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Sparing the Ortho-position in Nucleophilic Aromatic Substitution-Specific Displacement of the 4-SePh Group in 2,4-Bis(phenylseleno)nitrobenzene

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ABSTRACT: *Upon treatment of o- and p-(phenylseleno)nitrobenzenes with sodium methoxide quantitative exchange reactions took place, affording the corresponding methoxynitrobenzenes. Upon reaction between 2,4-bis(phenylseleno)nitrobenzene* **2** *and sodium methoxide, an unusual regiopure formation of 4-methoxy-2-(phenylseleno)nitrobenzene* **3** *was observed. This product remained unreactive toward an excess of sodium methoxide, thus preventing the formation of 2,4-dimethoxynitrobenzene* **6**. *The nature of the reactants and of the intermediate Meisenheimer complexes was examined by synthetic investigations, x-ray crystallography, and DFT calculations. We found that the observed selectivity can be understood in terms of traditional resonance considerations.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:101–108, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20519

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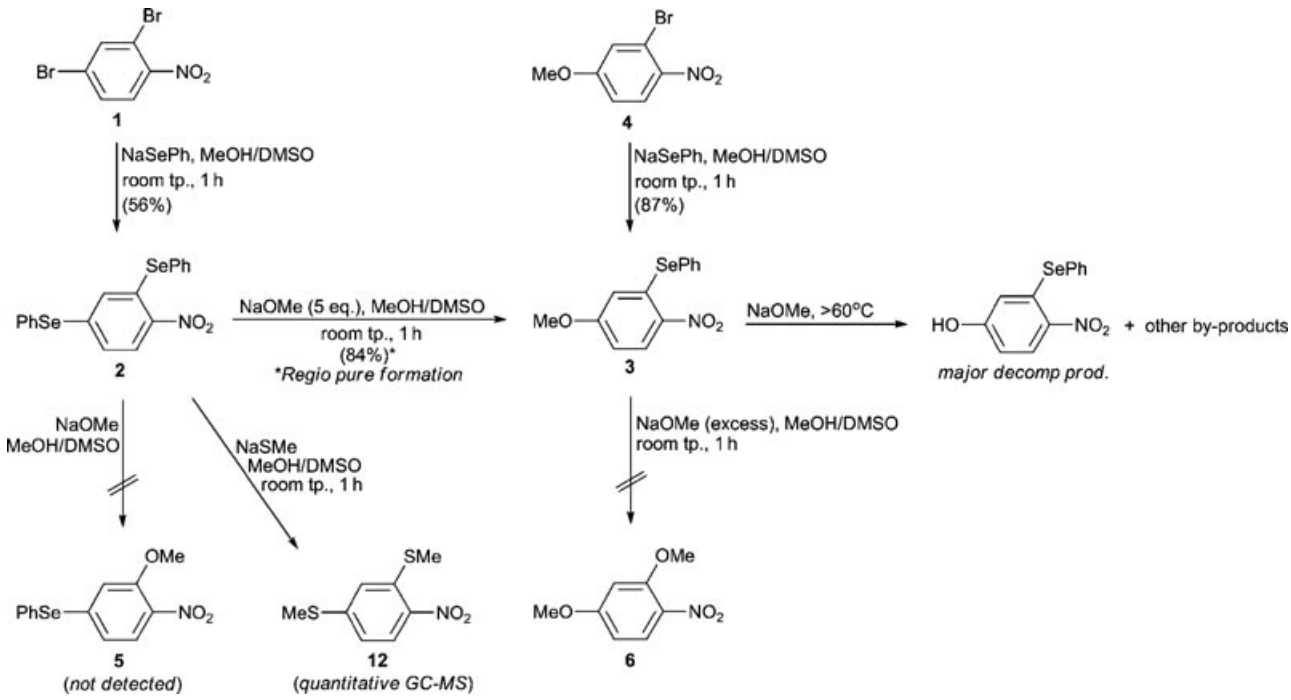
INTRODUCTION

The phenylselenide ion has been intensively used as a tool in organic synthesis [1] since it is a powerful nucleophilic species sufficiently reactive to effect nucleophilic aromatic substitution [2], a central route to selenium containing materials. Recently, in a study of the reactivity of halonitrobenzenes toward the phenylselenyl anion, sodium phenylselenide was prepared by rapid and precise reduction of diphenyl diselenide with hydrazine-sodium methoxide [3]. By addition of an excess of sodium methoxide to the reaction mixture, a regiopure product, 4-methoxy-2-(phenylseleno)nitrobenzene **3**, formed and remained stable even in the presence of a large excess of sodium methoxide. The present paper addresses the mechanistic reasons for the selectivity of the reaction.



