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Preliminary communication

ALKALI METAL PROMOTED TRANSFER OF DIMETHYLSILYLENE FROM DODECAMETHYLCYCLOHEXASILANE TO SILANES AND DIENES

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Summary

Addition of sodium/potassium alloy to THF solutions containing dodecamethylcyclohexasilane and a diene or a silane, affords silacyclopentenes and disilanes, respectively.

The diverse chemistry of cyclic polysilanes is a subject of much current interest. Among the more remarkable, but not uncommon, reactions of the catenated polysilanes is the extrusion of a silylene unit from within the silicon skeleton. For example, West and coworkers have observed that alkali metals induce an equilibrium redistribution between permethylcyclopolysilanes of five-, six- and seven-membered rings [1]. Photolytic elimination of dimethylsilylene from both the five- and six-membered rings has been studied by Ishikawa and Kumada [2] and others [3]. We now report that sodium/potassium alloy promotes the transfer of a dimethylsilylene fragment from dodecamethylcyclohexasilane to butadienes and silanes.

In a typical experiment, Na/K alloy (0.1 g, 3 mmol) is added to a solution of THF containing the polysilane (1.25 g, 3.6 mmol) and a five-fold excess of triethylsilane at room temperature. After stirring for 12 h, chromatographic analysis of the reaction mixture indicates the formation of 1,1,1-triethyl-2,2-dimethyldisilane [4] in 60% yield based on the 10% decrease in cyclohexasilane concentration. Minor amounts of cyclopentasilane and lower molecular weight polysilanes are also formed. Continued stirring for several days eventually leads to the complete disappearance [5] of the five- and six-membered polysilane rings and to isolation of the disilane product in 20% yield. The same product, resulting from the insertion of dimethylsilylene into the silicon—hydrogen bond of triethylsilane, is formed also in the photolysis of the permethylcyclopolysilanes [2]. The similarity of the two pathways for polysilane decomposition and the formation of the Si—H insertion product in both pro-

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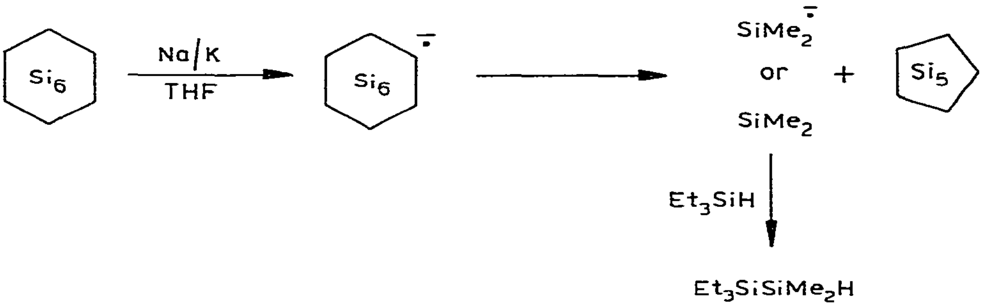
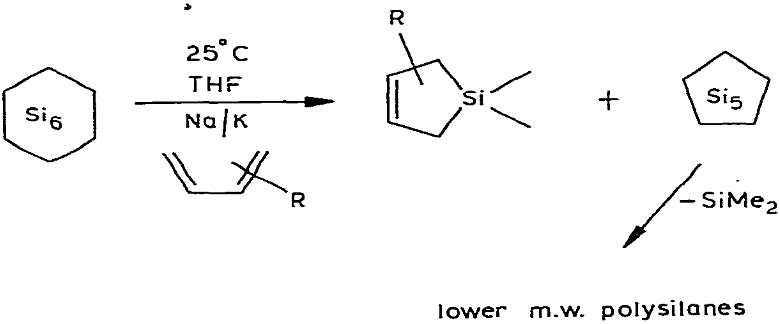
cesses, suggests that dimethylsilylene or its radical anion is an intermediate in the Na/K promoted reaction of the cyclohexasilane. While other mechanisms are conceivable and have not been excluded, we currently favor the one involving a dimethylsilylene pathway.



