ORGANIC
LETTERS

2005
Vol. 7, No. 15
3139−3141

Silyl Migration in the Photochemical Reactions of 2-Trimethylsilylmethylphenyl Ketones

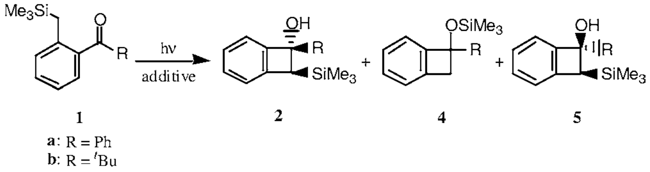
Masaichi Saito, Akitomo Saito, Yuko Ishikawa, and Michikazu Yoshioka*

*Department of Chemistry, Faculty of Science, Saitama University, Shomo-okubo,
Sakura-ku, Saitama-city, Saitama, 338-8570 Japan*

masaichi@chem.saitama-u.ac.jp

Received March 30, 2005 *(Revised Manuscript Received June 7, 2005)*

ABSTRACT



Irradiation of 2-trimethylsilylmethylphenyl ketones 1 gives benzocyclobutenols 2 and 5 together with siloxybenzocyclobutenes 4. Compound 4 arises from the novel photoinduced 1,5-silyl migration of 1. Irradiation of 1 in the presence of magnesium perchlorate gives the less hindered benzocyclobutenols 5 without the formation of 4. The mechanism of the photochemical reaction of 1 is discussed.

For many years, much attention has been focused on silyl migrations since they display characteristics not normally seen in carbon chemistry as well as in view of their synthetic usefulness.[1] It is well-known that silyl groups generally have high migratory aptitude. Among silyl migrations, those from carbon to oxygen have been often observed and extensively studied because of the greater bond strength of the Si−O bonds (ca. 112 kcal) than those of Si−C (ca. 73 kcal).[2] They may be roughly grouped into two categories: ionic and neutral rearrangements involving radicals and sigmatropic rearrangements. Although the 1,2- to 1,4-silyl migrations from carbon to oxygen have been well studied,[1] only a few 1,5-silyl migrations have been reported.[3−6] In the course of our studies on the effect of heteroatom functionalities on the photochemical reactions of *o*-alkylaryl ketones,[7] we report herein the 1,5-silyl migration from carbon to oxygen in the photochemical reaction of 2-trimethylsilylmethylphenyl ketones.

Irradiation of 2-trimethylsilylmethylbenzophene (**1a**) with a high-pressure mercury lamp gives benzocyclobutenol **2a** (58%) via hydrogen abstraction from the trimethylsilylmethyl group by the carbonyl oxygen, as in the case of *o*-alkylaryl ketones (Scheme 1).[8,9] Previous studies have shown that formation of the benzocyclobutenols proceeds via *E*-photo-

---

[1] For examples of reviews, see: (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) Brook, A. G.; Bassindale, A. R. *Molecular Rearrangements of Organosilicon* Compounds, In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 149. (c) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons: New York, 1999. (d) Kira, M.; Iwamoto, T. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Interscience: New York, 2001; Vol. 3, p 853.

[2] For approximate bond energies for silicon, see: Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214 and references therein.

[3] Casey, C. P.; Jones, C. R.; Tukada, H. *J. Org. Chem.* **1981**, *46*, 2089.

[4] (a) Pirrung, M. C.; Lee, Y. R. *Tetrahedron Lett.* **1993**, *51*, 8217. (b) Pirrung, M. C.; Fallon, L.; Zhu, J.; Lee, Y. R. *J. Am. Chem. Soc.* **2001**, *123*, 3638.

[5] (a) Lee, Y. R.; Lee, C. P.; Jeon, Y. T.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Kim, J. C.; Lee, J. G. *Tetrahedron Lett.* **1993**, *37*, 5855. (b) Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. K.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304.

[6] (a) Weber, W. P.; Felix, R. A.; Willard, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 1420. (b) Weber, W. P.; Willard, A. K. *J. Org. Chem.* **1971**, *36*, 1620.

