

The photolyses of $1a$ (19 mM) and $1b$ (16 mM) in degassed methylcyclohexane- d_{14} with a spiral, low pressure, mercury lamp (125W) at -72°C were followed separately by ^1H NMR spectroscopy using a known amount of dioxane as a standard. Two sets of new signals, ascribable to disilenes $Z-2a$ and $E-2a$,⁵ soon appeared upon irradiation at the expense of those due to $1a$ or $1b$. In both cases, the combined yield of $Z-2a$ and $E-2a$ was nearly quantitative at 70% conversion of starting material (Fig. 1), and the initial ratio of $Z-2a$ to $E-2a$ changed to a photo-stationary ratio of ca. 3.5:1 on further irradiation (Fig. 2). Prolonged irradiation (>2 h) resulted in the gradual decomposition^{1b} of $Z-2a$ and $E-2a$ at similar rates. The initial ratios of $Z-2a:E-2a$ are significantly different in the two cases: 7.1:1 for $1a$ and 0.38:1 for $1b$. These ratios are to be compared with that ($Z-2a:E-2a=1.6:1$) observed at the initial stage of the photolysis of 2-*t*-butyl-2-mesityl-hexamethyltrisilane (3)³ under the same conditions as those employed for $1a$ and $1b$ (see Fig. 2).⁶

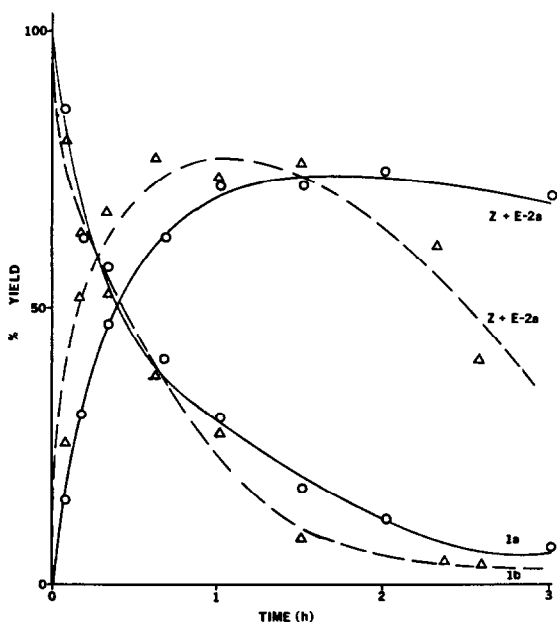


Fig. 1. Time course of the photolysis of $1a$ (—○—) and $1b$ (---△---) at -72°C .

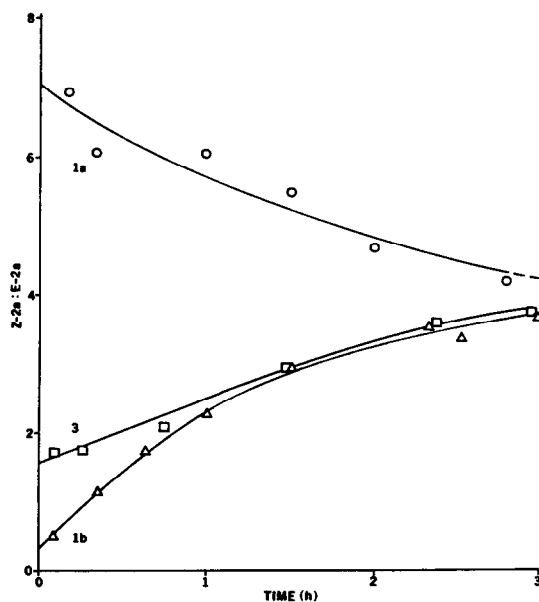
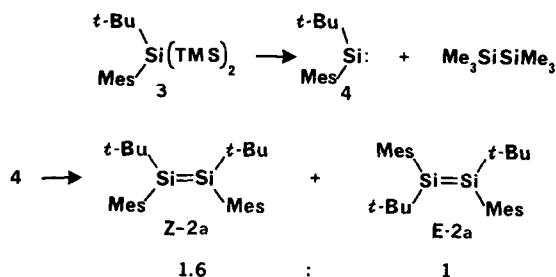


Fig. 2. Ratio of $Z-2a : E-2a$ during the photolysis of $1a$ (○), $1b$ (△) and 3 (□) at -72°C .

