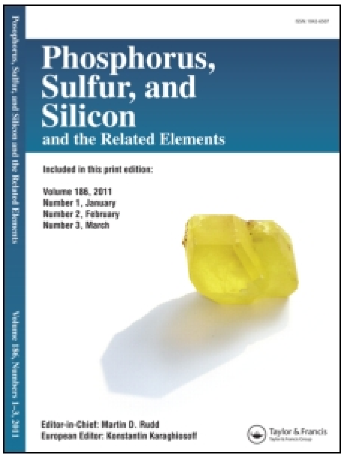

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Three-, Four- and Five-Membered Rings From Disilenes

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THREE-, FOUR- AND FIVE-MEMBERED RINGS FROM DISILENES

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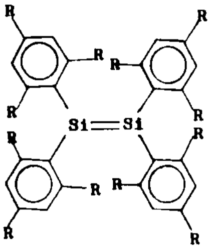
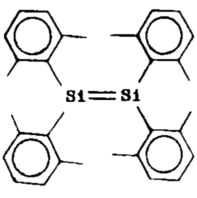
Abstract Disilenes, $R_2Si=SiR_2$, react with many substances to produce cyclic compounds containing two silicon atoms and one or more heteroatoms. Most of these products are new ring systems, and some show abnormal structures with short Si-Si bonds, suggesting unusual chemical bonding.

INTRODUCTION

The first stable compound containing a silicon-silicon double bond, tetramesityldisilene (1) was discovered in 1981.[1] Since that time a number of disilenes have been isolated, for example 2-7, and a fairly extensive reaction chemistry of disilenes is beginning to emerge.[2,3]



1, R = Me
2, R = i-Pr



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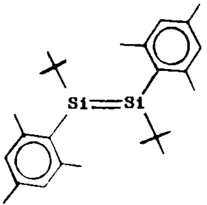
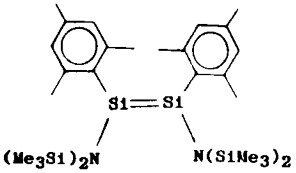
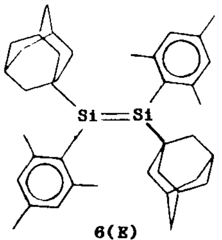


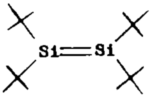
4(E)



5(Z)



6(E)



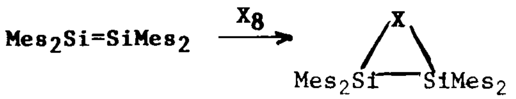
7

Disilenes are most conveniently synthesized by photolysis of the corresponding trisilanes[4] [Eq. (1)], although other methods of

$$RR'Si(SiMe_3)_2 \xrightarrow[\text{pentane,}-60^\circ C]{h\nu,\ 254\text{ nm}} Me_3SiSiMe_3 + [RR'Si] \rightarrow RR'Si{=}SiRR' \quad (1)$$

preparation are also successful.[5] Disilenes with two different substituents on each silicon, such as the dimesityldi-*tert*-butyldisilenes (**3**), form *cis-trans* isomers; often one or both stereoisomers can be obtained in pure form. The synthesis, structure, bonding, reactivity and isomerism of disilenes is discussed in several recent reviews.[2]

Although stable disilenes are protected against polymerization by the presence of sterically hindering substituent groups on silicon, they are nevertheless highly reactive toward a variety of electrophilic and nucleophilic reagents. Like the olefins of organic chemistry, the disilenes typically undergo addition reactions, in which the pi component of the double bond between the silicon atoms is broken.[3] Many of the addition reactions yield noncyclic products, but others lead to ring systems. These compounds, containing two silicon atoms and one, two or three heteroatoms, will be the subject of this paper [Eq. (2)].

