ORGANIC LETTERS

2001
Vol. 3, No. 9
1277−1280

Photoallylation and Photoreduction of Cyclohexylidenepropanedinitrile by Use of Allyltrimethylsilane via Photoinduced Electron Transfer: Control of the Product Ratio Depending on pK_a Values of Additives

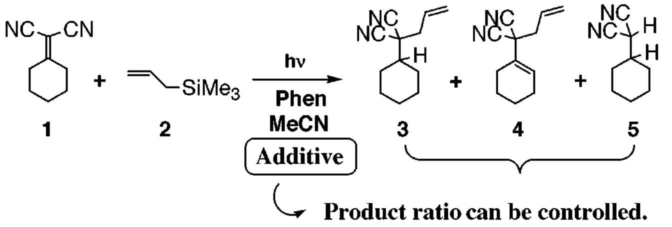
Tomoo Hayamizu, Munehiro Ikeda, Hajime Maeda, and Kazuhiko Mizuno*

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

mizuno@chem.osakafu-u.ac.jp

Received December 18, 2000

ABSTRACT



Irradiation of an acetonitrile solution containing cyclohexylidenepropanedinitrile (1) and allyltrimethylsilane (2) in the presence of phenanthrene afforded two kinds of allylated products (3, 4) and a reduction product (5). The product ratio of 3, 4, and 5 dramatically changed depending on the pK_a values of additives.

Photoinduced electron-transfer reactions between electron-rich and electron-poor molecules has been utilized as a useful method for the efficient C−C bond formation for the past two decades.[1] We and others have developed the photoinduced alkylation, allylation, arylmethylation, and silylation of a variety of electron-deficient compounds by use of group 14 organometallic compounds via electron transfer.[2−9] In these photoreactions, the radical anions or free radicals generated from electron-deficient molecules and the radical cations of group 14 organometallic compounds have been postulated as reactive intermediates. However, it is not easy to control the stereo-, regio-, and chemoselectivities because the mechanism in some cases is still equivocal. We now report the control of the product ratio by means of additives in the photoallylation and reduction of cyclohexylidenepropanedinitrile (**1**) using allyltrimethylsilane (**2**).

Irradiation of an acetonitrile (8 mL) solution containing **1** (0.68 mmol) and an excess of **2** (1.75 mmol) in the presence

---

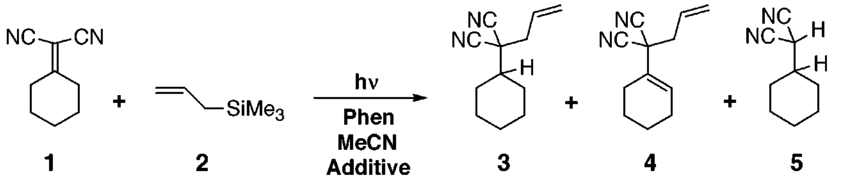
[1] Review articles for general photoinduced electron transfer: (a) Fox, M., Chanon, M., Eds. *Photoinduced Electron Transfer, Part A−D*; Elsevier: Amsterdam, 1988. (b) Mattay, J., Ed. *Photoinduced Electron-Transfer I−V:* (*Top. Curr. Chem.* 156, 158, 159, 163, 168); *Electron-Transfer I, II*: (*Top. Curr. Chem.* 169, 177); Springer: Berlin, 1990−1996. (c) Mariano, P. S., Ed. *Advances in Electron-Transfer Chemistry*; JAI Press: Greenwich, CT, 1991−1996; Vols. 1−5, and references therein.

[2] Review articles for photoinduced electron-transfer reaction of organosilicon compounds: (a) Kako, M.; Nakadaira, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2403. (b) Mizuno, K.; Tamai, T.; Sugimoto, A.; Maeda, H. In *Advances in Electron-Transfer Chemistry*, Vol. 6; Mariano, P. S., Ed.; JAI Press: New York, 1999; pp 131−165. (c) Kato, M.; Nakadaira, Y. *Coord. Chem. Rev.* **1998**, *87*, 176. (d) Mizuno, K.; Otsuji, Y. *Top. Curr. Chem.* **1994**, *169*, 301. (e) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.

[3] (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (c) Borg, R. M.; Mariano, P. S. *Tetrahedron Lett.* **1986**, 2821. (d) Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738. (e) Cho, I. C.; Tu, C. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 3594.

