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PHOTOLYSIS AND THERMOLYSIS OF 1,2,3-TRISILACYCLOPENTENE. REGIOSPECIFIC AND NON-REGIOSPECIFIC SILYLENE EXTRUSION[#,1]

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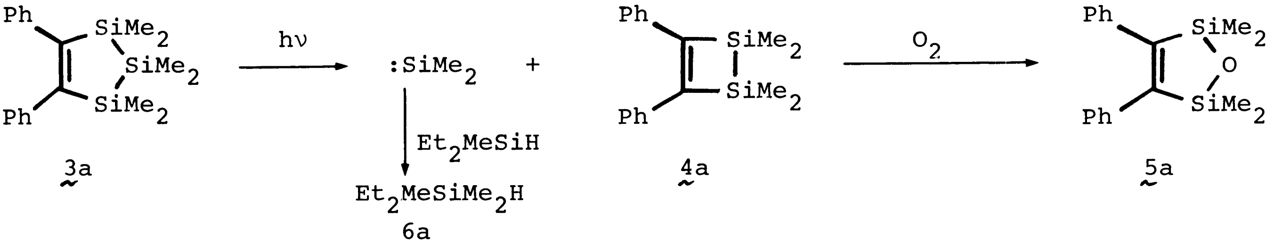
1,2,3-Trisilacyclopent-4-ene generates silylene to give 1,2-disilacyclobut-3-ene on both photolysis and thermolysis. The silylene arises from either the central or the terminal silicon atom of the ring depending on the nature of substituents on the central silicon atom on photolysis, but the central silicon is ejected as silylene regiospecifically on thermolysis.

We have reported previously that 1,2,3-trisilacycloheptane derivatives (1) extrude the central silicon atom as a silylene photochemically to give the corresponding 1,2-disilacyclohexanes (2) with retention of the configuration.[2]

In relation to the cheletropic silylene extrusion of 1, the reaction of 1,2,3-trisilacyclopentene (3) seemed to be of great interest, since the mechanism and products of the reaction might be affected by the π-bonding which linked cyclically to a trisilanylene unit. In this letter, we report the regiochemistry of photochemical and thermal silylene extrusion reactions of 3. The thermolysis of 1,2-disilacyclobutene (4a) is also reported.

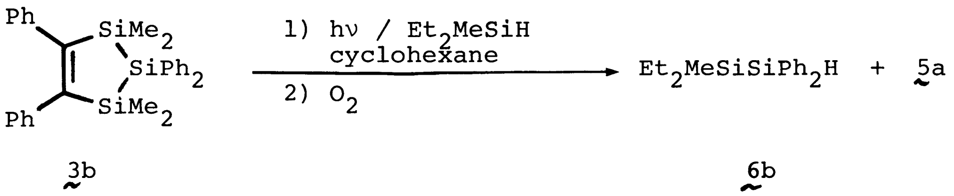
Irradiation of a cyclohexane solution of 1,1,2,2,3,3-hexamethyl-4,5-diphenyl-1,2,3-trisilacyclopent-4-ene (3a) in the presence of diethylmethylsilane for 18 h gave 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disiacyclobut-3-ene (4a) and 1,1-diethyl-1,2,2-trimethyldisilane (6a) in 86 and 78% yield, respectively.[3] Being extremely prone to oxidation, the former was isolated and identified as disiloxane 5a after aerial oxidation of the photo-products.[4] Therefore, 3a undergoes a ring-contraction reaction similarly to 1, together with extrusion of dimethylsilylene.

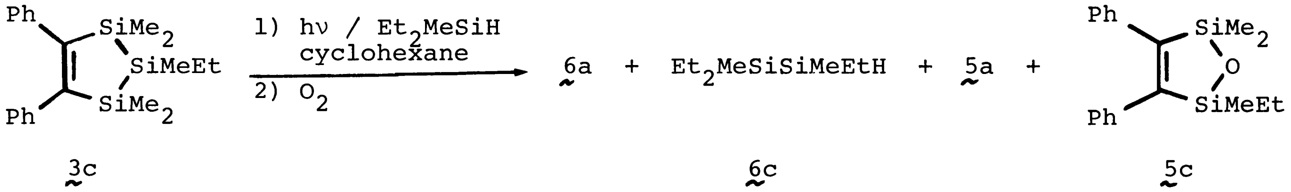


Next, the photolysis of diphenyl- (3b) and ethyl-substituted derivatives (3c) of 3a at the central silicon, prepared by silylene insertion into the Si-Si bond of 4a,[4,5] was examined in order to assign which silicon of the trisilanylene unit is eliminated as a silylene.

