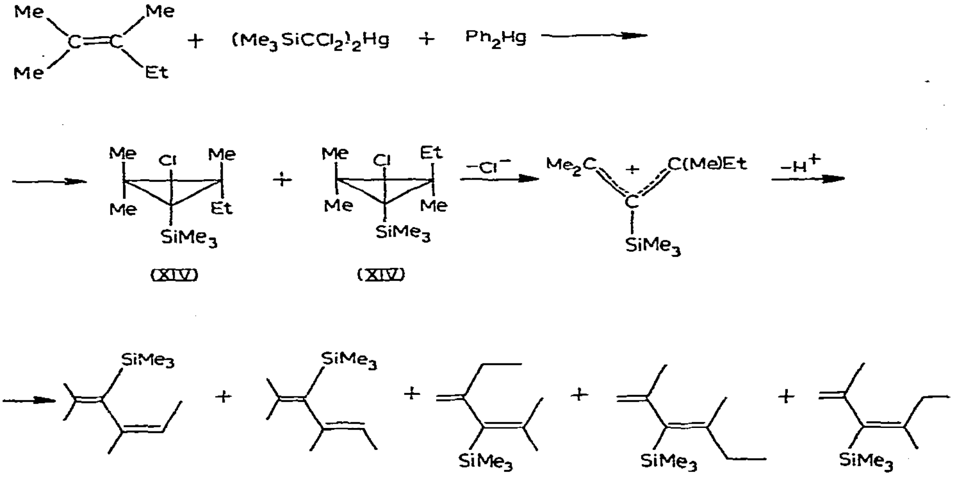
$$Me_3SiCCl_2HgCl+Ph_2Hg \rightleftarrows PhHgCCl_2SiMe_3+PhHgCl \qquad (7)$$

$$2\,PhHgCCl_2SiMe_3 \rightleftarrows Ph_2Hg + Hg(CCl_2SiMe_3)_2 \qquad (8)$$

Several other trimethylsilylchlorocarbene transfer reactions were carried out using the bis(trimethylsilyldichloromethyl)mercury/diphenylmercury system. Reaction of this reagent pair with cyclooctene in chlorobenzene solution for 8 days at 125–135° gave 9-chloro-9-trimethylsilylbicyclo[6.1.0]nonane in 73% yield and phenylmercuric chloride (98%). Reaction of this two-mercurial system with an excess of allyltrimethylsilane in bromobenzene solution for 3 days at 135–155° resulted in the formation of metallic mercury (7%), phenylmercuric chloride (83%), 1-chloro-1-trimethylsilyl-2-trimethylsilylmethylcyclopropane [(II), (37%)], trimethyl(dichloromethyl)silane (3%), trimethyl(trichlorovinyl)silane (3%), as well as other minor products. (The reaction which gives the trichlorovinylsilane will be discussed below.) A similar reaction with 1-heptene gave the expected 1-n-pentyl-2-chloro-2-trimethylsilylcyclopropane in 41% yield. The Me_3SiCCl adduct of 2,3-dimethyl-2-pentene was not sufficiently stable thermally to survive the rather drastic reaction conditions (11 days at 120° in chlorobenzene solution). Two major products were obtained in ca. 11% combined yield, and for these the formula $C_{11}H_{22}Si$ was indicated by mass spectral and combustion analysis. Their mixture could not be resolved by GLC, but an NMR spectrum of the mixture supported a butadiene structure; the major isomer contains one ethyl group, two methyl groups and two vinyl hydrogens with different environments and the minor isomer contains four methyl groups and one vinyl proton which has the same chemical shift as one of the vinyl protons of the major isomer. Such compounds would arise from the expected 1,1,2-trimethyl-2-ethyl-3-chloro-3-trimethylsilylcyclopropane as indicated below[20]. Other minor products with GLC retention



(II)



times similar to those of the major products were present as well and this suggests that most, if not all, of the possible butadiene isomers were formed to a small extent.

Another useful reaction of dihalocarbenes is their insertion into the silicon–hydrogen bond of organosilicon hydrides[21]. Such a reaction was also found to occur with $(Me_3SiCCl_2)_2Hg$. When an equimolar mixture of this mercurial and diphenylmercury was heated with a tenfold excess of triethylsilane at 126° for 3 days in chlorobenzene solution, the expected insertion product, triethylsilyl(trimethylsilyl)chloromethane was produced in 42% yield, together with triethylsilyl(trimethylsilyl)methane in 7% yield. Triethylchlorosilane also was present. Phenylmercuric chloride was not isolated; instead the mercury charged was present as metallic mercury and diphenylmercury. The known reactivity of triethylsilane as a reducing agent serves to explain these findings [eqns. (9) and (10)]. By extending the reaction time to 6 days

$$Et_3SiCHClSiMe_3 + Et_3SiH \rightarrow Et_3SiCH_2SiMe_3 + Et_3SiCl \tag{9}$$

$$PhHgCl + Et_3SiH \rightarrow Et_3SiCl + [PhHgH] \rightarrow \tfrac{1}{2}\,Ph_2Hg + \tfrac{1}{2}\,Hg + \tfrac{1}{2}\,H_2 \tag{10}$$

under these conditions, it was possible to make reaction (9) go nearly to completion, giving triethylsilyl(trimethylsilyl)methane in 80% yield.