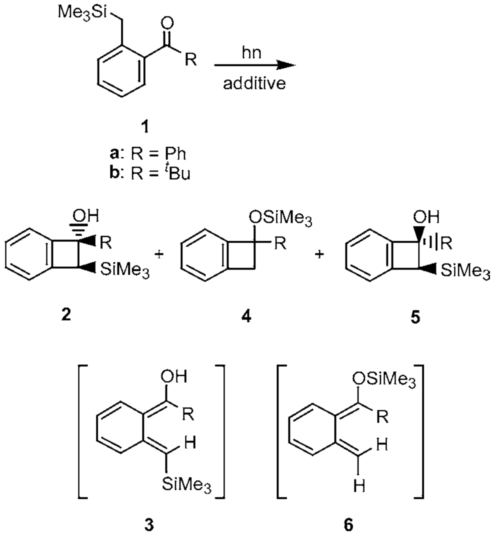
[7] Saito, M.; Kamei, Y.; Kuribara, K.; Yoshioka, M.; Hasegawa, T., *J. Org. Chem.* **1998**, *63*, 9013.

[8] (a) Matsuura, T.; Kitaura, Y. *Tetrahedron. Lett.* **1967**, *34*, 3309. (b) Matsuura, T.; Kitaura, Y. *Tetrahedron* **1969**, *25*, 4487.

[9] **General Procedure for Photolysis of 1.** A solution of **1** was placed in a glass vessel into which was placed a Pyrex water jacket to cool a lamp inserted in it and irradiated with a 100 or 450 W high-pressure mercury lamp under argon. The reaction vessel was kept at about 20−30 °C during irradiation. After irradiation, the solvent was removed and the residue was chromatographed on silica gel. The irradiation conditions and the solvent used for chromatography are shown in Table S1 in the Supporting Information.

10.1021/ol050673s CCC: $30.25

Scheme 1. Photochemical Reactions of **1**



ketone	solvent	irradiation period (h)	additive	isolated yields (%)		
				2	**4**	**5**
1a	benzene	12	none	58	-	-
1a	benzene	88	none	8	10	12
1a	CH_3CN	3	none	50	-	5
1a	CH_3CN	90	$Mg(ClO_4)_2$	-	-	62
1b	hexane	18	none	62	-	-
1b	hexane	70	none	45	28	-
1b	CH_3CN	18	none	65	-	-
1b	CH_3CN	60	$Mg(ClO_4)_2$	-	-	65

enols **3**.[10] Thus, we assume that our observed product **2** comes from this intermediate. This would lead to formation of the isomer wherein the phenyl and the trimethylsilylmethyl groups are cis. Benzocyclobutenol **2a** is thermally unstable and converted to the starting ketone over 1 day at room temperature via *E*-xylylenol **3a**.[11,12] Prolonged irradiation of **1a**, however, gives siloxybenzocyclobutene **4a** (10%) and less hindered benzocyclobutenol **5a** (12%) together with **2a** (8%) (Scheme 1).[9] In ^{1}H NMR, the trimethylsilyl protons of **2a** appear at higher field (−0.29 ppm) compared to those for **5a** (0.14 ppm) because of the strong shielding effect of the phenyl group located in a syn fashion. Siloxybenzocyclobutene **4a** probably arises from siloxyxylylene **6a** formed by the photoinduced 1,5-migration of a trimethylsilyl group to the carbonyl oxygen. Although the benzocyclobutenol **2a** reverts to the starting ketone **1a** through the xylylenol **3a** by intermolecular 1,5-hydrogen shift,[12] the siloxyxylylene **6a** formed by 1,5-silyl migration cyclizes to siloxybenzocyclobutene **4a** because it lacks hydrogen to undergo 1,5-shift. The hindered benzocyclobutenols are unstable and revert to the parent ketones.[13] The less hindered benzocyclobutenol **5a** arises from the photoinduced disrotatory cyclization of *E*-xylylenol **3a**. The formation of less hindered benzocyclobutenols upon extended irradiation has been reported.[13]

Irradiation of 2-trimethylsilylmethylpivalophenone (**1b**)[14] in hexane affords benzocyclobutenol **2b** (62%) (Scheme 1).[9] Prolonged irradiation of **1b**, however, gives siloxybenzocyclobutene **4b** (28%) and 2**b** (45%) (Scheme 1).[9] Benzocyclobutenol **2b** is also so labile as to revert to **1b** over 1 day at room temperature. The lack of formation of sioxybenzocyclobutenes **4** in short-time irradiation suggests that the thermal lability of the initially formed benzocyclobutenols **2** to revert to the starting ketones **1** plays an important role.

