Reactions of Oxasilacyclopropane. Generation of Silanediyl by Photo and Thermal Induced Cycloelimination

Wataru Ando,* Yoshitaka Hamada, and Akira Sekiguchi

Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 305, Japan

Dimesitylsilanediyl was generated from photolysis and pyrolysis of the oxasilacyclopropane (**1**) *via* a [3 → 2 + 1] cycloelimination reaction.

Photochemical or thermal treatment of epoxides is well known to cause [3→2+1] cycloelimination to produce carbenes and carbonyl compounds *via* carbonyl ylide intermediates.[1] However, the chemistry of the silicon analogues of epoxides is completely unknown because of the lack of such compounds. Recently, we succeeded in the preparation of a stable oxasilacyclopropane (**1**), the first silicon-containing epoxide, by the reaction of dimesitylsilanediyl with 1,1,3,3-tetramethylindan-2-one (**2**).[2] We now report our preliminary results on the photochemical and thermal reactions of the oxasilacyclopropane (**1**).

When an ethereal solution of (**1**) was photolysed (2537 Å) in the presence of methanol,† dimesitylmethoxysilane (**3a**) was formed in quantitative yield along with the indanone (**2**) (44%) and *o*-isopropyl-α-methylstyrene (**4**) (56%); see Scheme 1. The

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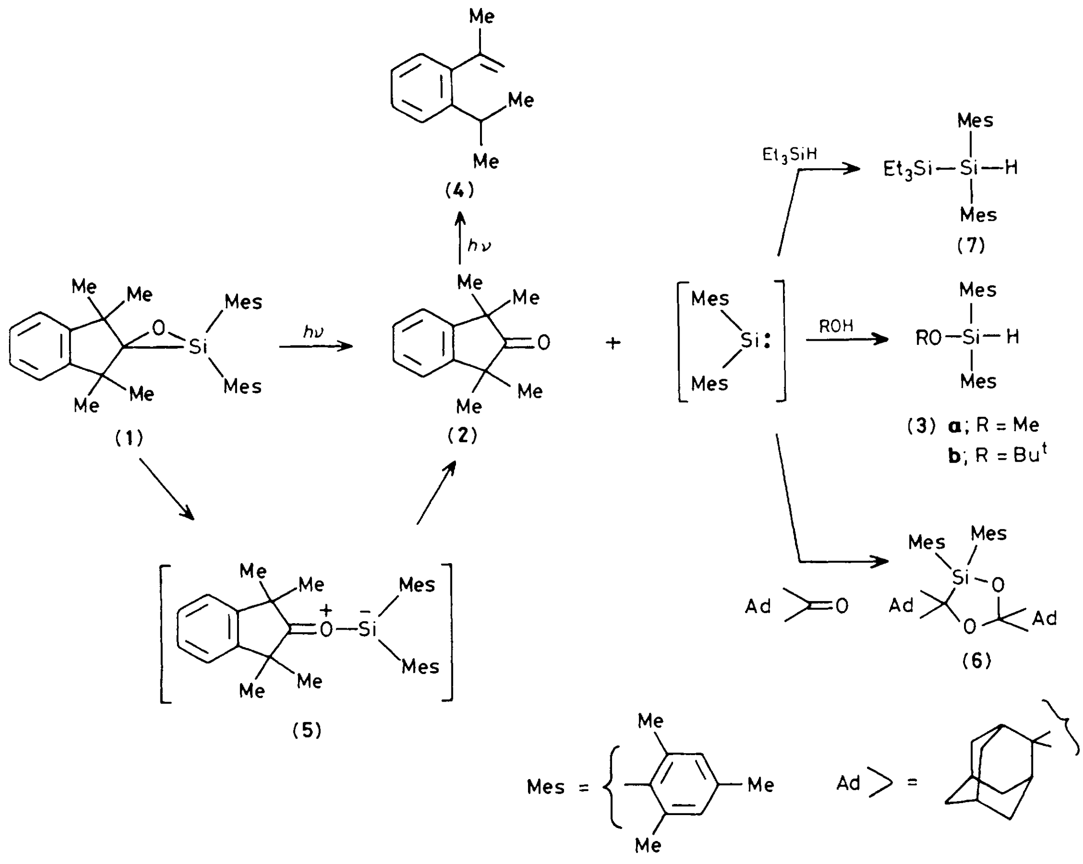
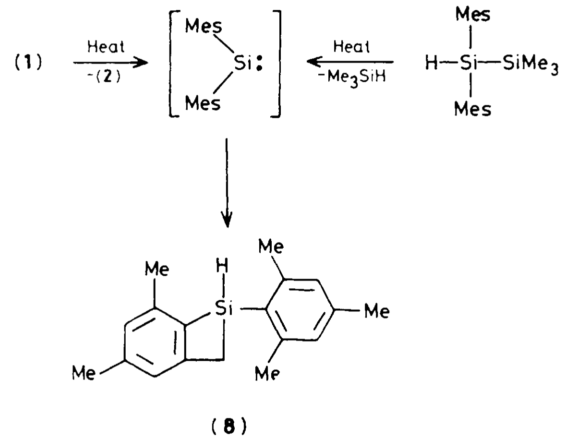
† U.v. spectrum of (**1**) in cyclohexane; λ_{max} 237 nm, log ϵ 4.68.