In many of these reactions trimethyl(dichloromethyl)silane was a by-product, and, as mentioned, we believed that a free radical process was responsible for its formation. To obtain more information concerning this point, the thermolysis of bis(trimethylsilyldichloromethyl)mercury at higher temperatures was investigated. When this mercurial was heated alone in an oil bath at 220°, a large number of products resulted. The expected "carbene dimer", 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene, was obtained in 14% yield, but the major products were trimethylchlorosilane (34%) and trimethyl(trichlorovinyl)silane (40%). Minor amounts of trimethyl(dichloromethyl)silane (2.5%), trimethyl(trichloromethyl)silane (4.5%) and several unidentified products also were present, and metallic mercury was produced. These products suggest that at this higher temperature the predominant decomposition process is homolytic cleavage of the C–Hg bond [eqn. (11)] followed by hydrogen atom abstraction [eqn. (12)], chlorine atom abstraction [eqn. (13)] and coupling reactions [eqn. (14)] by the trimethylsilyldichloromethyl radical formed. The tendency of most dialkylmercury compounds to decompose thermally to give free alkyl

$$(Me_3SiCCl_2)_2Hg \xrightarrow{220^\circ} 2\,Me_3Si\dot{C}Cl_2 + Hg \tag{11}$$

$$Me_3Si\dot{C}Cl_2 \xrightarrow{RH} Me_3SiCCl_2H \tag{12}$$

$$Me_3Si\dot{C}Cl_2 \xrightarrow{RCl} Me_3SiCCl_3 \tag{13}$$

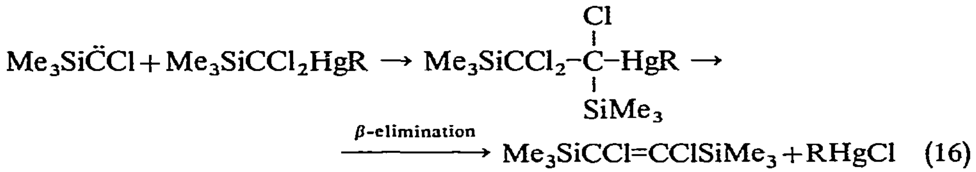
$$\begin{aligned} 2\,Me_3Si\dot{C}Cl_2 &\rightarrow [Me_3SiCCl_2CCl_2SiMe_3] \rightarrow \\ &\rightarrow Me_3SiCCl{=}CCl_2 + Me_3SiCl \end{aligned} \tag{14}$$

radicals and elemental mercury is well known, and examples of thermal β-elimination of trimethylchlorosilane from β-chloroethylsilicon compounds of the type shown in eqn. (14) have been noted previously[22]. Confirmation of such a homolytic cleavage mechanism was obtained when the pyrolysis of this mercurial was carried out at 220°

in diphenylmethane solution, *i.e.*, in a good hydrogen atom donor medium. In this case the principal product was trimethyl(dichloromethyl)silane (73%). Trimethyl(trichlorovinyl)silane and 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene again were formed, but in much lower yield, 13% and 4%, respectively.

The most probable route to 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene in these reactions is shown in eqn. (15) and (16). The insertion of dichlorocarbene into alkyl–mercury bonds is a known reaction[23], and to be noted especially in this connection is our recent report of the insertion of CCl_2 into the C–Hg bond of Me_3SiCCl_2–Hg compounds [eqn. (17)][24].

$$\mathrm{Me_3SiCCl_2HgCCl_2SiMe_3 \rightarrow Me_3Si\ddot{C}Cl + Me_3SiCCl_2HgCl} \qquad (15)$$



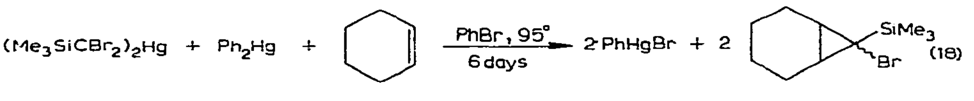
$$\mathrm{Me_3Si\ddot{C}Cl + Me_3SiCCl_2HgR \rightarrow Me_3SiCCl_2{-}\overset{\displaystyle Cl}{\underset{\displaystyle SiMe_3}{C}}{-}HgR \rightarrow \xrightarrow{\beta\text{-elimination}} Me_3SiCCl{=}CClSiMe_3 + RHgCl} \qquad (16)$$

$$\mathrm{Me_3SiCCl_2HgBr + CCl_2\ (via\ PhHgCCl_2Br) \rightarrow [Me_3SiCCl_2CCl_2HgBr] \rightarrow \underset{(82\%)}{Me_3SiCCl{=}CCl_2} + HgClBr} \qquad (17)$$

