Se-Demethylation from 8-dimethylamino-1-methylselanyl-naphthalene and its Se-oxide: an X-ray structure of a stable selenenic anhydride with a 8-dimethylamino-1-naphthyl ligand: peri Se · · · N interaction

**Hisashi Fujihara,**[*,b] **Hitomi Tanaka**[a] **and Naomichi Furukawa**[*,a]

[a] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
[b] Environmental Science Research Institute, Kinki University, Kowakae, Higashi-Osaka 577, Japan

Reaction of a selenoxide, 8-dimethylamino-1-methylseleninylnaphthalene 2, with acetic anhydride gave exclusively the Se-demethylated product, the corresponding selenoperacetate 3; the X-ray crystal structure of the stable selenenic anhydride 6 derived from hydrolysis of 3 shows the strong intramolecular interactions between selenium and nitrogen atoms.

In connection with the continuing interest in the Pummerer reaction of sulfoxides with acid anhydrides,[1] we reported earlier that the sulfoxide 1,5-dithiacyclooctane 1-oxide reacted with acetic anhydride to afford the remote α-acetoxylated sulfide via the intermediate formation of the dithia dication by trans-annular participation.[2] Surprisingly, we have now found that the reaction of 8-dimethylamino-1-methylseleninylnaphthalene 2 with acetic anhydride gave exclusively the Se-demethylated product, the corresponding selenoperacetate 3, which was converted into an isolable selenenic anhydride 6 upon hydrolysis, although the reaction of methyl phenyl selenoxide with acetic anhydride gives the acetoxymethyl phenyl selenide without demethylation.[3] This paper reports the novel Se-demethylation induced by a peri-amino nitrogen from either the reaction of 2 with carboxylic acid anhydrides or the reaction of 8-dimethylamino-1-methylselanylnaphthalene 1 with benzoyl peroxide and the observation of strong attractive interactions between selenium and nitrogen atoms in the crystal state of the selenenic anhydride 6 with the 8-dimethylamino-1-naphthyl ligand.

A new selenide 1 was synthesized from the reaction of 8-dimethylamino-1-naphthyllithium with MeSeCN. Reaction of 1 first with Bu^{t}OCl followed by alkaline hydrolysis gave the selenoxide 2. This when treated with acetic anhydride (2 equiv.) in benzene under an Ar atmosphere at room temperature for 12 h afforded the Se-demethylated product, the selenoperacetate 3, in quantitative yield (Scheme 1). Similar treatment of 2 with benzoic anhydride (2 equiv.) in chloroform gave the seleno-perbenzoate 4 (87%) and PhCO$_2$Me (82%) (Scheme 1). None of the Pummerer rearranged product was obtained in these reactions.

Scheme 1
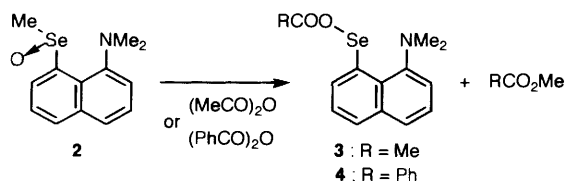
This new type of Se-demethylation was also found to proceed in the treatment of the selenide 1 with benzoyl peroxide (BPO; 1 equiv.) at room temperature which gave the seleno-perbenzoate 4 (88%), PhCO$_2$Me (78%), and a negligible amount of the Pummerer rearranged product 5 (3%) (Scheme 2). In contrast, it has been reported that the reaction of alkyl
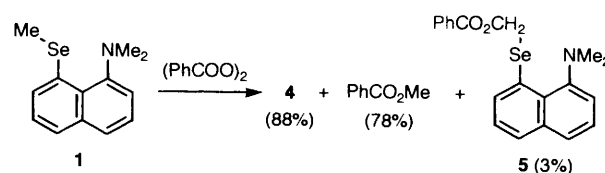
Scheme 2

phenyl selenides with benzoyl peroxide gives the tetravalent selenium compounds, hypervalent selenuranes, which, when heated, are converted into the α-benzoyloxyalkyl phenyl selenides.[4]

The mechanism in Scheme 3 is proposed to account for the Se-demethylation. Either the reaction of 1 with BPO or the reaction of 2 with acid anhydrides leads to the cation 7 stabilized by peri-nitrogen or the selenazolonaphthalene 8 as an intermediate. Subsequently, a carboxylate anion could attack on the carbon atom of the Se-methyl group of the selenazolonaphthalene 8.

