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Preliminary communication

ORGANOBORON COMPOUNDS AS SOURCES OF SILAETHYLENE INTERMEDIATES

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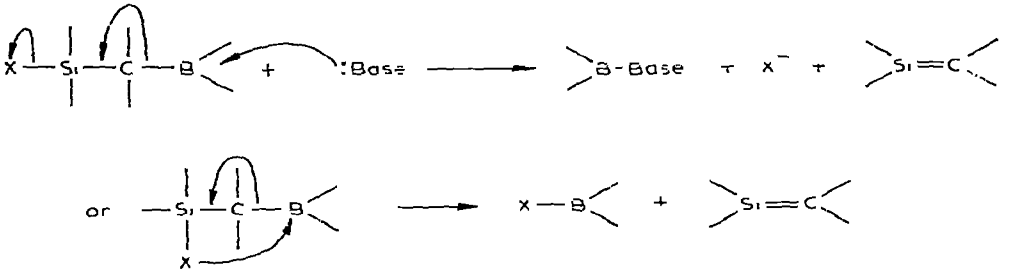
Summary

Possible generation of 1-silaethylene intermediates by base-catalyzed β-elimination reactions of $(Me_3SiOSiMe_2CH_2)_3B$ and $(C_6H_5Me_2SiOSiMe_2CH_2)_3B$ is discussed.

Interest in silaethylene intermediates has been expanding since Flowers and Gusel'nikov reported data for the kinetics of the gas phase thermal generation of 1,1-dimethyl-1-silaethylene from 1,1-dimethyl-1-silacyclobutane [1]. Recently, the chemistry of 1-silaethylene species generated from silacyclobutane systems by thermolysis [2] or photolysis [3,4] has been developed by Sommer and co-workers. Other reports of 1-silaethylene intermediates in the gas phase [5,6] in solution [7] and via photolysis [8] have appeared. The infrared band believed to be associated with the π interaction in 1,1-dimethyl-1-silaethylene has been observed at low temperatures [9]. Theoretical calculations concerning silaethylene species have been published [10,11].

Several years ago Brown and Cope [12] reported concerning an elimination reaction which occurred after hydroboration of certain functional allyl derivatives. It was observed that at 0° a β elimination reaction to give propylene was quite facile for good leaving groups such as tosylate and chloride. The elimination of poorer leaving groups such as ethoxide and phenoxide could be caused to occur at somewhat higher temperatures or under base catalysis. It seemed to us that such a β elimination reaction might have applicability in the generation of 1-silaethylene intermediates, i.e., eqn. 1 and 2. A base-catalyzed route to 1,1-dimethyl-1-silaethylene analogous to eqn. 1 involving the cleavage of the silicon—silicon bond of 1-halomethyl-1-phenyldisilanes was reported by Kumada and co-workers [13]. Reported herein are our initial results with the base-catalyzed approach using organoboron precursors.

A likely 1,1-dimethyl-1-silaethylene precursor, $(Me_3SiOSiMe_2CH_2)_3B$


(1)

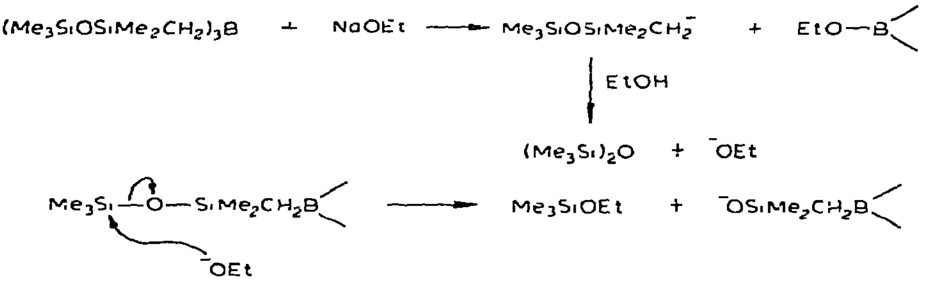
(2)

(I), was available [14]*. This compound was recovered unchanged from a THF solution that had been heated at reflux under nitrogen for several days. However, when it was treated with freshly prepared sodium ethoxide in refluxing ethanol the products indicated in eqn. 3 were formed. The yield

$$(Me_3SiOSiMe_2CH_2)_3B + 5\ NaOEt \xrightarrow[\text{2 days}]{\text{EtOH, reflux}} \underset{(66\%)}{Me_3SiOEt} + \underset{(53\%)}{(Me_3Si)_2O} \qquad (3)$$

of ethoxytrimethylsilane was calculated on the basis of the elimination of 3 moles of 1,1-dimethyl-1-silaethylene from I, followed by addition of ethanol to the intermediate. The yield of the disiloxane was calculated on the basis of the conversion of 3 moles of the intermediate silanol to 1.5 moles of disiloxane.