Bis(trimethylsilyldibromomethyl)mercury

Since in general α-elimination of Hg–Br from a halomethylmercury compound is a much more façile process than elimination of Hg–Cl[25], an investigation of $(Me_3SiCBr_2)_2Hg$ was of interest. An equimolar mixture of bis(trimethylsilyldibromomethyl)mercury[15] and diphenylmercury was heated with cyclohexene in chlorobenzene solution at reflux (115°). After 48 h the starting materials had been consumed (TLC) and phenylmercuric bromide was formed in 81% yield. The expected 7-bromo-7-trimethylsilylnorcarane, however, was present in only 36% yield, together with six minor products. Trimethyl(dibromomethyl)silane was not among these, nor was metallic mercury formed. Thus, as expected, bis(trimethylsilyldibromomethyl)mercury is a more reactive divalent carbon transfer agent than is its chlorine analog, but its application as a preparative reagent is undermined by the lesser stability of *x*-bromo-*x*-trimethylsilylcyclopropanes, as compared with the chlorine analogs.

Trimethylsilylbromocarbene could be generated from the mercurial at 95°, but longer reaction times were required; the results of an experiment with cyclohexene are summarized by eqn. (18). Both isomers of 7-bromo-7-trimethylsilylnorcarane were present, one in 48% yield, the other in 3% yield. Fewer by-products were formed at the lower temperature. It is apparent that bis(trimethylsilyldibromomethyl)mercury provides a useful route to trimethylsilylbromocarbene, and a more careful study of optimum reaction conditions should be worthwhile.



Bis(trimethylsilylbromomethyl)mercury

Bis(trimethylsilylbromomethyl)mercury was prepared[15] as a potential trimethylsilylcarbene source. However, this organomercury compound was very stable thermally; when it was heated, together with an equimolar quantity of diphenylmercury, in cyclohexene solution in a bomb tube at 160° for 7 days, phenylmercuric bromide was formed in only 19% yield and large amounts of starting mercurials were recovered. Some trimethylsilylcarbene-derived products were formed: *anti*-7-trimethylsilylnorcarane (9%), *trans*-1,2-bis(trimethylsilyl)ethylene (4%) and its *cis* isomer (1%), as well as five minor products. Thermolysis of $(Me_3SiCHBr)_2Hg$ at higher temperatures (190–210°) as the pure material gave over 20 volatile products: metallic mercury (60%), trimethyl(dibromomethyl)silane (15%), trimethyl(bromomethyl)silane (36%), *trans*-1,2-bis(trimethylsilyl)ethylene, methylmercuric bromide (8%). Clearly, homolytic cleavage of the C–Hg bond predominates at the higher temperatures.

CONCLUSIONS

This study has shown that $(Me_3SiCCl_2)_2Hg$ and $(Me_3SiCBr_2)_2Hg$ find limited application as divalent carbon transfer agents. They are very stable thermally in comparison to $PhHgCCl_3$ and $PhHgCBr_3$, requiring long reaction times at relatively high temperatures in their synthetic utilization. The high temperatures required introduce two complications: a minor one is that by-products from free radical decomposition of the mercurials are encountered; a major one is that some of the cyclopropane products, especially those with several alkyl substituents, have only limited thermal stability and do not survive the reaction conditions. However, these new silicon-substituted organomercury reagents do allow the preparation in fair to good yield of silicon-substituted cyclopropanes which would be difficult to prepare by other methods and as such may find useful application in organosilicon synthesis. On the other hand, $(Me_3SiCHBr)_2Hg$ does not appear to be a useful reagent: it is too stable, and when it does decompose, carbon–mercury bond homolysis is the major reaction course. A discussion of the factors which appear to be of importance in contributing to the stability of these reagents with respect to divalent carbon extrusion will be deferred until a later paper of this series.

EXPERIMENTAL

General Comments

IR spectra were recorded using a Perkin–Elmer Model 337 or 237B grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 NMR spectrometer. Unless otherwise stated, chloroform was used as internal standard and related to an external chloroform/TMS sample. Chemical shifts are expressed in δ units, ppm downfield from TMS. Mass spectra were obtained using a Hitachi–Perkin–Elmer RMU6D spectrometer. Gas-liquid partition chromatography (GLC) was used extensively for separation and purification of products and for yield determinations. Most of the GLC analyses reported here were performed using an F&M Model 5754 gas chromatograph with a 6 foot column containing 10% Dow Corning DC-200 silicone oil on 80–100 mesh Chromosorb W, with a temperature program of 40–190° at 6° per min. Yields were determined using the internal standard procedure.

