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# $S_{RN}1$ Reaction of Haloarenes with Benzenethiolate, Benzeneselenolate, and Benzenetellurolate Ions Promoted by $SmI_2$

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ABSTRACT: *$S_{RN}1$ reaction is of haloarenes with benzenethiolate, benzeneselenate, and benzenetellurolate ions can be carried out by use of samarium diiodide ($SmI_2$) as a promoter in DMF-THF to afford the corresponding ArZPh compounds in moderate to good yields.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:539–541, 2001

## INTRODUCTION

The aromatic radical nucleophilic substitution reaction ($S_{RN}1$) has been shown to be an excellent means for affecting the nucleophilic substitution of unactivated aromatic compounds possessing suitable leaving groups with many types of nucleophiles. The mechanism of the reaction is that of a chain process, and the propagation steps are shown in Scheme 1 [1].

Scheme 1 depicts a nucleophilic substitution in which radicals and radical anions are intermediates. However, this chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed [2]. When ET does not occur spontaneously, it can be induced by light [3], by solvated electrons [4], by cathodically generated electrons [5], or by certain inorganic salts [6].

Rossi [7] has reported the $S_{RN}1$ reactions of haloarenes with acetophenone enolate ions in DMSO by the use of $SmI_2$, because $SmI_2$ has been used as a one-electron reducing agent for many halides [8]. Herein, we wish to report that the $S_{RN}1$ reaction of some haloarenes with thiolate, selenate, and tellurate ions is promoted by $SmI_2$ (Scheme 2), and the results are summarized in Table 1.

## RESULTS AND DISCUSSION

$PhSe^-$ was prepared from diphenyl diselenide and two equivalents of $NaBH_4$. The dropwise addition of iodobenzene and a solution of $SmI_2$ in tetrahydrofuran (THF) to the solution, produced a 45% yield of the substitution product (diphenyl selenide) within 20 minutes (Table 1, entry1), whereas with a 1:0.5 ratio between substrate and $SmI_2$, the yield of substitution product was 42% (entry 2). When the nucleophilic reagent is the benzylselenolate anion, the ratio between substrate and $SmI_2$ is 1:1 and a 44% yield was obtained.

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Initiation Step:

$$ArX + e \longrightarrow (ArX)^{\overline{\cdot}} \qquad (1)$$

Propagation Step:

$$(ArX)^{\overline{\cdot}} \longrightarrow Ar^{\cdot} + X^{-} \qquad (2)$$

$$Ar^{\cdot} + Nu^{-} \longrightarrow (ArNu)^{\overline{\cdot}} \qquad (3)$$

$$(ArNu)^{\overline{\cdot}} + ArX \longrightarrow ArNu + (ArX)^{\overline{\cdot}} \qquad (4)$$

$$ArX + Nu^{-} \longrightarrow ArNu + X^{-}$$

**SCHEME 1**

$$ArX + PhZ^{-} \xrightarrow[THF-DMF]{SmI_2} ArZPh + X^{-}$$

**SCHEME 2**

With 2-bromopyridine and a 1:1 ratio (substrate to $SmI_2$), the corresponding product was obtained in 72% yield.

The reaction with 2-chloroquinoline as the substrate gave 51%, 66% and 50% yields (with $PhS^-$, $PhSe^-$, $PhTe^-$ as the nucleophilic reagent). The order of reactivities of the nucleophiles ($PhTe^- > PhSe^- > PhS^-$) increases as the nucleophiles become softer. Since aryl radicals are soft electrophiles, they react faster as the nucleophiles become softer.

The reaction of 1-bromonaphthalene with $SmI_2$ (with a substrate:$SmI_2$ ratio of 1:0.25) in 30 minutes gave the substitution product with a 62% yield (entry 11).