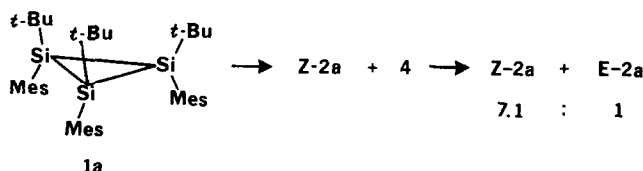
It has been established that 1) 2-aryl substituted trisilanes (e.g. 3 in Scheme 1) undergo photo-induced fragmentation to provide the corresponding silylenes (4) which in turn dimerize to form the disilenes ($2a$)⁷ and 2) cyclotrisilanes (1 mol) initially provide on photolysis disilenes (1 mol) and silylenes (1 mol), the latter species providing additional disilene (0.5 mol) in the manner already mentioned.¹ Therefore, it can be argued that, if 1) the initial ratio of $Z-2a$ to $E-2a$ observed during the photolysis of compound 3 represents the kinetic product distribution (1.6:1, see above) for silylene dimerization and 2) that silylene generated in the photolysis of 3 is in the same electronic state as that generated from the photolysis of $1a$,⁸ then the initial photo-induced cleavage of *cis,cis*-cyclotrisilane $1a$ proceeds with retention of configuration to

produce disilene $\underline{Z-2a}$ (Scheme 2, \underline{Z} to \underline{E} ratio: calcd based on the 1.6:1 distribution ratio, 6.9:1; observed, 7.1:1). For *cis*,*trans*-cyclotrisilane $\underline{1b}$, there are two modes of cleavage, a and b (Scheme 3), one of which is expected to be preferred over the other. If the above stereochemical course (retention) applies in the case of $\underline{1b}$ as well, then mode a is clearly favored over b as the initial ratio of $\underline{Z-2a}$ to $\underline{E-2a}$ is 0.38:1 (\underline{Z} to \underline{E} ratio: calcd for random, 0.75:1; for 4:1 preference, 0.39:1; for mode a only 0.26:1). Further work to corroborate this conclusion is in progress.

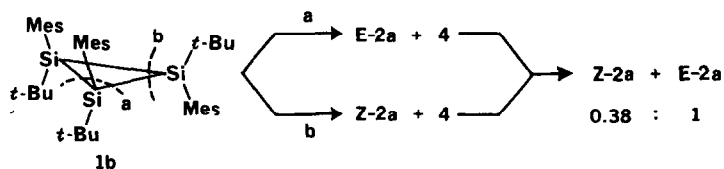
Scheme 1



Scheme 2



Scheme 3



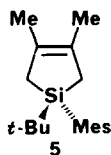
While $\underline{Z-2a}$ and $\underline{E-2b}$ are readily photo-isomerized (see above), thermal interconversion between $\underline{Z-2a}$ and $\underline{E-2a}$ is also observed on heating photolysis mixtures above room temperature. The conversion of $\underline{Z-2a}$ to $\underline{E-2a}$ is complete within 1 h at 100°C. The equilibrium ratio of $\underline{E-2a}$ to $\underline{Z-2a}$ at room temperature is 51.7:1. ($\Delta G^\circ = -2.3 \text{ kcal mol}^{-1}$). The kinetic parameters pertinent to this isomerization are: $k(79.3^\circ\text{C}) = (2.18 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$, $k(60.4^\circ\text{C}) = (3.03 \pm 0.11) \times 10^{-5} \text{ s}^{-1}$; $\Delta H^\ddagger = 23.4 \pm 0.9 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -9.4 \pm 2.7 \text{ cal K}^{-1} \text{ mol}^{-1}$. The mechanism of this isomerization involves solely rotation about the Si=Si double bond, since in the presence of the silylene trap 2,3-dimethylbutadiene at 80°C the rate of isomerization was not affected and no trapped products were formed, thus precluding a thermal dissociation-recombination pathway via the silylene.⁹ The above activation parameters are of obvious theoretical interest. However, we

defer discussion on this aspect until the behavior of ground and excited state potentials of disilene on rotation about the double bond has been adequately studied.¹⁰

