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# Synthesis of arylselenide ethers by photoinduced reactions of selenobenzamide, selenourea and selenocyanate anions with aryl halides

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ABSTRACT

Selenobenzamide ($^{-}$SeCNH(Ph), **1**), selenourea ($^{-}$SeCNH($NH_2$), **2**) and selenocyanate ($^{-}$SeCN, **3**) anions afford areneselenolate ions ($ArSe^{-}$) under photostimulation in the presence of *tert*-butoxide or 2-naphthoxide ions as electron donors (entrainment conditions) in DMSO. In a 'one-pot' procedure, $ArSe^{-}$ anions can be trapped by a subsequent aliphatic nucleophilic substitution giving aryl methyl selenides in good to excellent yields (67–100%). This simple approach is compatible with electron-donating and electron-withdrawing substituents, such as nitro and carbonyl groups.



## 1. Introduction

Organoselenium compounds have attracted considerable attention not only because of their versatility in organic synthetic procedures[1] but also as a result of their unique biological and medicinal activities, especially in cancer chemoprevention and as an antiviral or antioxidant in food and plants.[2,3]

Two main reactions are possible for the synthesis of organoselenides. One involves the use of electrophilic arylselenium halides with carbon and milder nucleophiles like aryl boronic acids, aryl siloxanes and aryl stannanes.[4] The most common procedure employs organoselenium anions in nucleophilic addition to alkyl or aryl halides. Due to their sensitivity to air oxidation, these powerful nucleophiles are usually prepared in situ from diaryl diselenides by reaction with reducing agents such as $NaBH_4$,[5] alkali metals,[6] or the expensive La, In, Yb, Sm and Zn in ionic liquid,[7,8] from deprotonation of arylselenols[9] and from insertion of elemental selenium into lithium or Grignard reagents.[10] This last methodology is widely used for the synthesis of organoselenium compounds. However, it is not compatible with functional groups susceptible to reduction, such as $NO_2$ or carbonyl groups. For aryl halides bearing a ketone or aldehyde group their ketal derivatization is required; then, their protecting groups must be removed after the Grignard reaction.[11]

Another approach for introducing a selenium atom into an aryl ring involves the diazotization of aromatic amines followed by reaction with KSeCN. The selenocyanate derivatives can be converted to selenols by reduction with $NaBH_4$ or hydrolysis in basic media.[12] Selenourea can also be used instead of KSeCN; however, the yields are modest.[13] There are few examples of the formation of ArSeCN including the reaction of hydrocarbons with $^{-}$SeCN in the presence of an oxidant such as bromide or CAN; for these electrophilic substitutions, a strong activation of the aromatic ring is required.[14] $Se^{2-}$ ion generated by the reduction of grey selenium with metallic sodium in liquid ammonia (−33 °C) or hydrazine in DMF (120 °C) is a powerful nucleophile towards aryl and hetero aryl halides, affording good yields of ArSeH or $Ar_2Se_2$.[15] Since we have successfully developed a procedure for the formation of arenethiolate anions involving the photoinduced reaction between thiourea and thioacetate ions with aryl halides,[16] we have considered extending this methodology to the selenium analogues. We herein report our results on the synthesis of arylselenide compounds by photoinduced reaction of selenium containing anions, such as selenobenzamide (**1**) selenourea (**2**) and selenocyanate (**3**) with aryl halides. Selenobenzamide was prepared by the addition of in situ generated $H_2Se$ to benzonitrile.[17] These anions can be generated by acid–base reaction in DMSO as solvent and would yield arene selenolate anions in the presence of aryl halides under mild conditions. These anions would render substitution products under photostimulation by the $S_{RN}1$ mechanism, which is a chain process, involving radicals and radical anions as intermediates. In these reactions, a compound bearing an adequate leaving group is substituted by a nucleophile. A wide variety of nucleophiles can be used, making the $S_{RN}1$ reaction a powerful synthetic tool.[18]