Scheme 1



Scheme 2

styrene (**4**) is evidently the photo-decomposition product of (**2**). The methoxysilane (**3a**) can be reasonably explained as an insertion product of dimesitylsilanediyl into the O–H bond of methanol. Similary, photolysis of (**1**) with t-butyl alcohol gave the t-butoxysilane (**3b**) in 86% yield in addition to (**2**) (39%), (**4**) (61%), and small amounts of dimesitylsilanol (14%) which was probably formed by hydrolysis of (**3b**). Photolysis of (**1**) in the presence of adamantanone yielded the dioxasilacyclopentane (**6**) in 65% yield.‡ Strong evidence for the existence of the dimesitylsilanediyl intermediate was presented by the reaction with triethylsilane, a well known reagent for trapping silanediyls. The disilane (**7**) was formed by the insertion of dimesitylsilanediyl into the Si–H bond, in 82% yield.‡ It is thus clear that compound (**1**) undergoes cycloelimination on photolysis to produce dimesitylsilanediyl and the ketone (**2**) either *via* the simultaneous cleavage of both the Si–O and the Si–C bonds or *via* the silyl carbonyl ylide (**5**). An attempt to trap the silyl carbonyl ylide (**5**) by a dipolarophile such as dimethyl acetylenedicarboxylate was not successful. These photochemical reaction sequences of the oxasilacyclopropane (**1**) are quite similar to those of other silicon-containing three-membered ring compounds, *e.g.* trisilacyclopropanes.[3] It is of interest that no product arising from cleavage of the Si–C and C–O bonds was obtained.

When a benzene solution of (**1**) was pyrolysed through a vertical Pyrex tube packed with Pyrex chips under flowing nitrogen at 520 °C, an interesting product, the benzosilacyclobutene (**8**) (40% yield) was formed as a white powder (m.p. 91.5—92.5 °C) along with the indanone (**2**) (94%) (Scheme 2). The structure of (**8**) was determined by its ^{1}H n.m.r., i.r., mass, and ^{13}C n.m.r. spectra: ^{1}H n.m.r. (CCl_4, δ) 6.94—6.74 (m, 4H, aromatic), 5.79 (br. s, Si-*H*, 1H), and 2.43 (br.s) and 2.38—2.19 (m) (17H, CH_3 and CH_2); ^{13}C n.m.r. ($CDCl_3$, δ) 151.3 (s), 144.8 (s), 141.6 (s), 140.8 (s), 140.1 (s), 139.6 (s), 128.7 (d), 128.5 (d), 128.0 (s), 126.9 (s), and 124.6 (d) (all aromatic C), 22.9 (q, CH_3), 21.9 (q, CH_3), 21.5 (q, CH_3), 21.1 (q, CH_3), and 18.1 p.p.m. (t, CH_2 of silacyclobutene); i.r. (NaCl) 2100 cm^{-1} (Si–H); *m/z* 266 (M^+). Elemental analyses were also consistent with structure (**8**). Alternatively, the benzosilacyclo-

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‡ Compounds (**6**) and (**7**) were independently prepared by the photolysis of 2,2-dimesitylhexamethyltrisilane with adamantanone and triethylsilane, respectively.

butene (**8**) can be prepared by the pyrolysis of 2,2-dimesityl-1,1,1-trimethyldisilane at 570 °C. The compound (**8**) is rationalised as the intramolecular insertion product of dimesitylsilanediyl into the C–H bond of *ortho*-methyl groups. Copyrolysis of (**1**) with methanol or triethylsilane also led to (**8**) instead of (**3a**) or (**7**), indicating that the intramolecular reaction of dimesitylsilanediyl prevails over the intermolecular reaction in the vapour phase.

In summary, the photochemical and thermal reactions of oxasilacyclopropane appear to be related to the cycloelimination of epoxides to give carbenes and carbonyl compounds, and involve silanediyl intermediates.

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