10.1021/ol000386i CCC: $20.00

Scheme 1



of phenanthrene (Phen) (0.14 mmol) as a sensitizer with a 300 W high-pressure mercury lamp through a Pyrex filter (>280 nm light) afforded two kinds of allylated products (**3**, **4**) and a reduction product (**5**) in a 1:31:68 ratio in 89% total yield (Scheme 1). In this photoreaction, the product ratio remarkably changed by varying the additives (Table 1). The addition of 4A molecular sieves suppressed the formation of **3** (entry 2). When methanol or water was added into the solution (entries 3 and 4), the product ratio of **3** slightly increased. In the cases of adding dimethyl malonate and malononitrile (entries 5 and 6), the formation of **3** increased and that of **4** decreased, although **5** was still obtained as a main product. When organic acids such as acetic acid and benzoic acid were added (entries 7 and 8), **3** was mainly obtained and the formation of **5** was effectively suppressed with the complete disappearance of **4**.[10] The addition of formic acid selectively gave **3** in high yield (entry 9).

Table 1. Additive Effect of Additives in the Photoallylation and the Photoreduction of **1**[a]

			product ratio[c]		
entry	additive[b]	pK_a	**3**	**4**	**5**
1	none		1	31	68
2	molecular sieves 4A[d]		0	44	56
3	H_2O	15.7	3	29	68
4	MeOH	15.0	4	29	67
5	$CH_2(CO_2Me)_2$	13.5	19	17	64
6	$CH_2(CN)_2$	11.2	33	1	66
7	$MeCO_2H$	4.8	69	0	31
8	$PhCO_2H$	4.2	77	0	23
9	HCO_2H	3.7	92	0	8

[a] Irradiation was carried out at room temperature for 8 h. [Phen] = 0.081 M, [**1**] = 0.085 M, [**2**] = 0.255 M. [b] MeCN:additive = 30:1 (wt %). [c] Determined by GC. [d] 10 mg/mL.

These results clearly showed that the pK_a values of the additives would affect the product ratios. The product ratios vs. pK_a values of additives were plotted (Figure 1).[11]

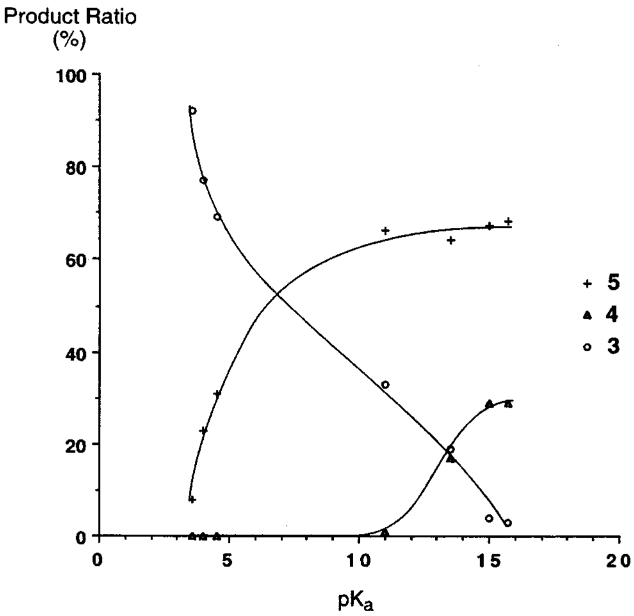


Figure 1. Plots of the product ratios vs. pK_a values of additives in the photoreaction of **1** with **2**.

From a mechanistic viewpoint, we examined the deuterium incorporation experiments using several deuterated com-

---

(4) (a) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 1507. (b) Mizuno, K.; Nakanishi, K.; Chosa, J.; Nguyen, T.; Otsuji, Y. *Tetrahedron Lett.* **1989**, *30*, 3689. (c) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 461. (d) Mizuno, K.; Terasaka, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 5819. (e) Mizuno, K.; Terasaka, K.; Yasueda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 145. (f) Mizuno, K.; Nakanishi, K.; Otsuji, Y. *Chem. Lett.* **1988**, 1833. (g) Mizuno, K.; Kobata, T.; Maeda, R.; Otsuji, Y. *Chem. Lett.* **1990**, 1821. (h) Mizuno, K.; Nakanishi, T.; Tachibana, A.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 344. (i) Mizuno, K.; Nakanishi, T.; Terasaka, T.; Yasueda, M.; Shima, K.; Otsuji, Y. *Tetrahedron* **1992**, *48*, 9673. (j) Nakanishi, K.; Mizuno, K.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2371. (k) Tamai, T.; Mizuno, K.; Hashida, I.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3747. (l) Mizuno, K.; Nakanishi, K.; Chosa, J.; Otsuji, Y. *J. Organomet. Chem.* **1994**, *26*, 461.