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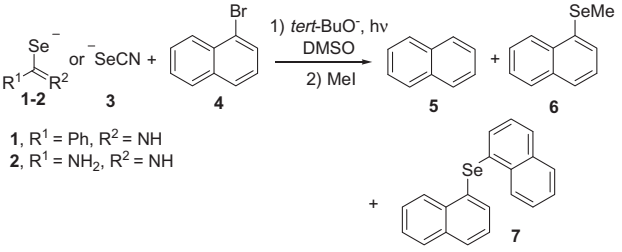
## 2. Results and discussion

### 2.1. Reaction of selenide anions 1–3 with 1-bromonaphthalene (4) in DMSO

We initiated our study with selenobenzamide anion (**1**) and 1-bromonaphthalene (**4**) as a model substrate.[19] Although anion **1** was unreactive towards **4** after 3 h of irradiation, the presence of 2.5 equiv of potassium *tert*-butoxide (*tert*-BuOK) triggered the reaction giving a mixture of naphthalene (**5**, 25%), methyl-1-naphthyl selenide (**6**, 54%) and bis(1-naphthyl) selenide (**7**, 17%), after quenching with MeI (Eq. 1). In this reaction *tert*-$BuO^-$ ion acted as an electron donor in the photoinduced electron transfer reaction (PET) (entrainment reactive). Similar results were found for the sulfur analogues thioacetate and thiobenzoate anions.[16d] The use of 2-naphthoxide ion as an electron donor improved the formation of aryl methyl selenide **6** up to 66% yield (Table 1, entries 1–3).




(1)

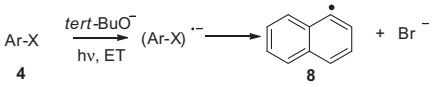
There was no reaction in the dark after 3 h and the photoinduced reaction was inhibited by the presence of the well-known radical trap 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Table 1, entries 4 and 5). In order to evaluate the nature of the PET reaction, electron acceptors better and worse than bromide **4**, 1-iodo and 1-chloronaphthalene respectively, were tested. As expected for an ET process, the iodo derivative was more reactive than **4** with a 100% of conversion while chloronaphthalene was the least reactive, with only a 46% consumption of the substrate. These results are in agreement with a photoinduced electron transfer reaction (Table 1, entries 6 and 7).

The lack of reaction between anion **1** and **4** under irradiation, the entrainment reaction in the presence of *tert*-$BuO^-$ or 2-naphthoxide ions under light catalysis, the inhibition by a radical trap, the reactivity order iodo > bromo > chloronaphthalene and the presence of a variable amount of naphthalene suggest a radical chain substitution mechanism ($S_{RN}1$) for the reaction between anion **1** and 1-naphthyl halides. This process involves an electron transfer from *tert*-BuOK to naphthyl halide as the initiation step, affording the corresponding radical anion. Subsequent fragmentation of the radical anion thus formed affords 1-naphthyl radical (**8**) and halide ions (Eq. 2). Coupling of radical **8** with anion **1** yields a new radical anion **9** (Eq. 3), which after fragmentation gives 1-naphthalene selenolate ion (**10**) (Eq. 4). Further reaction of selenide anion **10** with 1-naphthyl radical followed by electron transfer to **4** finally yields the disubstitution product bis(1-naphthyl) selenide (**7**) (Eq. 5). Hydrogen atom abstraction from the solvent by 1-naphthyl radicals gives the reduction product naphthalene (**5**) (Eq. 6). After irradiation, the reaction mixture is quenched by MeI to afford methyl-1-naphthyl selenide (**6**) (Eq. 7).

Assuming that the global efficiency of an $S_{RN}1$ process is the product of the initiation and the propagation efficiencies,[20] and considering that 20 mol % of TEMPO inhibited the reaction by just 30%, the low inhibiting effect of this radical trap can be attributed to a low initiation by *tert*-butoxide ion, or a low or even non-existent chain reaction.

