

Photochemistry of 1,2-Disila-3,5-cyclohexadienes

Sir:

In the previous communication,¹ we reported the photochemistry of 1-sila-2,4-cyclohexadienes, which showed similar photochemical transformation to 1,3-cyclohexadienes. In this paper, we describe photochemical reactions of another type of silicon analog of 1,3-cyclohexadiene, 1,2-disila-3,5-cyclohexadienes, which revealed a novel photochemistry leading to intriguing chemical species.

When a degassed C_6D_6 solution of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,5-cyclohexadiene (**1a**)² in an nmr tube was irradiated with a 450-W high-pressure mercury arc lamp with a Pyrex filter for 2 hr, a photoproduct with four Si-Me singlets at δ 0.70, 0.59, 0.58, and 0.39 ppm³ was obtained quantitatively. The photoproduct (**2a**) was extremely sensitive to both air and moisture and was not isolated in pure state. However, the following interesting transformations were observed by nmr. On heating the C_6D_6 solution of **2a** in the nmr tube, the intensities of four Si-Me signals decreased with concomitant increase of peaks due to a new product (**3a**), and finally **2a** was replaced by **3a** quantitatively. Furthermore, by irradiation, **3a** returned to **2a** again, and these interconversions can be effected repeatedly.⁴

The structure of **3a**, which was fairly stable to both air and moisture in contrast with **2a**, can be assigned to 5,5,6,6-tetramethyl-1,2,3,4-tetraphenyl-5,6-disilabicyclo[2.1.1]hex-2-ene by spectroscopic⁵ and chemical properties.⁶ Since **2a** is an isomer of **3a** with four magnetically nonequivalent Si-Me, 2,2,6,6-tetramethyl-1,3,4,5-tetraphenyl-2,6-disilabicyclo[3.1.0]hex-3-ene is the most probable structure of **2a**.

(1) Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Amer. Chem. Soc.*, **96**, 5621 (1974).

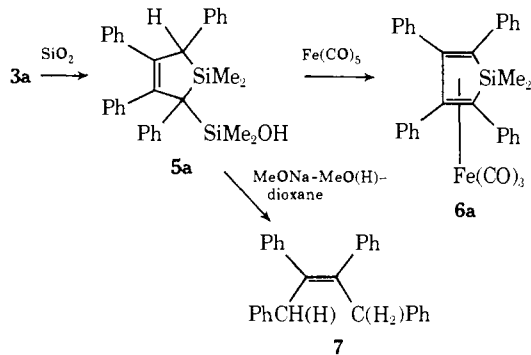
(2) Y. Nakadaira and H. Sakurai, *J. Organometal. Chem.*, **47**, 61 (1973).

(3) Nmr spectra were taken with Varian Associates HA-100 and A-60 spectrophotometers.

(4) A small amount of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene was formed in the photoproduct and the amount of this compound increased slightly on prolonged irradiation.

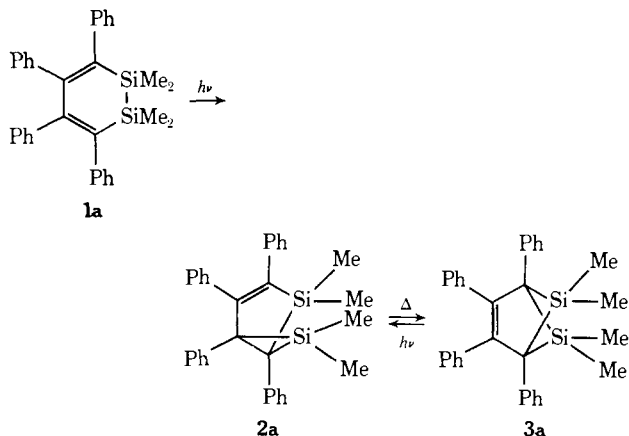
(5) Compound **3a**: M^+ 472; nmr δ (CCl_4) 0.65 (3 H, s, SiMe), 0.72 (H, s, SiMe), 6.5-7.1 (20 H, m); λ_{max}^{hexane} 223 (sh) (29,000), 330 (5900).

(6) Treatment of **3a** with silica gel gave a silanol (**5a**): M^+ 490(20), $M^+ - 75$ (18%), m/e 75 (SiMe₂OH, 100%); nmr δ (CCl_4) -0.64 (3 H, s, SiMe), -0.27 (3 H, s, SiMe), 0.02 (3 H, s, SiMe), 0.57 (3 H, s, SiMe), 3.77 (1 H, s, C-H), 6.7-7.8 (20 H, m); δ (acetone-*d*₆) 4.70 (1 H, s, OH), 3.95 (1 H, s, C-H); λ_{max}^{hexane} 225 (31,600), 260 (12,800), nearly quantitatively. **5a** was converted to an iron tricarbonyl complex⁷ by heating with iron pentacarbonyl in xylene in 9% yield. Desilylation of **5a** with NaOMe gave 1,2,3,4-tetraphenylbut-2-ene (**7**).⁸ Desilylation with MeOD afforded **7-d**.

