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PHOTOOXYGENATION OF SILACYCLOPENTADIENES: A NOVEL OXYGENATION PRODUCT, 2,4-DIOXA-3-SILABICYCLO[3.2.0]HEPT-6-ENE, AND ITS CYCLOREVERSION REACTIONS[1)]

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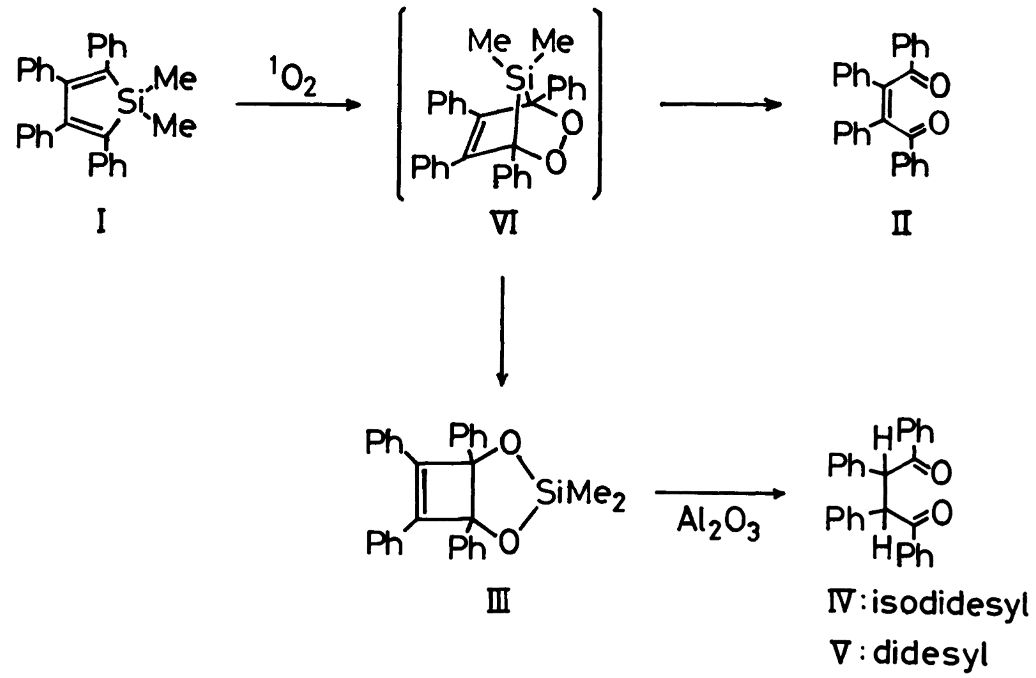
Photooxygenation of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene afforded 2,4-dioxa-3-silabicyc[3.2.0]hept-6-ene(III) together with dibenzoylstilbene. The former was converted to isodidesyl and didesyl by treatment on alumina. Valence bond isomerization of III to 1,3-dioxa-2-silacyclohepta-4,6-diene occurs both thermally and photochemically.

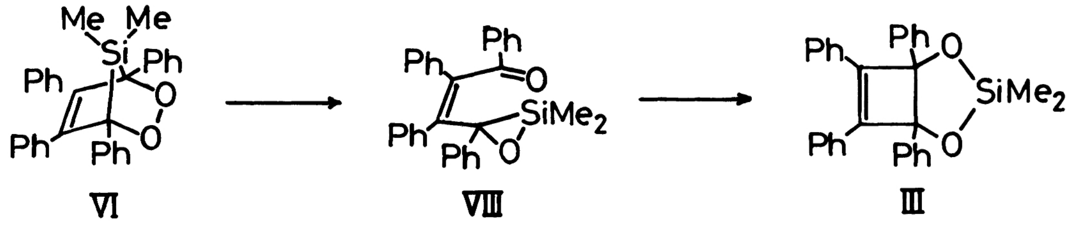
The reaction of singlet oxygen with cyclic dienes such as tetraphenylfuran and tetracyclone affords dibenzoylstilbene.[2)] In marked contrast, however, the silicon analogue, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (I) has been described to yield isodidesyl as a major product.[3)] The methyl groups on silicon were considered as the source of hydrogen for the reduction. This unusual behavior has stimulated us to study the photooxygenation of I in detail. We report here that the oxygenation of I with singlet oxygen actually gives dibenzoylstilbene (II) and 2,4-dioxa-3-silabicyclo[3.2.0]hept-6-ene (III). The latter is converted to isodidesyl (IV) afterward by treatment on an alumina column. An interesting interconversion of III into 1,3-dioxa-2-silacyclohepta-4,6-diene (VII) is also described.