SCHEME 1

RESULTS AND DISCUSSION

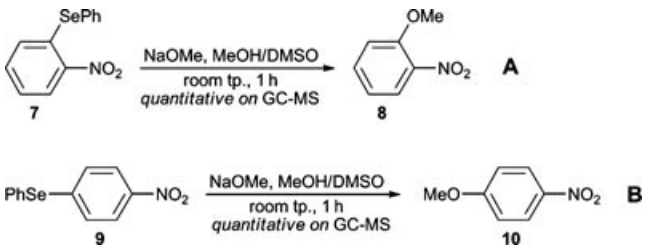
Regiospecific Isolation of 4-Methoxy-2-(phenylseleno)nitrobenzene

Not surprisingly, 2,4-dibromonitrobenzene **1** smoothly reacted at room temperature affording 2,4-bis(phenylseleno)nitrobenzene **2** without detectable by-products (Scheme 1). The yield was only limited by losses during work-up. However, the reaction between 2,4-bis(phenylseleno)nitrobenzene and 1 equivalent of methoxide substitution occurred only on the 4-position. 4-Methoxy-2-(phenylseleno) nitrobenzene **3** was formed in a completely regiopure fashion without sign of the other possible isomer 2-methoxy-4-(phenylseleno)nitrobenzene **5**. Even upon addition of a large excess (2.5–10 equivalents) of methoxide, there was no sign of the double-substituted product 2,4-dimethoxynitrobenzene **6**. The substitution pattern of **3** was confirmed since an unequivocal synthesis from 2-bromo-4-methoxynitrobenzene **5** and sodium phenylselenide yielded an identical product.

It was clear that the methoxide anion specifically attacked the phenylselenyl group para to the nitro group, and furthermore was unable to replace a second PhSe group after introduction of the first MeO-group. At elevated temperatures, it was possible to observe two entering methoxy groups, but under these circumstances decomposition reactions such as demethylations were observed in GC-MS.

Investigations of the Reactivity of (Phenylseleno)nitrobenzenes Toward Methoxide Attack

To obtain more information about the nature of the regiospecific exchange of the phenylselenyl group para to the nitro group, we made individual comparisons between the reactivities of phenylselenyl groups ortho and para to nitro groups by reacting 2-(phenylseleno)nitrobenzene **7** and 4-(phenylseleno)nitrobenzene **9**, respectively, with sodium methoxide. In both cases, a fast exchange and quantitative reaction occurred leading to 2-methoxynitrobenzene **8** (Scheme 2, **A**)



SCHEME 2

and 4-methoxynitrobenzene **10** (Scheme 2, **B**), respectively. These results show that it is the presence of a PhSe group that renders the PhSe group in the 2-position of **3** inert. The nitro-group might direct the initial attack, but it is not responsible for the inertness of the 2-PhSe group.

Crystal Structures of Ortho-Phenylselenylated Nitrobenzenes

Unfortunately, crystals of **3** could not be prepared in a quality suited for single crystal X-ray diffraction. However, high-quality crystals of similar ortho phenylselenylated nitrobenzenes of **7** and 1,3-dinitro-4,6-bis(phenylseleno)benzene **11** (prepared using standard conditions from 1,3-dibromo-4,6-dinitrobenzene) suitable for X-ray structure determination were prepared, and their crystal structures were determined. The structures (Fig. 1) will be compared with related compounds found in the literature to provide additional information about the exact geometries of the reaction centers during the observed phenylselenyl exchange reactions.

A strong through-space interaction between the O-atom of the nitro group and the Se-atom of an *ortho*-arylseleno substituent was evidenced by crystal structures of **7** and **11** as shown in Fig. 1. The nonbonded Se···O distance is 2.6517(13) Å in **7** and only slightly longer in **11** (2.6780(17) and 2.6732(18) Å). This is significantly shorter than the sum of van der Waals radii (3.42 Å). A search of the Cambridge Structural Database [4] (version 5.29, November 2007) shows that this trend is common for all types of *ortho*-selenenyl substituted nitrobenzenes [5]. (The lengths of the Se···O interactions in nine reported similar structures are in the region 2.3–2.7 Å.). The consequence of this unusually strong interaction between a selenium atom and an ortho nitro group on a benzene ring reveals itself in the unique stabilization of *o*-nitrobenzeneselenenic acid [6], which is the only stable selenenic acid reported. This ortho stabilization of the PhSe group might be one of the keys to the exclusive attack on the 4-position of 2,4-bis(phenylseleno)nitrobenzene.

