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Preliminary communication

HEXAMETHYLSILIRANE; RING CLEAVAGE BY GERMANIUM AND TIN HYDRIDES

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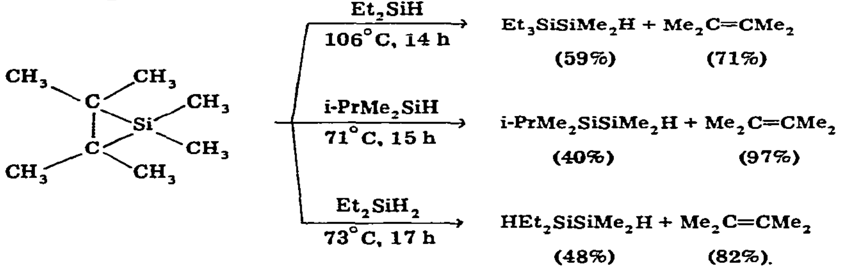
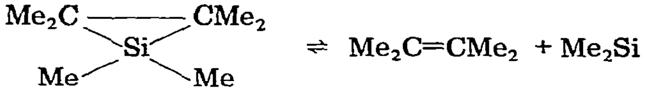
Summary

Under the appropriate conditions, organogermanium and organotin hydrides react with hexamethylsilirane to give ring-opening products of type $R_3GeSiMe_2(CMe_2CMe_2H)$ and $R_3SnSiMe_2(CMe_2CMe_2H)$, respectively.

The thermolysis of hexamethylsilirane in the presence of organosilicon hydrides resulted in the formation of products of dimethylsilylene insertion into the Si—H bond (Scheme 1) [1]. A mechanism involving the extrusion of dimethylsilylene from the silirane (eq. 1) followed by insertion of the divalent silicon intermediate into the Si—H bond (eq. 2) was suggested. There was no evidence for a direct reaction between the silicon hydrides and the silirane under these conditions, nor did UV irradiation initiate such a reaction in the case of triethylsilane. During the course of our further studies of the chemistry of hexamethylsilirane it became of interest to examine analogous reactions with organogermanium and organotin hydrides. If similar Me_2Si insertion into Ge—H and

SCHEME 1

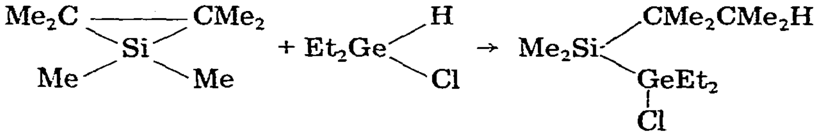



(1)

$$R_3SiH + Me_2Si \rightarrow R_3SiSiMe_2H \qquad (2)$$

Sn—H bonds were to occur, a new route to Group IV mixed element compounds of types $R_3GeSiMe_2H$, $HR_2GeSiMe_2H$, $R_3SnSiMe_2H$, $HR_2SnSiMe_2H$, etc., would provide a potentially useful addition to existing methods [2] for the synthesis of such compounds.

Our first experiments quickly showed that the reactions of hexamethylsilirane with organogermanium hydrides did not parallel those of this silacyclopropane with organosilicon hydrides. In one such example, NMR monitoring of the changes which occurred when equimolar quantities of hexamethylsilirane and diethylchlorogermane were mixed in THF solution showed that a reaction occurred at room temperature and that it was complete (when carried out on a 1.6 mmol scale) within 2 h. The product was isolated by GLC and identified as thexyldimethylsilyldiethylchlorogermane (I)*. Thus the reaction was one of ring cleavage (eq. 3) rather than of dimethylsilylene extrusion and trapping. Furthermore, it was the Ge—H bond, not the Ge—Cl bond, which reacted.


(3)

(I)

Further work, the results of which are summarized in Table 1, showed that

TABLE 1

REACTIONS OF HEXAMETHYLSILIRANE WITH ORGANOGERMANIUM AND ORGANOTIN HYDRIDES[a]

Hydride	Reaction time (h)[a]	Product[b] (% Yield)
Et_2ClGeH	2	$Et_2ClGeSiMe_2(CMe_2CHMe_2)$ (79)
$PhEtClGeH$	15	$PhEtClGeSiMe_2(CMe_2CHMe_2)$ (71)
Ph_2ClGeH	15	$Ph_2ClGeSiMe_2(CMe_2CHMe_2)$ (89)
Ph_2ClGeH	15	Treatment of crude product with CH_3MgI in ether gave $Ph_2MeGeSiMe_2(CMe_2CHMe_2)$ (89)
Ph_2ClGeH	15	Treatment of crude product with EtMgI in ether gave $Ph_2EtGeSiMe_2(CMe_2CHMe_2)$ (82)
Ph_3GeH	15	$Ph_3GeSiMe_2(CMe_2CHMe_2)$ (80)
$PhCl_2GeH$	2	$PhCl_2GeSiMe_2(CMe_2CHMe_2)$ (70)
n-Bu_3GeH	2[c]	n-$Bu_3GeSiMe_2(CMe_2CHMe_2)$ (70)
n-Bu_3SnH	2[c]	n-$Bu_3SnSiMe_2(CMe_2CHMe_2)$ (61)
n-Bu_3SnH	18[d]	n-$Bu_3SnSiMe_2(CMe_2CHMe_2)$ (60)
Et_3SnH	2	$Et_3SnSiMe_2(CMe_2CHMe_2)$ (60)