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References and Footnotes

- (a) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J.F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (b) Masamune, S.; Tobita, H.; Murakami, S. *Ibid.* **1983**, *105*, 6524. (c) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781.
- For instance, see: (a) Masamune, S.; Murakami, S.; Snow, J.T.; Tobita, H. *Organomet.* **1984**, *3*, 333. Cf.; (b) Fink, J.F.; Michalczyk, M.J.; Haller, K.J.; West, R.; Michl, J. *J. Chem. Soc. Chem. Commun.* **1983**, 1010.
- Michalczyk, M.J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.
- ¹H NMR (250 MHz, C₆D₆, r.t.) of **1a** shows the presence of three-fold symmetry: δ 1.44 (s, 27H, t-Bu), 2.06 (s, 9H, p-Me), 2.40 (s, 18H, o-Me), 6.67 (s, 6H, Ar-H). All the o-Me's are chemical shift equivalent, cf. those of **1b**. Mass spectrum (electron impact): found 555.3301; calcd for M-C₄H₉, 555.3299. ¹H NMR (C₆D₆, r.t.) of **1b** is consistent with the slow rotation of the two cis-oriented aryl groups along the Si-C bond: δ 0.96 (s, 9H, t-Bu), 1.34 (s, 18H t-Bu), 2.11 (s, 6H, p-Me), 2.14 (s, 3H, p-Me), 2.66 and 2.93 (s and s, 12H, o-Me), 2.99 (s, 6H, o-Me), 6.74 and 6.85 (s and s, 4H, Ar-H), 6.89 (s, 2H, Ar-H). Mass spectrum (electron impact): found 555.3295; calcd for M-C₄H₉, 555.3299.
- Z-2a**: ¹H NMR (250 MHz, methylcyclohexane-d₁₄) δ (relative to dioxane, 3.53) 1.29 (s, 18H, t-Bu), 2.07 (s, 6H, p-Me), 2.54 (s, 12H, o-Me), 6.60 (s, 4H, Ar-H). **E-2a**: ¹H NMR (250 MHz, methylcyclohexane-d₁₄) δ 0.96 (s, 18H, t-Bu), 2.23 (s, 6H, p-Me), 2.74 (s, 12H, o-Me), 6.86 (s, 4H, ArH). The isolation and full characterization of **Z-** and **E-2a** will be documented elsewhere. The chemical shifts of **Z-2a** and **E-2a** in C₆D₆ agreed with those reported.³
- The statement made in the recent report³ on the preparation of **Z-** and **E-2a** that "photolysis of [**3**] at -80°C produced more than 95% of the pale yellow disilene [**2a**], mostly as the trans isomer [**E-2a**]." seemed to conflict with our results observed in the photolysis **1a** and **1b**. Immediately after the appearance of this paper, we prepared compound **3** and observed its photolysis under homogeneous conditions with the results indicated in Fig. 2.
- West, R.; Fink, M.J.; Michl, J. *Science* **1981**, 214.
- The latter assumption seems reasonable since the two processes, if concerted, are formally analogous in the Woodward-Hoffman sense, being of the type [$\sigma_{2s} + \sigma_{2s} (\pi_{2s})$].
- The silylene **4** generated from photolysis of **1b** was readily trapped to provide compound **5**: ¹H-NMR (250 MHz, C₆D₆) δ 0.97 (s, 9H, t-Bu), 1.58 (d, 2H, J_{AB}=17 Hz, -CH_AH_B-), 1.73 (s, 6H, Me), 1.82 (d, 2H, J_{AB}=17 Hz, -CH_AH_B-), 2.15 (s, 3H, p-Me), 2.33 (s, 6H, o-Me), 6.79 (s, 2H, ArH), GC-MS; 286 (M⁺, 20.7%) 229 (M⁺-t-Bu, 51.5), 110 (C₆H₁₀Si⁺, 100).



- For recent calculations related to this subject, see a) Lischka, H.; Kohler, H.-J. *Chem. Phys. Lett.* **1982**, *85*, 467. b) Poirier, R.A.; Goddard, J.D. *Chem. Phys. Lett.* **1981**, *80*, 37. c) Daudel, R.; Kari, R.E.; Poirier, R.A.; Goddard, J.D.; Csizmadia, I.G.; *J. Mol. Struct.* **1978**, *50*, 115.

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