*Comparison of the X-ray Crystal Structure and the Calculated Geometry of o-PhSe-$C_6H_4NO_2$ (**7**)*

A strong interaction between the oxygen of the nitro group and the selenium in the ortho position

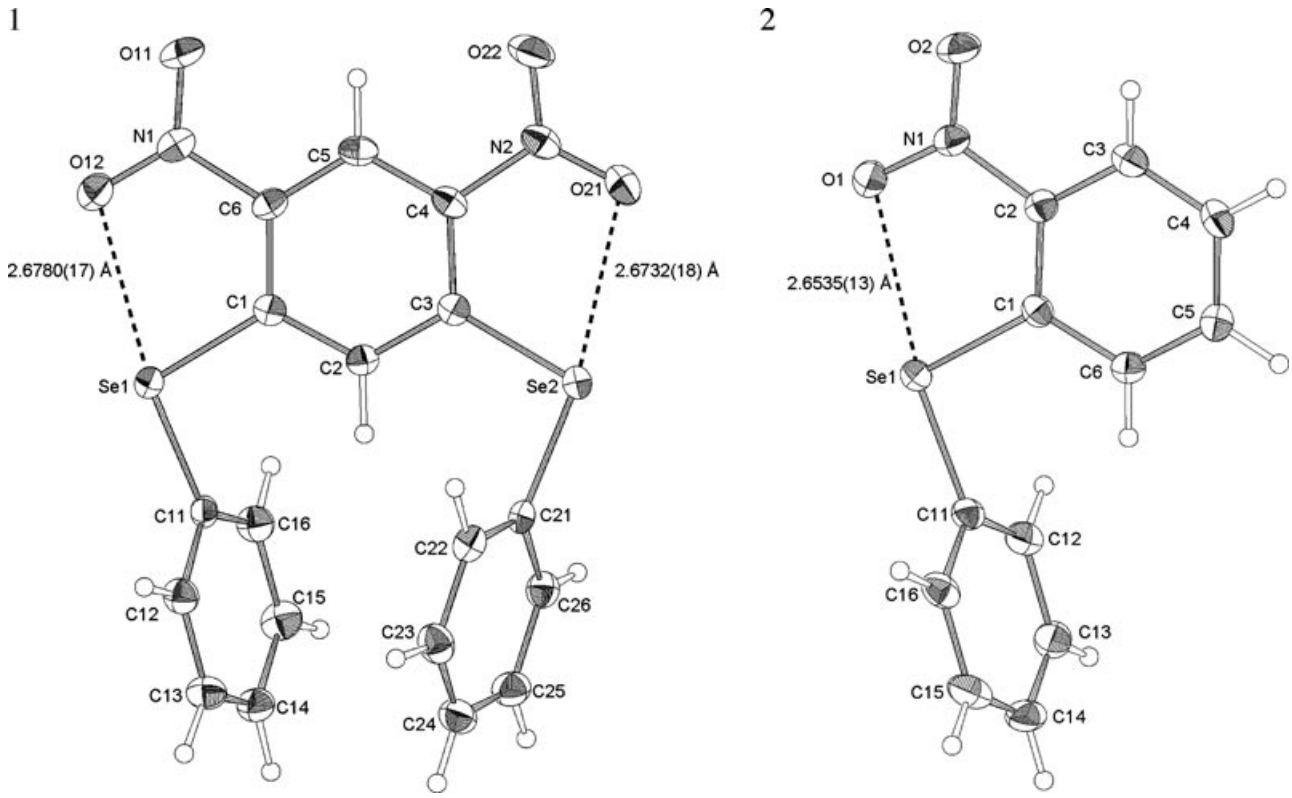


FIGURE 1 ORTEP II drawings showing the structure and atomic labeling of (1) compound **11** and (2) **7**. The thermal ellipsoids are drawn at 50% probability and the hydrogen atoms as spheres with an arbitrary radius.

