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A New Oxidative *Se*-Dealkylation in Seleno-Pummerer Reaction of 1,8-Bis(methylseleno)naphthalene and Naphtho[1,8-*b,c*]-1,5-diselenocin Induced by Peri-Selenium Participation

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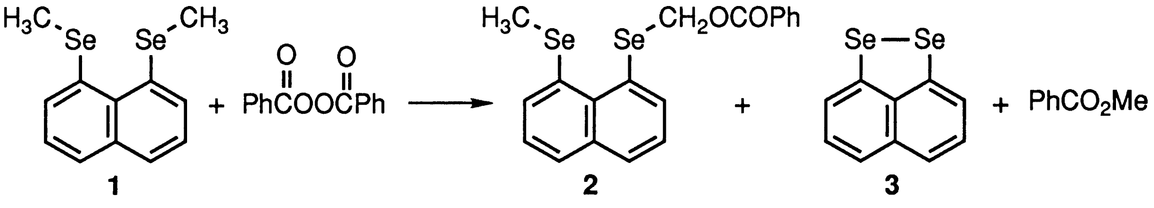
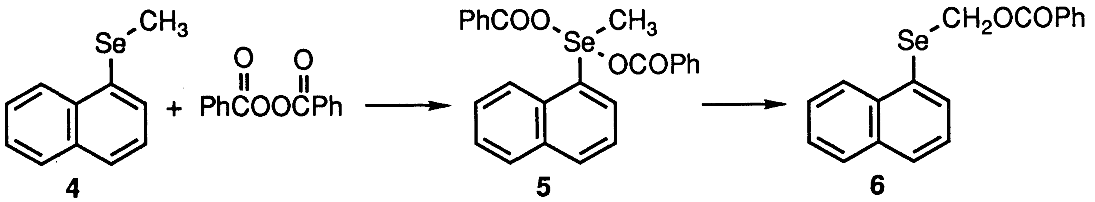
A new type of oxidative *Se*-dealkylation reaction was found in either the reaction of 1,8-bis(methylseleno)naphthalene and naphtho[1,8-*b,c*]-1,5-diselenocin with benzoyl peroxide or the reaction of their *Se*-oxides with carboxylic acid anhydrides.

Mechanism and synthetic application for the Pummerer reactions of organosulfur compounds have been extensively studied.1) However, the Pummerer-type reaction of organoselenium compounds has received little attention.2) We have now found the *Se*-demethylation in either the reaction of 1,8-bis(methylseleno)naphthalene (**1**) with benzoyl peroxide or the reaction of its *Se*-oxide (**7**) with carboxylic acid anhydrides under unusually mild conditions, although the reaction of methyl phenyl selenoxide with acetic anhydride gives the α-acetoxymethyl phenyl selenide without demethylation.2) While, a cyclic bis-selenide, naphtho[1,8-*b,c*]-1,5-diselenocin (**11**), or its oxide underwent readily the Claisen-type rearrangement *via* C-Se bond cleavage to give 2-allyl-substituted naphtho-1,8-diselenide on treatment with benzoyl peroxide or acetic anhydride.

The reaction of bis-selenide **1**3) (126 mg, 0.4 mmol) with benzoyl peroxide (BPO; 97 mg, 0.4 mmol) was carried out in CCl_4 (11 ml) under an Ar atmosphere at 0 °C for 15 h. After the usual work-up, the residue was purified by silica-gel column chromatography and further purified by preparative liquid chromatography to give the α-benzoyloxylated product (**2**) (36%) together with naphtho[1,8-*c,d*]-1,2-diselenole (**3**) as the demethylated product (33%) and methyl benzoate (Scheme 1).4) Interestingly, thus the rearrangement and the *Se*-demethylation reactions of **1** with BPO proceed readily without heating. However, it has been reported that the reaction of alkyl phenyl selenides with BPO gives the tetravalent selenium compounds which convert on heating to the α-benzoyloxyalkyl phenyl selenides.5) Actually, 1-methylselenonaphthalene (**4**)3) was reacted with 1 equiv of BPO at room temperature to afford exclusively the hypervalent selenurane (**5**) as a white solid, in which the ^{77}Se NMR spectrum of **5** in $CHCl_3$ shows a singlet at δ 804.8, as is characteristic of a selenurane.2,6) A refluxing solution of selenurane **5** in CCl_4 for 15 h gave the Pummerer-type rearranged product (**6**) (78%) and the selenide **4** (20%) (Scheme 2),6) however, no demethylation was found at all.

