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[23] National Science Foundation Postdoctoral Fellow, 1971–1972.

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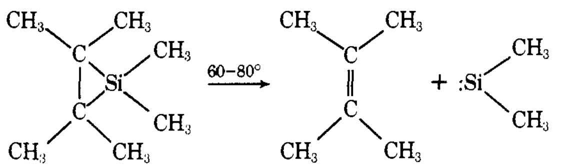
Generation of Dimethylsilylene under Mild Conditions by the Thermolysis of Hexamethylsilirane

Sir:

The generation of divalent silicon species, the silylenes, and their chemical reactivity have received much attention in recent years.[1] Pyrolytic and photolytic processes have served in their production, but these are not wholly satisfactory. The thermolysis reactions require high temperatures, ca. 300°, for substituted 7-silanorbornadienes[2] and ca. 200–250° for polydimethylsilanes with terminal methoxy substituents.[3] The photolysis of $Me(Me_2Si)_nMe$ ($n = 4$–8)[4] and c-$(Me_{12}Si_6)$[5] produces dimethylsilylene at 25–45°, but in such reactions it is possible that the final products obtained will be determined by secondary photoprocesses involving the initial products or by other chemistry involving excited states of the initial products. Clearly, a less strenuous thermal route would be a useful addition to the known procedures of silylene generation.

We have found that hexamethylsilirane, **1**, whose preparation we reported recently,[6] decomposes at around 60–80° to generate dimethylsilylene, eq 1. The initial indication of such a mode of decomposition was provided by the mass spectrum of hexamethylsilirane which showed no molecular ion. The largest fragment, *m/e* 84, was attributable to $[Me_2C{=}CMe_2]^+$. An experiment in which the decomposition of hexamethylsilirane in benzene-d_6 under argon at 60° was monitored by proton NMR spectroscopy showed that two products were formed when hexamethylsilirane decomposed: tetramethylethylene (δ 1.78 ppm) and a methylsilicon compound (δ 0.28 ppm). The half-life of the silirane under these conditions was 11 hr. In a larger scale experiment carried out in benzene (15 hr at 73°), the tetramethylethylene yield was determined by gas chromatography (GLC) to be 77%, and this product was isolated and identified by comparison of its GLC retention time, NMR spectrum, and refractive index with those of an authentic sample. Invariably lower yields of tetramethylethylene (46% in one such experiment) were obtained when the thermolysis of hexamethylsilirane was carried out in THF. The organosilicon product of the decomposition was isolated as a nonvolatile oil, probably polymeric polydimethylsilylene.



(1)

1

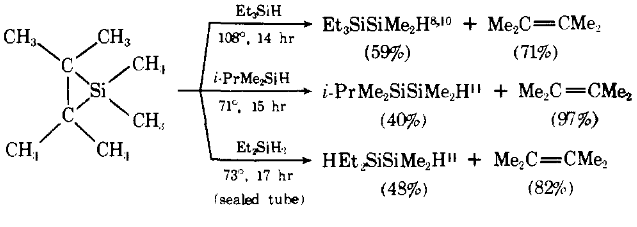
Dimethylsilylene produced in the thermolysis of hexamethylsilirane may be trapped by various substrates when the decomposition is carried out in their presence. The hexamethylsilirane may be used in the form of the THF solution in which it is formed,[6] as the neat reagent, or in benzene solution. Orientational experiments are required to determine which of these possibilities gives the best results for a given type of substrate. Also, the optimum substrate/hexamethylsilirane ratio must be determined in such experiments for the different types of substrate used.

Our initial trapping experiments have been carried out with classes of substrates which had been shown by previous workers to react with dimethylsilylene. The reaction of dimethylsilylene with dimethyldimethoxysilane is described in detail to illustrate the procedure used. (It must be emphasized that all operations must be carried out under an atmosphere of dry argon or nitrogen since hexamethylsilirane is highly reactive toward atmospheric oxygen and moisture.[6] All substrates and solvents used must be degassed prior to their mixing with the silirane.)

Seven milliliters of a solution of hexamethylsilirane in THF[6] was concentrated at room temperature and 65–70 mmHg during a 3-hr period to remove THF and argon was admitted into the flask containing the silirane which remained. An aliquot of the silirane was added to benzene-d_6 containing toluene as internal standard and the amount of silirane present was determined by NMR. An added check was provided by methanolysis of the silirane[6] in the NMR sample and determination of the yield of the methanolysis product, $MeOSiMe_2CMe_2CHMe_2$, by GLC. In this way it was established that 1.18 mmol of hexamethylsilirane was available for reaction. To this was added 75 mmol of degassed dimethyldimethoxysilane[7] and the resulting solution was heated at 73° for 15 hr, with stirring under argon. Subsequent GLC analysis showed that tetramethylethylene was present in 95% yield and that the Si–OMe insertion product, $MeOSiMe_2SiMe_2OMe$,[8,9] had been formed in 71% yield.