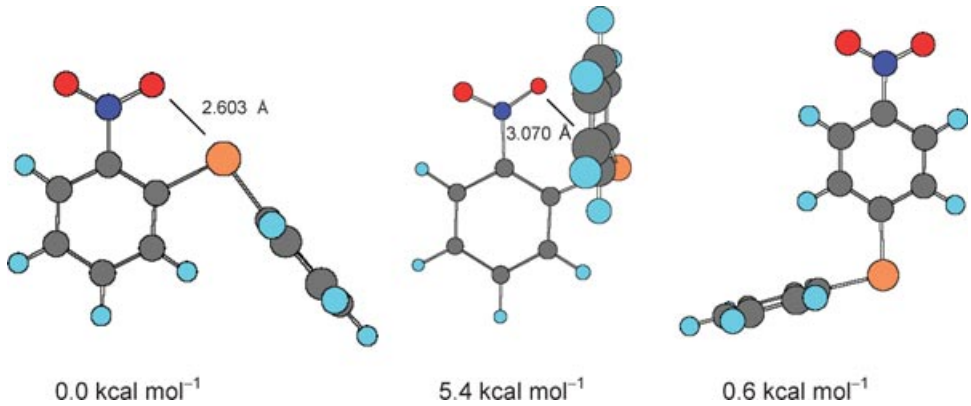


FIGURE 2 Calculated geometries (B3LYP/6–31G(d)) of *o*-(phenylselenonitro)benzene **7** in two different conformations together with the para-isomer in the lowest energy conformation.

was found by X-ray crystallography with a distance between the oxygen and the selenium of only 2.6517(13) Å as indicated in Fig. 1. This value agrees well with the distance of 2.60 Å obtained at the B3LYP/6–31G(d) level of theory and since a regular Se—O bond distance is of the order of 1.68 Å [7]. No indication of a formal chemical bond between the nitro group and the PhSe group was found. The agreement between the calculated geometry and the experimental structure seems to apply for most of the structural parameters. The torsional angles associated with the nitro group are in both cases close to 0°, and in both cases the planes defined by the phenyl groups are perpendicular (more so in the case of the calculated geometry (92°), than in the case of the experimental structure (102°)).

Relative Energies of a Series of $PhSeC_6H_4NO_2$ Isomers

In the attempt to locate a global minimum structure of *o*-PhSe-$C_6H_4NO_2$ a high-energy conformer (by 5.4 kcal mol^{-1}) was identified, where the nitro group is highly distorted away from the plane of the phenyl group. In this geometry, the PhSe group points away instead of pointing along the main phenyl group. Both conformers are shown in Fig. 2. The ortho and the para isomers are roughly equally stable, at the B3LYP/6–31G(d) level, with the para isomer having slightly lower energy by 0.6 kcal mol^{-1}. This indicates that the interaction between the PhSe group and the nitro group only just overcomes the steric repulsion between the ortho substituents. The calculated geometrical features of the para isomer are similar to those of the ortho isomer. The geometry of the para isomer is included in Fig. 2.

A strong interaction between the nitro group and the PhSe group could lead to a (hypothetical) transfer of an oxygen atom from the nitro group to the PhSe group, resulting in the formation of a selenoxide with a nitroso substituent. The calculated geometry of this compound is shown in Fig. 3. It lies substantially higher in energy (by 22.3 kcal mol^{-1}), and the formation of the nitroso compound in Fig. 3 does therefore seem very unlikely even in the case of a strong NO_2–SePh interaction. The nitroso compound does also exist in two conformers of very different stability (Fig. 3). One has the Se=O bond pointing away from the nitroso group. This gives rise to a stabilization of 7.7 kcal mol^{-1} because of the dipole–dipole stabilization that results from having the dipolar groups Se=O and N=O pointing in different directions as indicated in Fig. 3.

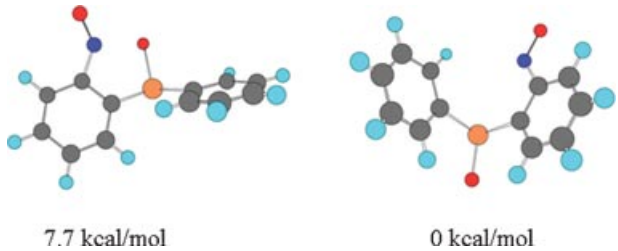


FIGURE 3 Calculated geometries (B3LYP/6–31G(d)) of the nitroso compounds that would result from the transfer of an oxygen atom from the nitro group to the selenium atom. The lowest energy conformer lies 22.3 kcal mol^{-1} higher in energy compared to the nitro-compound.