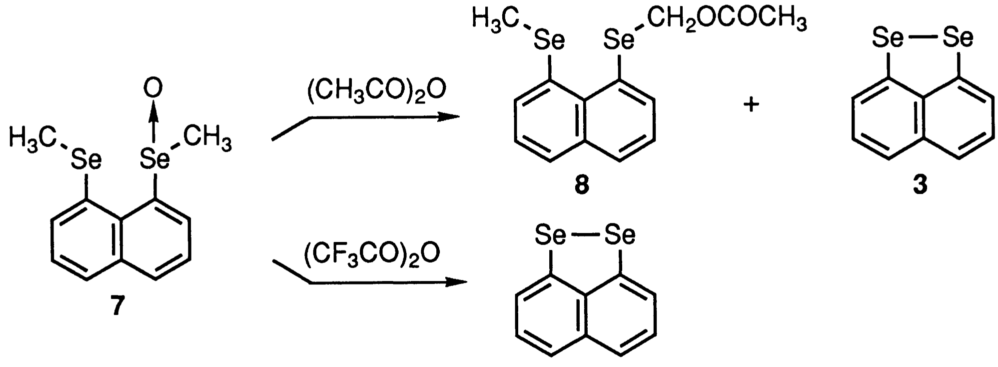


Scheme 1.



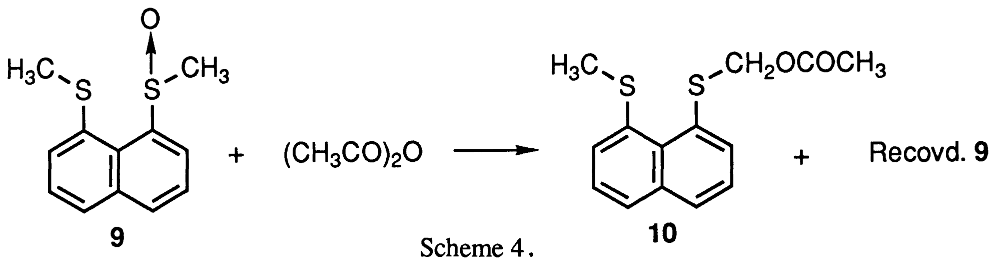
Scheme 2.

Meanwhile, the selenoxide (**7**) was reacted with acetic anhydride (1 equiv.) in benzene at room temperature for 3 h under an Ar stream to afford the α-acetoxylated selenide (**8**) (39%) and the diselenide (**3**) (34%) (Scheme 3).[7,8] Similar treatment of **7** with benzoic anhydride (1 equiv.) in CCl_4 led to the Pummerer rearranged product **2** (20%), diselenide **3** (40%), and methyl benzoate (15%). In contrast, reaction of **7** with trifluoroacetic anhydride in benzene at room temperature resulted in a smooth demethylation to the diselenide **3** (73%) without formation of the rearranged products.



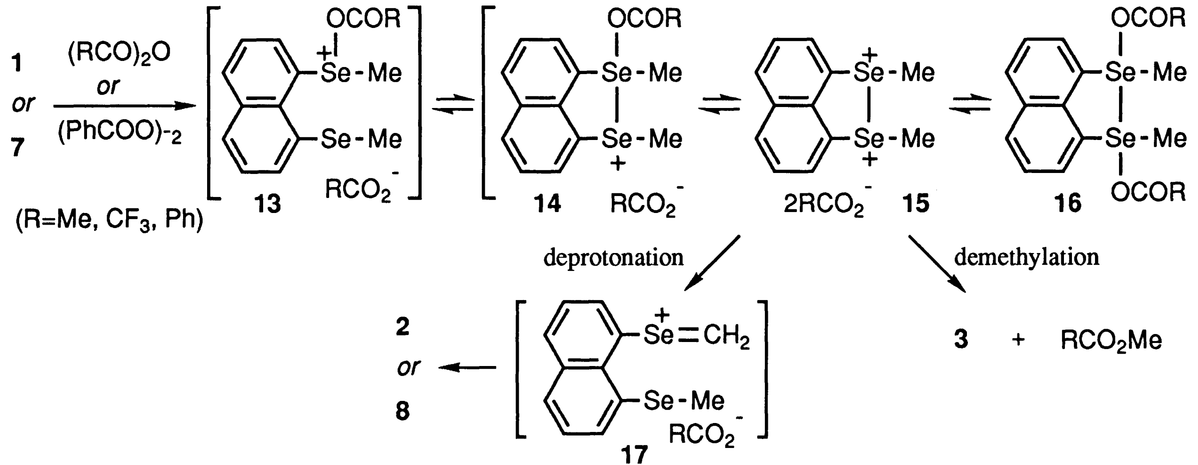
Scheme 3.