**TABLE 1** Reaction of Haloarenes (1 mmol) with Benzenethiolate, Benzeneselenolate and Benzenetellurolate Anions (1mmol) Stimulated by $SmI_2$

| *Entry* | *ArX*[a] | *PhZ*$^-$ | *SmI*$_2$ *(mmol)* | *Reaction Time (min)* | *ArZPh*[b] *(%)* |
|---|---|---|---|---|---|
| 1 | PhI | $PhSe^-$ | 1.0 | 20 | 45 |
| 2 | PhI | $PhSe^-$ | 0.5 | 20 | 42 |
| 3 | PhI | $PhCH_2Se^-$ | 1.0 | 20 | 44 |
| 4 | 2-BrPyr | $PhSe^-$ | 1.0 | 30 | 72 |
| 5 | 2-ClQuin | $PhS^-$ | 0.5 | 30 | 51 |
| 6 | 2-ClQuin | $PhSe^-$ | 0.5 | 30 | 66 |
| 7 | 2-ClQuin | $PhTe^-$ | 0.5 | 15 | 50 |
| 8 | 1-BrNaph | $PhS^-$ | 1.0 | 30 | 43 |
| 9 | 1-BrNaph | $PhSe^-$ | 1.0 | 30 | 67 |
| 10 | 1-BrNaph | $PhSe^-$ | 0.5 | 30 | 72 |
| 11 | 1-BrNaph | $PhSe^-$ | 0.25 | 30 | 62 |
| 12 | 1-BrNaph | $PhTe^-$ | 1.0 | 15 | 75 |
| 13 | 1-BrAdam | $PhS^-$ | 1.5 | 30 | 38 |
| 14 | 1-BrAdam | $PhSe^-$ | 1.5 | 30 | 62 |
| 15 | 1-BrAdam | $PhTe^-$ | 1.5 | 30 | 52 |

[a] PhI, iodobenzene; 2-BrPyr, 2-bromopyridine; 2-ClQuin, 2-chloroquinoline; 1-BrNaph, 1-bromonaphthalene; 1-BrAdam, 1-bromoadamantane.

[b] Isolated yield.

Even when the substrate was 1-bromoadamantane, the reaction still occurred but in relatively low yield (entries 13–15).

The actual mechanism of the reaction has not been clarified yet, but, according to the fact that the yield of substitution product obtained (62%) in the presence of a stoichiometric amount of $SmI_2$ (entry 11), the result may be an indication of a chain process.

## *EXPERIMENTAL*

Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use. Dimethylformamide (DMF) was distilled under reduced pressure. $^1$H NMR spectra were recorded with a Bruker AC-80 spectrometer, using tetramethylsilane (TMS) as an internal standard. IR spectra were determined on PE-683 spectrometer. Aryl halides were commercially available and were purified before use. Diselenides were prepared according to the literature [9].

### *Typical Procedure*

The reactions were carried out in a 50 mL three-neck round-bottomed flask equipped with a nitrogen inlet tube and a magnetic stirrer. To 12 mL of dry and degassed DMF under nitrogen was added 1.0 mmol of $NaBH_4$ and 0.5 mmol of PhSeSePh. After the solution had been warmed for 2 hours at 70°C, 1.0 mmol PhI was added (in 2 mL THF), and then 1 mmol of $SmI_2$ solution (20 mL THF) was dropped to this mixture by use of a syringe. After 20 minutes, the reaction was quenched by addition of ammonium nitrate in excess and 20 mL of water, and the mixture was extracted with ether. The ether extract was washed twice with water and dried. The solvents were removed under reduced pressure. The residue was purified by preparative TLC on silica gel (cyclohexane as eluent).

## *DATA OF PRODUCTS*

**1:** *Diphenyl selenide* oil [10]; $\upsilon_{max}/cm^{-1}$ 3100, 3080, 3040, 2960, 1600, 1500, 1480, 1460, 1380, 1185, 1020, 1000, 910, 690; $\delta_H \sim 6.95$–7.56 (m, ArH).

