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Intramolecular oxyselenenylation and deselenenylation reactions in water, conducted by employing polymer-supported arylselenenyl bromide

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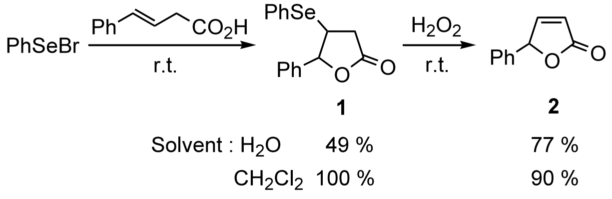
Abstract—After immobilizing arylselenenyl bromide on polymer resin, the oxyselenenylation reaction of olefin was carried out in water. An amphiphilic polymer-supported arylselenenyl bromide was employed, and various intramolecular oxyselenenylation and deselenenylation reactions proceeded smoothly in water in fair chemical yields (up to an 83% yield). © 2003 Elsevier Science Ltd. All rights reserved.

The use of organoselenium reagents in an organic synthesis is now commonly accepted as a powerful tool for introducing new functional groups into organic substrates.[1] Recently, several polymer-supported selenoreagents were prepared, and their applications to solid-phase organic synthesis and the combinatorial approach were then reported by us[2] and by other groups.[3]

Owing to today's environmental concerns about harmful and volatile organic solvents, the use of organic transformations in water is presently undergoing a very rapid growth.[4] However in selenium chemistry, most organoselenium reagents are insoluble or decomposed in water. For example, phenylselenenyl bromide, which is a representative electrophilic selenoreagent, is easily decomposed in water,[5] but only a few transformations employing selenoreagents in aqueous organic solvent have been reported.[6] We wish to report here the first example of the oxyselenenylation and the subsequent deselenenylation reactions in water, conducted by employing polymer-supported arylselenenyl bromide.

We first employed phenylselenenyl bromide, which was not immobilized, in order to examine the intramolecular oxyselenenylation (namely, selenolactonization) and the subsequent deselenenylation reactions in water according to Scheme 1. In this scheme, the selenolactonization reaction did not proceed smoothly in water, so that the yield of the corresponding selenolactone **1** (49% yield) was decreased significantly as compared with the yield obtained in dichloromethane (100% yield). In the case of carrying out in water, we also obtained diphenyl diselenide (36% yield), which was produced by the decomposition of phenylselenenyl bromide in water.[5b] On the other hand, the subsequent oxidative deselenenylation reaction proceeded smoothly in water to provide **2** in 77% yield, which was comparable to the yield obtained in dichloromethane (90% yield).

We then carried out this two-step transformation in water by employing polymer-supported arylselenenyl bromide as follows (Scheme 2). We stirred **3a**, which was prepared from aminomethyl-polystyrene resin[2a] (182 mg, 0.24 mmol) and (*E*)-styrylacetic acid (136 mg, 0.84 mmol) in water (3 ml) at room temperature for 15 h, and the corresponding polymer-supported selenolactone **4a** was then obtained. Subsequently, through the



Scheme 1.

Keywords: polymer-supported; selenium; solid-phase; oxyselenenylation; water.

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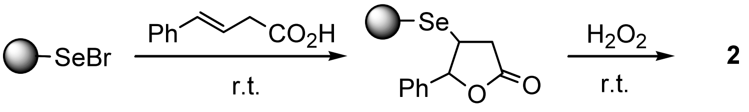
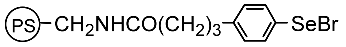
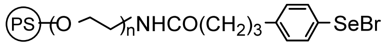


3a, 3b **4a, 4b**

Scheme 2.

Table 1. Selenolactonization and deselenenylation reactions of (*E*)-styrylacetic acid

Entry	●–SeBr		Total Yield of **2** /%[a] Solvent : H_2O	CH_2Cl_2
1	PhSeBr		38[b]	90[b]
2		**3a**[c]	59	46
3		**3b**[c]	62	44

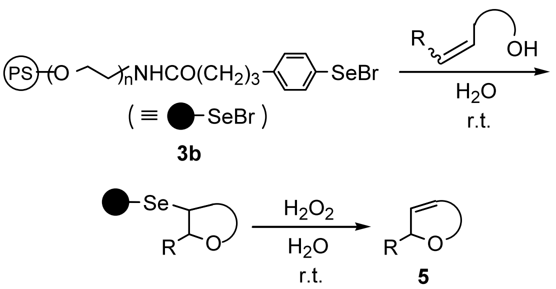
[a] Isolated yield.

[b] Total yield of selenolactonization and deselenenylation reactions shown in Scheme 1.

[c] PS: Polystyrene.

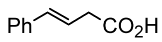
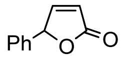
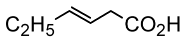
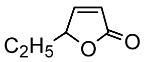
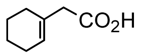
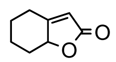
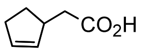
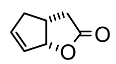
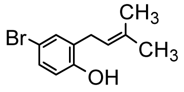
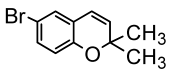
oxidation of **4a**, which was collected by filtration, with 30% hydrogen peroxide (0.11 ml, 1.0 mmol) in water (3 ml) at room temperature for 15 h followed by the usual workup and by purification, the deselenenylation product **2** (23 mg, 0.14 mmol) was obtained in a 59% yield (Table 1, entry 2), which was higher than the yield obtained by using phenylselenenyl bromide (entry 1). This is probably because the decomposition of the bromoselenenyl group in water is suppressed by immobilizing the selenogroup on the polymer-backbone due to its hydrophobicity. Especially in this case, the yield of **2** obtained in water exceeded the yield obtained in dichloromethane using **3a** (46% yield). Although we have no definitive explanation at the moment for high yield obtained in water, the hydrophobic cohesion of organic substrates in water could be responsible. This is the first example of oxyselenenylation and deselenenylation reactions performed in water. In this method, it should be noted that the selenocompound could be easily recovered entirely by filtration after the deselenenylation process.

Encouraged by these results, we then proceeded to use amphiphilic polymer-supported **3b**, which was prepared from poly(ethylene glycol)-polystyrene graft co-polymer resin (ArgoGel®-NH_2), similar to the preparation of **3a**.[2a] In this case, the corresponding selenolactonization and deselenenylation reaction proceeded more smoothly in water with rapid resin decolorization than those using **3a**, due to its amphiphilic property (62% yield; entry 3).



Scheme 3.

Table 2. Various intramolecular oxyselenenylation and deselenenylation reactions in water using **3b**

Entry	Olefin	**5**	Total Yield of **5** /%[a]
1			62
2			61
3			47
4			41
5			83

[a] Isolated yield.

By employing **3b**, we subsequently performed various intramolecular oxyselenenylation and deselenenylation reactions in water (Scheme 3, Table 2). Not only the selenolactonization and deselenenylation reactions, but also the intramolecular selenoetherification and deselenenylation reactions, proceeded smoothly in water to afford the corresponding deselenenylation products **5** in fair total yields (up to an 83% yield; entry 5). This method of realizing reactions in aqueous media by immobilizing reagents, which are decomposed in water, may be an effective approach to expanding the range of organic syntheses carried out in water.

We are currently trying to apply this method to other reactions, and to the catalytic version. The results will be reported in due course.

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