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Photoinduced Reduction of Group 16 Heteroatom Compounds with the Aid of Samarium Diiodide

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Abstract: *A novel photoinduced reduction of group 16 heteroatom compounds such as organic selenides, tosylates, and tellurides has been developed. In particular, organic selenides, which can not be reduced with SmI$_2$ in the dark (or even in the presence of HMPA), undergo reductive cleavage efficiently by using the SmI$_2$–hν system.* © 1998 Elsevier Science Ltd. All rights reserved.

The utility of organic selenium compounds for effecting a wide variety of synthetic transformations is now well-established;[1] therefore, the reductive cleavage reactions of C–Se bonds are of great importance in utilizing these as a last step always deal with the resulting organic selenides. Compared to the C–S bond reduction procedures, however, the C–Se bond reduction procedures are limited to several methods, which include Raney-nickel reduction, metal boride reduction, and radical reduction using tin hydrides.[2] Recently we have developed a novel photoinduced reduction system using samarium diiodide (SmI$_2$–$h\nu$),[3] the reducing ability of which is comparable to that of the SmI$_2$–HMPA system[4] in the reduction of organic halides. Herein we report a useful C–Se bond cleavage reaction by use of the SmI$_2$–$h\nu$ system.

The reduction of dodecyl phenyl chalcogenides with SmI$_2$ was examined upon irradiation with a tungsten lamp through filters and the results were compared with those conducted in the dark. As can be seen from eq 1, the SmI$_2$–$h\nu$ system is extremely effective for the reduction of selenides. While the reductive cleavage of C–Se bonds took place exclusively at the C(sp^3)–Se bond, the cleavage of C–Te bonds occurred at both C(sp^3)–Te and C(sp^2)–Te bonds. Unfortunately, the photoinduced reduction of sulfides with SmI$_2$ did not proceed at all under the conditions employed (40 °C). Since the starting selenides and tellurides exhibit no absorption in the regions of the wavelength over 400 nm and 500 nm, respectively, the C–Se bond and C–Te bond reduction may proceed *via* electron-transfer from the excited SmI$_2$ to the selenides and tellurides.[5] It was reported that the reduction of ^{n}C$_{12}$H$_{25}$SePh and ^{n}C$_{12}$H$_{25}$TePh with SmI$_2$–HMPA in refluxing THF for 20 h and 4.5 h afforded 6% and 63% of dodecane, respectively.[6] These results clearly indicate that the SmI$_2$–$h\nu$ system exhibits the higher reducing ability toward selenides, compared to the SmI$_2$–HMPA system.

$$\underset{0.5\ \text{mmol}}{{}^{n}\text{C}_{12}\text{H}_{25}\text{X}} \xrightarrow[\text{THF (20 mL), 40 °C}]{\text{SmI}_2\ \text{(4 mmol)},\ h\nu} \xrightarrow{\text{H}^+} {}^{n}\text{C}_{12}\text{H}_{26} \qquad (1)$$

X	$h\nu$, nm	Yield, %	
		$h\nu$	dark
SPh	>300	no reaction	—
SePh	>400	99	no reaction
TePh	>500	38	trace

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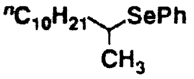
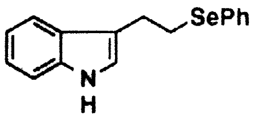
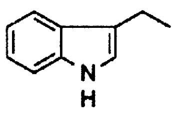
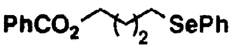
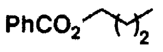
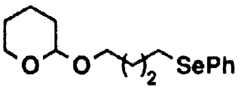
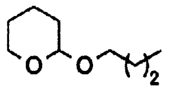
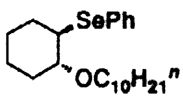
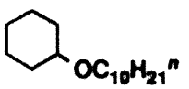
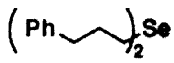
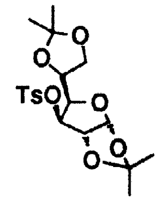
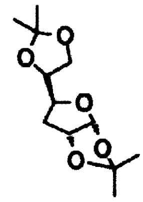
Representative results of the photoinduced reduction of selenides with SmI_2 are shown in Table 1. Secondary alkyl selenides such as *s*-dodecyl phenyl selenide and heterocyclic selenides such as 3-{2'-(phenylseleno)ethyl}indole underwent reductive deselenation smoothly (Runs 1-2). In these reactions, the PhSe-moiety could be recovered as $(PhSe)_2$ *via* the hydrolysis of $PhSeSmI_2$, followed by the air-oxidation during workups. In the case of *cis*-styryl undecyl selenide, the reduction also took place selectively at the C(sp^3)–Se bond (Run 3). Functionalities such as esters and ethers tolerate the reaction conditions (Run 4-6). With bis(3-phenylpropyl) selenide, both 3-phenylpropyl groups could be converted to propylbenzene quantitatively (Run 7). This reaction may proceed *via* the formation of $Ph(CH_2)_3SeSmI_2$ as a key intermediate.

The C–Se bond reduction procedure is also applicable to the reductive cleavage of the C–O bond of organic tosylates, as indicated in Runs 8-9. Although the reduction of dodecyl tosylate with SmI_2 in the dark afforded only 9% of dodecane,[7] the same reduction upon irradiation with visible light gave rise to 99% of dodecane. Similarly, a tosylated diacetone-D-glucose underwent the reductive cleavage of the C–OTs bond.

Table 1. Photoinduced Reduction of Selenides and Tosylates with SmI_2[a]

Run	Substrate	Yield, %	
1		$^nC_{12}H_{26}$	83
2			81
3		$^nC_{11}H_{24}$	79
4			68
5			84
6			84
7			97
8	$^nC_{12}H_{25}OTs$	$^nC_{12}H_{26}$	99
9			77

[a] Reaction conditions: substrate (0.25 mmol), SmI_2 (2 mmol), THF (10 mL), 67 °C, 10-16 h. Irradiation with a tungsten lamp (500 W) through Pyrex.

In summary, we have demonstrated the ability of the SmI_2–$h\nu$ system to serve as a useful reducing system for organic selenides and tosylates. We are further investigating applications of this methodology to different classes of substrates.

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