A distinct difference in reactivity between **7** and the sulfoxide (**9**) was observed; *i.e.*, heating the mixture of **9** with a large excess of acetic anhydride at 110 °C for 72 h, however did not yield the demethylated product, naphtho[1,8-*c,d*]-1,2-dithiole; only the α-acetoxylated sulfide (**10**) (18%), the recovered sulfoxide **9** (54%), and complex products were formed (Scheme 4).[7,9,10] Thus, the reaction of **9** with $(CH_3CO)_2O$ required high temperature and longer reaction time.



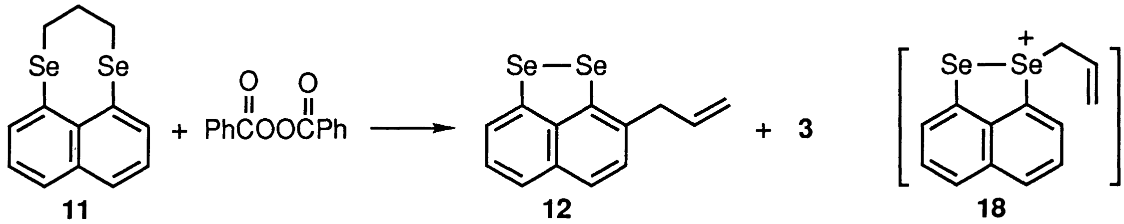
Scheme 4.

The unusual seleno-Pummerer reaction of diseleno *peri*-bridged naphthalenes under mild conditions seems to be ascribed to the interaction between the two-selenium atoms of **1** and **7**. Such interaction can be supported by the ^{77}Se NMR spectroscopic observation, since the proton-decoupled ^{77}Se NMR spectra of unsymmetrical diseleno naphthalenes showed the satellite peaks due to the ^{77}Se-^{77}Se coupling; *e.g.*, large coupling constants of $J_{Se\text{-}Se}$ = 203 Hz for **7** and of $J_{Se\text{-}Se}$ = 310 Hz for **8**.[11] The seleno-Pummerer reactions described above may proceed as follows. Either the reaction of **1** with BPO or the reaction of **7** with acid anhydrides leads to the selenonium cation (**13**) which is stabilized by the selenium participation to form the selenonio selenurane (**14**), or the diselena dication (**15**), or the bis-selenurane (**16**) as intermediate (Scheme 5). Rearrangement could proceed *via* addition of a carboxylate anion ($CH_3CO_2^-$ or $PhCO_2^-$) to the alkylidene selenonium ion (**17**) generated from α-proton abstraction of **14** or **15** or **16** by a carboxylate anion. Alternatively, demethylation may occur in either the substitution of the carbon atom of the methyl group of **14** or **15** by a carboxylate anion, or the ligand coupling reaction in **16**. Since $CF_3CO_2^-$ ion is much weaker base compared to $CH_3CO_2^-$ ion, it is reasonable that the demethylation predominated in the reaction of **7** with $(CF_3CO)_2O$.



Scheme 5.

Surprisingly, the rearranged product, 2-allyl-naphtho[1,8-*c*,*d*]-1,2-diselenole (**12**) (65%), and the diselenide **3** (19%) were obtained when cyclic bis-selenide **11**7) (1 equiv.) and BPO (1 equiv.) were allowed to react in equimolar amounts in CCl_4 under an Ar atmosphere at -20 °C for 12 h.12) Thus, a new rearrangement accompanied by dealkylation from **11** was found (Scheme 6). Similar result was obtained from the reaction of the monoselenoxide of **11** with acetic anhydride. The structure of **12** was determined on the basis of NMR (^1H, ^{13}C, ^{77}Se, and ^1H-^1H and ^1H-^{13}C COSY) spectroscopy, and mass spectrometry. Probably, the compound **12** forms *via* the Claisen-type rearrangement pathyway from the intermediate **18**.13) The studies of the mechanism for this new type of rearrangement and dealkylation are in progress.



Scheme 6.

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2) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1986), Vol. 1; "Selenium Reagents and Intermediates in Organic Synthesis," C. Paulmier, Pergamon Press (1986).

3) H. Fujihara, M. Yabe, J.-J. Chiu, and N. Furukawa, *Tetrahedron Lett.*, **32**, 4345 (1991).