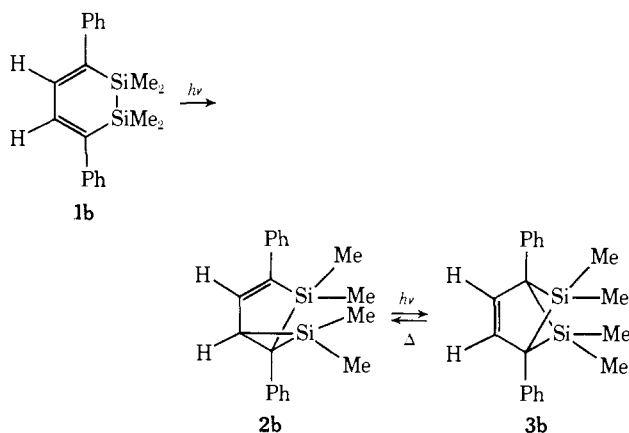


(7) J.-C. Brunet, B. Resibois, and J. Bertrand, *Bull. Soc. Chim. Fr.*, 3424 (1969).

(8) N. Tanaka, T. Ogata, Y. Uratani, Y. Nakadaira, and H. Sakurai, *Inorg. Nucl. Chem. Lett.*, **8**, 1041 (1972).



1,1,2,2-Tetramethyl-3,6-diphenyl-1,2-disila-3,5-cyclohexadiene (**1b**),⁹ the diphenyl analog of **1a**, behaved in a somewhat different way from **1a**. Thus, irradiation of **1b** in C_6D_6 afforded a photoproduct, whose structure can be assigned to 2,2,6,6-tetramethyl-1,3-diphenyl-2,6-disilabicyclo[3.1.0]hex-3-ene (**2b**) from the nmr spectrum. Compound **2b** had resonances (C_6D_6) at δ -0.15, 0.09, 0.13, and 0.41 ascribable to four Si-Me groups, 2.78 (1 H, d, $J = 4.0$ Hz, methine proton), 7.13 (coupled with the signal at δ 2.78) and aromatic multiplets. However, further irradiation resulted in the formation of a new product (**3b**)



with two Si-Me singlets at δ 0.31 and 0.60 and a sharp singlet at δ 6.53 due to an olefinic proton. Structure of **3b** can be reasonably assigned to 5,5,6,6-tetramethyl-1,4-diphenyl-5,6-disila[2.1.1]hex-2-ene. Figure 1 shows an nmr spectrum of a mixture of **1b**, **2b**, and **3b**.

Irradiation of **1b** for 6 hr at room temperature afforded a 6:1 mixture of **2b** and **3b**, but additional irradiation for 10 hr gave rise to a 1:4 mixture of **2b** and **3b**. On heating a 2:1 photomixture of **2b** and **3b** at 105° for 3 hr, the ratio changed to 4:1. Therefore, **2b** is thermally more stable than **3b**, contrary to the thermal interchange, **2a** \rightarrow **3a**.

These thermal and photochemical isomerizations should be regarded as the first example of vinylsilacyclopentene rearrangement.¹⁰ 1,6-Di-

(9) **1b** was prepared by the reaction of 1,4-dithio-1,4-diphenylbutadiene with 1,2-dichloro-1,1,2,2-tetramethyl-1,2-disilane in THF: mp $47-49^\circ$; M^+ 320; nmr δ ($CDCl_3$) 0.27 (12 H, s, SiMe), 6.74 (2 H, s, =CH), 7.3 (10 H, m).

(10) Similar rearrangement has been proposed in the formation of a silacyclopentene by the addition of a silylene to a 1,3-diene, but no evidence of vinylsilacyclopentene has been presented. For a pertinent review, see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

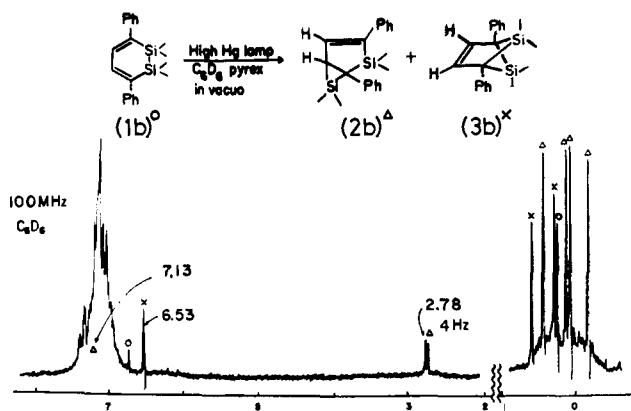


Figure 1. The nmr spectrum of a photomixture of **2b** and **3b** containing a small amount of **1b** in degassed C_6D_6 .

silahexa-1,3,5-trienes ($Me_2Si=CPh-CR=CR-CPh=SiMe_2$, $R = H, Ph$) are the possible intermediates in these photochemical reactions in view of similar behavior of **1a** and **1b** to those of 1,3-cyclohexadiene and 1-sila-2,4-cyclohexadienes.¹

Results of the trapping experiments of these intermediates as well as of kinetic study on the novel vinylsilacyclopropane-silacyclopentene rearrangement will be reported shortly.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. The work was supported in part by a Grant-in-Aid of the Ministry of Education.

