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Oxidation of sterically-crowded selones using chloramine-T: generation and skeletal rearrangement of selone *Se*-imides

Kazuaki Shimada,^{a,*} Keiichi Kodaki,^a Takashi Nanae,^a Shigenobu Aoyagi,^a Yuji Takikawa^a and Chizuko Kabuto^b

^aDepartment of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka, Iwate 020-8551, Japan ^bInstrumental Analysis Center for Chemistry, Faculty of Science, Tohoku University, Sendai, Miyagi 980-8578, Japan

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Abstract

Treatment of sterically-crowded bornane-2-selones possessing substituted bornane skeletons with chloramine-T afforded several products originated from intermediary selone *Se*-imides, and the direct observation of the intermediates was performed by NMR monitoring at low temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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Much interest has been concentrated on the oxidized variants of thiones A in the light of their heterocumulene-like structures and novel reactivities, and recently, the synthetic methods, reactivities, and synthetic uses of thione *S*-imides C have been widely studied. However, in spite of their potentiality as new reactive intermediates and building blocks for various heterocyclic compounds, studies on selone *Se*-imides D have been limited due to the difficulties incurred in

^{*} Corresponding author. Tel: +00-81-19-621-6324; fax: +00-81-19-621-6347; e-mail: shimada@iwate-u.ac.jp

preparation and treatment.¹ Especially, no studies on the isolation or detection of **D** have been reported to date. In the course of our current work on the generation of highly reactive chalcogenocarbonyl species, we attempted the chloramine-T oxidation of selones **B** possessing substituted bornane skeletons according to the kinetic protection methodology. In this paper, we would like to describe the generation, direct NMR observation, and thermal skeletal rearrangement of selone *Se*-imides **D**.

Ketones **1a**,**b** bearing substituents at the C-3 position of the bornane skeleton were at first prepared from *d*-camphor (**1c**),² and **1a**,**b** were then converted into selones **2a**,**b** or thiones **3a**,**b** by using bis(1,5-cyclooctanediylboryl) selenide or Lawesson's reagent, respectively.^{3,4}

When a methanolic solution of sterically-crowded selone 2a or 2b was treated with chloramine-T (2.2 mol amt.) at -78° C, the original deep-blue color of the solution of 3 immediately turned colorless, and selenenamides 6 (6a: 44% from 2a, 6b: 35% from 2b) were obtained along with trace amounts of ketones 1a,b and diselenide 8a or triselenide 8b, respectively, after usual workup.⁵ In all cases, neither selenaziridines nor *p*-toluenesulfonylimines were found in the crude reaction mixture. The structure of 6b was determined by X-ray crystallographic analysis, and the ORTEP drawing of 6b is shown in Fig. 1.⁶



Figure 1. ORTEP drawing of 6b

Furthermore, when a CDCl₃ solution of selone **2b** was treated with a CD₃OD solution of chloramine-T (2.2 mol amt.) at -78° C in an NMR tube and the reaction was monitored by NMR measurements, the NMR signals of **2b** (¹³C NMR: $\delta = 298$ ppm, ⁷⁷Se NMR: $\delta = 1644$ ppm) were quickly extinguished and a new signal assigned to the selenocarbonyl carbon of **4b** was just observed at $\delta = 273$ ppm in the ¹³C NMR spectrum and at $\delta = 1204$ ppm in the ⁷⁷Se NMR spectrum at -78 to -50° C range. Subsequently, when the temperature of the reaction mixture was raised from -50° C to 0° C, the signals of **4b** completely disappeared and a new set of sp^2 carbon signals of the *exo*-methylene group of selenenamide **6b** appeared at $\delta = 163$ and 102 ppm in the ¹³C NMR spectrum and a new sole selenium signal at $\delta = 723$ ppm in the ⁷⁷Se NMR spectrum.⁷ In addition, the signals of byproducts, such as **1b** or **8b**, were not observed throughout the NMR monitoring experiments. These results strongly indicated that selone *Se*-imide **4b** possessing a single geometry was generated in the reaction mixture at low temperature and that **4b** caused skeletal rearrangement to give **6b** exclusively.

