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Highly Efficient and Chemoselective Reductive Bis-silylation of Quinones by Silyltellurides

Shigeru Yamago,* Hiroshi Miyazoe, Kazunori Iida, and Jun-ichi Yoshida*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

yamago@sbchem.kyoto-u.ac.jp

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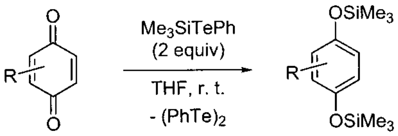
ABSTRACT



Silyltellurides serve as new silicon-based chemoselective reducing agents and reduce quinones to the corresponding bis-silylated hydroquinones. The reaction proceeds under ambient thermal conditions without the need of any additional promoters or catalysts and gives the products in excellent yields. Several control experiments suggest that the reaction is initiated by a single electron transfer from silyltellurides to quinones.

Silicon-based reducing agents have attracted a great deal of attention recently because of their low toxicity compared to the corresponding tin-based reagents.[1] However, since the currently used reagents are limited primarily to silyl hydride reagents, development of new silicon-based reducing agents with improved reactivity and selectivity is consequently highly desirable. We have recently shown that the thermal reaction of silyl tellurides with carbonyl compounds generates α-siloxy carbon radicals, which are useful intermediates for C−C bond formations.[2] While investigating the reactivity of silyl tellurides with carbonyl compounds, we discovered a new type of reductive bis-silylation of quinones.[3,4] We report here a highly efficient and chemoselective thermal reaction of silyl tellurides with quinones (Figure 1) that is the first example of the use of the silyltellurides as silicon-based reducing agents.

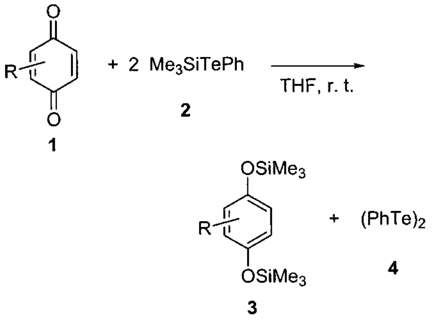


Figure 1. Reductive bis-silylation of quinones.

The feasibility of the reaction was initially examined with 1,4-benzoquinone (**1a**, R = H) and trimethylsilylphenyl-

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(1) (a) Weber, W. P. In *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 273−338. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 1479−1526. (c) Brook, M. A. In *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons: New York, 2000, pp 171−188 and 401−422. (d) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (e) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(2) Miyazoe, H.; Yamago, S.; Yoshida, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3669.

(3) (a) Wiberg, N.; Weith, M. *Chem. Ber.* **1971**, *104*, 3191. (b) Matsumoto, H.; Koike, S.; Matsubara, I.; Nakano, T.; Nagai, Y. *Chem. Lett.* **1982**, 533. (c) Lecea, B.; Aizpurua, J. M.; Palomo, C. *Tetrahedron* **1985**, *41*, 4657. (d) Bakola-Christianopoulou, M. N. *J. Organomet. Chem.* **1986**, *308*, C24. (e) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K.; Tonogaki-Kubota, M.; Kobayashi, T. *Chem. Lett.* **1994**, 1439. (f) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Organometallics* **1997**, *16*, 5223.

(4) Stepwise bis-silylation by the reduction of quinones followed by silylation has been also reported. (a) Rasmussen, J. K.; Krepski, L. R.; Heilmann, S. M.; Smith, H. K., II; Tumey, M. L. *Synthesis* **1983**, 457. (b) Boudjouk, P.; So, J. H. *Synth. Commun.* **1986**, *16*, 775.

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telluride (**2**).[5] Thus, when **1a** and **2** (2.2 equiv) were mixed in THF at room temperature, the red color corresponding to the diphenyl ditelluride appeared immediately, and the bis-silylated 1,4-dihydroquinone (**3a**, R = H) and diphenyl ditelluride (**4**) were isolated in quantitative yields (Table 1, entry 5).[6] When 1 equiv of **2** was used, half of the quinone was converted to **3a**, indicating that the second silylation reaction was faster than the first. While the reaction proceeded in various solvents, the rate of the reaction was faster in polar solvents than in nonpolar ones. For example, the reaction in CD_3CN was completed in about 0.5 h, while that in C_6D_6 required 2 h for completion.

Table 1. Reductive Bis-Silylation of Quinones with Silyltellurides[a]

entry	quinone	E_{red} (V vs SCE)[b]	yield (%)
1	2,3-dichloro-4,5-dicyano-1,4-benzoquinone	0.49	66[c]
2	2,3,5,6-tetrachloro-1,4-benzoquinone	0.00	96
3	2,6-dichloro-1,4-benzoquinone	−0.20	95
4	1,2-naphthoquinone	−0.39	82
5	1,4-benzoquinone	−0.54	100
6	2,3-dimethoxy-5-methyl-1,4-benzoquinone	−0.67	100
7	1,4-naphthoquinone	−0.72	98
8	duroquinone	−0.86	91
9	anthraquinone	−0.96	97

[a] Typical procedures: a THF solution of quinone (ca. 0.5 M) and **2** (2.2 equiv) was stirred for 0.5−1 h at room temperature. [b] Reduction potential was measured in a 0.1 M Bu_4NClO_4 solution of CH_3CN by cyclic voltammetry using glassy carbon as working electrodes. [c] Isolated as the corresponding dihydroquinone because the silylated product was hydrolytically unstable.

