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CYCLOADDITION OF STABLE DISILENES TO TERMINAL ACETYLENES

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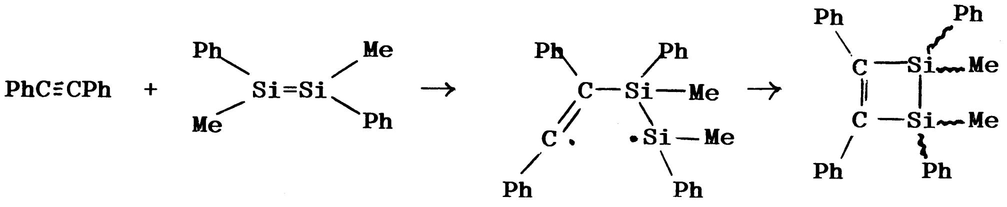
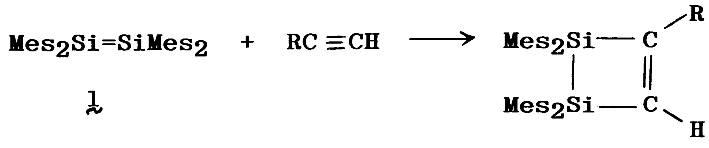
Tetramesityldisilene and trans-1,2-di-t-butyl-1,2-dimesityldisilene (**3**) react with various 1-alkynes to give air-stable disilacyclobutenes. The cycloaddition of **3** to alkynes produces equal amounts of both stereoisomers, consistent with a stepwise mechanism.

A recent communication by Nakadaira, Sato and Sakurai1) reports that the cycloaddition of transient cis- or trans-1,2-dimethyl-1,2-diphenyldisilene, generated thermolytically at 300 °C, adds to diphenylacetylene stereoselectively, but not stereospecifically. These authors suggest that the addition takes place through a diradical intermediate:

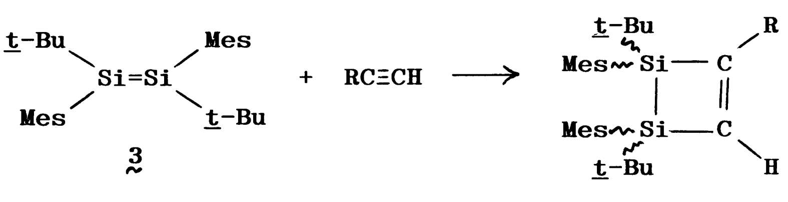


In our continuing study of chemical reactions of stable disilenes,2) we have investigated the reactions of two stable disilenes with several acetylenes. In benzene solution at 80 °C, tetramesityldisilene (**1**) cycloadds to phenylacetylene, ethoxyacetylene, carbomethoxyacetylene and trimethylsilylacetylene to give disilacyclobutenes **2a**-**d**, and trans-1,2-di-t-butyl-1,2-dimesityldisilene (**3**) adds similarly to phenylacetylene and ethoxyacetylene producing **4a**,**b**.3) Reactions are generally complete within 10 min; the products were isolated as colorless crystalline solids after recrystallization from hexane. Unlike disilacyclobutanes which have been reported earlier1,4) **2a**-**d** and **4a**-**b** do not react with



1

2a, R = Ph
2b, R = OEt
2c, R = CO_2Me
2d, R = $SiMe_3$

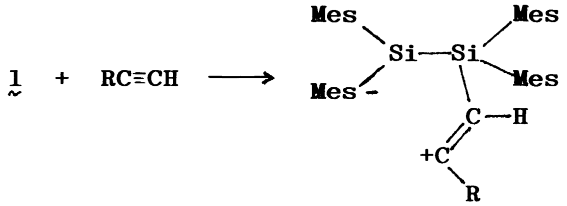


3

4a, R = Ph
4b, R = OEt

atmospheric oxygen, since they are sterically protected by the bulky groups on silicon. No reaction was observed between 1 and n-$C_4H_9C\equiv CH$, $PhC\equiv CSiMe_3$, $CH_3C\equiv CH$, $HC\equiv CH$, $PhC\equiv CPh$, $PhC\equiv CSiMe_3$ or $MeO_2CC\equiv CCO_2Me$, even when refluxed 18 h in benzene.

The reaction of 3 with $PhC\equiv CH$ and $EtOC\equiv CH$ yielded in both cases approximately equal amounts of the two stereoisomeric products, which were separated by GLC. Thus the reaction differs from the cycloadditions involving PhMeSi=SiMePh, which show moderate stereoselectivity. It is possible that the cycloaddition of 3 proceeds through a radical intermediate, as suggested for the high-temperature reaction of Sakurai and coworkers,$^{1)}$ but that the diradical is much longer-lived for the hindered disilenes so that stereoselectivity is completely lost. However, since only polar alkynes react with 1, an ionic mechanism may also be considered, perhaps one in which the alkyne reacts as a nucleophile to give a dipolar intermediate such as 5. Similar dipolar species appear to be involved in cycloaddition reactions of silenes.$^{5)}$ Further studies will be needed to elucidate the mechanism of alkyne cycloaddition to stable disilenes.



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2) For reviews on disilene chemistry see R. West, Pure Appl. Chem., 56, 1, 163-173 (1984); R. West, M. J. Fink, M. J. Michalczyk, D. J. De Young, and J. Michl in Organosilicon and Biorganosilicon Chemistry, H. Sakurai, Ed., Ellis Horwood Ltd., Part 1, Chap. 1, pp. 3-14 (1985); G. Raabe and J. Michl, Chem. Rev., 85, 419-509 (1985).
3) Reaction mixtures contained 0.6 mmol each of disilene and alkyne. Identity of all compounds was confirmed by NMR spectroscopy, exact mass determination by MS, and in most cases also by elemental analysis.
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