Steric congested benzocyclobutenols are known to isomerize to the corresponding less hindered benzocyclobutenols in the presence of acid.[15] The transformation of benzocyclobutenols **2** to the less hindered isomers **5** was examined. Treatment of **2** with magnesium perchlorate in acetonitrile at room temperature gives **5** and **1** (Scheme 2).[16] In ^{1}H NMR, the protons of the trimethylsilyl and *tert*-butyl groups of **2b** resonate at lower field (0.19 and 1.07 ppm, respectively) than those for **5b** (0.04 and 0.98 ppm, respectively) because of the van der Waals repulsion caused by steric congestion in **2b**.[17] The benzocyclobutenol **5** is thermally stable and does not decompose in solution even at 80 °C.

Scheme 2. Isomerization of **2**

$$\mathbf{2} \xrightarrow[CH_3CN]{Mg(ClO_4)_2} \mathbf{1} + \mathbf{5}$$

	isolated yields (%)	
	1	**5**
2a	20	51
2b	4	46

Irradiation of **1** with a high-pressure mercury lamp in the presence of magnesium perchlorate (1 eq) in acetonitrile gives the less hindered benzocyclobutenol **5** with no formation of **4** (Scheme 1).[18]

Since irradiation of **1** in the absence of magnesium perchlorate initially gives the unstable benzocyclobutenol **2**, the exclusive formation of **5** in the presence of magnesium perchlorate suggests that the initially formed **2** should convert to **5** faster than the reversion to the starting ketone **1**. The formation of the siloxybenzocyclobutene **4** in prolonged irradiation can be explained by the fact that the ketone **1** undergoes both hydrogen abstraction and silyl migration from

---

(10) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709.

(11) Very recently, *cis*-1,2-diphenylbenzocyclobutenol was found to be stable below 0 °C in solution; see: Sobczak, M.; Wagner, P. J. *Tetrahedron Lett.* **1998**, 2523.

(12) Iida, K.; Komada, K.; Saito, M.; Yoshioka, M. *J. Org. Chem.* **1999**, *64*, 7407.

(13) Sobczak, M.; Wagner, P. J. *Tetrahedron Lett.* **1998**, 2523.

(14) Kobayashi, K.; Kawakita, M.; Uchida, M.; Nishimura, K.; Mannami, T.; Irisawa, S.; Morikawa, O.; Konishi, H. *J. Org. Chem.* **1999**, *64*, 3557.

(15) Coll, G.; Costa, A.; Deyá, P. M.; Flexas, F.; Rotger, C.; Saá, J. M. *J. Org.* Chem. **1992**, 57, 6222.

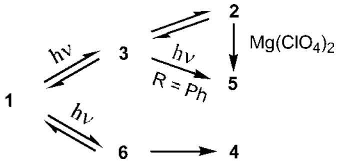
(16) Isomerization of **2** to **1** occurred via *E*-xylylenol **3** competitively.

(17) Atta-ur-Rahman, H. E. J. In *Nuclear Magnetic Resonance: Basic Principles*; Springer-Verlag: New York, 1986.

(18) Irradiation of **1** in acetonitrile without magnesium perchlorate gave **2**.

the *o*-trimethylsilylmethyl group to the carbonyl oxygen and that the unstable benzocyclobutenol **2** formed by hydrogen abstraction reverts to the starting ketone (Scheme 3). In the photochemical reaction of **1**, the hydrogen abstraction proceeds much faster than the silyl migration.

Scheme 3



In summary, the 2-trimethylsilylmethylphenyl ketone underwent both photoinduced hydrogen abstraction and silyl migration from the trimethylsilylmethyl group to the carbonyl oxygen to form the benzocyclobutenol and the siloxybenzocyclobutene. The former process is much more predominant than the latter. It is interesting to compare the present results with previous studies of *o*-formylbenzyltrialkylmetallanes. *o*-Formylbenzyltrialkylsilane and -germane underwent no photoinduced 1,5-silyl and germyl migrations. On the contrary, *o*-formylbenzyltrialkylstannane underwent 1,5-stannyl migration and the resulting stannoxyxylylene was trapped by the dienophile.[19]

Acknowledgment. This work was partially supported by a Grant-in Aid for Encouragement of Young Scientists No. 10740288 (M.S.) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Detailed descriptions of experimental procedures and spectral data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL050673S

---

[19] Sano, H.; Asanuma, D.; Kosugi, M. *Chem. Commun.* **1999**, 1559.