Nucleophilic Aromatic Substitution: The Meisenheimer Complexes

We have calculated the geometries of the Meisenheimer complexes that would result from nucleophilic attack of hydrogen selenide on both

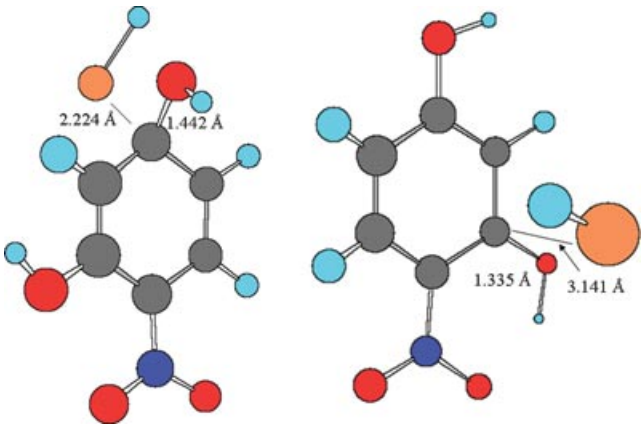
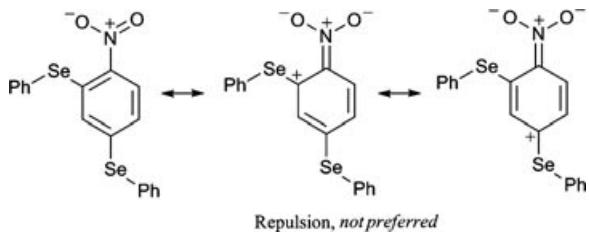


FIGURE 4 Calculated geometries (B3LYP/6–31G(d)) that result from the attempts to locate the intermediate Meisenheimer complexes in nucleophilic aromatic substitution in the para (left) and the ortho (right) positions. Only the para species resembles a Meisenheimer complex.

of the hydroxy groups of a model compound; 2,4-dihydroxynitrobenzene. The starting guess in these calculations had C—O and C—Se distances that are close to those of regular covalent bonds. This was done to investigate whether the reason for the resistance against nucleophilic attack of methoxide at 2 in the ortho position is determined by the energetics of an intermediate Meisenheimer complex. A substantially higher energy of the ortho isomer over the para would agree with the sole substitution of the para substitutent. It can be seen from Fig. 4 that para attack results in a complex, where the carbon-Se bond is somewhat longer (2.22 Å) than in regular alkylseleno-substituted arenes. This finding contrasts that for the ortho isomer; in that case it was not possible to optimize a geometry that meets our expectations on how a Meisenheimer complex should look regardless of the initial trial structure. The carbon-Se bond is very long in the case of the ortho isomer (3.141 Å), and the calculated geometry more closely resembles a van der Waals complex of the reactants. The energy of the van der Waals complex is 18 kcal mol^{-1} lower than that of the intermediate that results from para attack and reflects the lower energy of the reactants. It seems that the ortho isomer does not form stable intermediates in the case of nucleophillic attack.

Charge Distributions in 2,4-Bis(phenylseleno)nitrobenzene and 2-(Phenylseleno)-4-methoxynitrobenzene Accounting for the Exclusive Para-Substitution

The charge distributions of the central compounds were explored by the calculation

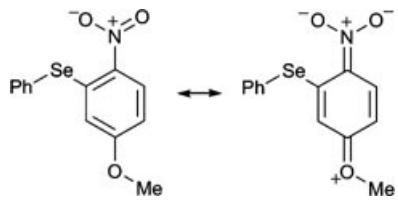


SCHEME 3

of the Mulliken charges. In the case of 2,4-diphenylselenonitrobenzene, the results can be taken to indicate that the amount of positive charge at C2 is about half of the positive charge on C4, making the attack of a nucleophile much more attractive at C4. The fact that it is much more favorable for the molecule to position a higher degree of positive charge on C4 can be understood in terms of a classical resonance picture. The charged nature of the nitro group simply makes it unfavorable to place a positive charge at the adjacent carbon. This idea is illustrated in Scheme 3.

