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REACTIONS OF SILYLENES WITH 1,4-DIPHENYL-1,3-BUTADIENE AND 1-METHYL-1,2,3,4,5-PENTAPHENYLSILOLE. A NOVEL SILYLENE-SILYLENE EXCHANGE REACTION1)

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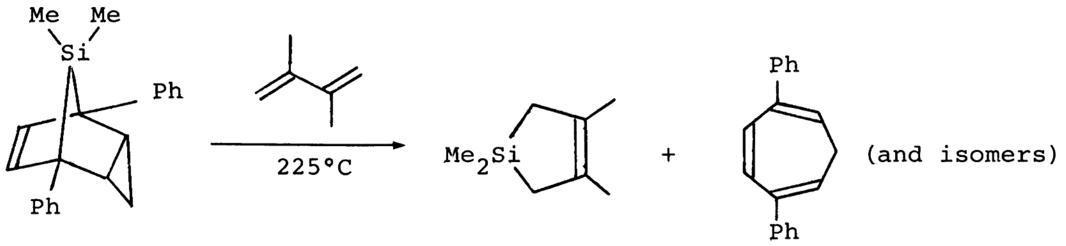
Thermally generated dimethylsilylene reacts with 1,4-diphenyl-1,3-butadiene to give 1,1-dimethyl-4,5-diphenyl-1-silacyclo-2-pentene. A mechanism involving homolytic C-C bond cleavage of the intermediate vinylsilacyclopropane is suggested. Dimethylsilylene also undergoes a novel silylene-silylene exchange reaction with 1-methyl-1,2,3,4,5-pentaphenylsilole.

As Tortorelli and Jones have described recently,2) the chemistry of silylenes, the second-row counterpart of carbenes, remains unexplored.3) For example, one of the most fundamental reactions such as addition of silylenes to olefins and dienes has not been elucidated satisfactorily.

More recently, Schriewer and Neumann4) reported results of interesting stereochemical studies of the reaction of germylenes to dienes, where concerted 1,4-additions of a linear [2+4] cheletropic type to certain dienes such as (1E, 3E)-1,4-diphenyl-1,3-butadiene (**1**) were demonstrated. We report in this paper that the thermally generated dimethylsilylene gives a product of an entirely different type in the reaction with **1**.

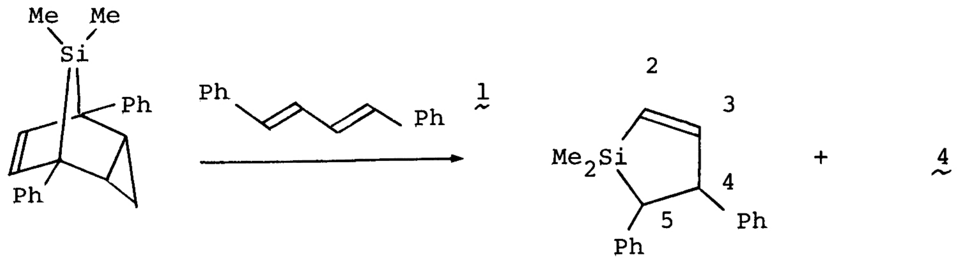
Addition of dimethylsilylene to 2,3-dimethylbutadiene gives 1,1,3,4-tetramethyl-1-silacyclopent-3-ene, arising from formal 1,4-addition of the silylene to the butadiene.3) We have reported previously that 1,5-diphenyl-8,8-dimethyl-8-silatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**)5) is a good photochemical silylene generator. The compound also proved to give dimethylsilylene under pyrolytic conditions. Thus a sealed-tube-thermolysis of the silylene generator in the presence of 2,3-dimethyl-1,3-butadiene at 225°C for 4 h actually gave the expected 1,1,3,4-tetramethyl-1-silacyclopent-3-ene in 34.6% yield, by formal 1,4-addition.



2 **4**

We thought therefore that addition of the silylene to **1** could also afford a similar silacyclopentene by formal 1,4-addition. Then in order to study stereochemistry of the addition reaction of dimethylsilylene to conjugated dienes, thermolysis of **2** in the presence of **1** under the same conditions has been conducted.

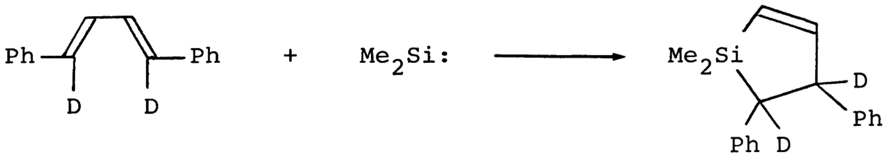
However, contrary to our expectation, a product obtained in 66.6% yield as a colorless oil was a mixture of two isomeric 1,1-dimethyl-4,5-diphenyl-1-silacyclopent-2-enes (**3**). A mixture of isomeric diphenylcycloheptatrienes (**4**)[5)] was also detected.



