doi:10.1246/cl.2012.766

Iodide-promoted Deselenylation of *β*-Chloro- and *β*-Oxyselenides to Form Alkenes and Selenenyl Iodides

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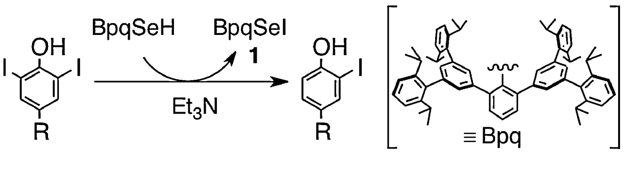
(Received March 21, 2012; CL-120241; E-mail: goto@chem.titech.ac.jp)

Deselenylation reaction of *β*-chloro- and *β*-oxyselenides proceeded efficiently by treatment with tetrabutylammonium iodide (TBAI) to afford alkenes in good yields. It was established that selenenyl iodides were formed in these reactions. Catalytic transformation of *β*-chloro- and *β*-oxyselenides to alkenes was also developed.

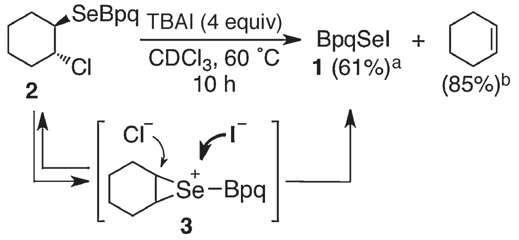
Organoselenium compounds constitute a useful and versatile class of reagents that has been widely utilized in organic syntheses.[1] Among a number of selenium-based synthetic methodologies developed to date, alkene formation involving release of organoselenium moieties provides an important tool for synthetic chemistry. *syn*-Elimination of selenoxides is the most common one, which proceeds under mild conditions to form a carbon–carbon double bond stereospecifically.[2] *β*-Oxyselenides serve as a potential alkene precursor,[3] which undergo *anti*-elimination upon treatment with acid,[3a] mesyl chloride in the presence of amine,[3b] and chlorotrimethylsilane–sodium iodide reagent.[3c] *β*-Chloro- and *β*-bromoselenides are also known to lead to alkenes by the reaction with selenolate nucleophile.[4]

In the course of our studies concerning biologically relevant organoselenium intermediates,[5] we have recently succeeded in the synthesis of a selenenyl iodide (RSeI) by taking advantage of a bowl-shaped substituent, a Bpq group (Scheme 1).[6] Although selenenyl iodides usually undergo facile disproportionation to form diselenides and iodine,[7] BpqSeI (**1**) was proved to have remarkable thermal stability. In a model study of a thyroid hormone-activating enzyme by utilizing selenenyl iodide **1**, it was suggested that selenium and iodine inherently have a high affinity, which plays a key role in the deiodination reaction of 2,6-diiodophenol derivatives by selenols.[6] It was envisioned that their affinity could also be applied to novel deselenylation reactions to produce alkenes. In this communication, we report an efficient deselenylative alkene formation from *β*-chloro- and *β*-oxyselenides promoted by an iodide ion, which can be performed with a catalytic amount of iodide source.

To test the hypothesis that the affinity between selenium and iodine would serve as a driving force for deselenylative alkene formation, we first examined the reaction of *β*-chloroselenide **2** bearing a Bpq group with an iodide source. Treatment of **2** with four equivalents of tetrabutylammonium iodide (TBAI) in $CDCl_3$ at 60 °C afforded cyclohexene in a good yield along with selenenyl iodide **1** (Scheme 2). It has been suggested that *β*-chloroselenides are in equilibrium with the corresponding seleniranium cation.[8] Attack of an iodide ion to the selenium atom of the seleniranium cation **3** is considered to result in the formation of **1** and cyclohexene, which predominates over the attack of a chloride ion to the carbon atom of **3** to produce the starting material **2**.



Scheme 1.

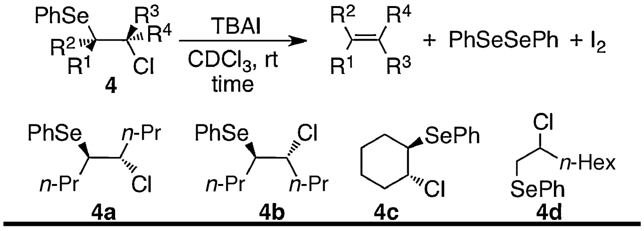


[a]Isolated yield. [b]Estimated by GC.

Scheme 2.

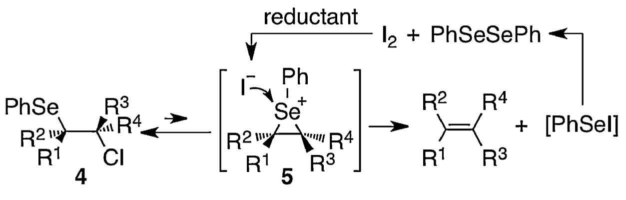
The generality of this deselenylative alkene formation was investigated by using *β*-chloroselenides **4a**–**4d** bearing a phenylseleno group (Table 1). Reaction of **4a** with 1.5 equivalents of TBAI in $CDCl_3$ at room temperature completed within 15 min to give stereospecifically *trans*-4-octene in 98% yield (Entry 1). Its stereoisomer **4b** yielded *cis*-4-octene in 93% yield upon treatment with 2.5 equivalents of TBAI for 1 h (Entry 2). In the case of **4c** and **4d**, deselenylation reaction proceeded somewhat slower, but the corresponding alkenes were obtained in good yields by increasing the amount of TBAI (Entries 3

Table 1. Deselenylation of *β*-chloroselenides **4a**–**4d** with TBAI

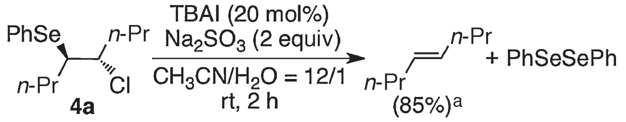


Entry	4	TBAI /equiv	Time	Product	Yield/%[a]
1	**4a**	1.5	15 min	*trans*-4-octene	98
2	**4b**	2.5	1 h	*cis*-4-octene	93
3	**4c**	5.0	10 h	cyclohexene	90
4	**4d**	6.0	20 h	1-octene	94

[a]Estimated by GC.