Once the para phenylseleno substituent has been replaced by a methoxy group, the effect is self-enhancing because of a substantially higher degree of stabilization (through overlap between carbon and oxygen) of a positive charge at a carbon atom next to a methoxy group (Scheme 4).

This further reduces the tendency for ortho attack. This is inline with the findings for the corresponding methanethiolate reaction performed on 2, where exchange of both PhSe-groups utilizing two equivalents of NaMeS smoothly took place and only 2,4-bis(methylthio)nitrobenzene 12 could be observed after reaction (Scheme 1). This meant that substitution of one PhSe-group in para did not reduce the tendency for exchange with NaMeS in the ortho position. Furthermore, there was no observed ortho/para–selectivity upon reaction of 2 with a limiting amount of NaSMe. This strengthens the hypothesis involving the charges on carbon a sulfur-based species analogous to 2 would be less influenced by the resonance effects shown in Scheme 4.



SCHEME 4

We note that the exchange involving NaSMe could involve free radicals and thus an entirely different mechanism. The observation is therefore not an unequivocal proof.

CONCLUSIONS

An unusual regioselectivity was observed upon methoxide exchange of PhSe groups in the bis(phenylseleno)nitrobenzene **2**, forming solely the product **3** with only the *p*-PhSe group substituted with a MeO group, even upon treatment with a large excess of methoxide. The mechanistic reasons for the observed regioselectivity are to be found in the electronic characteristics of the PhSe substituent. The drawback of using excess of methoxide is rapid exchange of PhSe groups in (phenylseleno)nitrobenzenes. However, when the NaSePh reagent is generated from our procedure, it can be performed as a titration (yellow to colorless) of diphenyl diselenide with methoxide in the presence of hydrazine. Diselenides polluted with namely triselenides and higher selenides can cause an unsharp titration end-point, but these species can be avoided using our procedure. By purification of diselenides via the tosylate salt of the corresponding seleninic acid [8], unnecessary addition of an excess of methoxide can be avoided in cases where this may cause serious damage. It was possible to obtain X-ray structures of two new ortho (phenylseleno)nitrobenzenes **7** and **11**, which afforded additional information about the nonbonded interaction between the ortho nitro group and selenium, which resembles a partial five-membered ring since the Se···O distance is 2.65 Å, much shorter that the sum of van der Waals radii. We have verified that the selectivity is not a result of this interaction.

EXPERIMENTAL

2,4-Dibromonitrobenzene **1**

1,3-Dibromobenzene (7.81 g, 33 mmol) was added to an ice-cooled mixture of concentrated sulfuric acid (11 mL) and concentrated nitric acid (11 mL) at such a rate that the temperature was kept at 20°C. The reaction mixture was effectively stirred at room temperature for 30 min and then cooled at 0°C while ice (25 g) was added in small portions. The yellow precipitate was filtered off, washed with water and dried in a vacuum oven (80°C, 1 mBar). Recrystallization from hexane (70 mL) afforded **1** (7.93 g, 85%) as light-yellow needles; mp: 61–62°C (lit. [9], ref 61°C); ^{1}H NMR ($CDCl_3$): δ 7.60 (dd, $J = 2.0$, 8.7 Hz, 1 H), 7.76 (d, $J = 8.7$ Hz, 1 H), 7.93 (d, $J = 2.0$ Hz, 1 H).

2,4-Bis(phenylseleno)nitrobenzene **2**

To a stirred solution containing diphenyl diselenide (1.56 g, 5 mmol) and hydrazine hydrate (0.14 g, 2.75 mmol) in DMSO (8 mL) was added 25% methanolic sodium methoxide (approximately 2 g, the last 0.2 g added dropwise with intervals of 5 s until a precise titration end-point yellow to colorless was reached) in a nitrogen atmosphere. Compound **1** (1.46 g, 5 mmol) was added, and stirring was maintained at room temperature for 3 h. The red-brown reaction mixture was diluted with water (75 mL) and extracted with ether (3 × 25 mL). The pooled etheral phases were washed with water (2 × 15 mL), filtered through alumina (basic, 10 g) by means of ether, and evaporated. Recrystallization from toluene (80 mL) and drying in a vacuum oven (60°C, 1 mBar) gave **2** as yellow crystals; mp 96–97°C (found: C, 50.18; H, 3.06; N, 3.14. $C_{18}H_{13}NO_2Se_2$ requires C, 49.90; H, 3.02; N, 3.23); ^{1}H NMR ($CDCl_3$): δ 6.77 (d, $J = 1.9$ Hz, 1 H), 7.08–7.12 (m, 1 H), 7.19–7.32 (m, 5 H), 7.34–7.41 (m, 3 H), 7.49 (dd, $J = 1.4$, 6.0 Hz, 2 H), 8.10 (d, $J = 8.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 125.90, 126.18, 127.28, 129.17, 129.26, 129.35, 129.61, 129.75, 129.78, 129.89, 129.91, 135.73, 136.89, 143.74; ^{77}Se NMR [10] ($CDCl_3$): δ 450, 497. MS: EI (*m/z*, relative intensity): 435 (M^+, 100), 388 (7), 342 (30), 308 (18).