2 **3**; a = trans, b = cis

In the mass spectrum of the former oily product, a parent peak at m/e 264, corresponding to the 1:1 adduct between dimethylsilylene and the butadiene **1** was observed. The ^{1}H NMR spectrum of the major product (**3a**) in $CDCl_3$ shows two kinds of singlets due to Si-Me groups with an equal intensity at δ -0.09 and 0.26 ppm, and two kinds of doublets of doublets due to vinyl protons at δ 6.88 (C_3-H) and 6.16 (C_2-H) ppm. Furthermore a doublet of triplets and a doublet due to two different benzyl protons appear at δ 4.17 (C_4-H) and 2.39 (C_5-H) ppm, respectively. Another multiplet at around 7.0-7.5 ppm is assigned to those of aromatic protons.[6)] In the UV spectrum, no absorption due to styrene nor stilbene chromophore was observed. These spectral data show clearly that the product is 1,1-dimethyl-4,5-diphenyl-1-silacyclopent-2-ene (**3**) but not its isomeric 1,1-dimethyl-2,5-diphenyl-1-silacyclo-pent-3-ene (**5**). Two benzyl protons of the trans isomer (**3a**) should appear at higher field than the corresponding protons of the cis isomer (**3b**) in ^{1}H NMR because of the expected diamagnetic shielding due to the syn phenyl groups. Comparison of ^{1}H NMR data[6)] indicates clearly **3a** to be the trans. The **3a**/**3b** ratio of 4.6/1 is also reasonable as a preferential formation of the trans isomer.

In order to confirm the above result further, **2** was thermolyzed in the presence of the dideuterated butadiene (**6**) under the same conditions. The corresponding dideuterated silacyclopentene was obtained as an oil in 59.4% yield. In the mass spectrum of the deuterated product, the parent peak shifted to m/e 266. In the NMR spectrum in carbon tetrachloride, the peak corresponding to two kinds of benzyl protons disappeared but two doublets at δ 6.16 and 6.88 ppm due to vinyl protons still remained unchanged. These spectral characteristics show the silacyclopentene obtained to be 4,5-dideuterio-4,5-diphenyl-1-silacyclopent-2-ene (**7**). Again, the silacyclopentene (**7**) was found to be composed of two isomers with a ratio of ca. 5:1.

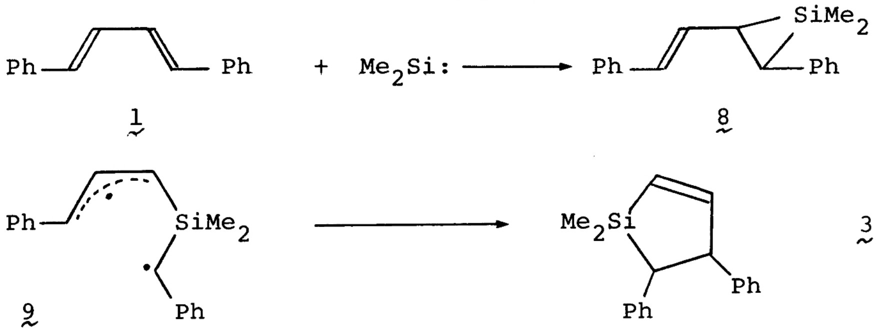


6 **7**

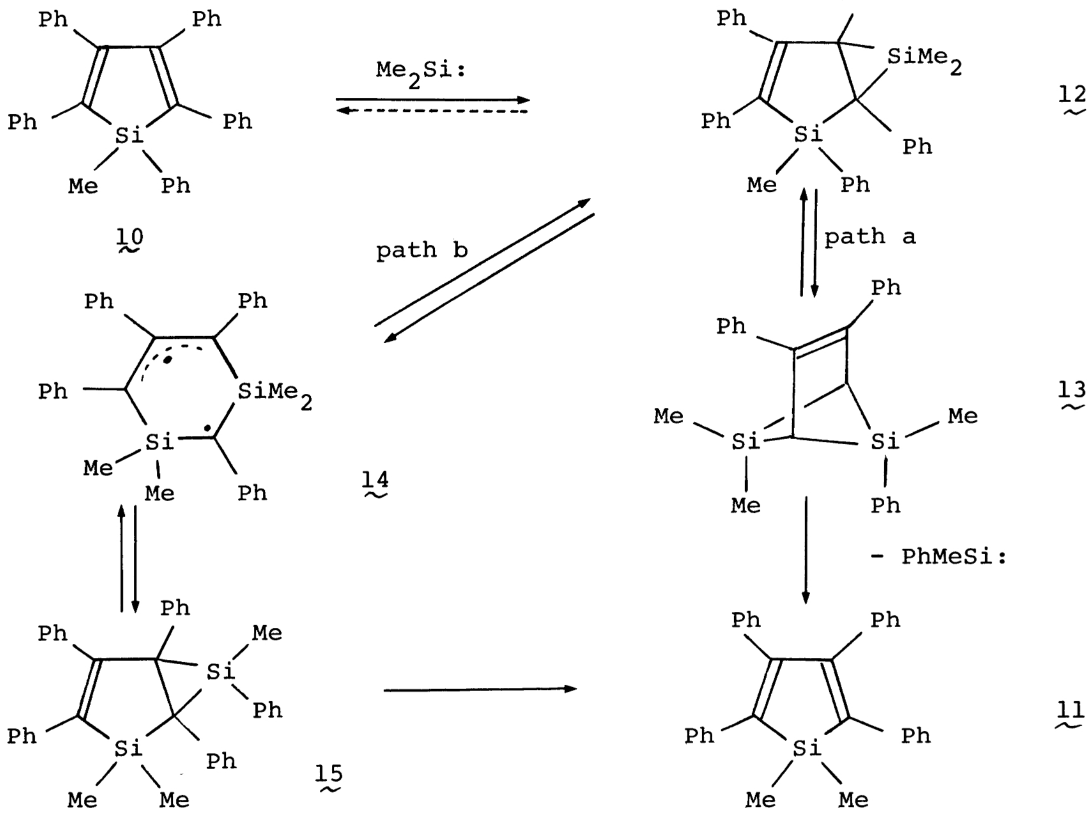
Furthermore, 3 was obtained also by the reaction of 1 and 1.2 molar equivalent amount of another silylene generator, 1,2-dimethoxy-1,1,2,2-tetramethyldisilane, in benzene in a sealed tube at 250°C for 12 h in 20% yield (3a/3b = 5.3/1).