All solvents were dried prior to use. Bromobenzene, chlorobenzene and n-decane were dried over anhydrous calcium chloride and then distilled. Benzene and cyclooctene were dried over and distilled from calcium hydride. Cyclohexene was distilled from lithium aluminum hydride. The preparation of the starting mercurials is described in previous papers of this series[14,15].

Mercurial thermolyses generally were carried out in a dry 50 ml three-necked round bottom flask equipped with a magnetic stirring unit, a thermometer and a reflux condenser topped with a gas inlet tube. The solid organomercury reagents were added to the flask and the system was evacuated for several hours. Prepurified nitrogen then was introduced and a nitrogen atmosphere was maintained during the reaction. Solvent and substrate were added and the reaction mixture was stirred and heated as specified. The progress of the reactions was monitored by thin layer chromatography (TLC) using Eastman silica gel TLC sheet, type K301-R. The sheet was developed using 20% benzene in cyclohexane. After it had been dried, the sheet was visualized in an iodine chamber followed by spraying with 10% sodium sulfide in 50% aq. ethanol.

In cases where higher temperatures were needed, the reactions were carried out in a heavy walled Pyrex bomb tube which was heated in a steel casing wrapped with chromel wire and insulation. The temperature control was approximately ± 10°.

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with cyclohexene in n-decane

A solution of $(Me_3SiCCl_2)_2Hg$ (2.52 g, 4.92 mmol), diphenylmercury (1.83 g, 5.15 mmol) and cyclohexene (8.60 g, 0.10 mol) in 25 ml of n-decane was heated at reflux (118°) under nitrogen. After 10 days, TLC indicated that less than 5% of $(Me_3SiCCl_2)_2Hg$ remained. The yellow reaction mixture was filtered from 2.21 g of white phenylmercuric chloride and metallic mercury. This mixture was extracted with hot *N*,*N*-dimethylformamide (DMF), leaving 0.074 g (4%) of metallic mercury, indicating a 2.14 g (68%) yield of phenylmercuric chloride. The filtrate was trap-to-trap distilled at 5×10^{-5} mm into a receiver at −78°. The pot residue, a yellow oily solid, 0.41 g, consisted (TLC) mainly of phenylmercuric chloride, giving a total yield of 82%. GLC analysis showed the presence of trimethylchlorosilane (yield not determined), trimethyl(dichloromethyl)silane (16%), 7-chloro-7-trimethylsilylnorcarane (62%) and assumed bis(3-cyclohexenyl)methane. The known compounds were identified by comparison of their GLC retention times and IR spectra with those of authentic samples. 7-Chloro-7-trimethylsilylnorcarane had n_D^{25} 1.4794. (Found: C, 59.53; H, 9.54; Cl, 17.26. $C_{10}H_{19}ClSi$ calcd.: C, 59.23; H, 9.44; Cl, 17.48%.) NMR (in $CHCl_3$): δ 0.02 (s, 9 H, Me_3Si); 0.87–2.0 ppm (m, 10 H). IR (liq. film): 2990 (sh), 2940 s, 2900 (sh), 2870 (sh), 2855 m, 2650 w, 1462 m, 1450 m, 1400 w, 1350 w, 1315 w, 1268 (sh), 1258 s, 1230 w, 1180 w, 1170 w, 1138 w, 1085 w, 1050 m, 1040 m, 990 m, 950 w, 930 s, 870 s, 845 s, 825 w, 805 m, 775 w, 765 m, 745 m, 735 m, 690 m, 655 m and 625 m cm^{-1}.

In a similar experiment a mixture of 2.07 mmol of diphenylmercury and 2.10 mmol of $(Me_3SiCCl_2)_2Hg$ was refluxed (119°) with cyclohexene in chlorobenzene solution for 8 days to give metallic mercury (4%), phenylmercuric chloride (quantitative), and 7-chloro-7-trimethylsilylnorcarane (63%), as well as other minor products.

In another reaction, 3.03 mmol of $(Me_3SiCCl_2)_2Hg$ and 63.5 mmol of cyclohexene in 20 ml of bromobenzene were stirred and heated at reflux (120°) for 6 days. The volatile products were trimethyl(dichloromethyl)silane (35%), 7-chloro-7-trimethylsilylnorcarane (24%) and bis(3-cyclohexenyl)methane (4%). The solid products contained elemental mercury in about 8% yield. The solids were extracted with hexane and chloroform to give white crystals whose IR spectrum and TLC behavior were identical with those of authentic[14] Me_3SiCCl_2HgCl. No reaction occurred when $(Me_3SiCCl_2)_2Hg$ (2.72 mmol) was heated in refluxing cyclohexene (28 ml) for one week; mercurial recovery was quantitative.