Organosilicon hydrides also react readily with silylenes,[1] and we have intercepted the dimethylsilylene released in hexamethylsilirane thermolysis with several substrates containing Si–H bonds. In all cases no inert diluent was present and the silicon hydride, present in large excess, served as reaction medium. The results are shown in Scheme I. Finally, we have examined reactions of hexamethylsilirane with 1,3-dienes which have been shown to react with silylenes,[1] via 1,2-addition followed by subsequent rearrangement of the initially formed vinylsilacyclopropanes, usually to 1-silacyclopent-3-enes.[12] Here the results were not straightforward. The best product yield with 2,3-dimethyl-1,3-butadiene was obtained when a THF solution containing the silirane and 5.3 molar equivalents of the diene was heated at 66° for 17 hr. Tetramethylethylene was obtained in 37% yield and 1,1,3,4-tetramethyl-1-silacyclopent-3-ene[8,13] in

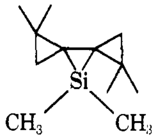
Scheme I



34% yield. An increase in the diene concentration resulted in a decrease in the yield of the silacyclopentene, and none of this product was obtained when the hexamethylsilirane–2,3-dimethyl-1,3-butadiene reaction was carried out (15 hr at 70°) in the absence of a diluent, although the tetramethylethylene yield was 40%. With some other dienes (e.g., *trans,trans*-2,4-hexadiene) no dimethylsilylene adducts were obtained under the conditions found to be successful with 2,3-dimethyl-1,3-butadiene. One may speculate that the unconverted 1,3 diene present in these reactions intercepts either a diradical intermediate[12a,b] of the rearrangement of the vinylsilacyclopropane or reacts (by cycloaddition?) with the product of the rearrangement. Further experiments are required on this point.

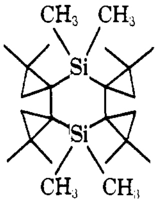
This new, mild route to dimethylsilylene may allow the development of new silylene chemistry, and experiments directed toward this goal are in progress. However, it should be recognized that the scope of the application of hexamethylsilirane will be limited by the extremely high reactivity of the silacyclopropane ring system toward many classes of compounds,[6,14-16] among which are some which might react with silylenes. In those cases reactions with the silirane starting material would preclude observation of the desired silylene reactions.

This thermal dimethylsilylene extrusion from hexamethylsilirane finds parallels in some known cases of sulfur extrusion from thiiranes[17] and in thermal difluorocarbene extrusion from *gem*-difluorocyclopropanes.[18] The other known silacyclopropanes[14] are much more thermally stable than hexamethylsilirane and do not serve as sources of dimethylsilylene at these low temperatures. Thus when **2**



2

was heated in triethylsilane solution at reflux for 17 hr, no $Et_3SiSiMe_2H$ was obtained. Instead, a 20% yield of a dimer of **2**, presumably **3**, was formed, along with nonvolatile polymeric material.



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No information concerning the mechanism of dimethylsilylene extrusion from hexamethylsilirane is available at present. A concerted process, the reverse of singlet state silylene addition to the $C{=}C$ bond,[12] seems a good possibility, but a stepwise process proceeding via the diradical $\cdot SiMe_2CMe_2CMe_2\cdot$ also must be considered.

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Macrocyclic Ligand Ring Size Effects on Complex Stabilities and Kinetics. Copper(II) Complexes of Cyclic Polythiaethers

Sir:

Much recent interest has centered on the unusually large stabilities of macrocyclic ligand complexes, particularly those of the cyclic polyethers (crown ethers) and cyclic tetramines, as compared to the corresponding open-chain species, and the dependency of these stabilities on ligand ring size.[1-4] Busch and co-workers[2] have attributed these enhanced stabilities to factors which they have called *multiple juxtapositional fixedness* (essentially configurational effects) in which emphasis has been placed on the relative rigidity of the complexed cyclic ligands resulting in an apparent increase in the difficulty of sequentially breaking the metal-donor atom bonds. Hinz and Margerum,[5] in dealing with a series of tetramines, have suggested that an additional and more dominant contribution arises in hydrogen-bonding ligands from the fact that the free cyclic species are less extensively solvated than their open-chain analogues and, thus, are thermodynamically more favored to exist in the complexed state since less solvation energy (primarily an enthalpic contribution) is involved. However, their study was unable to differentiate specifically between the contributions of solvation effects and configurational effects in the complexes studied, particularly since each of these effects likely contain both enthalpic and entropic contributions.

To date the supporting evidence for these effects has been limited to thermodynamic and indirect kinetic data. Direct kinetic data have been difficult to obtain since the cyclic polyethers form extremely labile complexes[6] while the polyamines protonate in the pH regions accessible to the solvated metal ions of general interest thereby introducing interfering electrostatic and conformational effects which are difficult to isolate.[7] A recent attempt to eliminate polyamine protonation by operating in 0.2-2.0 *M* NaOH media