

Photochemical Reaction of 2-Aryl-1,2-benzisoselenazol-3(2H)-ones

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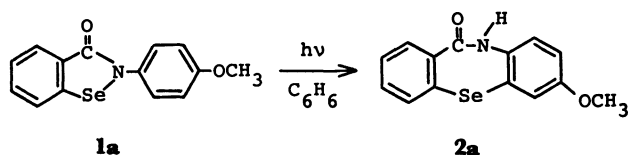
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The photochemical reaction of 2-aryl-1,2-benzisoselenazol-3(2H)-ones (**1**) in benzene was found to give dibenzo[*b,f*][1,4]selenazepin-11(10H)-ones (**2**). On the other hand, the photochemical reaction of **1** in *t*-butyl alcohol afforded 2-(2-hydroxy-2-methylpropylseleno)benzanilide, 2-(methylseleno)benzanilide, and 2-aryl-1,2-benzisoselenazol-3(2H)-one 1-oxides together with the photoisomer **2**. Mechanisms for these reactions are proposed.

Attention regarding the photochemistry of five-membered heterocyclic ring systems continues to be strong because of their use in heterocycle syntheses and studies concerning the reaction mechanisms.¹⁾ Recently, we have reported a novel photoisomerization of 2-aryl-1,2-benzisothiazol-3(2H)-ones to dibenzo[*b,f*][1,4]thiazepin-11(10H)-ones.²⁾ In our systematic investigation of the photochemical reactions of benzisothiazolinones and their analogues, we have studied the photochemical reactions of 2-aryl-1,2-benzisoselenazol-3(2H)-ones, selenium analogues of 2-aryl-1,2-benzisothiazol-3(2H)-ones. The results are described herein.

When a solution containing 2-(4-methoxyphenyl)-1,2-benzisoselenazol-3(2H)-one (**1a**) in benzene was irradiated under argon with 300-nm light, a single photoproduct was obtained. The assignment of this material as 7-methoxydibenzo[*b,f*][1,4]selenazepin-11(10H)-one (**2a**) was made on the basis of spectral data.



Some related 2-aryl-1,2-benzisoselenazol-3(2H)-ones (**1**) were also irradiated under similar conditions to give dibenzo[*b,f*][1,4]selenazepin-11(10H)-ones (**2**) as the only isolable photoproducts. The results are summarized in Table 1.

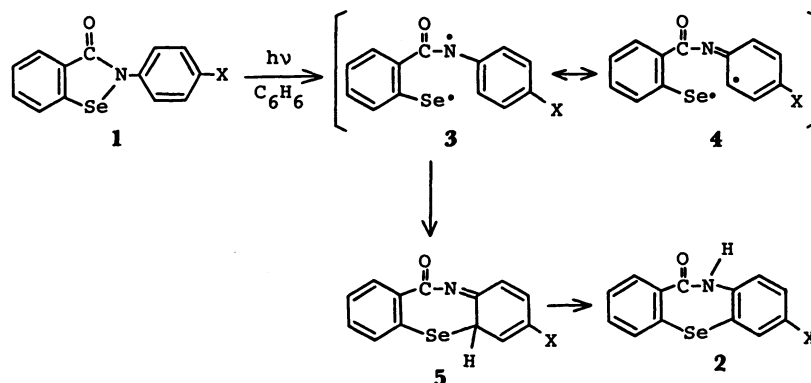
The present results show a very similar feature to that of photochemical reactions of 2-aryl-1,2-benzisothiazol-3(2H)-ones.²⁾ Therefore, the reaction mechanism of **1** is similar to that proposed in the photoisomerization of 2-aryl-1,2-benzisothiazol-3(2H)-ones²⁾ and is outlined in Scheme 1. The photoexcited **1** undergoes a homolytic cleavage of the weakest bond (Se–N) in the molecule to give biradical (**3**). The initially formed biradical recombines at the ortho-position of the *N*-aryl group to give a cyclized product (**5**). A subsequent 1,7-hydrogen shift of the intermediate **5** leads to the final product **2**. The last step of the sequence can proceed by either a thermal or photochemical hydrogen shift.

Recently, Rokach, and Hammel reported that small amounts of a photo-ring expansion product were formed together with 3-phenyl-2(3H)-thiazolone upon irradiation of 2-phenyl-3(2H)-isothiazolone.³⁾ However, we could not detect the corresponding 3-aryl-

Table 1. Photochemical Reaction of **1** in Benzene^{a)}

X in 1	Product	Yield/% ^{b)}
1a OCH ₃	2a	55
1b CH ₃	2b	33
1c H	2c	42

a) The irradiation was carried out on a 2.85×10^{-3} M (1 M = 1 mol dm⁻³) solution of **1** in benzene under argon using a 450-W medium-pressure mercury lamp (Hanovia) through a Pyrex filter (>300 nm). b) The yields are based on the starting materials consumed.

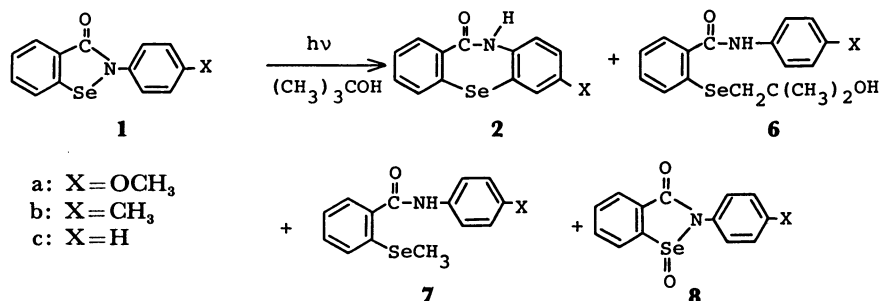


Scheme 1.