(5) (a) Kyushin, S.; Masuda, Y.; Matsushima, K.; Nakadaira, Y.; Ohashi, M. *Tetrahedron Lett.* **1990**, *31*, 6395. (b) Kyushin, S.; Otani, S.; Takahashi, T.; Nakadaira, Y.; Ohashi, M. *Chem. Lett.* **1991**, 775.

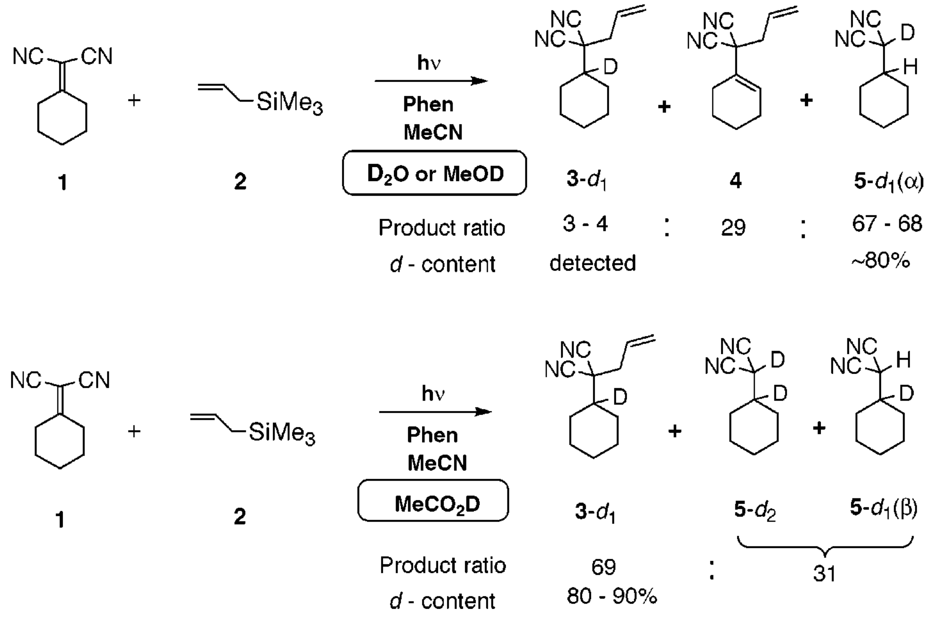
(6) (a) Mella, M.; Fassani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 6210. (b) Mella, M.; Fassani, E.; Albini, A. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 383. (c) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (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.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.

(7) Pandey, G.; Sesha, K. S.; Rao, P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2669.

(8) (a) Kubo, Y.; Imaoka, T.; Shiragami, T.; Araki, T. *Chem. Lett.* **1986**, 1749. (b) Maruyama, K.; Imahori, H.; Osuka, A.; Takuwa, A.; Tagawa, H. *Chem. Lett.* **1986**, 1719. (c) Takuwa, A.; Tagawa, H.; Iwamoto, H.; Soga, O.; Maruyama, K. *Chem. Lett.* **1987**, 1091. (d) Takuwa, A.; Nishigaichi, Y.; Iwamoto, H. *Chem. Lett.* **1990**, 639. (e) Takuwa, A.; Nishigaichi, Y.; Iwamoto, H. *Chem. Lett.* **1991**, 1013. (f) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435. (g) Hasegawa, E.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099. (h) Zang, X. M.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 1655. (i) Jeon, Y. T.; Lee, C. P.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8847. (j) Xu, W.; Zhang, X. M.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8863. (k) Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3280. (l) Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235.

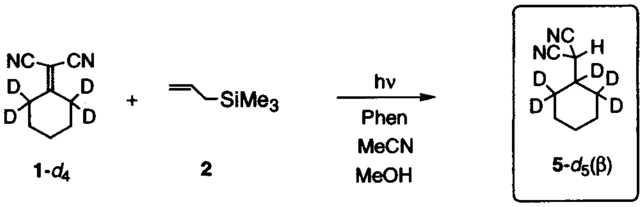
(9) (a) Mochida, K.; Kochi, J. K.; Chen, K. S.; Wan, J. K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2927. (b) Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1986**, 25.

