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# Electronic and steric effects of silyl groups in silicon-directed Norrish type cleavages

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## Abstract

Sterically congested *cis*-2-(*t*-butyl)-3-(organosilyl)cyclohexanones were irradiated with UV light to give a mixture of Norrish type I and II products, as well as the corresponding *trans*-2-(*t*-butyl)-3-(organosilyl)cyclohexanones. In comparison with the *trans* isomers, the quantum yields and rate constants of the photolytic reactions were greater for the *cis* isomers.

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**Keywords:** Silicon; Norrish type cleavage; Electronic effect; Photolysis;  $\sigma$ - $\pi$  Hyperconjugation

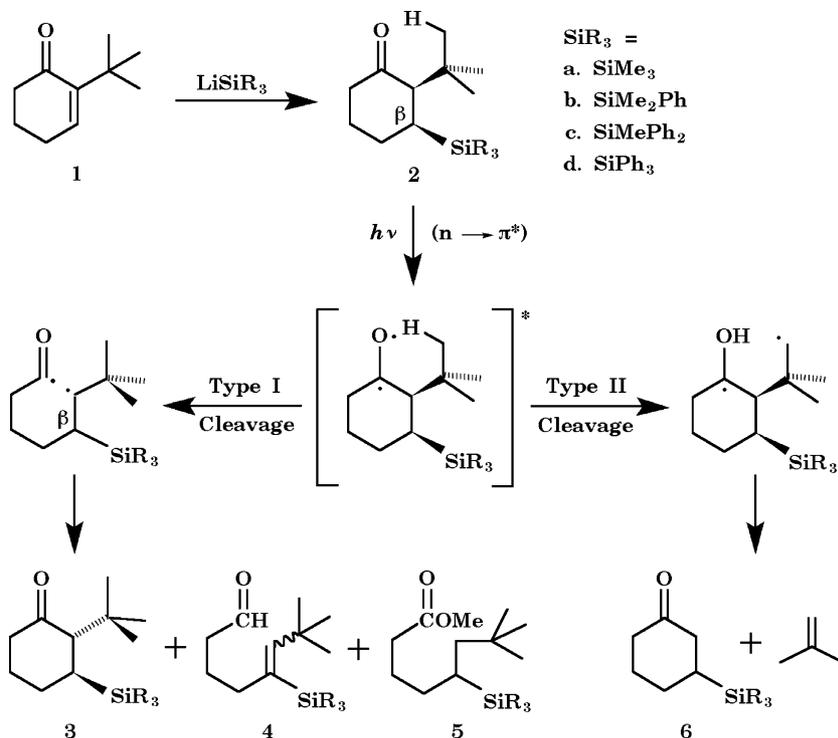
Irradiation of  $\alpha,\beta$ -disubstituted cycloalkanones with UV light may lead to products through the Norrish type I and type II cleavages. The *cis* isomers may undergo epimerization to give the corresponding *trans* isomers [1]; this process has been used in organic synthesis [2]. On the other hand, a  $\beta$ -Me<sub>3</sub>Si group in cycloalkanones can direct the Norrish type I cleavage to give an excellent regioselectivity for a C<sub>1</sub>-C<sub>2</sub> bond cleavage, as well as to increase the quantum yield and the reaction rate [3]. This reaction involves biradical intermediates, in which the  $\beta$ -Me<sub>3</sub>Si group can stabilize the carboradical (see Scheme 1) [4,5]. Two factors may contribute to the stabilizing effect: the ' $\sigma$ - $\pi$  hyperconjugation' [6–11] and ' $p$ - $d$  homoconjugation' [12,13]. Considering the potential applicability of this recently developed silicon-directed reaction [14], we investigated the geometric factor associated with the alignment between the Si-C<sub>3</sub> and the C<sub>2</sub>-C<sub>1</sub> bonds in the Si-C<sub>3</sub>-C<sub>2</sub>-C<sub>1</sub>=O moiety. Herein we report our findings that the electronic and the steric effects resulting from a silyl group exhibited strong impact on Norrish type cleavages during photolysis of  $\beta$ -silyl cyclohexanones.