The scope of the current reaction was examined, and the results are summarized in Table 1. Several kinds of quinones with various substitution patterns were found to react with **2** to afford **3** in good to excellent yields. In all cases, mono-, di-, tri-, and tetrasubstituted quinones gave the desired adducts. It is worth noting that not only 1,4-quinones but also 1,2-quinones were reduced to give the corresponding bis-silylated 1,2-hydroquinones (entry 4). The reaction rate was found to be sensitive to the electronic character of the substituents, and the quinones of higher reduction potential tend to react faster than those bearing electron-releasing substituents. Indeed, thin-layer chromatography analysis indicated that the reaction proceeded in about 10 min with quinones whose reduction potential is higher than −0.4 V vs SCE (entries 1−4). The reactivity of the quinones whose reduction potential is lower than −0.4 V was slightly less, but in all cases the reaction was completed within 0.5 h (entries 5−9).

To further clarify the synthetic utility of the current reaction, we next examined the compatibility of functional groups. The reaction of duroquinone (1.0 equiv) and **2** (2.0 equiv) was conducted in the presence of 2 equiv of the compounds listed in Figure 2. We found that the reaction occurred selectively with the quinone and that the additives were recovered quantitatively in all cases (>90%), while the reaction of **2** with duroquinone took place in high yield (>90% yield). The results indicate that the reaction is compatible with various functional groups, e.g., alkyl and aryl halides, aldehydes, α,*β*-unsaturated carbonyl compounds, and nitro groups. The selective reduction of quinones in the presence of an alkyl iodide is worth noting, because the reactivity of the free triethylsilyl radical toward duroquinone and primary alkyl iodides is known to be almost identical ($k = 10^9\ M^{-1}\ s^{-1}$).[7]

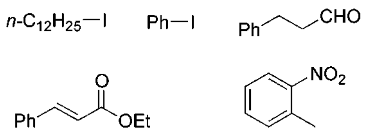
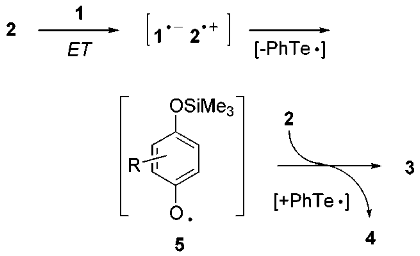


Figure 2. Functional groups that are compatible with the reductive bis-silylation.

Since we have already reported that the reaction of **2** with carbonyl compounds generates the α-siloxy carbon radicals, we propose the mechanism as depicted in Scheme 1. An initial electron transfer (ET) from **2** to the quinone generates a radical ion pair, and the subsequent O−Si bond formation in the ion pair generates the phenoxy radical **5**.[8] The radical **5** further reacts with **2** to give **3** and **4**.[9] An alternative possibility, which includes the generation of trimethylsilyl radical from **2** and the subsequent reaction of the radical

Scheme 1. Possible Reaction Mechanism



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[5] (a) Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879. (b) Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1985**, *26*, 453.

[6] **Typical Reaction Procedure.** A mixture of **1a** (54.2 mg, 0.50 mmol) and **2** (302.4 mg, 1.09 mmol) in THF (1.0 mL) was stirred at room temperature for 0.5 h. Removal of the solvent followed by purification on silica gel afforded **3a** as a white solid (127.2 mg, 0.50 mmol, 100%).

[7] (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119. (b) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

[8] When s a 1:1 mixture of **2** and 2,6-di-*tert*-butyl-1,4-benzoquinone was dissolved in EtCN at 20−30 °C, a characteristic ESR signal corresponding to the phenoxy radical species was observed at $g = 2.0044$ with aH = 0.092 mT. For such radical species, see: (a) Chen, K. S.; Foster, T.; Wan, J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1288. (b) Alberti, A.; Chatgilialoglu, C. *Tetrahedron* **1990**, *46*, 3963.

[9] See ref 2 for the analogous reaction of TEMPO free radical with **2**.

with the quinone to generate **5**, was less likely for the following reasons. First, since the reactivity of the trimethylsilyl radical toward duroquinone and primary alkyl iodidies is almost the same, the observed chemoselectivity ruled out the possibility of generation of the free trimethylsilyl radical. Indeed, the calculated homolytic bond dissociation energy of **2**, 232 kJ/mol, is too high for the Si−Te bond to undergo homolysis under the reaction conditions.[10] Second, the observed solvent effect is consistent with the involvement of the polar intermediate, e.g., radical ion pairs. Third, the reactivity of the quinones correlates well with their reduction potential; the quinones of higher reduction potential react faster than those with lower reduction potential. The oxidation potential of **2** is 0.94 V vs SCE, which is higher than the reduction potential of the quinones. However, the preassociation of **2** and the quinones may considerably enhance the ET processes.[11] Obviously, further studies are needed to clarify the detail reaction mechanism.

In conclusion, the silyltellurides serve as highly reactive and chemoselective silicon-based reducing agents for the reduction of quinones and provide easy access to the bis-silylated hydroquinones. Since protected hydroquinones are important intermediates for the synthesis of complex quinoid compounds,[12,13] the current method provides a new and efficient approach for the synthesis of this class of compounds.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. We thank Professor S. Okazaki and Professor M. Oyama, Department of Material Chemistry of Kyoto University, for the ESR measurement and valuable discussions and Dr. C. Chatgilialoglu, I.Co.C.E.A. of Consiglio Nazionale delle Ricerche, Bologna, for valuable discussions and suggestions.

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(10) Calculation was carried out with Gaussian 98 programs. Geometry optimizations were performed with the hybrid B3LYP density functional with a Hey-Wadt effective core potential (ECP) and outermost valence electron basis set for tellurium and 6-31G(d) basis set for the rest. *Gaussian 98, Revision A.7*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; W. Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) For an excellent review of such processes, see: Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1.

(12) Greeves, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, pp 1−24.

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