4-Methoxy-2-(phenylseleno)nitrobenzene **3**

Compound **2** (0.87 g, 2 mmol) was suspended in DMSO (5 mL). Sodium methoxide (5 M in methanol, 1 mL, 5 mmol) was added, and the resulting solution was stirred for 1 h (at this point of time TLC showed total consumption of **2**). The dark-orange reaction mixture was diluted with water (15 mL) and extracted with ether (3 × 10 mL). The combined etheral phases were washed with water (5 mL), filtered through aluminum oxide (6 g) by means of ether, and the solvent was evaporated in vacuo (GC-MS showed no products arising from methoxide substitution ortho to the nitro group) to give the regiospecific product **3** (0.52 g, 84%) identical to the product synthesized below.

Unequivocal Synthesis of **3**

A sodium phenylselenide solution (1 M in MeOH-DMSO 1:4, 10 mL, 10 mmol) was prepared by the standard procedure as a titration at room temperature with a sharp end-point (yellow to colorless). 2-Bromo-4-methoxynitrobenzene (2.32 g, 10 mmol) was added in one portion. Stirring was maintained at room temperature for 1 h under nitrogen. The dark-orange reaction mixture was diluted with water

(70 mL) and extracted with ether (3 × 25 mL). The combined organic phases were washed with water (2 × 15 mL), filtered through alumina (neutral, 6 g) by means of ether, and the solvent evaporated in vacuo. Recrystallization from hexane (40 mL) and drying (vacuum oven, 50°C) gave **3** (2.69 g, 87%) as yellow crystals; mp 76–77°C (found: C, 50.89; H, 3.68, N 4.47. $C_{13}H_{11}NO_3Se$ requires C, 50.66; H, 3.60; N, 4.54); mass spectrum (EI; *m/z*, relative intensity): 309 (M^+, 100), 248 (7), 232 (9), 216 (93); ^{1}H-NMR ($CDCl_3$): δ 3.57 (3H, s), 6.35 (1H, d, *J* 2.7 Hz), 6.72 (1H, dd, *J* 9.2, 2.7 Hz), 7.42–7.53 (3H, m), 7.67–7.72 (2H, m), 8.19 (1H, d, *J* 9.2 Hz); ^{13}Se-NMR ($CDCl_3$): δ 55.51, 106.15, 115.88, 124.43, 125.30, 126.42, 128.73, 137.31, 138.24, 168.42; ^{77}Se-NMR ($CDCl_3$): δ 504.

2-Methoxynitrobenzene **8** *and 4-Methoxynitrobenzene* **10**

2-(Phenylseleno)nitrobenzene **7** (0.28 g, 1 mmol, experiment **A**) or 4-(phenylseleno)nitrobenzene **9** (0.28 g, 1 mmol, experiment **B**) were suspended in DMSO (5 mL). Sodium methoxide (5 M in methanol, 0.24 mL, 1.2 mmol) was added, and the resulting solutions were stirred for 1 h (at this point of time TLC showed total consumption of the corresponding (phenylseleno)nitrobenzene). Samples for GC-MS were obtained by quench in water and extraction with *tert*-butyl methyl ether. TLC and GC-MS showed full conversion of starting materials, indicating clean formations of **8** and **10**, respectively.

