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STEREOCHEMISTRY OF THERMAL [2+2] CYCLOADDITION OF DISILENE WITH ACETYLENE[1)]

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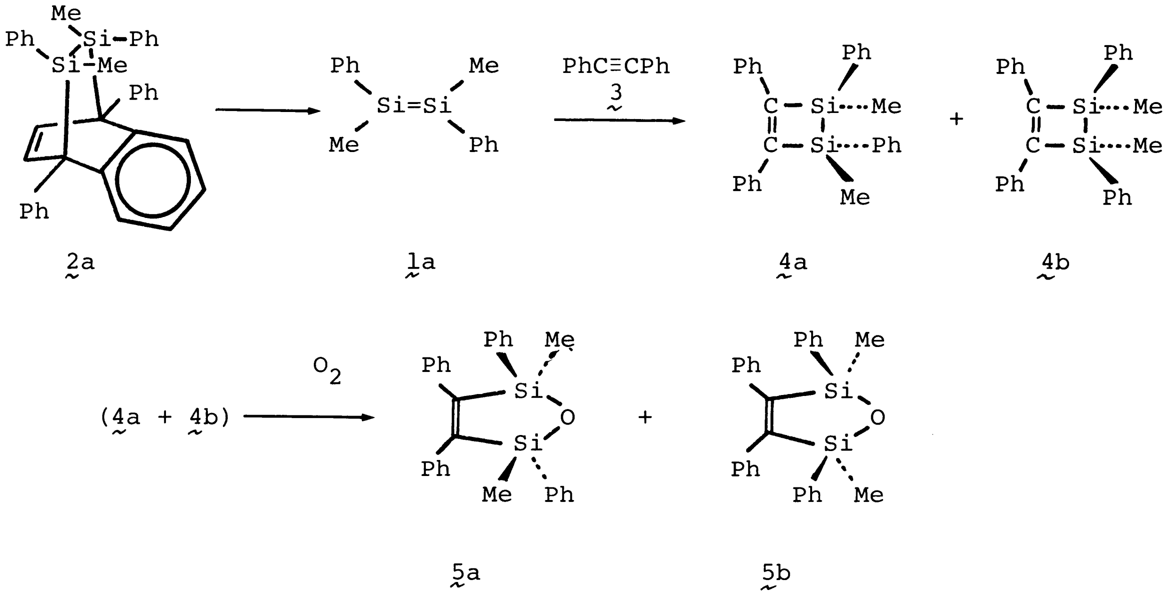
The reaction of diphenylacetylene with thermally generated cis- and trans-1,2-dimethyl-1,2-diphenyldisilene at 300 °C gave a mixture of the [2+2] cycloadducts in a stereoselective but not completely stereospecific manner. A stepwise radical mechanism is suggested.

Recently, a considerable interest has been focussed on the silicon-silicon double-bonded species, disilenes, since the isolation of stable crystalline disilene derivatives by West, Masamune and their coworkers.[2)] However, much remained uncovered in the chemistry of disilenes. Comparison of the chemical behaviors of disilenes with those of olefins is of special interest.

Previously, we have reported that cis- and trans-1,2-dimethyl-1,2-diphenyldisilenes (**1**), generated respectively, from cis- and trans-7,8-dimethyl-1,4,7,8-tetraphenyl-2,3-benzo-7,8-disila[2.2.2]bicyclooctadiene (**2**), undergo highly stereoselective [4+2] cycloaddition with anthracenes.[3)] The cis-trans isomerization of the Si-Si double bond is indicated to be slow enough to give the products in a highly stereoselective way. On the other hand, disilene is also known to undergo efficient [2+2] cycloaddition with acetylene to give disilacyclobutene.[4)] The [4+2] cycloaddition may be regarded as a thermally allowed and fast reaction even for the disilene, while the [2+2] one may not be. Therefore, stereochemical studies on the [2+2] cycloaddition of disilene seemed to be very interesting.

A trans disilene precursor (**2a**) was pyrolyzed in the presence of 1.1 equivalent of diphenylacetylene (**3**) at 300 °C for 17.5 h. Since disilacyclobutenes are air-sensitive,[4)] resulting products (**4**) were oxidized before TLC separation on silica gel. 1,3-Dimethyl-1,3,4,5-tetraphenyl-1,3-disila-2-oxacyclopent-4-ene (**5**) was thus obtained in 70% yield as a 63:37 mixture of two isomers (**5a** and **5b**) which could not be separated each other but structures were determined unequivocally to be trans (**5a**) and cis (**5b**) isomers by ^{1}H NMR and mass spectra.[5)]



The stereochemistry of oxidation of the Si-Si bonds is known to be retention of configuration.[6)] Therefore, the ratio of trans to cis for 5 should be the same as that of 4. Unfortunately, all the attempts to delineate the stereochemistry of 5, such as epoxidation with metachloroperbenzoic acid and oxidation with osmium tetroxide of the double bond, failed. We tentatively assign the dominant isomer with a longer retention time on GLC as the trans isomer (5a) and the other as the cis (5b).

Pyrolysis of the cis disilene precursor (2b) under the same conditions afforded a 38:62 mixture of 5a and 5b in 73% yield. These results indicate that [2+2] cycloaddition proceeds stereoselectively but in a lesser extent as compared with [4+2] cycloaddition. However, there is a possibility that the disilene isomerizes before the possibly slow [2+2] cycloaddition reaction.