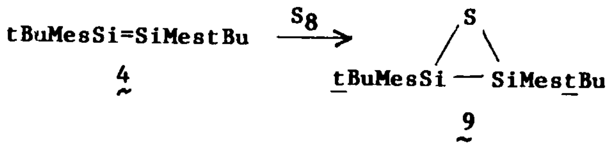


(2)

8a, X = S; **8b**, X = Se

REACTIONS WITH CHALCOGENS

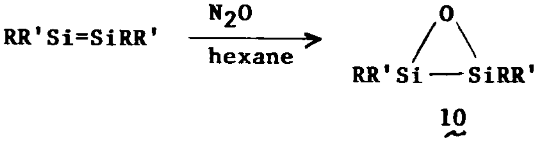
Disilenes react with sulfur or selenium to give, as principal products, three-membered rings.[6] The reaction of **E-4** with sulfur [Eq. (3)] takes place stereospecifically to give a single, pre-



(3)

sumably trans, product, **9**. The crystal structure of the thiirane **8a** has been determined, and will be discussed below.

The corresponding oxygen-containing three-membered ring, **10**, can be made by treating disilenes with dinitrogen oxide [Eq. (4)].[7]



(4)

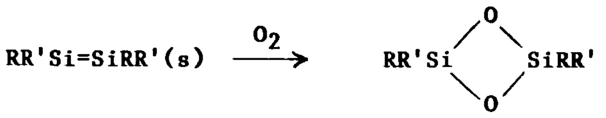
Disilaoxiranes (**10**) are also produced in small amounts in the dioxygen oxidation of disilenes in solution.

REACTION WITH DIOXYGEN

1,3-Cyclodisiloxanes

Disilenes react with triplet dioxygen to give cyclic products of unusual interest. When solid, crystalline or powdered disilenes are exposed to air, they slowly take up oxygen, the rate depending on the nature of the groups attached to silicon. Reaction is complete in a few minutes for the most reactive disilenes such as

1 and **3**, but requires hours for **4**, and days for the highly-hindered compounds **2** and **6**. In every case the final product is the 1,3-cyclodisiloxane **11** [Eq. (5)].[8,9]



11

(5)

Cyclic siloxanes are among the best known of organosilicon compounds, being manufactured in multiton quantities as principal intermediates in the industrial synthesis of silicone polymers. However, all previously known cyclic siloxanes consist of six-membered or larger rings; these are the first examples of four-membered ring cyclosiloxanes.

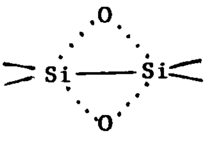
The structures of four of the cyclodisiloxanes, those from oxidation of **1**, *E*-**4**, *Z*-**5** and **7**, have been established by x-ray crystallography.[10] The four-membered rings have abnormally small Si—O—Si bond angles, less than 90° in some compounds (Table I). Even more striking are the silicon-silicon distances

TABLE I Structural parameters for cyclodisiloxanes, $RR'SiO_2SiRR'$.

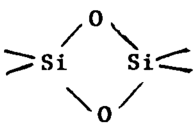
R	R'	<SiOSi,°	Si-Si,pm	Ref.
Mesityl	Mesityl	86.2	230.6	10
Mesityl	t-Butyl(E)	91.9	239.6	10
Mesityl	$N(SiMe_3)_2$(E)	84.4,89.7	234.9	10
t-Butyl	t-Butyl	95.8	245.3	11

across the ring, which range from 230 to 246 pm. These values are near that for a normal Si-Si sigma bond, about 235 pm. The oxidation takes place stereospecifically, with isomers **E**-**4** and **Z**-**5** giving the corresponding stereoisomers of the cyclodisiloxanes.

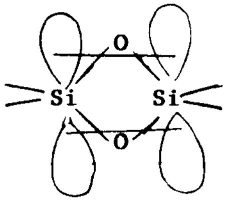
Several different models have been suggested to account for the unusual structures of the cyclodisiloxanes.[12] One possibility is that a sigma bond exists between the silicon atoms, with some electron-deficiency in the Si-O sigma bonds (A). Another, and more likely possibility is that oxygen-oxygen repulsion dominates the structure, forcing the silicon atoms together but with no bonding interaction between them (B). Most of the many *ab initio* calculations done on these rings favor model B; but recently a third model (C) has been proposed by Grev and Schaeffer,[13] in which there is *pi-bonding, but no sigma bonding* between the silicons.