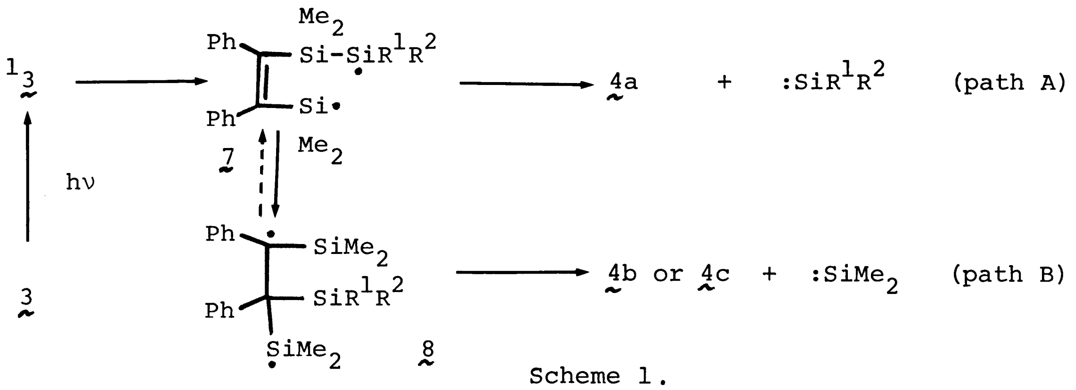
[#] Dedicated to Professor Tadashi Suehiro on the occasion of his 60th birthday.

Photolysis of a cyclohexane solution of 3b in the presence of diethylmethylsilane, as a silylene trap, for 38 h[3)] followed by aerial oxidation resulted in the formation of 5a and 6b in 63 and 25% yield, respectively. Therefore the central silicon was ejected as diphenylsilylene. In contrast, under similar conditions 3c afforded disiloxanes 5a and 5c in 27 and 35% yield, respectively, together with hydrodisilanes 6a and 6c, which were identified by means of GC-MS.[6)] Therefore, in this case, both central and terminal silicon atoms were extruded as silylenes. Qualitatively, addition of piperylene, as a triplet quencher, affected neither the reactivity of 3c nor the relative ratio of 4a to 4c.





These results may be explained in terms of a stepwise radical mechanism for the silylene extrusion shown in Scheme 1. Irradiation of 3 induces homolysis of the Si-Si bond to give a silyl diradical (7), probably by way of the excited singlet state. The diradical intermediate (7) extrudes a silylene to give 4, through two possible paths A and B. Path A involves elimination of the central silicon from 7, possibly assisted by the attack of another radical center in the mode of an S_H2-type reaction.[7)] In path B, intramolecular addition of a disilylanyl radical to the π-bond leads to a diradical (8), from which the terminal silicon atom is evolved as a silylene. Recently, we have demonstrated a similar addition-elimination mechanism for the photochemical generation of dimethylsilylene from phenylpentamethyldisilane[8a)] and dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene.[8b)]



Scheme 1.

The regioselectivity in the photolysis of 3b and 3c seems to be a result of a subtle balance of the substituent effects. The expected stabilizing influence of

Table 1. Photolysis and Thermolysis of 1,2,3-Trisilacyclopentene (3)

Compound	Reaction conditions (Conversion / %)	Products (yield / %)		
		1,2-Disilacyclobutene[a]	Hydrodisilane[b]	Acetylene
3a	hν, cyclohexane (20)	4a (86)	6a (78)	
3b	hν, cyclohexane (37)	4a (63)	6b (25)	
3c	hν, hexane (55)	4a (27) + 4c (35)	6a + 6c[c]	
3a	720 °C, 10^{-3} mmHg (79)	4a (60)		9 (24) + 10 (tr)
3b	650 °C, 10^{-3} mmHg (55)	4a (55)		9 (5) + 10 (10)
3c	700 °C, 10^{-3} mmHg (100)	4a (39)		9 (11) + 10 (6)
3c	650 °C 10^{-3} mmHg (95)	4a (32)[d]		9 (16) + 10 (4)

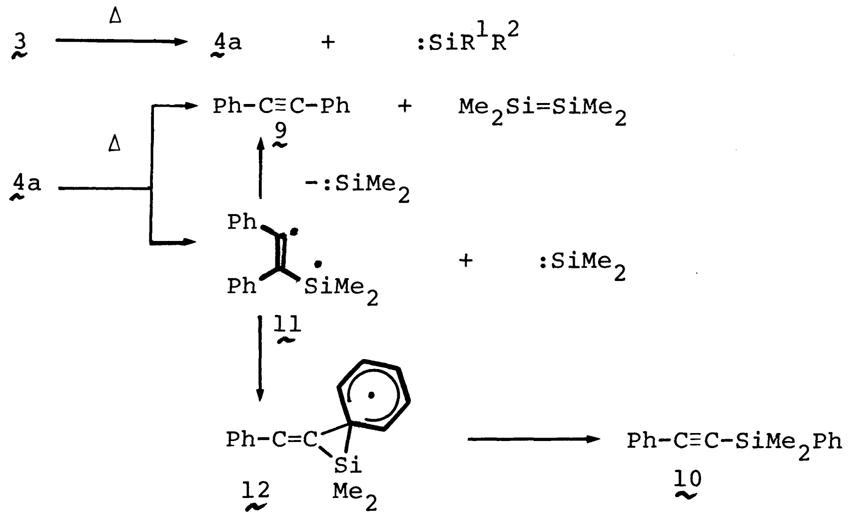
a) Isolated as cyclic disiloxanes (5) by TLC on SiO_2. b) Silylenes were trapped by diethylmethylsilane. c) Relative ratio of 6a and 6c was shown to be around 1:1 by VPC. d) 4c was detected only by means of GC-MS.

