

## Nucleophilic Substitutions on Silane Cation Radicals: Stepwise or Concerted?

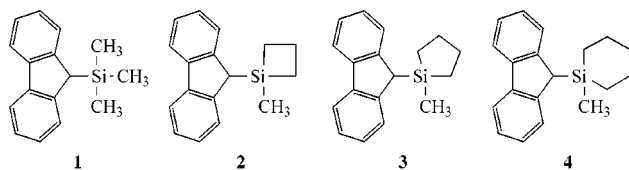
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Received May 16, 2001

A variety of organosilane cation radicals have recently been shown to react with nucleophiles via a bimolecular substitution mechanism.<sup>1–4</sup> Left unresolved by these studies is whether the substitution reactions are stepwise or concerted. Herein we present a combination of kinetic data, structure–reactivity comparisons, and stereochemical experiments that favor a concerted substitution mechanism.

If silane cation radical substitutions proceed via a stepwise mechanism involving pentacoordinate intermediates that have significant lifetimes then, in principle, it should be possible to kinetically detect their intermediacy, even if they cannot be directly observed. In this case, the rate of reaction of the cation radicals with nucleophiles will exceed the rate of leaving-group departure. Obviously, a concerted substitution mechanism requires these rates to be identical. Silanes **1–4** were prepared for this kinetic test. These silanes have an advantage over previously studied systems in that transient absorption spectroscopy can be used to follow both reaction of the silane cation radicals with nucleophiles and displacement of the 9-fluorenyl radical ( $\lambda_{\text{max}} = 503 \text{ nm}$ ).<sup>5</sup>



Loss of the fluorenyl group in **1–4** was confirmed by preparative photooxidation experiments with 9,10-dicyanoanthracene (DCA) as a photooxidant in  $\text{CH}_3\text{OH}$  (or  $\text{CH}_3\text{O}^2\text{H}$ ). In all cases, fluorene (or fluorene-9-<sup>2</sup>H) was formed in quantitative yield. Following previous precedent,<sup>1</sup> the reaction is presumed to proceed by initial electron transfer from **1–4** to the singlet excited state of DCA to produce cation radicals  $1^{+\bullet}$ – $4^{+\bullet}$ . The silane cation radicals then react with methanol to produce a methoxysilane and the 9-fluorenyl radical. The radical is subsequently reduced by DCA anion radical to produce the 9-fluorenyl anion, which is protonated by  $\text{CH}_3\text{OH}$ (<sup>2</sup>H) to give fluorene(9-

<sup>2</sup>H).<sup>6</sup> This hypothesis is supported by nanosecond transient absorption experiments, as described below.

Pulsed laser excitation (343 nm, 15 ns, 3 mJ) of dioxygen-saturated dichloromethane solutions containing silanes **1–4** (~20 mM), *N*-methylquinolinium hexafluorophosphate (NMQ) as a photosensitizer,<sup>1c</sup> and toluene (~1 M) as a co-donor, all resulted in the formation of similar transient species with  $\lambda_{\text{max}} \approx 640 \text{ nm}$ , similar to that of fluorene cation radical.<sup>7</sup> We assign the transients to  $1^{+\bullet}$ – $4^{+\bullet}$  based on this and the fact that they all reacted with 1,2,4,5-tetramethoxybenzene (TMB) with diffusion-controlled rates to produce  $\text{TMB}^{+\bullet}$  ( $\lambda_{\text{max}} = 460 \text{ nm}$ ).<sup>8</sup> All of the cation radicals reacted with a variety of nucleophiles with clean second-order kinetics. As shown in Table 1, the rate constants for reaction of  $1^{+\bullet}$ – $4^{+\bullet}$  with nucleophiles ( $k_1$ , monitored at 640 nm) and the rate constants for growth of the 9-fluorenyl radical ( $k_2$ , monitored at 503 nm in argon-saturated solutions) were found to be indistinguishable within experimental error.

It is especially noteworthy that  $k_1 = k_2$  for silacyclobutane cation radical  $2^{+\bullet}$ . Making the traditional assumptions that nucleophilic addition and leaving-group departure occur from axial positions and that steric constraints require the silacyclobutane ring to bridge one axial and one equatorial position,<sup>9</sup> then a stepwise mechanism would require nucleophilic addition to  $2^{+\bullet}$  to form a pentacoordinate intermediate, followed by pseudorotation before departure of the fluorenyl radical. Thus,  $k_1 = k_2$  for  $2^{+\bullet}$  requires either nucleophilic addition to be reversible, or that both pseudorotation and leaving-group departure are rapid relative to nucleophilic attack. At the highest nucleophile concentrations used, where the lifetime of  $2^{+\bullet}$  is shortest, our kinetic data require that the lifetime of the hypothetical intermediate be  $\leq 50 \text{ ns}$ .