A

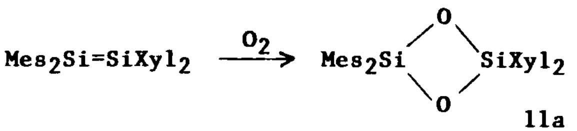


B



C

To provide some experimental information about this bonding question, the ^{29}Si-^{29}Si NMR coupling constant was determined for an unsymmetrically-substituted cyclodisiloxane, **11a**, prepared by oxidation of the corresponding [Eq. (6)] disilene.[14] Because



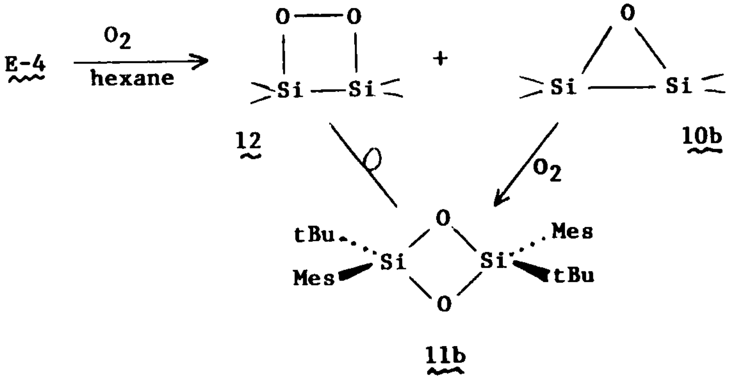
(6)

11a

the two silicon atoms in **11a** have different chemical shifts, the ^{29}Si-^{29}Si coupling constant between them can be determined. Directly-bonded silicon atoms show $^{1}J_{Si-Si}$ = 80 Hz, while open-chain siloxanes, Si—O—Si, have two-bond J_{Si-Si} values of 1 to 10 Hz. The value of 3.8 Hz observed for **11a** indicates that there is not a classical Si-Si single bond between the silicons. It is therefore inconsistent with model (A), but consistent either with (B) or with (C). In the latter case the pi-bonding between silicons would not provide the Fermi contact needed for coupling of the nuclear spins.

1,2-Dioxetanes and Disilaoxiranes

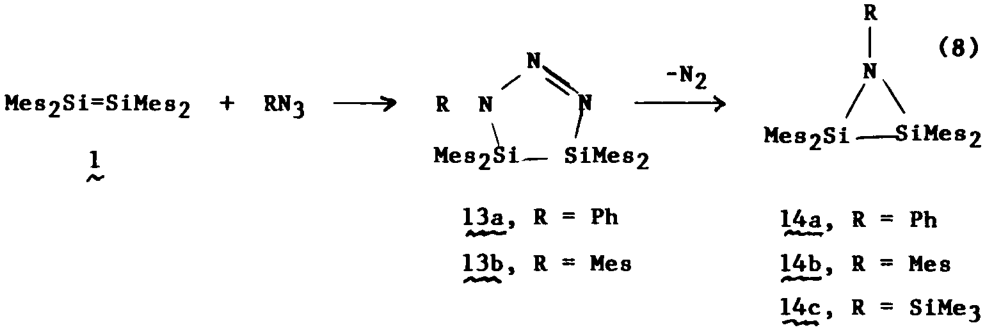
The reaction of disilenes with dioxygen in solution is more complicated. For example, **E-4** reacts with O_2 in hexane solution to give as major product the 1,2-dioxetane **12**; the minor product is the oxirane (epoxide), **10b**.[15] If excess oxygen is present **10b** undergoes further oxidation to the cyclodisiloxane **11b** [Eq. (7)]. The 1,2-dioxetane slowly, and spontaneously, rearranges to the same 1,3-cyclodisiloxane. All of the reactions are highly stereoselective, with the **E** configuration being maintained in **10b**, **12** and **11b**. The mechanisms of these unprecedented transformations are under intensive study.