4) **2**: FT-IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 5.67 (s, 2H), 7.33-7.81 (m, 8H), 7.98-8.07 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.0, 66.0, 125.9, 126.0, 128.0, 128.4, 128.5, 129.9, 130.0, 131.6, 133.2, 133.7, 135.4, 135.5, 135.6, 165.9; ^{77}Se NMR ($CDCl_3$) δ 234.8, 421.5 (relative to Me_2Se); MS, *m/z* 436 (M^+). Anal. Found: C, 52.82; H, 3.84%. Calcd for $C_{19}H_{16}O_2Se_2$: C, 52.55; H, 3.71%.

5) Y. Okamoto, K. L. Chellappa, and R. Homsany, *J. Org. Chem.*, **38**, 3172 (1973).

6) **5**: FT-IR (KBr) 1694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.87 (s, 3H), 7.42-8.37 (m, 17H); ^{13}C NMR ($CDCl_3$) δ 35.8, 122.0, 124.6, 126.1, 126.9, 127.7, 128.3, 129.3, 130.0, 130.2, 130.3, 131.7, 133.2, 133.9, 136.7, 171.0; ^{77}Se NMR ($CDCl_3$) δ 804.8 (relative to Me_2Se).
6: FT-IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.79 (s, 2H), 7.36-8.41 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 62.7, 123.9, 125.8, 126.3, 126.7, 126.8, 127.9, 128.4, 128.6, 128.9, 129.4, 129.6, 129.7, 133.3, 134.0, 134.5, 165.9; ^{77}Se NMR ($CDCl_3$) δ 341.0 (relative to Me_2Se); MS, *m/z* 342 (M^+).

7) Compound **7** was obtained by the oxidation of **1**[3] with peracid and the selenide **11** was prepared by the reaction of disodium naphtho[1,8-*c*,*d*]-1,2-diselenolate with 1,3-dibromopropane. The compounds, **7**, **9**, and **11**, and the oxide of **11** were fully characterized by ^{1}H, ^{13}C, ^{77}Se, mass spectroscopy and microanalysis.

8) **8**: FT-IR (neat) 1744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3H), 2.32 (s, 3H), 5.44 (s, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.72 (d, J = 7.5 Hz, 2H), 7.80 (d, J = 7.5 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.2, 21.1, 65.6, 125.9, 126.0, 128.1, 129.8, 130.0, 131.9, 132.1, 134.9, 135.5, 135.6, 170.3; ^{77}Se NMR ($CDCl_3$) δ 233.0, 421.4 (relative to Me_2Se); MS, *m/z* 374 (M^+). Anal. Found: C, 45.09; H, 3.76%. Calcd for $C_{14}H_{14}O_2Se_2$: C, 45.18; H, 3.79%.

9) When the reaction was carried out at higher than 110 °C, a complex mixture was obtained; The different behavior was also found in the electrochemical oxidation of **1** and the bis-sulfide, 1,8-bis(methylthio)-naphthalene (**19**); *i.e.*, the cyclic voltammogram of **1** shows the reversible oxidation wave by peri-selenium interaction, while that of **19** shows an irreversible oxidation.[3]

10) **10**: ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H), 2.52 (s, 3H), 5.36 (s, 2H), 7.37-7.46 (m, 3H), 7.64-7.67 (m, 1H), 7.78-7.84 (m, 2H); MS, *m/z* 278 (M^+).

11) The ^{77}Se-^{77}Se coupling can be attributed to the *p*-orbital overlap between two selenium atoms.[2]

12) **12**: ^{1}H NMR ($CDCl_3$) δ 3.35 (d, J = 6.5 Hz, 2H), 5.18-5.23 (m, 2H), 5.88-5.96 (m, 1H), 7.14 (d, J = 8 Hz, 1H), 7.20 (t, J = 8 Hz, 1H), 7.34 (d, J = 8 Hz, 1H), 7.44 (d, J = 8 Hz, 1H), 7.49 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 41.1, 117.8, 121.3, 123.4, 124.7, 126.7, 128.9, 132.9, 133.8, 136.5, 137.7, 140.0, 140.6; ^{77}Se NMR ($CDCl_3$) δ 389.9, 437.0 (relative to Me_2Se); MS, *m/z* 326 (M^+); The Pummerer-type rearranged product, α-benzoyloxylated selenide of **11**, was obtained in a low yield.

13) H. Kwart and J. L. Schwartz, *J. Org. Chem.*, **39**, 1575 (1974) and references therein.

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