A reaction of 3.8 mmol of Me_3SiCCl_2HgCl, 4.05 mmol of diphenylmercury and 21.5 mmol of cyclohexene in 15 ml of bromobenzene at 123° for 9 days gave phenylmercuric chloride (74%) contaminated with a small (6%) amount of mercury, as well as Me_3SiCCl_2H (14%), 7-chloro-7-trimethylsilylnorcarane (46%) and bis(3-cyclohexenyl)methane (2%). A similar reaction carried out without added diphenylmercury gave no 7-chloro-7-trimethylsilylnorcarane. The only volatile product in any amount was trimethyl(dichloromethyl)silane.

Reduction of 7-chloro-7-trimethylsilylnorcarane with tri-n-butyltin hydride

A mixture of 0.48 g (2.36 mmol) of 7-chloro-7-trimethylsilylnorcarane and 1.016 g (3.5 mmol) of tri-n-butyltin hydride was heated and stirred (under nitrogen) at 135–145° for 16 h. Trap-to-trap distillation at 10^{-4} mm was followed by GLC analysis of the distillate (10% Carbowax 20M on Chromosorb W, 60–190° at 6° per min) showed the presence of 1.80 mmol of *syn*-7-trimethylsilylnorcarane (76%), 0.14 mmol of *anti*-7-trimethylsilylnorcarane (6%) and tri-n-butyltin chloride in greater than 90% yield. The trimethylsilylnorcaranes were identified by comparison of their GLC retention times and infrared spectra with those of authentic samples[10].

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with cyclooctene

Cyclooctene (12.21 g, 99 mmol) and 5.1 mmol each of the two organomercury compounds were heated at 125–135° in 15 ml of chlorobenzene for 7 days, until TLC showed that the mercurials had been consumed (>95%). Filtration gave 2.75 g of phenylmercuric chloride contaminated with 0.014 g of metallic mercury. Trap-to-trap distillation of the filtrate left 0.37 g of phenylmercuric chloride (total yield, 98%) and some yellow oil. GLC analysis of the distillate showed the presence of 9-chloro-9-trimethylsilylbicyclo[6.1.0]nonane in 73% yield and also of two minor products, each present in less than 5% yield. (One of these may have been the other product isomer.) The product, a white solid with m.p. 41–42° (sealed tube) was purified by sublimation at room temperature (0.6 mm). (Found: C, 62.67; H, 10.05; Cl, 15.34. $C_{12}H_{23}ClSi$ calcd.: C, 62.43; H, 10.04; Cl, 15.36%.) NMR (in $CHCl_3$): δ 0.15 (s, 9 H, Me_3Si) and 1.23–2.08 ppm (m, 12 H). IR (CCl_4/CS_2 composite): 2980 m, 2932 s, 2860 s, 2690 w, 1480 m, 1460 m, 1410 w, 1370 w, 1270 w, 1267 s, 1238 w, 1218 w, 1190 w, 1165 w, 1155 w, 1070 m, 1031 m, 1022 (sh), 905 s, 880 w, 858 s, 840 s, 820 w, 778 w, 758 m, 745 m, 690 m, and 622 m cm^{-1}.

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with allyltrimethylsilane

A 6.39/6.97 mmol mixture of these mercurials and 88.5 mmol of allyltrimethylsilane in 15 ml of bromobenzene was heated at 135° for 3 days. The solids consisted of PhHgCl (83% yield) and metallic mercury (7%). The trap-to-trap distilled (at 0.001 mm) filtrate was shown by GLC analysis to contain 1-chloro-1-trimethylsilyl-2-trimethylsilylmethylcyclopropane (II) in 37% yield, as well as trimethyl(dichloromethyl)silane (2%), trimethyl(trichlorovinyl)silane (3%) and over ten higher-boiling minor products. The main product, (I), had n_D^{25} 1.4512 (isolation by GLC). (Found: C, 51.18; H, 10.11; Cl, 14.80. $C_{10}H_{23}ClSi_2$ calcd.: C, 51.13; H, 9.87; Cl, 15.09%.) IR (liq. film): 3060 w, 2990 (sh), 2960 s, 2920 w, 2900 m, 2880 (sh), 2800 w, 1445 w, 1410 m, 1370 m, 1300 w, 1270 (sh), 1255 s, 1230 w, 1205 w, 1185 w, 1140 w, 1062 m, 1045 (sh), 1032 m, 942 m, 840–870 s, 758 (sh), 750 m, 700 m, and 628 m cm^{-1}.