1,3-Dinitro-4,6-bis(phenylseleno)benzene **11**

To a sodium selenophenolate solution (20 mmol) in DMSO (20 mmol) prepared by the standard procedure, 1,3-dibromo-4,6-dinitrobenzene [11] (3.26 g, 10 mmol) was added and stirring was maintained for 3 h at room temperature under nitrogen. The dark-orange reaction mixture was diluted with water (150 mL) and extracted with ether:toluene (1:2, 3 × 100 mL). The combined organic phases were washed with water (2 × 40 mL), filtered through alumina (neutral, 10 g) by means of ether, and the solvent was evaporated in vacuo. Recrystallization from toluene (100 mL) and drying (vacuum oven, 70°C) gave **11** (3.49 g, 73%) as yellow crystals; mp 215–216°C; (found: C 45.19; H 2.48; N 5.84. $C_{18}H_{12}N_2O_4Se_2$ requires C 45.21; H 2.53; N 5.86); mass spectrum (EI; *m/z*, relative intensity): 480 (M^+, 100), 450 (4), 384 (17), 306 (30). ^{1}H NMR ($CDCl_3$): δ 7.34–7.38 (m, 4H), 7.43–7.51 (m, 4H), 7.59–7.64 (m, 2H), 7.98 (s, 1H), 8.92 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 118.83, 126.57, 128.28, 128.99, 129.32, 131.45, 137.24, 146.25; ^{77}Se-NMR ($CDCl_3$): δ 514. Single crystals of **7** and **11** were prepared by slow crystallization from diluted toluene solutions.

X-ray crystallography

Single crystal X-ray diffraction data were collected on crystals of compound **7** and **11** cooled to 122.0(5) K on an Enraf-Nonius CAD4 diffractometer [12], employing Cu Kα radiation. Data reductions were performed with the DREAR suite of programs [13]. All reflections were corrected for background, Lorentz and polarization effects. Absorption corrections were performed using the numerical Gaussian integration procedure [14]. The structures were solved by Patterson and Fourier methods using SHELXS97 [15] and refined by full matrix least-squares on $|F|^2$-values against all reflections with SHELXL97 [16]. The non-hydrogen atoms were refined with anisotropic displacement parameters. Positional and isotropic displacement parameters were refined for all hydrogen atoms. An extinction parameter was introduced for both refinements.

Crystal data for **7**. $C_{12}H_9NO_2Se$, $M_w = 278.16$ g mol^{-1}, crystal dimensions $0.35 \times 0.15 \times 0.06$ mm^3, monoclinic, space group $P2_1/c$, $a = 9.0947(8)$, $b = 14.969(3)$, $c = 8.0496(14)$ Å, $\beta = 98.129(11)°$, $V = 1084.9(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.703$ g cm^{-3}, μ(Cu Kα) = 4.559 mm^{-1}, $4.91 < \theta < 75.90°$, of 8976 measured reflections, 2232 were independent ($R_{int} = 0.0336$) and 2204 observed with $I > 2\sigma(I)$; $R1 = 0.020$, $wR2 = 0.0576$, GOF = 1.014 for 182 parameters, $\Delta\rho_{max/min} = 0.281/-0.465$.

Crystal data for **11**. $C_{18}H_{12}N_2O_4Se_2$, $M_w = 478.22$ g mol^{-1}, crystal dimensions $0.35 \times 0.25 \times 0.09$ mm^3, orthorhombic, space group *Pbca*, $a = 10.5072(15)$, $b = 27.715(3)$, $c = 11.7420(12)$ Å, $V = 3419.4(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.858$ g cm^{-3}, μ(Cu Kα) = 5.659 mm^{-1}, $3.19 < \theta < 74.94°$, of 7713 measured reflections, 3522 were independent ($R_{int} = 0.0292$) and 3293 observed with $I > 2\sigma(I)$; $R1 = 0.0256$, $wR2 = 0.0677$, GOF = 1.137 for 284 parameters, $\Delta\rho_{max/min} = 0.429/-0.760$.

DFT Computations

The geometries and vibrational frequencies were calculated at the B3LYP/6–31G(d) level of theory with the GAUSSIAN 98 suite of programs [17]. The relative energies were calculated as the difference between the sums of the electronic energy and the zero-point vibrational energy scaled by 1.008 as prescribed by Scott and Radom [18]. Archive entries

related to the calculated geometries are available from the authors upon request.

Supplementary Data

Atomic coordinates, thermal parameters, and bond lengths and angles for compounds **7** and **11** have been deposited in the Cambridge Crystallographic Data Center, CCDC nos. CCDC 703709 and 703710. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK on request (fax: +44–1223–336–033; E-mail: deposit@ccdc.cam.ac.uk or URL: http://www.ccdc.cam.ac.uk).

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