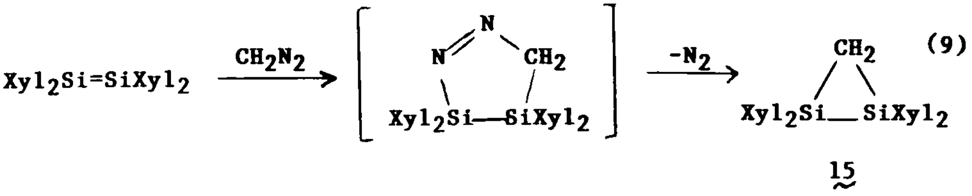
(7)

Reactions with Azides and Diazomethane

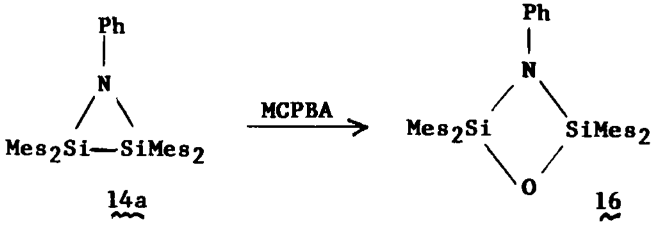
Covalent azides are known to react with olefins by 1,3 dipolar cycloaddition to give five-membered rings. The reaction of azides with disilenes appears to take a similar course. Phenyl azide and mesityl azide reaction with **1** to give initially the intensely purple-colored cyclic products **13a** and **13b** respectively [Eq. (8)]. These compounds are relatively unstable, losing dinitrogen to give the three-membered ring azadisiliranes **14ab**. With trimethylsilyl azide only the final product **14c** is observed, apparently because loss of N_2 from the five-membered ring is very rapid.[16]



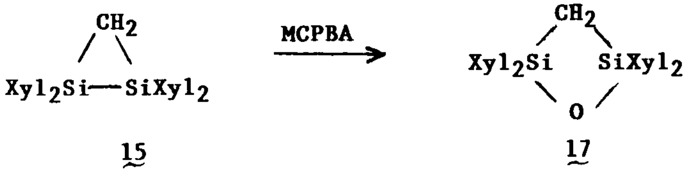
The reaction of **2** with diazomethane, leading to the disilacyclopropane **15**,[17] may also take place by 1,3-dipolar cycloaddition and loss of nitrogen [Eq. (9)]. All of these cyclic com-



pounds represent novel ring systems. As shown in equations (10) and (11), peracid oxidation of the three-membered rings leads to

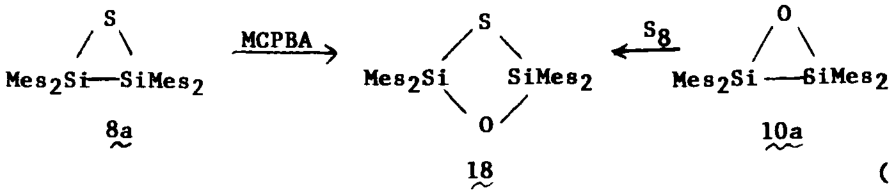


(10)



(11)

additional new kinds of ring systems, the four-membered rings 16 and 17. A related new ring, the thiaoxetane 18, can be obtained either by oxidation of the thiirane 8a or sulfurization of 10 [Eq. (12)].[16]



(12)

Structures of Three-Membered Rings

X-ray crystallographic studies have now been carried out on four different three-membered ring compounds containing two silicon compounds, 8a, 10a, 14c and 15, as well as for the trisilacyclopropane $(Xyl_2Si)_3$.[18] As an example, the ORTEP diagram for the structure of 10a is shown in Figure 1. The results, listed in Table II, are of unusual interest.