the phenyl substituent on silyl radicals and silylenes probably makes the diphenylsilylene more stable than dialkylsilylenes.[9)]

On flash vacuum thermolysis (720 °C, 10^{-3}mmHg), 3a also evolves dimethylsilylene to give 4a in 60% yield, which is converted to and identified as 5a.[10)] In the thermolysis, diphenylacetylene (9) is produced also in an appreciable amount (24%) together with (dimethylphenylsilyl)phenylacetylene (10).

$$3 \xrightarrow[\text{2) } O_2]{\text{1) FVP}} 5 + \text{Ph-C}\equiv\text{C-Ph}\ (9) + \text{PhMe}_2\text{Si-C}\equiv\text{C-Ph}\ (10)$$

The latter two products are conceivable to be secondary products arising from the thermolysis of 4a once formed. Indeed, the supporting evidence comes from the fact that thermolysis of 4a (700 °C, 10^{-3}mmHg, 93% conversion) gave both acetylenes 9 and 10 in 39 and 12% yields, respectively. In order to examine regioselectivity



Scheme 2.

of the thermal extrusion of the silylene unit, **3b** and **3c** were thermolyzed under similar conditions. The results obtained are summarized in Table 1. In contrast to the photolysis, the silylene generated from **3** arised exclusively from the central silicon of the ring. Further studies are required, but at the present time, these results suggest a reaction mechanism shown in Scheme 2. The regiospecific thermal extrusion of silylene from **3** may be rationalized best in terms of a concerted process rather than a stepwise radical process. On the other hand, **4** thus formed may undergo either [2 + 2] cycloreversion to yield **9** and tetramethyldisilene,[4)] or extrusion of a silylene to form a diradical **11** which can rearrange to **10** through **12**.[11)]

We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

References

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2) H. Sakurai, Y. Kobayashi, and Y. Nakadaira, J. Am. Chem. Soc., 93, 5272 (1971); 96, 2659 (1974).
3) A solution of cyclic trisilane (**3**) was placed and degassed in a quartz tube containing more than a 10 fold excess amount of diethylmethylsilane. After being sealed, the sample tube was irradiated externally with a 10W low pressure Hg lamp.
4) H. Sakurai, T. Kobayashi, and Y. Nakadaira, J. Organomet. Chem., 162, C43 (1978).
See also H. Watanabe, K. Higuchi, M. Kobayashi, and Y. Nagai, J. Chem. Soc., Chem. Commun., 1978, 1029.
5) Thermolysis of the silylene precursor, 7-ethyl-7-methyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene in the presence of **4a** in an evacuated sealed tube at 390 °C for 1 h gave **3c** in 42% yield followed by TLC and GLC separation. **3c**: colorless crystals; mp 76.5-79.5 °C; ^{1}H-NMR ($CDCl_3$) δ_{ppm} 0.21 (6H, s, SiMe), 0.22 (6H, s, SiMe), 0.34 (3H, s, SiMe), 0.8-1.4 (5H, m, Et), 6.6-7.2 (10H, m, arom.); UV (n-Hexane) λ_{max} 223nm (37 900, shoulder); MS m/e (%) M^+366 (100); high-resolution MS, found 366.1650, calcd for $C_{21}H_{30}Si_3$ 366.1654.
6) **5c**: mp 36-39 °C; ^{1}H-NMR ($CDCl_3$) δ_{ppm} 0.34 (3H, s, SiMe), 0.35 (3H, s, $SiMe_3$), 0.39 (3H, s, SiMe), 0.63-1.16 (5H, m, Et), 6.8-7.2 (10H, m, arom.); MS m/e (%) M^+ 324 (37), 295 (100); high-resolution MS, found 324.1372, calcd for $C_{19}H_{24}OSi_2$ 324.1365.
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8) a) H. Sakurai, Y. Nakadaira, M. Kira, H. Sugiyama, K. Yoshida, and T. Takiguchi, J. Organomet. Chem., 184, C36 (1980); b) M. Kira, K. Sakamoto and H. Sakurai, J. Am. Chem. Soc., 105, 7469 (1983).
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10) Dimethylsilylene was detected as 1,2,4,4-tetramethyl-4-silacyclopenetene in an independent sealed-tube thermolysis of **3a** in the presence of 2,3-dimethyl-1,3-butadiene.
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