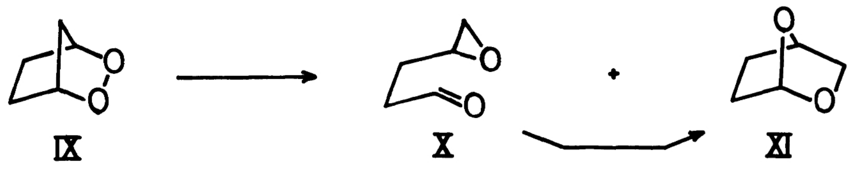
The silacyclopentadiene (I) in carbon disulfide was irradiated with a high pressure mercury lamp in an NMR tube at low temperature (Dry Ice-MeOH) under a constant stream of oxygen, the oxygenation reaction being monitored by means of NMR spectroscopy. During the reaction, two new Si-Me signals with an equal intensity appeared and the intensity of the peaks increased with consumption of I. However, during the course of oxygenation, no signal due to IV was detected on the NMR spectra of the reaction mixture. After disappearance of the NMR signals due to I, the reaction mixture was concentrated under reduced pressure and submitted to TLC on silica gel to afford II (20%) and a white crystal having a molecular formula of $C_{30}H_{26}O_2Si$ (29%), but IV was not detected at this stage. At first, we thought the white crystal to be the expected endoperoxide (VI) from the spectroscopic data, but single-crystal X-ray diffraction study on the compound demonstrated clearly that the structure should be assigned to 3,3-dimethyl-1,5,6,7-tetraphenyl-2,4-dioxa-3-silabicyclo[3.2.0]heptene (III).[4)] Spectroscopic data obtained for the compound cannot distinguish III from VI. The ORTEP drawing of the molecular structure of III is shown in Figure 1.

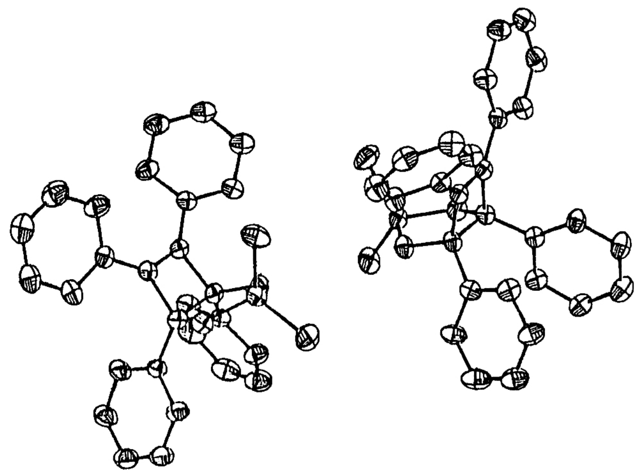


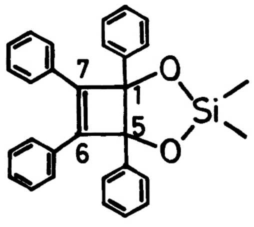
Interestingly, treatment of III on alumina TLC afforded IV and didesyl (V) in 35 and 19% yield, respectively.[3,7] This indicates that in oxygenation of I, IV is formed indirectly from III by the hydrolytic cleavage and that hydrogen abstraction from the Si-Me groups by the oxy radical derived from the endoperoxide (VI), as suggested previously, was highly unlikely.[3]

Formation of III from I is interesting. Although not demanded, the following explanation accounts for the reaction mechanism reasonably. Singlet oxygen adds I to form VI which gives II with concomitant elimination of dimethylsilylene. At the same time, VI is conceivable to rearrange to VIII competitively. A silaoxirane (VIII) then cyclizes to give III with cleavage of a highly strained Si-C bond as shown in the Scheme. This reaction is reminiscent of the formation of X and XI from the thermolysis of an endoperoxide (IX)[9].