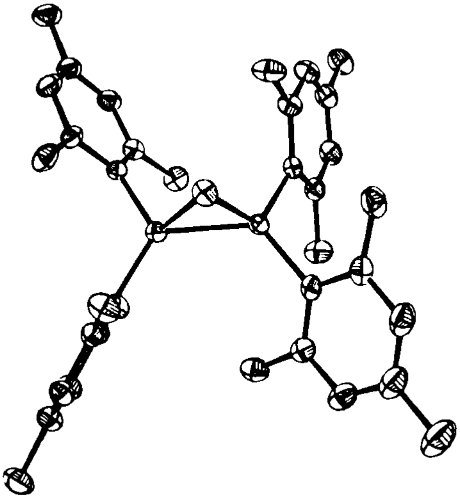


Figure 1

TABLE II. Si-Si bond lengths (pm) and sum of bond angles about silicon[a] in three-membered rings, RR'SiXSiRR'.

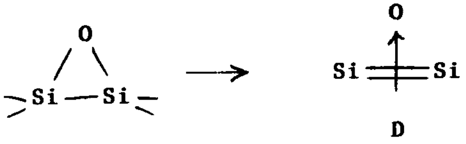
Compound	Si-Si, pm	$\Sigma\angle$(Si),[a]	Ref.
$(Xyl_2Si)_3$	237.5-242.5	346.5-349.5	18
$(Mes_2Si)_2S$, 8a	228.9	357.4	6
$(Xyl_2Si)_2CH_2$, 15	227.2	357.4,357.7	17
$(Mes_2Si)_2NSiMe_3$, 14	223.0	357,358	16
$(Mes_2Si)_2O$, 10a	222.8	359.9	7

---

[a] Sum of angles RSiR', RSiSi, R'SiSi.

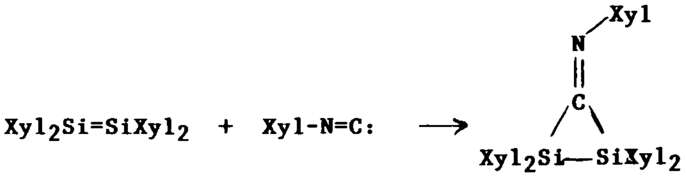
The first point to be noted is that the silicon-silicon distances are abnormal. In trisilacyclopropane the Si-Si bond lengths are near 240 pm, a little longer than the unconstrained Si-Si single-bond length of 235 pm. Therefore it is surprising that in the other three compounds, the Si-Si distances are shorter than the usual single-bond distance; for **14c** and **10a** the Si-Si separation is actually closer to that for a Si=Si double bond, 215 pm, than for a single bond. Moreover, the arrangement around silicon in the heterorings is remarkable. In $(Xyl_2Si)_3$ the organic groups are bent away from the plane of the Si_3 ring, as expected for a cyclopropane structure. But for the other compounds the carbon atoms attached to silicon are nearly, or (for **10a**) completely coplanar with the Si-Si vector.[7] Thus in **10a** the arrangement about silicon is quite similar to that in the corresponding disilene, with just a slight lengthening of the Si-Si distance.

Theoretical studies on disilaoxirane and related materials are being carried out by various groups. Qualitatively, the short Si-Si bond length and planar arrangement of groups around silicon in **10a** can be rationalized by a contribution of a pi-complex form D to the structure.



Reaction with Isocyanides: A Disilacyclopropanimine

Although disilenes react with diazomethane as described above, no unambiguous reaction of a carbene with a disilene has yet been reported. Disilenes react however with isocyanides, to give disilacyclopropanimines.[19] In one case the product, **19**, has been decisively identified by x-ray crystallography [Eq. (13)]. Since all other three- and four-membered rings described here are colorless, it is remarkable that disilacyclopropamimines are bright red, with λ_{max} = 510 nm for **19**. The reason underlying this unusual long-wavelength absorption is not yet understood.



19

(13)

SUMMARY

Stable disilenes, although stabilized toward polymerization by the presence of sterically-hindering substituents, are nevertheless highly reactive toward a wide variety of reagents. In many cases, reactions of disilenes proceed by cycloaddition to give three-, four- or five-membered rings containing heteroatoms: N, O, C, S or Se are known so far. Nearly all of these products represent new cyclic systems which have not been obtainable through other syntheses, and several show unusual structural or physical properties. Many other reactions remain to be tried; the cycloaddition reactions of disilenes are likely to provide numerous other examples of novel and interesting systems.