Displaying a similar behaviour to anion **1**, selenourea anion (**2**) was not reactive towards **4** under irradiation; however, in the presence of *tert*-$BuO^-$ or 2-naphthoxide ions, it afforded products **5** and **6**. 2-Naphthoxide ion showed a better performance compared to *tert*-$BuO^-$ ion, improving the conversion and yield of selenide **6**, formed in 67% and 24% yield respectively (Table 1, entries 8–10).

The reactivity of thiourea anion with 1-bromonaphthalene was previously studied. This anion is able to initiate and maintain the catalytic cycle of an $S_{RN}1$ reaction, completed in 15 min with 91% of conversion.[16a] By contrast, entrainment was necessary for the reaction with selenourea anion (**2**), even when the yield of selenide **6** is comparable to its sulfide analogue, the overall process is slower, needing up to 3 h for a complete conversion. It was also reported that the thiocyanate anion is unreactive both in the initiation step as an electron donor and in addition to 1-naphthyl radicals generated by a photostimulated entrainment reaction with *tert*-BuOK.[16b] However, its selenium analogue, $^-SeCN$ (**3**), in the presence of **4** and *tert*-BuOK yielded a mixture of naphthalene (5%), methyl-1-naphthyl selenide (61%) and bis(1-naphthyl) selenide (27%) after 3 h of irradiation. This reaction did not occur in the absence of *tert*-BuOK (Table 1, entries 11 and 12).

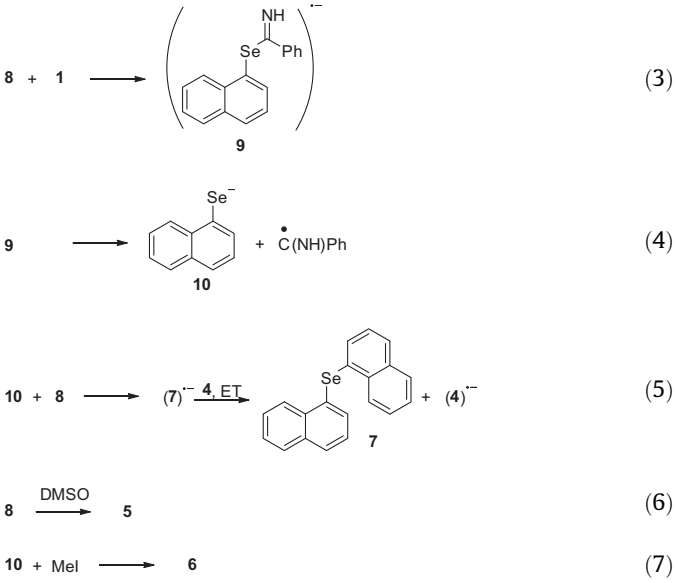



(2)

**Table 1**
Reactions of selenium nucleophiles **1–3** with 1-halonaphthalene in DMSO[a]

| Entry | RSe⁻ | ArX, condition, additive | Product yield[b] (%) | | | |
|---|---|---|---|---|---|---|
| | | | Convn | ArH (**5**) | ArSeMe (**6**) | ArSeAr (**7**) |
| 1 | **1** | 1-$BrC_{10}H_7$, hν | — | — | — | — |
| 2 | **1** | 1-$BrC_{10}H_7$, hν, *tert*-BuOK (2.5 equiv) | 96 | 25 | 54 | 17 |
| 3 | **1** | 1-$BrC_{10}H_7$, hν, 2-naphthoxide (2.5 equiv) | 100 | 21 | 66 | 9 |
| 4 | **1** | 1-$BrC_{10}H_7$, dark, *tert*-BuOK (2.5 equiv) | — | — | — | — |
| 5 | **1** | 1-$BrC_{10}H_7$, hν, *tert*-BuOK (2.5 equiv), TEMPO (0.2 equiv) | 67 | 11 | 49 | 7 |
| 6 | **1** | 1-$IC_{10}H_7$, hν, *tert*-BuOK (2.5 equiv) | 100 | 47 | 53 | — |
| 7 | **1** | 1-$ClC_{10}H_7$, hν, *tert*-BuOK (2.5 equiv) | 46 | 15 | 31 | — |
| 8 | **2** | 1-$BrC_{10}H_7$, hν | — | — | — | — |
| 9 | **2** | 1-$BrC_{10}H_7$, hν, *tert*-BuOK (1.5 equiv) | 46 | 15 | 24 | — |
| 10 | **2** | 1-$BrC_{10}H_7$, hν, 2-naphthoxide (2.5 equiv) | 100 | 31 | 67 | — |
| 11 | **3** | 1-$BrC_{10}H_7$, hν | — | — | — | — |
| 12 | **3** | 1-$BrC_{10}H_7$, hν, *tert*-BuOK (5 equiv) | 91 | 4 | 61 | 27 |