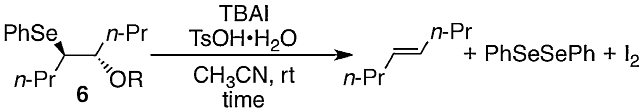
Scheme 3.



[a]Estimated by GC.

Scheme 4.

Table 2. Deselenylation of β-oxyselenides **6a**–**6c** with TBAI



6

a: R = OH
b: R = OMe
c: R = OAc

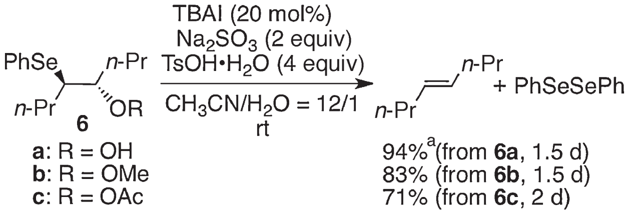
Entry	**6**	TBAI /equiv	$TsOH \cdot H_2O$ /equiv	Time	Yield/%[a]
1	**6a**	2.0	4.0	10 min	98
2	**6b**	2.0	4.0	10 min	98
3	**6c**	2.0	4.0	40 min	93
4	**6a**	2.0	—	24 h	n.d.[b]
5	**6a**	—	4.0	3 d	72

[a]All yields of *trans*-4-octene were estimated by GC. [b]Not detected.

and 4).[9] Besides the alkenes, diphenyl diselenide and iodine were formed in all cases, both of which are likely to be formed through disproportionation of phenylselenenyl iodide (PhSeI).

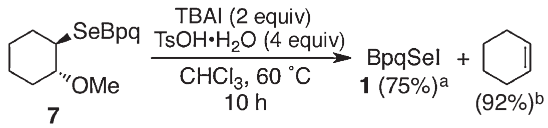
By taking advantage of the facile disproportionation of PhSeI, deselenylation reaction with a catalytic amount of iodide source was successfully developed. Since iodine can be easily reduced to iodide ions, iodine formed through disproportionation of PhSeI would be converted to iodide ions in the presence of appropriate reductant, which could react again with seleniranium cation **5** to establish a catalytic cycle (Scheme 3). Indeed, the reaction of **4a** with 20 mol % of TBAI and two equivalents of sodium sulfite at room temperature gave *trans*-4-octene in 85% yield after 2 h (Scheme 4). It is notable that this reaction can be performed under mild conditions free from iodine.

The iodide-promoted deselenylation reaction was applicable to β-oxyselenides **6a**–**6c** with various oxy functionalities. Reaction of **6a**–**6c** with two equivalents of TBAI in the presence of $TsOH \cdot H_2O$ at room temperature gave *trans*-4-octene along with diphenyl diselenide and iodine (Table 2, Entries 1–3). Although the reaction of **6c** took somewhat longer time, all the reactions proceeded almost quantitatively. Control experiments performed in the absence of either TBAI or $TsOH \cdot H_2O$ confirmed that the presence of both reagents is necessary for smooth formation of the alkene. No reaction was observed upon treatment of **6a** with two equivalents of TBAI (Entry 4). Reaction of **6a** with four equivalents of $TsOH \cdot H_2O$ proceeded sluggishly, affording *trans*-4-octene in 72% after 3 days (Entry 5).



[a]All yields were estimated by GC.

Scheme 5.



[a]Isolated yield. [b]Estimated by GC.

Scheme 6.

Catalytic deselenylation of β-oxyselenides **6a**–**6c** was also achieved to produce *trans*-4-octene in good to excellent yields, although longer reaction times were necessary for these catalytic reactions (Scheme 5).

A related alkene synthesis from β-oxyselenides by use of chlorotrimethylsilane–sodium iodide reagent has been reported by Clive et al.[3c] Although they suggested that HI, formed by adventitious hydrolysis, may play a role, the reaction mechanism was not elucidated. In the present study, the formation of a selenenyl iodide was established by the reaction of β-methoxyselenide **7** bearing a Bpq group with TBAI in the presence of $TsOH \cdot H_2O$ to produce selenenyl iodide **1** (Scheme 6). Deselenylation of β-oxyselenides is considered to proceed in a similar manner to that of β-chloroselenides, except that assistance of acid is necessary for efficient generation of the seleniranium cation intermediates from the former.

In summary, iodide has been found to promote deselenylation reaction of β-chloro- and β-oxyselenides to afford alkenes efficiently with formation of selenenyl iodides.[10] A catalytic version of the transformation has been also developed. Further studies on application of the high affinity between selenium and iodine to synthetic chemistry are currently in progress.

This work was partly supported by Grants-in-Aid for the Global COE Program for Education and Research Center for Emergence of New Molecular Chemistry and for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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9 When the reaction of **4d** with TBAI (Table 1, Entry 4) was monitored by ^{1}H NMR, the regioisomer of **4d** ($ClCH_2CH(SePh)$–*n*-Hex) was not observed during the course of the reaction.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.