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PHOTO-INDUCED FRAGMENTATION OF TRI-t-BUTYL-TRIMESITYL-CYCLOTRISILANES AND E,Z-INTERCONVERSION OF DI-t-BUTYL-DIMESITYL-DISILENES

Shu Murakami, Scott Collins, and Satoru Masamune*

Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139

Abstract: The stereochemical course of the titled photo-conversion to yield Z-and E-substituted disilenes and the photochemical and thermal interconversion of the latter two compounds are described.

Symmetrically substituted cyclotrisilanes (l_{\star} , R=R^{\prime}) undergo photolysis to provide the corresponding disilenes (2, R=R') nearly quantitatively, based on the stoichiometry shown below (eq 1).¹ Therefore, the use of a less symmetrically substituted cyclotrisilane (1, R \neq R²) should



lead to the formation of a mixture of \underline{Z} and \underline{E} disilenes ($\underline{Z}-\underline{2}$ and $\underline{E}-\underline{2}$), thereby providing an opportunity to disclose the stereochemical course of this photo-fragmentation. The ground-state conformations of both $\underline{Z-2}$ and $\underline{E-2}$ are expected to be nearly coplanar (with a slightly twisted Si=Si bond).² This note describes 1) the synthesis of cis,cis- and cis,trans-1,2,3-tri-t-butyl-1,2,3trimesitylcyclotrisilanes ($\frac{1}{10}$ and $\frac{1}{10}$) and 2) the stereochemical course of the photoconversion of la and lb to Z-and E-1,2-di-t-butyl-1,2-dimesityl-disilenes (Z-2a and E-2a). The photochemical and thermal interconversion of the latter two compounds is also discussed. These results complement those recently reported by Michalczyk, West, and Michl,³ although some discrepancies are noted.

The synthesis of l_{a} and l_{b} follows a method developed earlier. la,2a Thus, reaction of t-butylmesityldichlorosilane (9.1 mmol in 10 mL of DME) with lithium napthalenide (20 mmoL in 25 mL of DME) (addition at -78° C and warming to room temperature) provided, after the usual work-up, lamp 189-191°C, and 1b mp 267-268.5°C, in 7 and 38% yield, respectively. The stereostructures (eq 1) assigned to these compounds are based on high-resolution mass and ¹H NMR (250 MHz) spectral data.⁴ It is worth noting that the UV and visible absorption maxima of λ_m (cyclohexane) 379 (ϵ 460) and 412 (550)] are considerably red shifted as compared with those of $\frac{1}{10} [\lambda_{max}]$ (cyclohexane) 334 (1000) and 363 (990)], the latter values being normal for this type of cyclotrisilane.^{la}

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The photolyses of $\frac{1}{10}$ (19 mM) and $\frac{1}{10}$ (16 mM) in degassed methylcyclohexane-d₁₄ 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 <u>Z-2a</u> and <u>E-2a</u>, ⁵ soon appeared upon irradiation at the expense of those due to <u>la</u> or <u>lb</u>. In both cases, the combined yield of <u>Z-2a</u> and <u>E-2a</u> was nearly quantitative at 70% conversion of starting material (Fig. 1), and the initial ratio of <u>Z-2a</u> to <u>E-2a</u> 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 <u>Z-2a</u> and <u>E-2a</u> at similar rates . The initial ratios of <u>Z-2a:E-2a</u> are significantly different in the two cases: 7.1:1 for <u>la</u> and 0.38:1 for <u>lb</u>. These ratios are to be compared with that (<u>Z-2a:E-2a=1.6:1</u>) observed at the initial stage of the photolysis of 2-<u>t</u>butyl-2-mesityl-hexamethyltrisilane (3)³ under the same conditions as those employed for <u>la</u> and <u>lb</u> (see Fig. 2).⁶



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 \underline{Z} -2a to \underline{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 \underline{la} ,⁸ then the initial photo-induced cleavage of cis,cis-cyclotrisilane \underline{la} proceeds with retention of configuration to <u>produce disilene Z-2a</u> (Scheme 2, <u>Z</u> to <u>E</u> ratio: calcd based on the 1.6:1 distribution ratio, 6.9:1; observed, 7.1:1). For cis,trans-cyclotrisilane l_{D} , 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 l_{D} as well, then mode a is clearly favored over b as the initial ratio of <u>Z-2a</u> to <u>E-2a</u> is 0.38:1 (<u>Z</u> to <u>E</u> 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.



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°C) = (2.18 ± 0.06) x 10⁻⁴s⁻¹, k (60.4°C) = (3.03 ± 0.11) x 10⁻⁵s⁻¹; $\Delta H^{\pm} = 23.4 \pm 0.9 \text{ kcal mol}^{-1}$; $\Delta S^{\pm} = -9.4 \pm 2.7 \text{ cal } K^{-1} \text{ mol}^{-1}$. 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

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- 3.
- 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 4. are chemical shift equivalent, cf. those of 1b. Mass spectrum (electron impact): found 555.3301; calcd for $M-C_4H_9$, 555.3299. ¹H NMR (C_6D_6 , r.t.) of 1b is consistent with the slow 1200rotation 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,
- 5. 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 C_6D_6 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 la and lb. 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. <u>Science</u> 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, C_6D_6) & 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 ($C_6H_{10}Si^+$, 100). 9.



10. 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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