[a] 1-$XC_{10}H_7$: 0.05 M, selenium-centred nucleophiles ($RSe^-$): 0.25 M, under $N_2$ atmosphere, irradiation time: 3 h with a high-pressure Hg lamp. The reactions were quenched by the addition of MeI.
[B] Determined by GC using $(PhSe)_2$ as internal standard, error 5%. The conversion (convn) was determined by quantification of the recovered substrate.



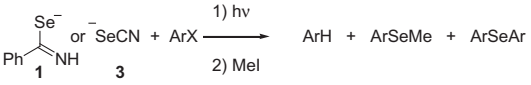

## 2.2. Synthesis of aryl methyl selenides by the photoinduced reactions of selenide anions 1 and 3 with aryl halides in DMSO

The observed reactivity of selenobenzamide anion towards 1-bromonaphthalene under irradiation encouraged us to further explore the potential of this anion in the synthesis of selenide compounds. The selenourea anion was not considered due to its low reactivity, high cost, low stability and its air sensitive nature. Quite a few examples of the use of $^{-}$SeCN were also included because of its air-stable and commercially available potassium salt. Table 2 summarizes the results obtained in the photoinduced reactions of **1** and **3** with a variety of aryl halides.

From Table 2, it is possible to conclude that this methodology is appropriate for substrates bearing electron-donating and electron-withdrawing groups. In these cases, the arene selenide ions obtained by the $S_{RN}1$ reaction were quenched by MeI to afford aryl methyl selenide (ArSeMe) derivatives in good to excellent yields (66–100%). Diaryl selenide (ArSeAr) was formed as a side product and in most cases the ratio $Ar_2Se$/ArSeMe was higher for anion **3**. This finding can be ascribed to a higher reactivity towards aryl radicals of the arene selenide ion ($ArSe^{-}$) formed during the course of the reaction, compared to $^{-}$SeCN. When halo ketones were used as substrates, anion **3** was not reactive and the mass balance was poor (results not shown). However, anion **1** gave very good to excellent yields of the corresponding ArSeMe products. This latter result is better than those provided by the Grignard methodology, which needs protection of the carbonyl moiety. Furthermore, our procedure was also successful with aryl halides bearing a nitro group; not requiring the expensive or non-commercially available amines shows another advantage of the present methodology. Finally, our results are comparable with those obtained with $Na_2Se$ as nucleophile; however, this anion must be formed in situ by the reduction of metallic selenium in liquid ammonia as solvent (−33 °C).[15a]

In conclusion, we have developed a new approach to the preparation of $ArSe^{-}$ anions in DMSO by photoinduced reaction of the acid–base generated anions **1** and **3** with a variety of aryl halides and in the presence of *tert*-BuOK as an entrainment reagent. Subsequent substitution with MeI affords ArSeMe derivatives from good to excellent yields. This simple methodology is compatible with both electron-donating and electron-withdrawing groups, including nitro and carbonyl groups.