This experiment does not establish unambigously the intermediacy of 1,1-dimethyl-1-silaethylene since the products formed could conceivably arise via alternative and/or competing pathways. Two of these are shown in eqns. 4 and 5. These were eliminated by means of an experiment in which tris(2,2,4-trimethyl-4-phenyl-3-oxa-2,4-disilapentyl)borane (II) was treated with sodium ethoxide in refluxing ethanol. The products indicated in eqn. 6 were obtained. Ethoxydimethylphenylsilane and phenylpentamethyldisiloxane were not present in the reaction mixture; their absence argues strongly against the reaction pathways indicated by eqns. 4 and 5.


(4)

(5)

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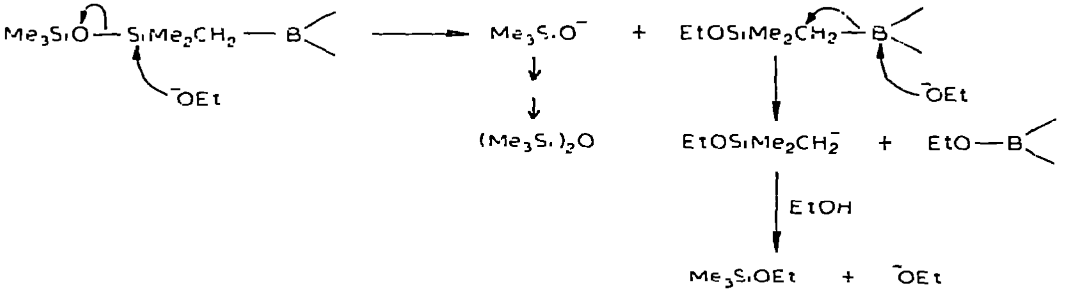
[*] I had n_D^{25} 1.4260 and b.p. 98-100°/0 01 mm (lit. 14, b.p. 110-113°/0.22 mm). NMR: (CCl$_4$, internal HCCl$_3$) δ 1.0,s, rel. intensity 2 H; 0.00, and −0.01 ppm,s, rel. intensity 15 H.

$$\underset{(II)}{(C_6H_5Me_2SiOSiMe_2CH_2)_3B} + 5\ NaOEt \xrightarrow[\text{2 days}]{\text{EtOH, reflux}} \underset{(40\%)}{Me_3SiOEt} + \underset{(55\%)}{(C_6H_5Me_2Si)_2O} \qquad (6)$$

A third reaction course in which a silaethylene intermediate is not involved must be considered, (eqn. 7)[*]. In order to test this alternative, 20 mmol of I was treated with 100 mmol of sodium phenoxide in 50 ml of refluxing ethanol for 2 days[**]. In addition to unreacted I, the complex reaction mixture contained trimethylethoxysilane (33% yield) and hexamethyldisiloxane (67% yield; yields based on I charged). If authentic trimethylphenoxysilane was deliberately added to the reaction mixture, a new, clearly resolved peak appeared in the GLC trace of the reaction mixture. This result suggests that little, if any, of the expected product based on the reaction pathway shown in eqn. 7 was present. The formation of the ethoxysilane in this reaction is nicely accomodated by eqn. 1 involving the formation of a 1-silaethylene intermediate which concurrently or subsequently reacts with ethanol.



(7)

These results indicate that a base-catalyzed β elimination reaction from organoboron compounds can be used in the formation of products derivable from 1-silaethylene intermediates. Our efforts in these areas are continuing and will be the subject of later reports.

Acknowledgments

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[*] The authors are indebted to Professor Paul R. Jones, North Texas State University, for the original suggestion of this alternative.

[**] A calculation based on the pK_a's of phenol and ethanol indicated that less than 0.1% of the phenoxide would be converted to phenol in the initial mixture via the acid—base equilibrium.

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