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with 1-heptene

A 6.07/6.35 mmol mixture of these mercurials and 61.5 mmol of 1-heptene (Chemical Samples, Inc.) in 12 ml of bromobenzene was heated at 121° for 9 days. The PhHgCl and metallic mercury yields were 77% and 8%, respectively. The trap-to-trap distilled volatiles contained (by GLC) 1-n-pentyl-2-chloro-2-trimethylsilylcyclopropane (40%), Me_3SiCCl_2H (2%) and six other minor products. The major product had n_D^{25} 1.4474. (Found: C, 60.40; H, 10.34; Cl, 16.74. $C_{11}H_{23}ClSi$ calcd.: C, 60.37; H, 10.59; Cl, 16.20%.)

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with 2,3-dimethyl-2-pentene

The two mercurials (4.4 mmol each) and 71.5 mmol of the olefin (Chemical Samples, Inc.) in 23 ml of chlorobenzene were heated at 120° for 11 days. The usual work-up was followed by GLC analysis of the distilled volatile products. Two major products were present which could not be completely resolved using several different GLC columns and at least eleven other compounds were observed, all present in very low yield. The major products (ca. 11% combined yield) were collected and characterized as the mixture. (Found: C, 72.03; H, 12.11. $C_{11}H_{22}Si$ calcd.: C, 72.44; H, 12.16%.) IR (liq. film): 3090 w, 3010 (sh), 2980 s, 2920 m, 2870 w, 1640 m, 1620 m, 1460 m, 1410 w, 1375 m, 1262 (sh), 1255 s, 1075 w, 1020 w, 1000 w, 905 w, 900 m, 885 m, 840 s, 760 m, 690 m, and 640 w cm^{-1}. NMR (in $CHCl_3$; a mixture of both isomers A and B, richer in A): δ 0.07 (s, Me_3Si of B), 0.10 (s, Me_3Si of A), 0.99 (t, J 7 Hz, $MeCH_2$ of A, further split by longe-range coupling), 2.1 (q, J 7 Hz, $MeCH_2$ of A, further split by long-range coupling), 1.58–1.83 (m, alkyl groups of A and B), 4.31 (s, greatly split, vinylic H of A), 4.75 ppm (s, greatly split, vinylic H of A and B). These data do not permit a definite structural assignment to A and B, but it is apparent that A contains an ethyl group and two vinylic hydrogens, while B contains one vinylic hydrogen. Mass spectrum: molecular ion at m/e 182, other major fragments at m/e 73 (Me_3Si^+), 97 ($Me_2SiC{\equiv}CMe^+$) and 167 ([$M{-}CH_3^+$]).

Reaction of bis(trimethylsilyldichloromethyl)mercury/diphenylmercury with triethylsilane

A 5.0/5.12 mmol mixture of the two mercurials and 12.73 g (0.11 mol) of triethylsilane (Peninsular ChemResearch) in 20 ml of chlorobenzene was heated at 126° for 72 h. At the end of this time, no phenylmercuric chloride was visible, but a large amount of metallic mercury was present. TLC showed that all of the $(Me_3SiCCl_2)_2Hg$

had been consumed, but diphenylmercury was still present in large amount; a trace amount of PhHgCl was present. Filtration under nitrogen gave 0.998 g (4.97 mmol) of metallic mercury [99% yield based on conversion of the expected PhHgCl to Hg and Ph_2Hg, eqn. (10)]. Trap-to-trap distillation of the filtrate at 3×10^{-5} mm left 1.76 g (99%) of white, solid diphenylmercury, m.p. 125–126°. GLC analysis of the distillate showed the presence of triethylchlorosilane (56% yield, based on available Cl), $Et_3SiCHClSiMe_3$ (42%), $Et_3SiCH_2SiMe_3$ (4%) and two minor products. The major product had n_D^{25} 1.4675. (Found: C, 50.63; H, 10.62; Cl, 14.74. $C_{10}H_{25}ClSi_2$ calcd.: C, 50.69; H, 10.63; Cl, 14.96%.) IR (liq. film): 2955 s, 2910 m, 2880 m, 1460 w, 1420 w, 1270 (sh), 1268 s, 1050 m, 1020 m, 1015 m, 975 w, 865 s, 842 s, 804 m, 765 m, 752 w, 730 w, 712 w, 695 w, 672 w, and 628 w cm^{-1}. NMR (in $CHCl_3$): δ 0.185 (s, 9 H, Me_3Si), 0.52–1.20 (m, 15 H, Et_3Si), 2.6 ppm (s, 1 H, CHCl). The other two products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples.