**Table 2**
Reactions of selenium nucleophiles **1** and **3** with aryl halides (ArX) in DMSO[a]




| Entry | $RSe^{-}$ | ArX | Products yield[b] (%) | | | |
|---|---|---|---|---|---|---|
| | | | Convn | ArH | ArSeMe | ArSeAr |
| 1 | **1** | 1-$IC_{10}H_7$ | 100 | 47 | 53 | — |
| 2[c] | **3** | 1-$IC_{10}H_7$ | 100 | 7 | 67 | 27 |
| 3 | **1** | PhI | 100 | — | 100 | — |
| 4 | **1** | *p*-$MeOC_6H_4I$ | 100 | — | 99 | — |
| 5[c] | **3** | *p*-$MeOC_6H_4I$ | 97 | 11 | 66 | 21 |
| 6 | **1** | *o*-$MeC_6H_4I$ | 100 | — | 100 | — |
| 7[c] | **3** | *o*-$MeC_6H_4I$ | 65 | — | 55 | 10 |
| 8[d] | **1** | *p*-$BrC_6H_4COMe$ | 100 | 2 | 98 | — |
| 9[d] | **1** | *p*-$BrC_6H_4COPh$ | 96 | 2 | 93[e] | — |
| 10 | **1** | *p*-$NO_2C_6H_4I$ | 100 | — | 20 | — |
| 11[c] | **3** | *p*-$NO_2C_6H_4I$ | 100 | — | 75 | — |

[a] ArX: 0.05 M, selenium-centred nucleophiles ($RSe^{-}$): 0.25 M in the presence of 0.125 M of *tert*-BuOK unless otherwise indicated, under $N_2$ atmosphere, irradiation time: 3 h with high-pressure Hg lamp. The reactions were quenched by the addition of MeI.

[b] Determined by GC using $(PhSe)_2$ as internal standard, error 5%. The conversion (convn) was determined by quantification of the recovered substrate.

[c] 0.25 M of *tert*-BuOK.

[d] ArX: 0.1 M, **1**: 0.125 M.

[e] Reference 21.

## Acknowledgements

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.11.115.

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19. *Representative experimental procedure*: The photochemical reaction was carried out in a three-necked, 10 mL Schlenk tube equipped with a nitrogen gas inlet and a magnetic stirrer. The flask was dried under vacuum, filled with nitrogen and then charged with 10 mL of dried DMSO. 3.75 mmol of *tert*-BuOK for selenobenzamide (3.25 mmol for anion selenourea and 2.5 mmol for KSeCN) was added to the degassed DMSO under nitrogen, then 2.5 mmol of the nucleophile **1**–**3** and 0.5 mmol of ArX were added to the reaction mixture. After 3 h of irradiation with a high-pressure Hg lamp, the reaction was quenched by the addition of MeI (6 equiv) in excess and 30 mL of water, and the mixture was then extracted with dichloromethane (3 × 20 mL). The organic extract was washed twice with water, dried and the products were quantified by GC with diphenyl diselenide as internal standard. The identity of all the products was confirmed by $^{1}H$ and $^{13}C$ NMR and MS spectrometry. All the aryl methyl selenides are known, otherwise indicated, and their data are in agreement with those reported.
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21. *4-Benzoylphenyl methyl selenide*: isolated by radial chromatography technique with petroleum ether/ethyl ether (95:5) as eluent from the crude product reaction mixture of selenourea anion and *p*-bromobenzophenone in the presence of 0.125 M *tert*-BuOK. White solid Mp 76–77 °C. $^{1}H$ NMR (400.16 MHz, $CDCl_3$): $\delta$ 2.42 (s, 3H); 7.46 (d, 2H, $J$ = 8.0 Hz); 7.48 (d, 2H, $J$ = 8.0 Hz); 7.58 (t, 1H, $J$ = 7.2 Hz); 7.70 (d, 2H, $J$ = 8.8 Hz); 7.78 (d, 2H, $J$ = 6.8 Hz). $^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta$ 6.5; 128.3; 128.6; 129.9; 130.6; 132.3; 134.8; 137.7; 139.4; 196.0. $_{77}Se$ NMR (76.32 MHz, $CDCl_3$): 216.41.MS: (EI, $m/z$) 278 (15); 276 (M+, 79); 274 (46); 201 (18); 199 (94); 197 (52); 105 (100); 77 (97). HRMS (EI) calcd for $C_{13}H_9SeO$ $[M]^+$: 276.0053; found: 276.0049.