Scheme 2

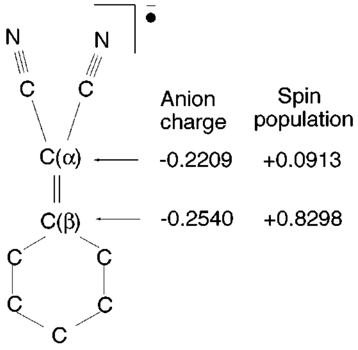


pounds. In acetonitrile-d_3, deuterated products were not obtained at all. However, the α-position to the cyano group of **5** was effectively deuterated by the addition of methanol-O-d_1 or D_2O into the acetonitrile solution. When acetic acid-O-d_1 was added, the deuterated product **3**-d_1 (d-content; 80−90%) at the β-position to the cyano group was obtained in a good yield. In this photoreaction, two kinds of deuterated **5** (**5**-d_2 and **5**-d_1(β)) were interestingly produced, the former was deuterated at both the α- and β-positions and the latter was only deuterated at the β-position (Scheme 2). Next, we searched the hydrogen source of the β-hydrogen of **5**-d_1(α). The reduction product **5** was not deuterated by allyltris(trideuteriomethyl)silane **2**-d_9 in either MeCN−MeOH or MeCN−$MeCO_2H$ solutions.[12] Finally, we found that the partially deuterated **5**-d_5 was obtained in the photoreaction of 2,2,6,6-tetradeuteriocyclohexylidenepropanedinitrile (**1**-d_4) with **2** in MeCN−MeOH (Scheme 3), but all products in MeCN−$MeCO_2H$ were not deuterated by **1**-d_4.

Scheme 3



From the result of the pK_a-dependent photoreactions and the deuterium incorporation experiment, we propose the mechanism for the allylation and the reduction of **1** shown in Scheme 4. The first step is the formation of Phen$^{\bullet+}$ and **1**$^{\bullet-}$ via one-electron transfer from the excited singlet state of Phen to **1**.[11,13,14] Then, the secondary electron transfer from



---

[10] The photoallylation of 1,1-dicyano-2-phenylethene by **2** in the presence of Phen was not affected by the addition of methanol and acetic acid: see ref 4a.

[11] No linear relationship between the product ratios and the pK_a values of the additives may suggest the participation of complex intermediates, although we have shown the radical ion intermediates in Scheme 4 as a simplified mechanism. We believe that the radical anion species are involved as important intermediates in this photoreaction. See ref 14.