When a methanolic solution of thione **3b** was treated with chloramine-T (2.2 mol amt.) at 40°C for 1 h in a similar manner as shown above, sulfenamide 7b (35%) was obtained along with an epimeric mixture of thione S-oxides 10b (23%, combined yield),³ trisulfide 9b (trace), p-toluenesulfonamide, and an epimeric mixture of sulfinylimides 11b (trace, 1:1). It was noteworthy that neither thione S-imide **5b**, thiaziridine, nor p-toluenesulfonylimine was found at all in the crude reaction mixture.¹ Treatment of **7b** with silica gel (excess) in hexane at rt gave **9b** in low yield along with the recovery of 7b, and further treatment of a methanolic solution of 7b with chloramine-T (1.1 mol amt.) at rt gave an epimeric mixture of **11b** (35%, about 1:1). An epimer of **11b** was purified by repeated recrystallization, and the structure of the crystalline epimer of **11b** was finally determined by X-ray crystallographic analysis. The ORTEP drawing of **11b** is shown in Fig. 2.⁸ Thus, it was clarified that 7b, 9b, and 11b possessed the same skeleton as those of 6 and 8 in the selenium series. A similar treatment of an ethanolic solution of **3a** with chloramine-T gave thione S-imide 5a (86%),⁹ and the signal of the thiocarbonyl carbon of 5a in ¹³C NMR was revealed at much higher field region ($\delta = 220$ ppm) than that of the selenocarbonyl carbon of 4b. Heating a toluene solution of 5a at refluxing temperature for 24 h also gave sulfenamide 7a (63%) along with a trace amount of *p*-toluenesulfonamide. It was assumed that the lower thermal stability of **5b** than that of **5a** might be attributed to the preferred *E*-geometry of the C=S moiety of **5b** due to the steric repulsion between the *p*-toluenesulfonyl group and the neighboring spiro-2-indanyl substituent, and the E-isomers of 5 were presumed to cause thermal skeletal rearrangement exclusively to give 7 through abstraction of the C-1 methyl proton. It was suggested that the selective formation of 6 from 4 even at about 0° C, in contrast with the requirement of high temperature for the same skeletal rearrangement from 5a to 7a, might be attributed to facile equilibration of the Se–N bond of 4 under mild reaction conditions.¹⁰



Figure 2. ORTEP drawing of 11b

All the results clearly showed evidence of the in situ generation of selone Se-imides 4 at the primary stage of the reaction of selones 2 with chloramine-T at low temperature. Furthermore, 4

caused thermal skeletal rearrangement to give selenenamides **6** through a similar reaction course to that from thione *S*-imides **5** to sulfenamides **7**. Formation of diselenide **8a** or triselenide **8b** was also explained by hydrolytic cleavage of **6** and the subsequent condensation of the resulting selenenic acids in a similar manner as mentioned in the case of the formation of trisulfide **9b**. In addition, the formation of *p*-toluenesulfonylimines through generation of the intermediary selenaziridines or thiaziridines, respectively, and subsequent thermal selenium or sulfur extrusion might also be sterically suppressed in these cases (Scheme 1).^{1,9b,11}



In conclusion, we have established the generation and direct observation of selone *Se*-imides **4** possessing sterically-crowded bornane skeletons. Further attempts for chemical conversion of **4** into the syntheses of various heterocycles are in progress in our laboratory.

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- 5. Treatment of **6b** with an excess amount of silica gel at rt overnight afforded **8b** (17%) and *p*-toluenesulfonamide along with the recovery of **6b**.
- 6. X-Ray crystallographic data for **6b**: $C_{25}H_{29}NO_2SSe$, FW = 486.53, colorless prism, orthorhombic, $P2_12_12_1$ (#19), a = 14.522(3), b = 15.754(3), c = 10.205(4) Å, V = 2334.8(9) Å³, $D_{calc} = 1.384$ g/cm³, $\mu(CuK\alpha) = 31.71$ cm⁻¹, R = 0.042, $R_w = 0.051$.
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- X-Ray crystallographic data for 11b: C₂₆H₃₁NO₃S, FW=437.60, colorless prism, orthorhombic, P2₁2₁2₁ (#19), a=17.853(2), b=18.248(2), c=7.427(3) Å, V=2419.6(9) Å³, Z=4, D_{calc}=1.201 g/cm³, μ(MoKα)=1.60 cm⁻¹, R=0.056, R_w=0.060.
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