By modifying Hudrlik's procedure, we treated 2-*t*-butyl-2-cyclohexen-1-one (**1**) [15] with LiSiMe<sub>3</sub> [16,17] at -78 to 0 °C to give a mixture of *cis*- and *trans*-cyclohexanones **2a** and **3a** in a ratio of 32:1, as determined by GC (see Scheme 2). After purification by medium pressure liquid chromatography, pure **2a** was isolated in 81% yield. For the preparation of **2b–2d** from **1**, we had to add cuprous cyanide to the reaction flask containing LiSiMe<sub>2</sub>Ph, LiSiMePh<sub>2</sub>, or LiSiPh<sub>3</sub>. After purification, we obtained pure **2b** in 75% yield, **2c** in 51% yield, and **2d** in 35% yield. On the other hand, we heated a 1.0 N HCl methanolic aqueous solution of *cis* compounds **2a–d** at reflux. The corresponding *trans* isomers **3a–d** were isolated in 95, 93, 85 and 65% yields, respectively. Thus the *trans* isomers **3a–d** were thermodynamically more stable than the corresponding *cis* isomers **2a–d**.

To realize the conformation of **2a–d** with the lowest total energies, we performed the MM2 [18] molecular modeling studies. Our results indicate that their most stable conformations held a chair form. For example, the conformation with the lowest energy for *cis* isomer **2d** had an axial *t*-butyl group and an equatorial silyl substituent (see **2d**<sub>Si-equat</sub> in Scheme 3). Furthermore, we obtained the lowest molecular energy of the *cis*- and the *trans*-cyclohexanones **2a–d** and **3a–d** by using the MM2, MNDO [19], and AM1 [19,20] programs. All of the results

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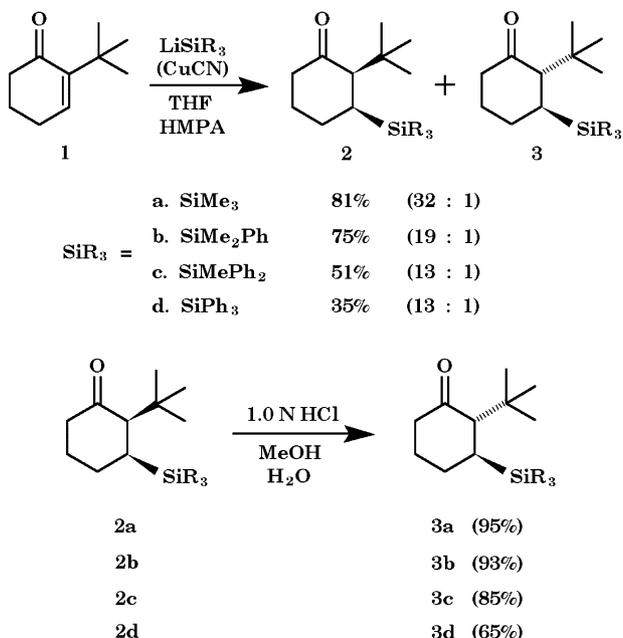
Scheme 1. Photolysis of *cis*-2-*t*-butyl-3-silylcyclohexan-1-ones (**2a–d**) to give a mixture of products from the isomerization, Norrish type I and type II processes.

indicate that the *trans* isomers **3a–d** were more stable than the *cis* isomers **2a–d**. The energy differences ranged from 7.06 to 8.71 kcal mol<sup>-1</sup> by the MM2 method (see Table 1). Both of the  $\alpha$ -*t*-butyl and the  $\beta$ -silyl groups in

the *trans* compounds **3a–d**, however, resided at axial positions.