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REFERENCES

1. R. West, M. J. Fink, and J. Michl, Science (Washington), 214, 1343 (1981).
2. a) R. West, Pure Appl Chem., 56, 163 (1984); b) R. West, M. J. Fink, M. J. Michalczyk, D. J. De Young, and J. Michl in Organosilicon and Bioorganosilicon Chemistry edited by H. Sakurai (Ellis Horwood, Chichester, England, 1985) p 3;

c) G. Raabe and J. Michl, Chem. Rev. 85, 420 (1985); d) R. West, Angew. Chem. Int. Ed. Engl., 26, 1201 (1987).

3. D. J. De Young, M. J. Fink, J. Michl and R. West, Main Group Metal Chem. 1, 19 (1987).
4. M. J. Fink, M. J. Michalczyk, K. J. Haller, J. Michl, and R. West, Organometallics, 3, 793 (1984); R. West, G. R. Gillette, and H. B. Yokelson, Inorg. Synth. 25, xxx (1988); G. R. Gillette, H. B. Yokelson, and R. West, Organomet. Synth., 4, 529 (1988).
5. S. Masamune, S. Murakami, J. T. Snow, H. Tobita, and D. J. Williams, Organometallics, 3, 333 (1984); S. Murakami, S. Collins, and S. Masamune, Tetrahedron Lett., 25, 2131 (1984).
6. R. West, D. J. De Young, and K. J. Haller, J. Am. Chem. Soc. 107, 4942 (1985).
7. H. B. Yokelson, A. J. Millevolte, G. R. Gillette, and R. West, J. Am. Chem. Soc., 109, 6865 (1987).
8. M. J. Fink, D. J. De Young, R. West, and J. Michl, J. Am. Chem. Soc. 105, 1070 (1983).
9. M. J. Michalczyk, R. West, and J. Michl, J. Chem. Soc., Chem. Commun., 1525 (1984).
10. M. J. Michalczyk, M. J. Fink, K. J. Haller, R. West, and J. Michl, Organometallics, 5, 531 (1986).
11. E. Pham, and R. West, unpublished studies.
12. E. A. Kirichenko, A. I. Ermakov, and I. N. Samsonova, Russ. J. Phys. Chem., 51, 1468 (1977)); T. Kudo and S. Nagase, J. Am. Chem. Soc., 107, 2589 (1985); S. M. Bachrach and A. Streitweiser, J. Am. Chem. Soc., 107, 1186 (1985); E. D. Jemmis, R. V. V. P. Kumar, N. R. S. Kumar, J. Chem. Soc., Dalton Trans., 271 (1987); I. Silaghi-Dimitrescu and I. Haiduc, Inorg. Chim. Acta, 112, 159 (1986); R. J. Brenstein and S. Scheiner, Int. J. Quantum Chem., 29, 1191 (1986).
13. R. Grev, and H. J. Schaefer, J. Am. Chem. Soc., 109, 6577 (1987).
14. H. B. Yokelson, A. Millevolte, B. Adams, and R. West, J. Am. Chem. Soc., 109, 4116 (1987).
15. R. West, H. B. Yokelson, G. R. Gillette, and A. J. Millevolte in Silicon Chemistry, edited by J. Y. Corey, E. R. Corey and P. P. Gaspar (Ellis Horwood, Chichester, England, 1988), Chap. 26, pp. 269-281.
16. G. R. Gillette, and R. West, unpublished investigations. Values given in Table II are preliminary.
17. S. Masamune, S. Murakami, and H. Tobita, J. Am. Chem. Soc., 105, 7776 (1983).
18. S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and J. F. Blount, J. Am. Chem. Soc. 104, 1150 (1982).
19. H. B. Yokelson, A. J. Millevolte, K. J. Haller, and R. West, J.C.S., Chem. Comm., 21, 1605 (1987).