The possibility of the selenazolonaphthalene 8 being formed is supported by the X-ray data, i.e. very short contacts are observed between Se and N atoms of the selenenic anhydride 6 (vide infra).

Scheme 3
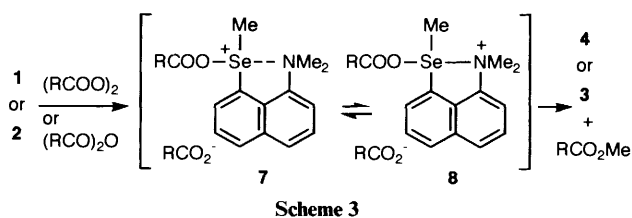
It is noteworthy that the selenoperacetate 3 was converted into the stable selenenic anhydride 6 which would be formed from the selenenic acid generated on the hydrolysis of 3. The ^{77}Se NMR spectrum of 6 in CDCl$_3$ exhibits a single resonance at δ 1191 (relative to Me$_2$Se). In general, selenenic acids and their anhydrides are usually generated in situ and used without isolation, because of their instability. On the other hand, ortho-nitro- and benzoyl-benzeneselenenic anhydrides have been isolated, where the compound is stabilized by an ortho-electron-withdrawing group such as a nitro or carbonyl group.[5]

The crystal structure of a new selenenic anhydride 6 was determined by X-ray diffraction analysis (Fig. 1). The bond lengths of Se–O are 1.856(7) Å [Se(1)–O] and 1.869(7) Å
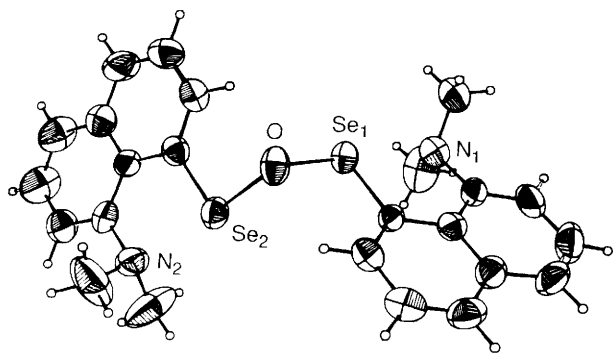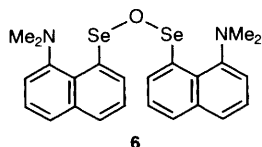
Fig. 1 The crystal structure of the selenenic anhydride **6**. For clarity, CHCl₃ as a crystal solvent is omitted.

6

[Se(2)–O]; the calculated single Se–O bond would be 1.82 Å.³ The Se(1)–O–Se(2) angle is 117.0(3)°. It is interesting to note that the intramolecular Se ∙∙∙ N contacts are 2.420(9) Å for Se(1)–N(1) and 2.447(9) Å for Se(2)–N(2) which are remarkably shorter than the sum of the van der Waals radii (3.5 Å) of the two elements. The angles of N ∙∙∙ Se ∙∙∙ O are 173.4(3)° for N(1)–Se(1)–O and 172.2(3)° for N(2)–Se(2)–O. This linear alignment of N ∙∙∙ Se ∙∙∙ O showed the hypervalent nature of selenium atoms.³ The X-ray data suggest that the selenenic anhydride **6** is considered to be stabilized by the *peri*-participation of the two nitrogen atoms. This would be the first X-ray crystal structure for selenenic anhydrides to our knowledge.

Experimental

Synthesis of 8-dimethylamino-1-methylselanylnaphthalene 1

To the lithium reagent prepared from 1-dimethylamino-naphthalene (3.53 g, 20.6 mmol) and BuLi (1.71 mol dm⁻³ in hexane; 13.5 cm³, 23.1 mmol) in anhydrous ether (60 cm³) was added a solution of methyl selenocyanate (MeSeCN; 2.79 g, 23.3 mmol) in anhydrous ether (10 cm³) under an Ar atmosphere at −20 °C. The mixture was stirred for 2 h at room temperature. After work-up, the crude product was purified by silica-gel column chromatography (eluent, hexane) to give **1** in 37% yield; mp 45 °C; δ_H(CDCl₃) 2.05 (s, 3 H), 2.60 (s, 6 H), 7.13–7.35 (m, 4 H) and 7.48–7.55 (m, 2 H); δ_C(CDCl₃) 7.2, 45.9, 119.0, 123.6, 124.7, 125.76, 125.82, 126.1, 129.8, 131.4, 135.7 and 151.5; δ_Se(CDCl₃) 260 (relative to Me₂Se); *m/z* 265 (M⁺) (Found: C, 59.3; H, 5.7; N, 5.2. C₁₃H₁₅NSe requires C, 59.09; H, 5.72; N, 5.30%).