To study the influence of a silyl group on the Norrish type reactions, we irradiated **2a–d** in anhydrous methanol containing NaHCO<sub>3</sub> in Pyrex by UV light with  $\lambda > 3000$  Å for 9.0–12 h. The isolated products and yields are listed in Table 2. The ratios of the products through Type I process to those through Type II process ranged from 2.4 to 3.8 [21]. In a series of control experiments, we monitored the photolytic reactions involving **2a** by detecting the products with GC. After 60 min, the reaction mixture contained isomer **3a** in 6% and a trace amount of photo-cleaved products. Irradiation for 180 min gave 15% of **3a**, 4% of Type I products, and 2% of a Type II product. After 12 h, we obtained 35% of **3a**, 32% of Type I products (i.e. **4a**+**5a**), and 13% of a Type II product (i.e. **6a**) [22]. Our findings on isomerization of the *cis* isomers **2** to the *trans* isomers **3** are in consistent with those involving non-silylated compounds reported by Barltrop and Coyle [23] as well as by Yang and Chen [24]. Moreover, we found that none of the *trans* isomers **3a–d** isomerized to give the corresponding *cis* isomers **2a–d**.

Furthermore, we measured the quantum yields and reaction rate constants for disappearance of the *cis* isomers **2a–d** (see Table 3). They were always greater than those of the corresponding *trans* isomers **3a–d**, respectively. For the  $\Phi_{cis}/\Phi_{trans}$ , the ratios were found



Scheme 2. Synthesis of *cis*- and *trans*-2-*t*-butyl-3-silylcyclohexan-1-ones.

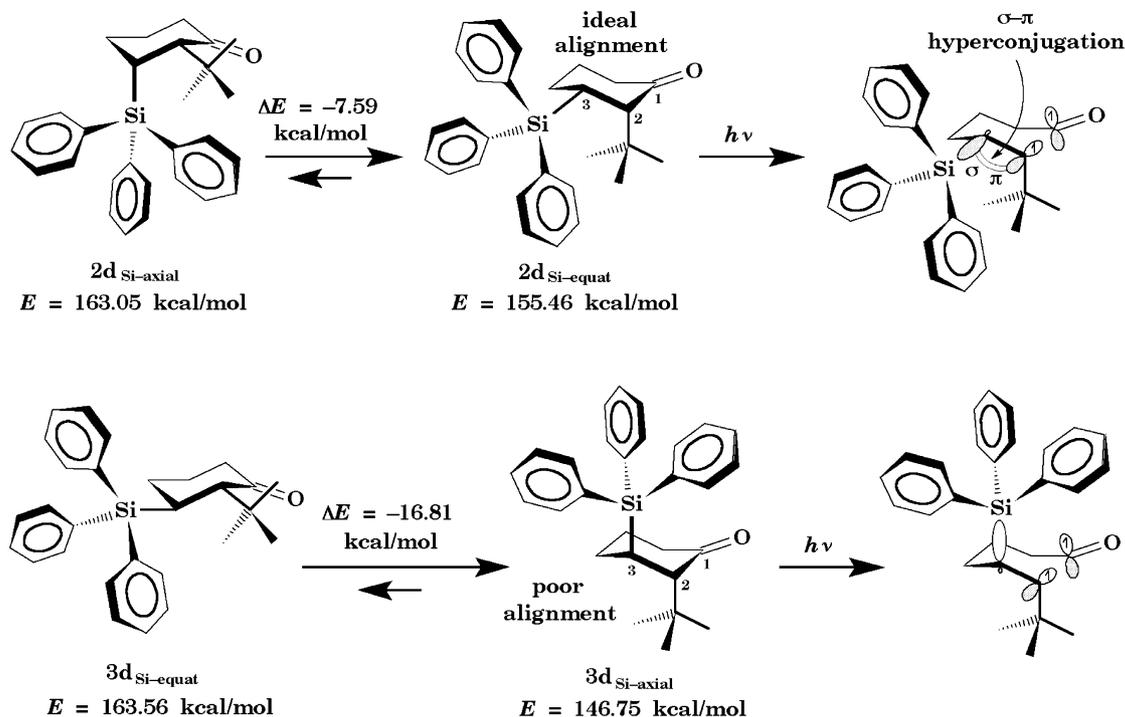
Scheme 3. Bond alignment in the photolysis of **2d** and **3d**.