[a] At room temperature in THF solution unless otherwise specified. [b] All products are new compounds which were characterized by CH analysis, IR and proton NMR spectroscopy and, in some cases, mass spectroscopy. A satisfactory analysis could not be obtained for the $PhCl_2GeH$ product due to its instability. [c] UV irradiation in pentane solution. [d] At 71°C in THF solution.

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*The thexyl group = 2,3-dimethyl-2-butyl, $(CH_3)_2CHC(CH_3)_2$, using the nomenclature of H.C. Brown [3].

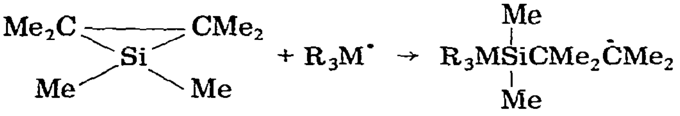
other germanium hydrides which contained Ge—Cl functionality, as well as triphenylgermane, react readily in similar fashion with hexamethylsilirane. All these reactions took place at room temperature, and the yields of the ring-opening products were good to excellent.

Tri-n-butylgermane also reacted with hexamethylsilirane in the sense of eq. 3. but a reaction time of 18 h, at 68°C gave the expected product, thexyldimethylsilyltri-n-butylgermane, in only 28% yield. However, a 70% yield of this compound was obtained in a reaction time of only 2 h, when a pentane solution containing hexamethylsilirane and an excess of tri-n-butylgermane in a quartz flask was irradiated with a 100 watt mercury vapor UV lamp.

Trialkyltin hydrides react with hexamethylsilirane as well. Thus, a 2 h irradiation of a pentane solution of the silirane and an excess of tri-n-butyltin hydride gave $(n\text{-}C_4H_9)_3SnSiMe_2(CMe_2CMe_2H)$ in 61% yield. A comparable (60%) yield of this product was obtained in a thermal reaction (18 h at 71°C in THF solution). On the other hand, triethyltin hydride reacted exothermally when it was added (dropwise) to a THF solution of hexamethylsilirane, giving the expected ring-opening product in 61% yield. Reverse addition (the silirane to the Et_3SnH) resulted in copious gas evolution and in formation of much hexamethylditin in addition to $Et_3SnSiMe_2(CMe_2CMe_2H)$.

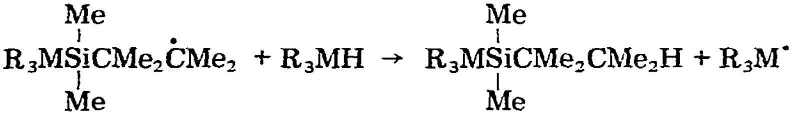
The possible mechanism of these reactions is of interest. Organogermanium hydrides of types RX_2GeH, R_2XGeH and R_3GeH appear to add to simple olefins and acetylene by a free radical chain mechanism [4], and their reactivity in the series X = Cl decreases in the order given. Trialkyltin hydrides, for the most part, also react with similar olefins and acetylenes by a free radical pathway [5]. Accordingly, we suggest that the reactions of the organogermanium and organotin hydrides listed in Table 1 with hexamethylsilirane also proceed by a radical chain mechanism (eq. 4—6),

$$R_2MH \rightarrow R_3M^\bullet + H^\bullet \quad (M = Ge\ or\ Sn) \qquad (4)$$



(5)

$$+ R_3M^\bullet \rightarrow R_3M\overset{Me}{\underset{Me}{Si}}CMe_2\dot{C}Me_2 \qquad (5)$$



(6)

$$R_3M\overset{Me}{\underset{Me}{Si}}CMe_2\dot{C}Me_2 + R_3MH \rightarrow R_3M\overset{Me}{\underset{Me}{Si}}CMe_2CMe_2H + R_3M^\bullet \qquad (6)$$

etc;

Both chlorogermanium hydrides and trialkyltin hydrides apparently can react with polar olefins and acetylenes (e.g., acrylonitrile) by a polar mechanism [4,5]. However, hexamethylsilirane, while hyper-reactive, is not a strongly polar molecule and many of its other reactions appear to follow a free radical mechanism. It may be noted that the unavoidable minor autoxidation of hexamethylsilirane which occurs during the course of its handling and transfer serves to produce its own catalyst for free radical processes, a peroxide of still unknown constitution [6]. Furthermore, UV irradiation, as mentioned above, was found to activate the reaction of tri-n-butylgermane with the silirane. On the basis of these considerations, we favor the free radical mechanism shown above.

Acknowledgements

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