Preparation of 8-dimethylamino-1-methylseleninylnaphthalene 2

To a solution of the selenide **1** (521 mg, 1.97 mmol) in MeOH (45 cm³) was added BuᵗOCl (225 mm³, 1.99 mmol) at −78 °C. The mixture was stirred at 0 °C for 2 h after which it was treated with 2 mol dm⁻³ aqueous NaOH. After work-up, the crude product was purified by recrystallization from benzene–hexane to give the selenoxide **2** (98% yield); mp 128–129 °C (decomp.); δ_H(CDCl₃) 2.55 (s, 3 H), 2.61 (s, 3 H), 2.88 (s, 3 H), 7.48 (dd, *J* 7.6, 1.0, 1 H), 7.56 (t, *J* 7.6, 1 H), 7.73 (t, *J* 7.6, 1 H), 7.81 (dd, *J* 7.6, 1.0, 1 H), 7.99 (d, *J* 7.6, 1 H) and 8.62 (dd, *J* 7.6, 1.0, 1 H); δ_C(CDCl₃) 39.4, 43.0, 49.3, 119.4, 124.9, 126.36, 126.41, 126.5, 127.2, 130.9, 135.4, 137.6 and 149.0; δ_Se(CDCl₃) 832; *m/z* 281

(M⁺) (Found: C, 55.3; H, 5.4; N, 4.9. C₁₃H₁₅NOSe requires C, 55.72; H, 5.40; N, 5.00%).

Reaction of the selenoxide 2 with acetic anhydride

A mixture of the selenoxide **2** (85 mg, 0.30 mmol) and acetic anhydrides (58 mm³, 0.62 mmol) in anhydrous benzene (1 cm³) was stirred under an Ar atmosphere at room temperature for 12 h. Evaporation then gave the selenoperacetate **3** in 98% yield; liquid; δ_H(CDCl₃) 2.20 (s, 3 H), 3.04 (s, 6 H), 7.39 (d, *J* 7.8, 1 H), 7.50 (t, *J* 7.8, 1 H), 7.58 (t, *J* 7.8, 1 H), 7.67 (d, *J* 7.8, 1 H), 7.80 (d, *J* 7.8, 1 H) and 7.86 (d, *J* 7.8, 1 H); δ_C(CDCl₃) 22.3, 50.4, 117.3, 123.0, 123.8, 125.9, 127.2, 127.9, 128.5, 134.2, 134.6, 148.1 and 175.3; δ_Se(CDCl₃) 1175 (Found: *m/z* 309.0288. Calc. for C₁₄H₁₅NO₂Se: 309.0269).

Reaction of the selenide 1 with benzoyl peroxide

Compound **1** (800 mg, 3.04 mmol) was treated with benzoyl peroxide (920 mg, 3.8 mmol) in dichloromethane (60 cm³) under an Ar atmosphere at room temperature for 2 h. Work-up then gave the selenoperbenzoate **4** (88% yield), methyl benzoate (78% yield), and the rearranged product **5** (3% yield). Compound **4** was a liquid; δ_H(CDCl₃) 3.10 (s, 6 H), 7.39–7.54 (m, 5 H), 7.58–7.71 (m, 2 H), 7.81 (d, *J* 7.5, 1 H), 8.02 (dd, *J* 7.5, 1.1, 1 H) and 8.17–8.20 (m, 2 H); δ_C(CDCl₃) 50.8, 117.3, 123.3, 123.9, 126.0, 127.4, 128.0, 128.1, 128.8, 129.6, 131.5, 133.1, 134.66, 134.71, 148.2 and 170.3; δ_Se(CDCl₃) 1183; *m/z* 371 (M⁺). Compound **5** was a liquid; δ_H(CDCl₃) 2.68 (s, 6 H), 5.82 (s, 2 H), 7.35–7.46 (m, 5 H), 7.53–7.58 (m, 1 H), 7.63–7.68 (m, 2 H), 7.81 (d, *J* 7.6, 1 H) and 8.08–8.12 (m, 2 H); δ_C(CDCl₃) 45.9, 61.4, 119.3, 124.4, 125.7, 125.8, 126.0, 126.5, 128.4, 129.8, 130.1, 130.4, 133.1, 135.7, 151.2 and 166.5; δ_Se(CDCl₃) 437; *m/z* 385 (M⁺) (Found: C, 62.8; H, 5.3; N, 3.4. C₂₀H₁₉NO₂Se requires C, 62.50; H, 4.98; N, 3.64%).