Table 1

The lowest molecular energy obtained by the MM2 calculations with the CVFF for *cis*- and *trans*-2-(*t*-butyl)-3-silylcyclohexanones

2- <i>t</i> -Butyl-3-silyl-cyclohexanone	<i>E</i> <sub>lowest</sub> (kcal mol <sup>-1</sup> )	Δ <i>E</i> <sup>a</sup> (kcal mol <sup>-1</sup> )
<b>2a</b>	37.66	7.56
<b>3a</b>	30.10	
<b>2b</b>	75.39	7.06
<b>3b</b>	68.33	
<b>2c</b>	115.16	7.26
<b>3c</b>	107.90	
<b>2d</b>	155.46	8.71
<b>3d</b>	146.75	

$$^a \Delta E = E_{cis-2} - E_{trans-3}$$

between 1.20 and 22.6; for the  $\tau_{cis}^{-1}/\tau_{trans}^{-1}$ , the ratios were found between 1.22 and 20.0. The biggest ratios are associated with the pair of **2d/3d**, which possess the triphenylsilyl group.

Table 2

Photolysis of *cis*-2-*t*-butyl-3-silylcyclohexan-1-ones **2a–d** with UV light ( $\lambda > 3000$  Å) for 9.0–12 h

Substrate	Products (isolated yield)		
	Isomerization	Through Type I	Through Type II
<b>2a</b>	<b>3a</b> (35%)	<b>4a</b> (4%) + <b>5a</b> (28%)	<b>6a</b> (13%)
<b>2b</b>	<b>3b</b> (28%)	<b>4b</b> (5%) + <b>5b</b> (46%)	<b>6b</b> (14%)
<b>2c</b>	<b>3c</b> (42%)	<b>4c</b> (6%) + <b>5c</b> (30%)	<b>6c</b> (15%)
<b>2d</b>	<b>3d</b> (40%)	<b>4d</b> (0%) + <b>5d</b> (45%)	<b>6d</b> (12%)

We consider two factors that may contribute to efficiency of the Norrish type cleavages of *cis* isomers **2**: (1) the repulsion of the two bulky groups (i.e.  $-\text{SiR}_3$  and  $-t\text{-Bu}$ ) at the adjacent positions with *cis* configuration; and (2) the better alignment between the Si–C<sub>3</sub> and the C<sub>2</sub>–C<sub>1</sub>O bonds (see Scheme 3). An ideal bond alignment in the structure of **2d<sub>Si-equat</sub>** allows the ‘ $\sigma$ – $\pi$  hyperconjugation’ to exert great influence on efficiency of  $\alpha$ -bond cleavage in the Norrish type I reaction. The steric effect resulting from the three phenyl groups attached to Si in **2d** leads it to the thermodynamically more stable conformational isomer **2d<sub>Si-equat</sub>**. Because

Table 3

Comparison of the quantum yields ( $\Phi$ ) and reaction rate constants ( $\tau^{-1}$ ) in the photolysis of *cis*- and *trans*-2-(*t*-butyl)-3-silylcyclohexanones (i.e. **2a–d** and **3a–d**)

Cyclohexanone	$\Phi$ <sup>a</sup>	$\Phi_{cis}/\Phi_{trans}$ <sup>b</sup>	$\tau^{-1} \times 10^8$ (s <sup>-1</sup> )	$\tau_{cis}^{-1}/\tau_{trans}^{-1}$ <sup>c</sup>
<b>2a</b>	0.414	2.74	0.22	1.22
<b>3a</b>	0.151		0.18	
<b>2b</b>	0.556	1.20	1.25	3.91
<b>3b</b>	0.464		0.32	
<b>2c</b>	0.678	2.63	1.31	1.85
<b>3c</b>	0.258		0.71	
<b>2d</b>	0.928	22.6	5.00	20.0
<b>3d</b>	0.041		0.25	

<sup>a</sup> Quantum yield of disappearance of **2** or **3**. 3-(Trimethylsilyl)cyclohexanone was used as an actinometry.