The reactivity of  $2^{+\bullet}$  relative to that of the other silane cation radicals is also noteworthy when compared to data for neutral silanes. The relative rate constants for reaction of 1-methylsilacyclobutane, 1-methylsilacyclopentane, triethylsilane, and 1-methylsilacyclohexane with hydroxide ion are 10<sup>6</sup>, 10, 1, and 0.1, respectively.<sup>9</sup> As the data in Table 1 clearly show, silane cation radicals  $1^{+\bullet}$ – $4^{+\bullet}$  do not follow this reactivity trend. Indeed, silacyclobutane cation radical  $2^{+\bullet}$  is slightly less reactive than the acyclic cation radical  $1^{+\bullet}$  – a  $> 10^6$  reversal of reactivity compared to the neutral silanes! This suggests a significant change in reaction mechanism.

Further mechanistic insight into the cation radical substitutions was provided by stereochemical experiments. *Cis*- and *trans*-1,3-dimethyl-1-(4-methoxybenzyl)silacyclobutane (**5,6**) were prepared for this purpose.<sup>10</sup> Photooxidation of these silanes using 1-cyano-4-methylnaphthalene as a photosensitizer and 4,4'-dimethylbiphenyl as a co-donor in  $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$  (2.5:1 v:v) produced 1,3-dimethyl-1-methoxysilacyclobutanes (**7,8**)<sup>11b</sup> as the silane substi-

(6) (a) The reduction potentials of fluorenyl radical and DCA are  $-0.76 \text{ V}$  and  $-0.91 \text{ V}$  vs SCE, respectively (ref 6, b and c), thus reduction of the fluorenyl radical by DCA radical anion is exothermic by approximately 3 kcal/mol. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (c) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(7) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988; p. 137.

(8) (a) The (irreversible) peak potentials for **1** and **2** obtained by cyclic voltammetry (150 mV/sec) using a platinum disk electrode in acetonitrile with ca. 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte were 1.60 and 1.54 V vs SCE, respectively. The oxidation potential of TMB is 0.88 V; hence, electron transfer from TMB to  $1^{+\bullet}$  and  $2^{+\bullet}$  is exothermic by approximately 15–17 kcal/mol.

(9) (a) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965. (b) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, D. W., Eds.; Pergamon: New York, 1979; Vol. 3, Chapter 13. (c) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43. (d) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989, Part 1, Chapter 13.

(1) (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 151. (c) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601. (d) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *Tetrahedron Lett.* **1993**, *34*, 2863. (e) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.

(2) Zhang, X.; Yeh, S.-R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(3) Schmittel, M.; Keller, M.; Burghart, A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2327.

(4) Kako, M.; Nakadaira, Y. *Coord. Chem. Rev.* **1998**, *176*, 87.

(5) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934.

**Table 1.** Rate Constants for Disappearance of Silane Cation Radicals  $1^{+}$ – $4^{+}$  ( $k_1$ ) and for Formation of the 9-Fluorenyl Radical ( $k_2$ ) in the Presence of Nucleophiles, and Relative Rate Constants (in bold)

nucleophile	rate constants ( $\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ )							
	$1^{+}$		$2^{+}$		$3^{+}$		$4^{+}$	
	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$
MeOH	1.7(3) <sup>a</sup> <b>1.0</b>	1.8(2)	1.0(1) <b>0.6</b>	1.2(1)	0.34(2) <b>0.2</b>	0.37(3)	0.24(2) <b>0.1</b>	0.26(2)
<i>i</i> -PrOH	0.89(4) <b>1.0</b>	0.90(8)	0.40(2) <b>0.5</b>	0.43(3)	0.21(9) <b>0.2</b>	0.22(2)	0.12(1) <b>0.1</b>	0.16(4)
<i>t</i> -BuOH	0.49(5) <b>1.0</b>	0.61(7)	0.35(3) <b>0.7</b>	0.36(2)	0.14(3) <b>0.3</b>	0.12(2)	0.08(1) <b>0.2</b>	0.09(1)
MeCN	1.0(1) <b>1.0</b>	1.1(1)	0.60(2) <b>0.6</b>	0.66(5)	0.26(4) <b>0.3</b>	0.27(2)	0.11(1) <b>0.1</b>	0.11(2)

<sup>a</sup> The standard deviation in the last digit is given in parentheses.

tation products. Methoxysilacyclobutanes **7** and **8** could be conveniently transformed back into the 4-methoxybenzylsilacyclobutanes by reaction with 4-methoxybenzyl lithium,<sup>12</sup> thus allowing a classic Walden cycle to be constructed.