Formation of the selenenic anhydride 6

The selenoperacetate **3** was treated with aqueous NaOH or silica gel in CH₂Cl₂–MeOH to give **6** in 96% yield. The selenenic anhydride **6** was recrystallized from CHCl₃–hexane. Compound **6** had mp 156–158 °C (decomp.); δ_H(CDCl₃) 2.77 (s, 12 H), 7.35 (d, *J* 7.7, 2 H), 7.44 (t, *J* 7.7, 2 H), 7.63 (d, *J* 4.2, 4 H), 7.75 (d, *J* 7.7, 2 H) and 8.17 (t, *J* 4.2, 2 H); δ_C(CDCl₃) 48.3, 118.1, 121.6, 123.2, 125.6, 126.5, 127.8, 128.9, 135.2, 139.1 and 150.0; δ_Se(CDCl₃) 1191 (Found: C, 55.9; H, 4.7; N, 5.3. C₂₄H₂₄-N₂OSe₂ requires C, 56.04; H, 4.70; N, 5.45%).

Crystal data for the selenenic anhydride 6·CHCl₃

Intensity data for a colourless cubic solvent (CHCl₃)-containing crystal (*ca*. 0.30 × 0.30 × 0.30 mm) were measured at 296 °C on an Enraf-Nonius CAD4 diffractometer fitted with Mo-Kα (graphite monochromator) radiation, λ = 0.710 73 Å. A total of 5271 reflections were measured (ω : 2θ scan technique, θ_max = 25°) of which 4930 were unique (R_amal = 0.028) and 3753 satisfied the *I* ⩾ 3σ(*I*) criterion of observability. Three reference reflections measured every 2 h indicated that after 37 h of X-ray exposure 23% crystal decomposition had occurred. Corrections were applied for the decay, for Lorentz and polarization effects and for absorption with the use of the empirical psi-scan procedure (transmission coefficients between 0.82 and 1.00). Crystals of C₂₄H₂₄N₂OSe₂·CHCl₃ are monoclinic, space group *P2₁/c*, with *a* = 9.390(1), *b* = 11.124(1), *c* = 25.622(2) Å, *β* = 93.17(1)°, *V* = 2672.0 Å³, *Z* = 4, *M* = 633.77, *D* = 1.58 g cm⁻³, μ = 30.6 cm⁻¹ and *F*(000) = 1264. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically in full-matrix least-squares calculations using the MolEN program package. The refinement (minimizing Σw(|F_o| − |F_c|)², w = 1.0) converged to *R* = 0.080 leaving a maximum residual electron density peak of 0.67 e Å⁻³ in the final difference map. Tables of fractional atomic coordinates,

bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

† For details of the scheme, see Instructions for Authors (1995), *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

References

1 *The Chemistry of the Sulphonium Group*, vol. 2, eds. C. J. M. Stirling and S. Patai, Wiley, New York, 1981.

2 H. Fujihara, A. Kawada and N. Furukawa, *Gazz. Chim. Ital.*, 1989, **119**, 617; H. Fujihara and N. Furukawa, *J. Mol. Struct. (Theochem)*, 1989, **186**, 261.

3 *The Chemistry of Organic Selenium and Tellurium Compounds*, vol. 1 and vol. 2, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986 and 1988.

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

5 H. J. Reich, W. W. Willis and S. Wollowitz, *Tetrahedron Lett.*, 1982, **23**, 3319; J. L. Kice, F. McAfee and H. Slebocka-Tilk, *Tetrahedron Lett.*, 1982, **23**, 3323.