These findings are accounted for only by the formation of a vinylsilacyclopropane (8) as an intermediate, followed by the cleavage of the carbon-carbon bond of the silacyclopropane moiety to afford the diradical intermediate (9) which is then transformed to the final product by an intramolecular recombination of the radical centers, as shown in the scheme 1.

Scheme 1.



Scheme 2.



Such a mechanism has been proposed for the reaction of silylene with cyclic dienes[7a,c] and cyclooctatetraene.[8] However, a carbon-carbon bond cleavage of a silacyclopropane has not been reported yet in the case of an acyclic system. The driving force for such rearrangement observed in the silacyclopropane of the present study can be attributed to the effect of phenyl groups to stabilize the radical centers.

Although reactions of silylenes with cyclic dienes such as cyclopentadiene[7c,d] and cyclooctadiene[7a] has been reported, the reaction with a cyclic diene containing a heteroatom has not been investigated yet, except for some furan derivatives.[7b,d] Herein, we report an interesting thermal reaction of dimethylsilylene with 1-methyl-1,2,3,4,5-pentaphenylsilole (**10**).

Thermolysis of a benzene solution of **2** in the presence of **10** in a sealed tube afforded an yellow crystal in 10% yield together with unreacted **10**. The mass spectrum of the crystal shows a parent peak of $C_{30}H_{26}Si$ at m/e 414, which is identified to be 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**11**) by comparing its NMR spectrum with that of an authentic sample.

The formation of **11** can be explained by two ways as follows (Scheme 2): (a) thermal 1,3-sigmatropic shift of **12** to give **13**, which loses phenylmethylsilylene to yield the silole (**11**), and (b) the carbon-carbon bond cleavage of the silacyclopropane (**12**) to lead to a diradical (**14**) which gives **15** followed by extrusion of the silylene to afford the silole (**11**). Although vinylsilacyclopropane-silacyclopentene rearrangement in a fashion of a concerted reaction (path a) is possible as previously reported,[9] a diradical process involving an intermediate (**14**) (path b) appears more likely in reference to the result of the acyclic system.

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6) 3: an oil (**3a** + **3b**, **3a**/**3b** = 4.6/1); MS m/e (%) M^+ 264 (49), 249 (22), 206 (33) 173 (100); high resolution MS found 264.1348, calcd for $C_{18}H_{20}Si$ 264.1333. ^1H NMR ($CDCl_3$) δ; **3a** (major isomer) -0.09 (s, 3H, $SiCH_3$), 0.26 (s, 3H, $SiCH_3$), 2.39 (d, 1H, $J_{4,5}$ = 6.8 Hz, C_5-H), 4.17 (ddd, 1H, $J_{2,4}$ = 2.4 Hz, $J_{3,4}$ = 2.2 Hz, $J_{4,5}$ = 6.8 Hz, C_4-H), 6.16 (dd, 1H, $J_{2,3}$ = 10.3 Hz, $J_{2,4}$ = 2.4 Hz, C_2-H), 6.88 (dd, 1H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ =2.2 Hz, C_3-H), 7.0-7.5 (m, 10H, ArH). **3b**: (minor isomer) 0.09 (s, 3H, $SiCH_3$), 0.24 (s, 3H, $SiCH_3$), 2.89 (d, 1H, $J_{4,5}$ = 8.4 Hz, C_5-H), 4.36 (ddd, 1H, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 8.4 Hz, C_4-H), 6.36 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{2,4}$ = 2.2 Hz, C_2-H), 7.0-7.5 (m, 11H, C_3-H and ArH).

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