<sup>b</sup> Quantum yield ratio of *cis* isomers **2** ( $\Phi_{cis}$ ) to *trans* isomers **3** ( $\Phi_{trans}$ ).

<sup>c</sup> Rate constant ratio of *cis* isomers **2** ( $\tau_{cis}^{-1}$ ) to *trans* isomers **3** ( $\tau_{trans}^{-1}$ ).

the phenyl groups are  $\sigma$  donors, their electronic effect contributes to stabilization of the carboradical by ' $\sigma$ - $\pi$  hyperconjugation.' On the other hand, their p orbitals participating in the ' $p$ - $d$ - $p$  homoconjugation' may also play a role in stabilization [21].

In conclusion, photolysis of various hindered *cis*- $\alpha$ -*t*-butyl- $\beta$ -organosilylcyclohexanones **2a-d** gave products through the Norrish type I and II cleavages as well as isomerization. The quantum yields and reaction rate constants of these reactions are bigger than those from the corresponding *trans* isomers **3a-d**. These results indicate that the ' $\sigma$ - $\pi$  hyperconjugation' plays an essential role on efficiency of the photolytic process.

### Acknowledgements

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- [22] Cyclohexanone **2a** (23 mg, 0.10 mmol, one equivalent), anhydrous granular sodium bicarbonate (17 mg, 0.20 mmol, two equivalents), and methanol (4.0 ml) were added into a 10-ml Pyrex tube, which was sealed with a septum. After being degassed by argon, this solution was irradiated with UV light that was filtered through a Pyrex glass sleeve. The reaction mixture was then diluted with diethyl ether (50 ml), and the ethereal mixture was washed with brine (20 ml), dried over MgSO<sub>4</sub> (s), filtered, and concentrated to give a colorless oil. Purification by HPLC afforded ketone **3a** (12 mg, 0.051 mmol) as a light yellow oil in 35% yield, alkenyl aldehyde **4a** (0.9 mg, 0.0040 mmol) as a light yellow oil in 4% yield, ester **5a** (7.2 mg, 0.028 mmol) as a yellow oil in 28% yield, and ketone **6a** (2.2 mg, 0.013 mmol) in 13% yield. For **3a**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  -0.06 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.94 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.45–2.35 (m, 8H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz)  $\delta$  -1.89 (SiCH<sub>3</sub>), 23.38, 24.75, 25.52, 29.49 (C(CH<sub>3</sub>)<sub>3</sub>), 34.73, 42.60 (C<sub>6</sub>), 59.80 (C<sub>2</sub>), 214.85 (CO); IR (neat) 1706 (s, C=O), 1249 (s, Si-CH<sub>3</sub>), 833 (s, Si-CH<sub>3</sub>) cm<sup>-1</sup>; exact mass Calc. for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 226.1753, Found (70 eV) 226.1754. For **4a**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.07 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.50–2.20 (m, 4H), 2.38 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>CO), 6.07 (s, 1H=CH), 9.75 (t, *J* = 2.0 Hz, 1H, OCH); IR (CHCl<sub>3</sub>) 2725 (w, H-C=O), 1722 (m, C=O), 1609 (w, C=C), 1248 (m, Si-CH<sub>3</sub>), 836 (m, Si-CH<sub>3</sub>) cm<sup>-1</sup>; exact mass Calc. for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 226.1753, Found (70 eV) 226.1759. For **5a**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  -0.02 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.50–0.65 (m, 1H), 0.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.95–1.70 (m, 6H), 2.25 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>CO), 3.64 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  -2.68 (SiCH<sub>3</sub>), 20.58, 24.50, 29.55, 31.96, 32.33, 34.50, 43.12, 51.27 (OCH<sub>3</sub>), 173.82 (CO); IR (CHCl<sub>3</sub>) 1730 (s, C=O), 1249 (m, Si-CH<sub>3</sub>), 834 (m, Si-CH<sub>3</sub>) cm<sup>-1</sup>; exact mass Calc. for C<sub>14</sub>H<sub>30</sub>O<sub>2</sub>Si: 258.2015, Found (70 eV) 258.2017.
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