Yasuhiro Nakadaira, Seiichi Kanouchi, Hideki Sakurai*
 Department of Chemistry
 Faculty of Science, Tohoku University
 Aramaki Aza-Aoba, Sendai 980, Japan
 Received April 24, 1974

Hot Molecule Effects in 1,4-Diradicals.¹ The Thermal Generation of a Norrish Type II Intermediate

Sir:

We wish to report the generation of the Norrish type II diradical **1** from cyclobutanol precursors.² Since the behavior of **1** generated by photoreaction of ketone **2** has been documented,³ this represents an ideal opportunity to compare in detail the behavior of diradicals generated by very different means. We find that the pyrolysis route involves a substantially less stereospecific cleavage to the product butenes.⁴ Explanations

(1) The Chemistry of Diradicals, V; for previous work see L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2849 (1973).

(2) Such pyrolyses have previously been studied by E. D. Feit, *Tetrahedron Lett.*, 1475 (1970).

(3) C. P. Casey and R. A. Boggs, *J. Amer. Chem. Soc.*, **94**, 6457 (1972).

(4) The 1,2,3-trimethylcyclobutanols were prepared as follows. Addition of dichloro ketene (generated *in situ* from dichloroacetyl chloride and triethylamine) to *cis*-2-butene at 0° yielded 2,2-dichloro-*cis*-3,4-dimethylcyclobutanone (48%).⁵ Dechlorination with Zn-HOAc produced *cis*-2,3-dimethylcyclobutanone (38%).⁶ The Grignard addition of CH_3MgI gave the cyclobutanol, **4**. Isomers **7** and **8** were synthesized by CH_3MgI addition to *trans*-2,3-dimethylcyclobutanone, which resulted from the isomerization of the *cis* ketone with NaOMe in MeOH.^{7,8} It is interesting to note that the mass spectra of the three isomers are identical, characteristic of common McLafferty-type intermediates.⁹ Pyrolyses of **4**, **7**, or **8** were conducted in a flash vacuum apparatus at 585° and ~2 Torr for varying lengths of time. The products were analyzed by vapor phase chromatography. The olefins did not isomerize under the reaction conditions. Packing

of this difference based on geometrical or structural features of the system are inadequate, and we suggest that the excess energy associated with the photochemical route is responsible for the result.

The stereochemical characteristics of several diradical reactions are given in Table I. It is clear from this table

Table I. Stereochemical Characteristics of Some Selected 1,4-Diradical Cleavage Reactions

Reactant	Method	Product	Product ratio	Ref
	$h\nu$	2-Butene-2-d	cis/trans = 10	3
	Δ	2-Butene	cis/trans = 1.8	b
	Δ	2-Butene	cis/trans = 2.3	a
	$h\nu$	2-Butene-2-d	trans/cis = 24	3
	Δ	2-Butene	trans/cis = 8.0	b
	Δ	2-Butene	trans/cis = 4.0	a
	Δ	2-Butene	trans/cis = 3.0	a

^a This work. ^b H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 3935, 4884 (1951).

that cyclobutane pyrolyses yield cleavage products with low stereochemical retention in the olefin moieties, while photochemical singlet reactions are apparently more stereospecific. With the exception of the present report, a diradical prepared by these two very different methods has not been described. Earlier, most of the photochemically derived diradicals involved tertiary radical centers, while many of the cyclobutane derived diradicals involved secondary centers. Several workers^{10,11} have ascribed the higher stereospecificity in the photoreactions to ponderal rotor effects caused by increasing alkyl substitution at the radical site but neglected differences in mode of generation. The present report demonstrates the importance of the latter.

the reaction vessel with quartz wool did not influence the results. Vpc analysis showed that cleavage proceeded eight-ten times faster than isomerization or back-abstraction to ketones, and the results in Table I are olefin ratios for low per cent conversion runs (<5%).

(5) W. T. Brady and J. P. Hieble, *J. Org. Chem.*, **36**, 2033 (1971).

(6) N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970).

(7) Nmr and microanalytical data are in agreement with these structures.

(8) (a) M. Julia, Y. Noël, and R. Guégan, *Bull. Soc. Chim. Fr.*, **35**, 3742 (1968); (b) E. D. Feit, private communication.

(9) (a) P. Ausloos and R. E. Ribbert, *J. Amer. Chem. Soc.*, **83**, 4897 (1961); (b) G. Eadon, *ibid.*, **94**, 8938 (1972).

(10) J. A. Berson, D. C. Tompkins, and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 5799 (1970).

(11) G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974).