At early reaction times,<sup>13</sup> GC analysis (HP Ultra 1, 50 m  $\times$  0.2 mm) showed that the photooxidations of **5** and **6** were >98% stereospecific, producing methoxysilacyclobutanes **7** and **8**, respectively. Reaction of **7** with 4-methoxybenzyl lithium produced silacyclobutane **6**. Similarly, reaction of **8** with 4-methoxybenzyl lithium produced silacyclobutane **5**. These data unequivocally demonstrate that the neutral and cation radical nucleophilic substitution reactions have opposite reaction stereochemistries. Nucleophilic substitutions on neutral silacyclobutanes are known to proceed with retention of configuration at silicon.<sup>9,11</sup> Consequently, the cation radical substitutions occur with inversion (Scheme 1). These stereochemical conclusions were independently supported by assignments of the relative stereochemical configurations of **5**–**8** from nOe studies.<sup>14</sup> Thus, irradiation of the C3-methyl protons in **5** led to a 6-fold enhancement of the benzylic methylene protons relative to the Si-methyl protons. The corresponding experiment with **6** led to a 3-fold enhancement of the Si-methyl protons relative to that of the benzylic methylene protons. Virtually identical, relative enhancements of the Si-methyl vs Si-methoxy groups were found in comparable nOe experiments with **7** and **8**.

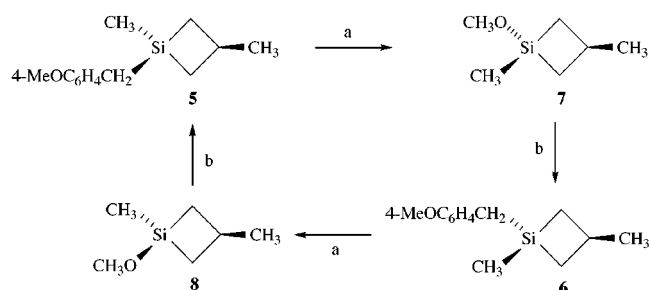
(10) Prepared by the reaction of a cis/trans mixture of 1-chloro-1,3-dimethylsilacyclobutane (Dubac, J.; Mazzerolles, P.; Serres, B. *Tetrahedron* **1974**, *30*, 749.) with 4-methoxybenzylmagnesium chloride followed by separation of **5** and **6** by using preparative gas chromatography on a 18'  $\times$  3/8" OD column packed with 5% SP-1200/1.75% Bentone 34 on 100/120 mesh Supelcoport (Supelco) at 170 °C (100 mL/min).

(11) (a) Dubac, J.; Mazzerolles, P.; Serres, B. *Tetrahedron Lett.* **1972**, 525. (b) Dubac, J.; Mazzerolles, P.; Serres, B. *Tetrahedron* **1974**, *30*, 749. (c) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Am. Chem. Soc.* **1974**, *96*, 2637. (d) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Org. Chem.* **1976**, *41*, 1534. (e) Dubac, J.; Mazzerolles, P.; Fagoaga, P. *J. Organomet. Chem.* **1977**, *139*, 271.

(12) Vanermen, G.; Toppet, S.; Van Beylen, M.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 707.

(13) Upon prolonged irradiation, silanes **7** and **8** underwent slow interconversion by an as yet unidentified isomerization mechanism. **7** and **8** are both stable in the unirradiated reaction medium. Neither **7** or **8** react with the singlet excited state of 1-cyano-4-methylnaphthalene as judged by fluorescence quenching experiments. We presume that either the anion radical of the sensitizer or a small amount of methoxide ion produced by reaction of the anion radical with methanol may act as a catalyst for the isomerization reaction.

(14) Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. *J. Am. Chem. Soc.* **1994**, *116*, 6037.

**Scheme 1**<sup>a</sup>

<sup>a</sup> (a) 1-cyano-4-methylnaphthalene, 4,4-dimethylbiphenyl, *hν*, CH<sub>3</sub>OH:CH<sub>2</sub>Cl<sub>2</sub> (b) 4-methoxybenzyl lithium, Et<sub>2</sub>O.

In conclusion, the opposite stereochemistries for nucleophilic substitutions on neutral silacyclobutanes vs their cation radicals establishes that the reactions proceed via different mechanisms. Substitutions on neutral silacyclobutanes have been proposed to proceed by a stepwise mechanism.<sup>9</sup> This rationalizes the retention of stereochemistry and the high reactivity of neutral silacyclobutanes toward nucleophiles, which can be explained by the release of bond angle strain during formation of the pentacoordinate intermediate. Silacyclobutane cation radicals react via an inversion mechanism, which explains why they do not show enhanced reactivity. Our kinetic data show that if a pentacoordinate intermediate is formed in silane cation radical substitutions, it must be very short-lived (<50 ns), even in the case where it is most likely to be observed,  $2^{+}$ . On the other hand, a concerted substitution mechanism fits the data without the need for ad hoc assumptions. Quantum chemical calculations predict a concerted mechanism for nucleophilic substitutions on silane cation radicals,<sup>15</sup> with a strong preference for an inversion pathway, consistent with experiment.

**Acknowledgment.** Research support was provided by a grant from the National Science Foundation (Grant No. CHE-9812719). J.P.D. thanks Professor S. Shaik (Hebrew University) for stimulating discussions during the course of this work.

JA011207A

(15) Shaik, S.; Reddy, A. C.; Ioffe, A.; Dinnocenzo, J. P.; Danovich, D.; Cho, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 3205.