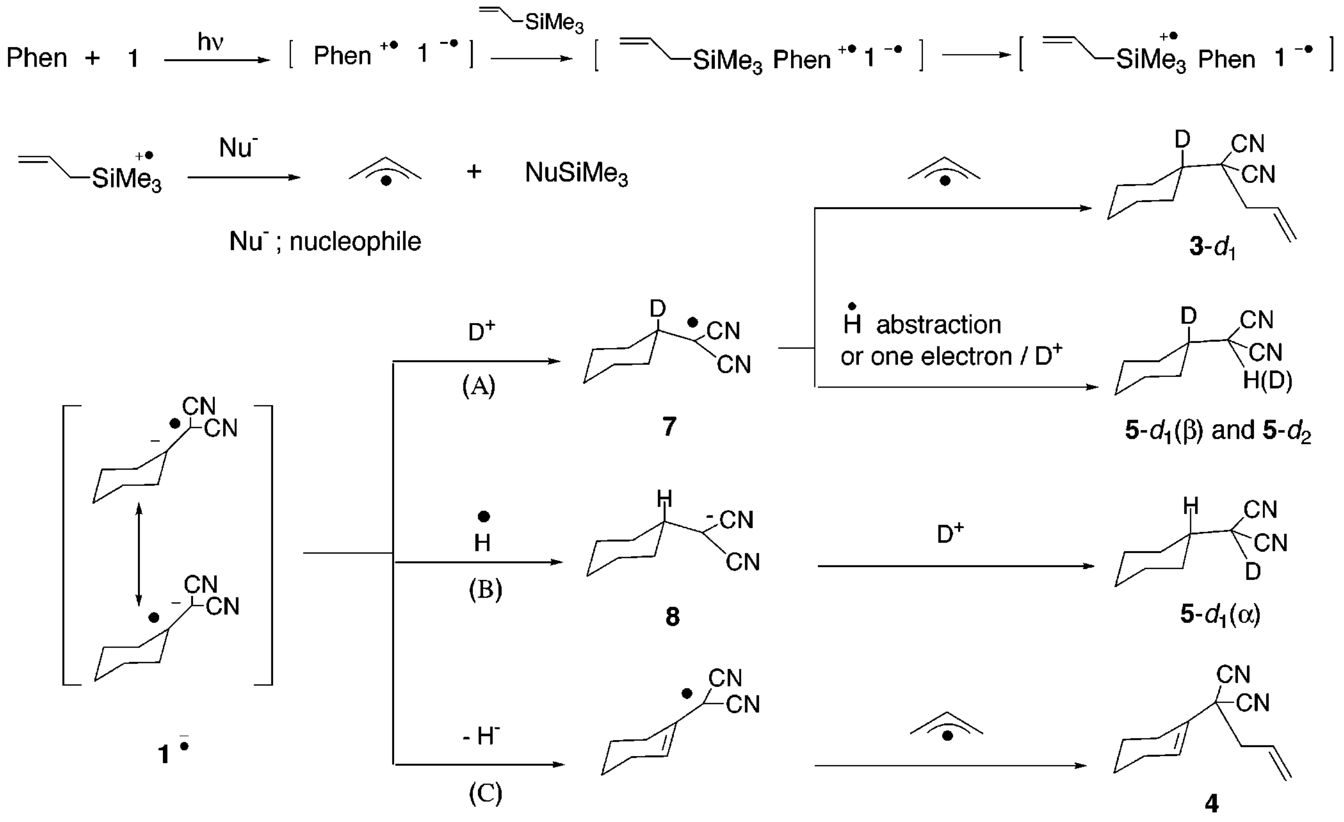
[12] The photobenzylation of **1** by use of benzyltrimethylsilane **6** similarly occurs to give the corresponding benzylated products, 1,1-dicyano-1-cyclohexyl-3-phenylpropane and 1,1-dicyano-1-(1′-cyclohexenyl)-3-phenylpropane, accompanying the formation of **5**. The photoreaction of **1** with α,α-dideuteriobenzyltrimethylsilane **6**-d_2 did not give a deuterated **5**. From these results, we have postulated that **5** could not be deuterated by α,α-dideuterioallyltrimethylsilane **2**-d_2.

[13] (a) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265. (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. (c) Arnold, D. A.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012.

[14] The formation of the radical cation of Phen is supported by the laser flash photolysis of an acetonitrile solution of **1** and pyrene in place of Phen with 355 nm excimer laser light. The radical cation of pyrene was observed at 450 nm as a transient absorption spectrum, although the radical cation of Phen and the radical anion of **1** were not observed. Hayamizu, T.; Mizuno, K.; Ichinose, N.; Majima, T. Unpublished result.

[15] The spin population of C(β) position on **1** calculated by PM3 calculation is about nine times as large as that of C(α), although the anion charges at both positions are nearly the same.

Scheme 4



2 to Phen$^{\bullet+}$ generates **2**$^{\bullet+}$, which gives the allyl radical by the nucleophile-assisted elimination of Me_3Si^+.[2b,4j,6e] In the presence of organic acids, the protonation at the β position to the cyano group of **1**$^{\bullet-}$ predominantly takes place to generate radical **7** (path A). The major pathway is the radical coupling of **7** with the allyl radical to give **3**. The minor pathway is a hydrogen abstraction of **7** or an electron transfer from **1**$^{\bullet-}$ to **7** followed by protonation to give **5**. On the other hand, in the presence of methanol or water, the hydrogen abstraction from the allylic position of **1** preferentially occurs to generate the carbanion **8**.[15] The protonation of **8** gives the reduction product **5** as a main product (path B). The formation of **4** can be explained by the elimination of hydride ion from **1**$^{\bullet-}$ followed by the radical coupling with allyl radical (path C).[16]

In conclusion, the product ratio in the photoinduced electron-transfer reaction of **1** by use of **2** can be controlled by the pK_a values of additives. Two possible pathways, protonation and hydrogen abstraction, for the reactivity of **1**$^{\bullet-}$ have been clarified by use of additives having different pK_a values and several deuterated compounds.

Acknowledgment. We are grateful to Dr. N. Ichinose and Prof. T. Majima (Osaka University) for the measurements of transient spectra of the pyrene−**1** system. Financial support from a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged.

OL000386I

---

[16] The yields of **4** and **5** (**4**:**5** = 53:47) increased and **3** was not produced when a high concentration of **1** (0.25 M) was used. A reviewer suggested that the result may support a hydride transfer mechanism.