**2:** *Phenyl benzyl selenide* oil [11]; $\upsilon_{max}/cm^{-1}$ 3105, 3080, 3040, 2950, 1590, 1500, 1485, 1460, 1390, 1180, 1020, 1000, 910, 760, 690; $\delta_H$ 3.80 (s,2H), 7.00–7.50 (m,10H).

**3:** *2-Phenylselenopyridine* oil [12]; $\upsilon_{max}/cm^{-1}$ 3080, 3020, 1600, 1460, 1440, 1030, 980, 750, 690; $\delta_H$ 7.20–8.70 (m, ArH).

**4:** *2-Phenylthioquinoline*, m.p. 52–54°C (lit. [12] 55–56°C); $\upsilon_{max}/cm^{-1}$ 3030, 3010, 1620, 1590, 1570, 1500, 1420, 1380, 1310, 1120, 1030, 960, 800, 690; $\delta_{\mathrm{H}}$ 7.26–8.50 (m, ArH).

**5:** *5-Phenylselenoquinoline* oil [12]; $\upsilon_{\max}$/cm$^{-1}$ 3030, 1620, 1590, 1570, 1500, 1420, 1380, 1310, 1120, 1030, 960, 800, 760, 690; $\delta_{\mathrm{H}} \sim 7.20$–8.35 (m, ArH).

**6:** *2-Phenyltelluroquinoline*, m.p. 42–45°C (lit. [12] 46–48°C); $\upsilon_{\max}$/cm$^{-1}$ 3030, 3010, 2980, 1620, 1590, 1570, 1500, 1410, 1380, 1310, 1030, 960, 810, 760, 690; $\delta_{\mathrm{H}} \sim 7.30$–8.40(m, ArH).

**7:** *1-Phenylthionaphthalene* oil [13]; $\upsilon_{\max}$/cm$^{-1}$ 3030, 1580, 1500, 1480, 1440, 1380, 1020, 970, 800, 770, 740, 690; $\delta_{\mathrm{H}} \sim 7.70$–8.90 (m, ArH).

**8:** *1-Phenylselenonaphthalene*, m.p. 50°C (lit. [14] 52–53°C); $\upsilon_{\max}$/cm$^{-1}$ 3030, 1580, 1500, 1480, 1440, 1380, 1010, 970, 770, 710, 690; $\delta_{\mathrm{H}} \wedge 7.00$–8.30 (m, ArH).

**9:** *Phenyltelluronaphthalene*, oil [15]; $\upsilon_{\max}$/cm$^{-1}$ 3030, 1600, 1480, 1440, 1380, 1010, 970, 770, 710, 690; $\delta_{\mathrm{H}} \sim 7.00$–8.35 (m, ArH).

**10:** *1-Phenylthioadamantane*, m.p. 68–71°C (lit. [16] 71.5-72°C); $\upsilon_{\max}$/cm$^{-1}$ 3060, 3040, 2950, 1590, 1580, 1500, 1450, 1380, 1350, 1270, 1220, 960, 690; $\delta_{\mathrm{H}} \sim 1.65$–2.40 (m, 15H), 7.08–7.85 (m, 5H).

**11:** *1-Phenylselenoadamantane*, low melting crystal m.p.(lit. [17] 35°C); $\upsilon_{\max}$/cm$^{-1}$ 3040, 2940, 1600, 1580, 1500, 1450, 1380, 1340, 1270, 950, 690; $\delta_{\mathrm{H}} \sim$ 1.60–2.22 (m, 15H), 7.10–7.95 (m, 5H).

**12:** *1-Phenyltelluroadamantane*, m.p. 110–112°C (lit. [17] 113–115°C); $\upsilon_{\max}$/cm$^{-1}$ 3040, 2945, 1590, 1500, 1450, 1380, 1340, 1280, 960, 690; $\delta_{\mathrm{H}} \wedge 1.65$–2.25 (m, 15H), $\sim$7.06–7.75 (m, 5H).

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