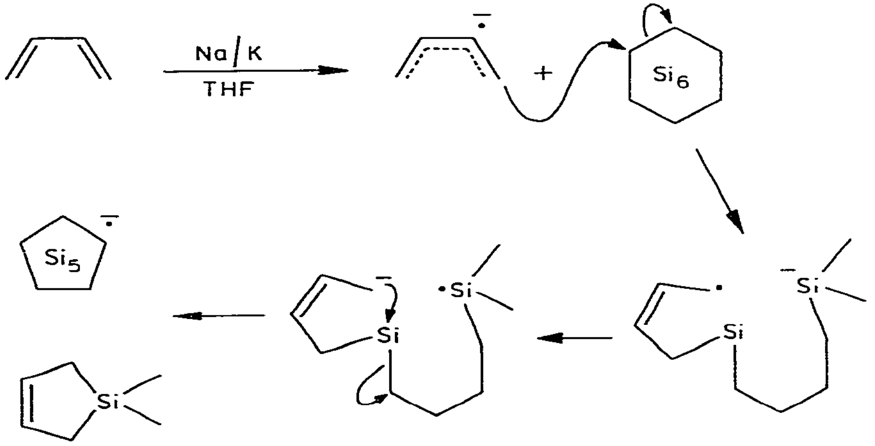
In order to obtain additional information concerning the possible role of the transient dimethylsilylene, dienes have been used as trapping agents. In the presence of a five-fold excess of acyclic conjugated dienes, but otherwise identical reaction conditions, the metal promoted decomposition of the cyclohexasilanes affords apparent dimethylsilylene adducts, silacyclopentenes. Yields [4] are typically 70—80% in the presence of 2-methylbutadiene, 2,3-dimethylbutadiene and 1-methylbutadiene and this procedure provides a new and convenient method for the synthesis of silacyclopentenes. Furthermore, when dienes are present in place of silicon hydrides, the cyclohexasilane and cyclopentasilane undergo rapid decomposition to lower molecular weight polysilanes. The reaction is complete in a few minutes.



We have examined the stereochemistry of silacyclopentene formation in order to obtain mechanistic details of the transfer of the dimethylsilylene unit to dienes. When either *E*,*E*- or *E*,*Z*-2,4-hexadienes are present in the reaction medium, the formation of 1,1,2,5-tetramethylsilacyclopentenes is non-stereospecific. Both *E*,*E*- and *E*,*Z*-hexadienes give the same ratio, 60/40, of *cis*- and *trans*-tetramethylsilacyclopentenes. Although non-stereospecific addition of silylenes to hexadienes is expected from the earlier work of Gaspar and Hwang [6], it is surprising that in the metal-induced formation of tetramethylsilacyclopentenes, the same ratio of *cis* to *trans* products is formed from both hexadiene diastereomers. Since the diene reagents could not be recovered from the reaction mixture, we were not able to determine if the 2,4-hexadienes undergo *E*-*Z* isomerization during the reaction.

It is noteworthy that when dienes are employed as trapping agents, even in large excess, addition of the metal alloy leads to rapid and complete disappearance of the dienes as well as the cyclic polysilanes. In contrast, when triethylsilane is the trapping agent, no reaction of the silicon—hydrogen bond, other than capture of the silylene, is observed. These and previous observations regarding the stereochemistry of silacyclopentene formation point to different mechanisms for the transfer of dimethylsilylene from permethylcyclohexasilane to silanes and to dienes.

If free dimethylsilylene, possibly formed in a sequence originating from the radical anion of cyclohexasilane, were the species producing both disilanes in the triethylsilane and silacyclopentenes in diene solutions, reaction rates and product yields should not display the dramatic dependence on the nature of the trapping agent. An alternative to this mechanism, available with the dienes but not with silicon hydrides, involves prior generation of a diene radical anion which attacks a silicon atom of the cyclopolysilane. The resulting open chain adduct could undergo an intramolecular electron transfer from the silyl anion to the allylic methylene, followed by another anionic displacement which gives a silacyclopentene and the cyclopentasilane. Continuation of the same cycle would account for the disappearance of the cyclopentasilane.



We note that the proposed mechanism for silacyclopentene formation is similar to one suggested by Weyenberg [7] for the disilylation of conjugated dienes with halosilanes and alkali metals. However, other mechanisms, possibly involving the addition of an initially formed silyl anion [8] to a diene, cannot be ruled out at this time.

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5 Over the long reaction times, secondary reactions between Na/K and cyclopolysilanes produce large amounts of lower molecular weight polysilanes. Such reactions apparently reduce the overall efficiency of dimethylsilylene transfer to triethylsilane.
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