A similar reaction was carried out (in n-decane solution) at 125° for 3 days; at the end of this time TLC showed that all of the $(Me_3SiCCl_2)_2Hg$ had reacted. The solution, now containing $Me_3SiCHClSiEt_3$ and excess of triethylsilane, was heated at reflux for another three days. Similar work-up gave metallic mercury (85%, based on all starting mercury compounds) and diphenylmercury in only 17% yield. The volatile products contained $Me_3SiCH_2SiEt_3$ (80%), triethylchlorosilane (85%), benzene (44%), as well as trimethylchlorosilane, hexamethyldisiloxane and other minor products. $Me_3SiCH_2SiEt_3$ had n_D^{25} 1.4419. (Found: C, 59.15; H, 12.95. $C_{10}H_{26}Si_2$ calcd.: C, 59.32; H, 12.94%.) IR (liq. film): 2955 s, 2910 s, 2880 s, 2800 w, 2730 w, 1460 m, 1415 m, 1378 w, 1265 (sh), 1253 s, 1060 s, 1020 s, 995 w, 860 s, 835 s, 775 s, 760 (sh), 725 m, 710 m, and 688 m cm^{-1}. NMR (in $CHCl_3$): δ 0.67 (s, 9 H, Me_3Si) and 0.37–1.4 ppm (m, 17 H, Et_3SiCH_2).

High temperature thermolysis of bis(trimethylsilyldichloromethyl)mercury

A dry, nitrogen-flushed 25 ml flask containing 3.00 g (5.85 mmol) of the mercurial attached to a short path distillation unit was immersed in an oil bath and heated under nitrogen at 220°. Some liquid distilled into the receiver and small droplets of mercury appeared on the sides of the still head. After ca. 60 min, the material remaining in the still pot was trap-to-trap distilled at 0.001 mm, leaving behind gray solid plus metallic mercury. GLC analysis of the distillate showed the presence of trimethylchlorosilane (34%), trimethyl(dichloromethyl)silane (2.5%), trimethyl(trichloromethyl)silane (4.5%), trimethyl(trichlorovinyl)silane (40%) and 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene (14%) [yields based on eqn. (11)–(14)]. The first four products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples. Trimethyl(trichlorovinyl)silane was known to us from another investigation[24]. The following data support the structure of 1,2-dichloro-1,2-bis(trimethylsilyl)ethylene, m.p. 48–49°. (Found: C, 39.62; H, 7.43. $C_8H_{18}Si_2Cl_2$ calcd.: C, 39.82; H, 7.52%.) Mass spectrum: molecular ion peaks at *m/e* 240, 242 and 244 in 9/6/1 ratio, indicating the presence of 2 chlorine atoms. Other major fragments: *m/e* 43, 45, 73 (Me_3Si^+), 93, 95 (Me_2SiCl^+) and 117, 119 ($Me_2SiC{\equiv}CCl^+$). IR (CCl_4/CS_2 composite): 2975 (sh), 2960 s, 2900 m, 2790 w, 1945 w, 1455 w, 1414 m, 1300 w, 1268 (sh), 1258 s, 860–850 s, 785 m, 765 s, 700 m, and 663 m cm^{-1}. NMR (in $CHCl_3$): δ 0.32 ppm (s, Me_3Si).

A similar thermolysis reaction carried out for 1 h at 220° with 4.87 mmol of the mercurial in the presence of 0.2 mol of diphenylmethane (Eastman) gave metallic mercury (90%) and, as volatiles, trimethylchlorosilane (3%), trimethyl(dichloromethyl)silane (73%), trimethyl(trichloromethyl)silane (1%), trimethyl(trichlorovinyl)silane (13%) and $Me_3SiCCl{=}CClSiMe_3$ (14%).

Reaction of bis(trimethylsilyldibromomethyl)mercury/diphenylmercury with cyclohexene

A mixture of 1.35 mmol of $(Me_3SiCBr_2)_2Hg$ and 1.85 mmol of diphenylmercury was heated at 95° with 26.5 mmol of cyclohexene in bromobenzene for 6 days. The mixture was filtered to remove phenylmercuric bromide and the filtrate was trap-to-trap distilled at 3×10^{-4} mm. GLC analysis of the filtrate to contain 7-bromo-7-trimethylsilylnorcarane, a single isomer, 48% and four very minor products. One of the latter, present in 2% yield, was identified tentatively by GLC peak enhancement as the other isomer of 7-bromo-7-trimethylsilylnorcarane, both isomers being available to us from another study[26]. The 7-bromo-7-trimethylsilylnorcarane isomer obtained as major product had n_D^{25} 1.4997. (Found: C, 48.63; H, 7.61; Br, 32.90. $C_{10}H_{19}BrSi$ calcd.: C, 48.58; H, 7.74; Br, 32.32%.) NMR (in $CHCl_3$): δ 0.03 (s, 9 H, Me_3Si) and 0.73–2.4 ppm (m, 10 H, tetramethylene unit and cyclopropyl protons).

A similar reaction carried out at 115° for 2 days gave 7-bromo-7-trimethylsilylnorcarane in 36% yield.