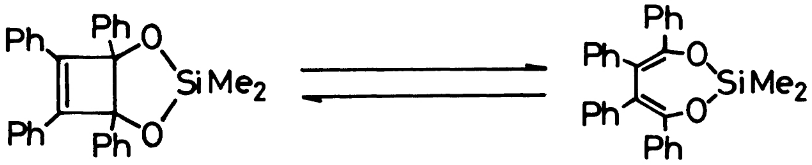




III

Figure 1. ORTEP drawing of the molecular structure of III which was determined by X-ray diffraction method. Crystal Data: a=13.822(2), b=9.892(1), c=21.701(2)Å, α =79.46(1), β =119.10(1), γ =107.83(1)°, space group=P$\bar{1}$(Z=4). The R value was reduced to 0.09 for 6837 observed reflections by anisotropic non-hydrogen atoms refinements. This figure shows two molecules in the unit cell and their molecular geometries are essentially the same except for the torsion of phenyl group. Selected bond lengths averaged among equivalent bonds over two independent molecules are: Si-O= 1.658(5), C(1)-C(5)= 1.60$_2$, C(1)-C(7)= 1.52$_7$, C(6)-C(7)= 1.35$_1$ Å.

Thermolysis of III took place readily at 190°C to give a valence isomer, 2,2-dimethyl-4,5,6,7-tetraphenyl-1,3-dioxa-2-silacyclohepta-4,6-diene (VII)$^{10)}$ in quantitative yield. Kinetic studies revealed the reation to be the first-order process for which following activation parameters were obtained: E_a = 36 kcal/mol, $\Delta S^{\ddagger}$ = 2.9 e.u.$^{11)}$ Irradiation of VII with a high pressure mercury lamp through a Pyrex filter induced the isomerization in the reverse direction to yield III. On the other hand, irradiation with a high pressure mercury lamp through a quartz wall gave a photochemically equilibrated mixture composed of III and VII in the ratio of 45:55.



III VII

It is interesting to note that the C_1-C_5 distance of 1.60$_2$ Å is longer than that of a normal carbon-carbon single bond, although other bond lengths are rather usual. Judging from the molecular geometry found in X-ray data, molecular orbitals of two phenyl groups can interact each other through an antibonding orbital of the C_1-C_5 bond. This should be the reason why the C_1-C_5 bond is lengthened.$^{12)}$ An example of phenyl interaction to cause bond elongation has been reported recently.[13)] Apparently, elongation of the bond is the factor to the enhanced reactivity in thermolysis of III.

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References

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4) III: mp 158-159°C; MS(%) M^+ 446(100); ^{1}HNMR (CS_2) δ 0.26 (3H, s, Si-CH_3), 0.57 (3H, s, Si-CH_3), 6.8-7.8 (20H, m, Ph) ppm; ^{13}CNMR ($CDCl_3$) δ 0.1 (q), 1.4 (q), 92.5 (s), 127.0 (d), 127.5 (d), 128.1 (d),1287 (d), 128.9 (d), 132.7 (s), 145.1 (s),138.7 (s) ppm; ^{29}SiNMR ($CDCl_3$) δ 31.3 ppm; UV (hexane) λ_{max}(log ε) 225 (4.54), 294 (4.19) nm. On the treatment with triphenyl phosphite ozonide in dichloromethane[5)] followed by TLC (SiO_2) separation, I gave III, II and V in 37, 17 and 7% yields, respectively. Similar results were also obtained by dye-sensitized photooxygenation (Rose-Bengal-coated SiO_2, W-lamp).[6)]

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7) IV: isodidesyl; ^{1}HNMR ($CDCl_3$) δ 5.39 (2H, s) ppm. V, didesyl; ^{1}HNMR ($CDCl_3$) δ 5.76 (2H, s) ppm. IV and V are diastereomeric each other [8)] and the equilibration with sodium methoxide shows that IV is thermodynamically more stable isomer.

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10) VII: mp 195-196°C; MS(%) M^+ 446 (100); ^{1}HNMR ($CDCl_3$) δ 0.21 (6H, s, Si-CH_3), 6.8-7.4 (20H, m, Ph) ppm ; ^{13}CNMR ($CDCl_3$) δ -2.2 (q), 124.8 (s), 126.0 (d), 127.4 (d), 127.5 (d), 127.6 (d), 129.3 (d), 131.8 (d), 138.8 (s), 139.1 (s), 148.8 (s) ppm; ^{29}SiNMR ($CDCl_3$) δ 20.6 ppm; UV (n-hexane) λ_{max}(log ε) 288 (4.21), 317 (4.26) nm.

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