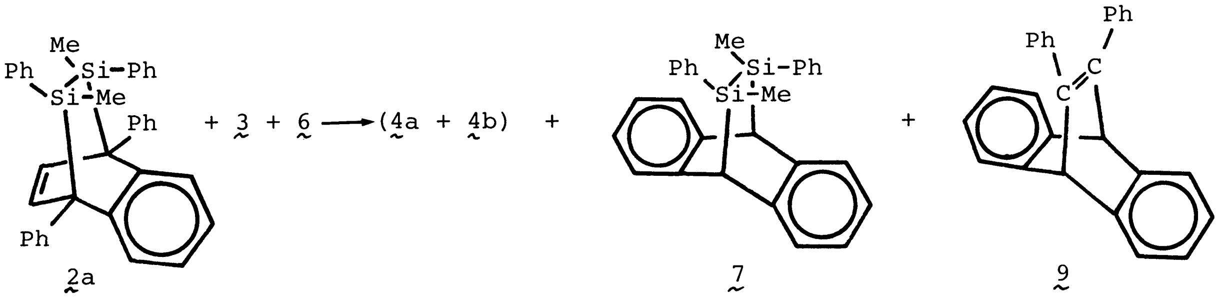
To shed light to the problem, we also pyrolyzed 2a in the presence of both 3 and anthracene (6). In addition to 4, dibenzodisilabicyclo[2.2.2]octadiene (7) and diphenyldibenzobicyclo[2.2.2]cyclooctatriene (8) were obtained. The Diels-Alder adduct (7) of the trans disilene with 6 was found to be the trans isomer with more than 90% stereospecificity.[3)] Both 4 and 7 were analyzed after oxidation to the corresponding disiloxanes, 5 and 8. Cycloaddition between 3 and 6 gives rise to the formation of 9. The results are summarized in Table 1.[7)]

In the case of an equimolar mixture of 2a, 3, and 6 (run 1), a considerable amount of the Diels-Alder adduct between 3 and 6 was obtained (31% yield) but the major product was 7 (42% yield). This means that anthracene reacts faster with

Table 1. Competitive cycloaddition reactions of disilene

Run	Substrates (equiv.)			Products (% yield)			
	2a	**3**	**6**	**5**	(**5a**:**5b**)	**7**a)	**8**
1	1	1	1	18	(62:38)	42	31
2	1	0.5	1.5	2.9	(56:44)	76	70
3	1	10		20	(61:39)		

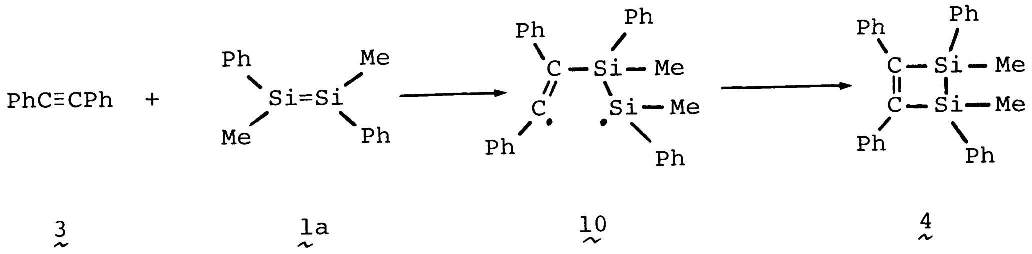
a) Determined after oxidation with trimethylamine oxide.



disilene than with diphenylacetylene. Under the conditions, **5** was obtained in 18% yield. Therefore, the rate of the formation of **7** is greater than that of **5** but the difference is not very much significant. The results indicate that rates of all the three cycloaddition reactions are rather comparable.

Interestingly, the ratio of **5a** to **5b** in run 3, where a 10 molar excess amount of **3** was subjected to react with **2a** in the absence of **6**, is almost the same as that in run 1. This indicates that the possibility of extensive isomerization before the reaction can be eliminated, although as expected, the product **5** was obtained in low yield less stereoselectively in the case of a deficient amount of **3** (run 2). Isomerization of **1a** to **1b** is a competing process but the rate is slower than cycloaddition processes.3)

Consequently, a reasonable mechanism of the present [2+2] cycloadditon reaction is a stepwise one involving a diradical intermediate (**10**). Outcomes of the



stereochemistry of the [2+2] cycloaddition suggest that either rotation of the Si-Si bond or inversion of the silyl radical center$^{8)}$ is slow in comparison with the ring closure process.

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4) H. Sakurai, T. Kobayashi, and Y. Nakadaira, J. Organomet. Chem., 162, C43 (1978); T. J. Barton and J. A. Kilgour, J. Am. Chem. Soc., 98, 7746 (1976).

5) A mixture of 5a and 5b: colorless crystals; MS m/e (%) 434 (M^+, 100), 419 (69), 197 (78), 178 (28). 5a: ^{1}H NMR (C_6D_6) δ 0.75 (s, 6H, SiMe), 6.7-7.9 (m, 20H, Ph). 5b: ^{1}H NMR (C_6D_6) δ 0.72 (s, 6H, SiMe), 6.7-7.9 (m, 20H, Ph).

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7) 8: colorless prisms; mp 217-218 °C; ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 2H, methine), 6.8-7.5 (m, 18H, arom); IR (KBr, cm^{-1}) 2950, 1590, 1475, 1445, 1430, 1150; MS m/e (%) 356 (M^+, 66), 279 (15), 178 (100); Found: C, 94.20; H, 5.71%. Calcd for $C_{28}H_{20}$: C, 94.35; H, 5.65%. 9: colorless prisms; mp 128-129 °C; ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6H, SiMe), 3.44 (s, 2H, methine), 6.4-7.4 (m, 18H, arom); IR (KBr, cm^{-1}) 1460, 1440, 1420, 1245, 1115, 1090, 1015, 835; MS m/e (%) 434 (M^+, 70), 287 (27), 255 (45), 241 (74), 197 (33), 178 (100); Found: C, 77.13; H, 6.20%. Calcd for $C_{28}H_{26}OSi$: C,77.37; H, 6.03%.

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