Reaction of bis(trimethylsilylbromomethyl)mercury/diphenylmercury with cyclohexene

A solution of 5.85 mmol of $(Me_3SiCHBr)_2Hg$ and 6.01 mmol of diphenylmercury in cyclohexene was heated in a bomb tube (with shaking) for 7 days at 160 ± 10°. The pale yellow solution then was filtered to remove phenylmercuric bromide (18%). Trap-to-trap distillation of the filtrate at 0.0001 mm was followed by GLC analysis of the distillate. The following were present: *anti*-7-trimethylsilylnorcarane (9%), *trans*-1,2-bis(trimethylsilyl)ethylene (ca. 4%), *cis*-1,2-bis(trimethylsilyl)ethylene (ca. 1%) and 5 other minor Me_3Si-containing (via IR) minor products. The three products were identified by comparison of their GLC retention times and infrared spectra with those of authentic samples available from our study of trimethylsilyldiazomethane[10]. The distillation residue (4.25 g of pale yellow solid plus some oil) was shown by TLC to contain large amounts of both starting mercurials and trace amounts of phenylmercuric bromide.

The $(Me_3SiCHBr)_2Hg/Ph_2Hg$ mixture survived a heating period of two weeks at 119° in bromobenzene solution. Only a trace amount of phenylmercuric bromide (by TLC) was formed.

ACKNOWLEDGEMENT

The authors are grateful to the Air Force Office of Scientific Research (SRC)-OAR (USAF Grant AFOSR-68-1350) for generous support of this work. This work was supported in part by Public Health Service Fellowship 5-F1-GM-28,934 (to E.M.H.).

REFERENCES

1 D. Seyferth and D. C. Mueller, *J. Organometal. Chem.*, 25 (1970) 293.
2 D. Seyferth and E. M. Hanson, *J. Amer. Chem. Soc.*, 90 (1968) 2438.
3 D. Seyferth, D. C. Mueller and R. L. Lambert, Jr., *J. Amer. Chem. Soc.*, 91 (1969) 1562.
4 D. C. Mueller and D. Seyferth, *J. Amer. Chem. Soc.*, 91 (1969) 1754.
5 P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, 86 (1964) 1442.
6 I. A. D'yakonov, I. B. Repinskaya and G. V. Golodnikov, *Zh. Obshch. Khim.*, 35 (1965) 199.
7 J. W. Connally and G. Urry, *J. Org. Chem.*, 29 (1964) 619.
8 J. W. Connally, *J. Organometal. Chem.*, 11 (1968) 429.
9 M. F. Lappert and J. Lorberth, *Chem. Commun.*, (1967) 836.
10 D. Seyferth, A. W. Dow, H. Menzel and T. C. Flood, *J. Amer. Chem. Soc.*, 90 (1968) 1080.
11 U. Schöllkopf and N. Rieber, *Angew. Chem.*, 79 (1967) 906.
12 K. D. Kaufmann, B. Auräth, S. Träger and K. Rühlmann, *Tetrahedron Lett.*, (1968) 4973.
13 A. G. Brook and P. F. Jones, *Chem. Commun.*, (1969) 1324; *Canad. J. Chem.*, 47 (1969) 4353.
14 D. Seyferth, E. M. Hanson and F. M. Armbrecht, Jr., *J. Organometal. Chem.*, 23 (1970) 361.
15 D. Seyferth, R. L. Lambert, Jr. and E. M. Hanson, *J. Organometal. Chem.*, 24 (1970) 647.
16 D. Seyferth, H. Yamazaki and D. L. Alleston, *J. Org. Chem.*, 28 (1963) 703.
17 H. G. Kuivila, *Advan. Organometal. Chem.*, 1 (1964) 47.
18 D. Seyferth and F. M. Armbrecht, Jr., *J. Amer. Chem. Soc.*, 91 (1969) 2616.
19 D. Seyferth, R. M. Turkel, M. A. Eisert and L. J. Todd, *J. Amer. Chem. Soc.*, 91 (1969) 5027.
20 S. R. Sandler, *J. Org. Chem.*, 32 (1967) 3876, and references cited therein.
21 D. Seyferth, J. M. Burlitch, H. Dertouzos and H. D. Simmons, Jr., *J. Organometal. Chem.*, 7 (1967) 405.
22 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, Chapter 4.
23 J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, 86 (1964) 524; 88 (1966) 3545.
24 D. Seyferth, E. M. Hanson, B. Prokai and R. J. Cross, *J. Organometal. Chem.*, 24 (1970) 33.
25 D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., J.-H. Treiber and S. R. Dowd, *J. Amer. Chem. Soc.*, 87 (1965) 4259.
26 D. Seyferth and R. L. Lambert, Jr., to be published.