2(3*H*)-benzisoselenazolone in the reaction mixture, as in the case similar to the photochemical reaction of 2-aryl-1,2-benzisothiazol-3(2*H*)-one reported recently from our laboratory.²⁾

Irradiation of **1** in *t*-butyl alcohol was also carried out. When a solution containing 2-(4-methoxyphenyl)-1,2-benzisoselenazol-3(2*H*)-one (**1a**) in *t*-butyl alcohol was irradiated under argon with 300 nm light,

the formation of four kinds of photoproducts was indicated by a TLC analysis. The products were separated by silica-gel chromatography and were assigned as **2a**, 4'-methoxy-2-(2-hydroxy-2-methylpropylseleno)benzanilide (**6a**), 4'-methoxy-2-(methylseleno)benzanilide (**7a**), and 2-(4-methoxyphenyl)-1,2-benzisoselenazol-3(2*H*)-one 1-oxide (**8a**) on the basis of their spectral data.



The irradiation of **1b** and **1c** was also carried out in *t*-butyl alcohol in a similar way and the corresponding four photoproducts **2**, **6**, **7**, and **8** were isolated. The results are summarized in Table 2.

The mechanism of the formation of **2** is the same as that proposed regarding the photochemical reaction of **1** in benzene (Scheme 1). Photoproduct **6** seems to be formed via a homolytic cleavage of the photoproduct **2** by the secondary photo-excitation, affording the biradical **9**. The phenyl radical in the biradical intermediate **9** abstracts a hydrogen atom from *t*-butyl alcohol to give a selenyl radical (**10**) and a 2-hydroxy-2-methylpropyl radical (**11**). The homo-

lytic recombination of these radical intermediates, **10** and **11** affords **6** (Scheme 2).

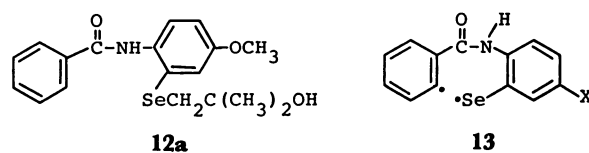
In order to obtain supporting evidence for this mechanism, the isolated **2a** was irradiated in *t*-butyl alcohol, and **6a** was obtained in 47% yield. However, **2a** did not change to **6a** in *t*-butyl alcohol by refluxing the mixture for 3 h and all of the starting material of **2a** was recovered. These findings indicate a secondary photochemical reaction route from **2** to **6**.

We could not detect such a reaction product as **12a** in the photolysis of **1a** in *t*-butyl alcohol. This indicates that **2** does not cleave homolytically to **13** but to **9**. However at present we can not propose any explanation.

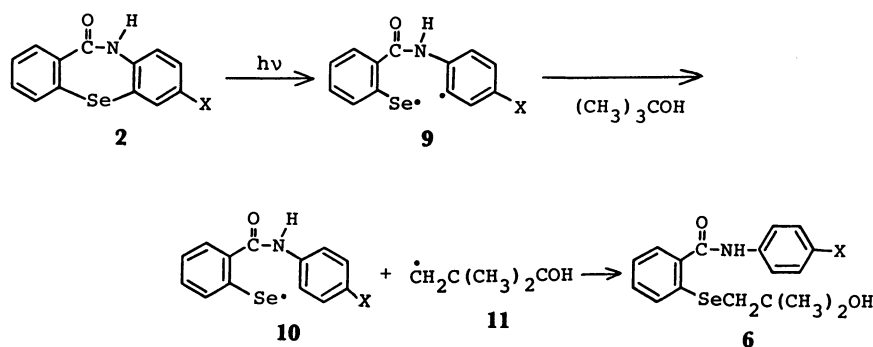
Table 2. Photochemical Reaction of **1** in *t*-Butyl Alcohol

X in 1	Product (Yield/% ^a)			
1a OCH ₃	2a 35	6a 17	8a 9	
1b CH ₃	2b 24	6b 8	8b 3	
1c H	2c 19	6c 8	8c 4	

a) The yields are based on the starting materials consumed.

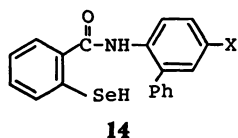


The photochemical cleavage of **2** to **9** suggests that the photochemical reaction of **1** in benzene has a



Scheme 2.

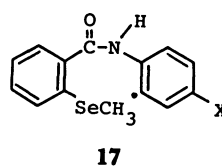
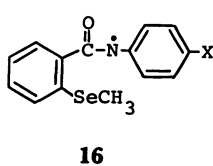
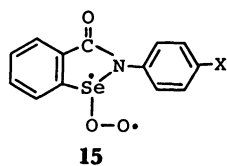
possibility of affording such a compound as **14**.



The absence of **14** in the photolysis of **1** in benzene means that **2** does not give **9** in a benzene solution or **9**, once formed, recombines to **2** again in a solvent cage faster than it reacts with the solvent benzene.

The formation of **7** is of considerable interest; however, it is very difficult to understand how the methyl group of compound **7** is introduced. It is certain that it comes from the methyl group of *t*-butyl alcohol, but the mechanism is not clear. One plausible interpretation is that formation of **7** is

closely related to the formation of a photooxidized product **8**. The mechanism of the formation of **8** is a direct photooxidation, as we reported previously regarding the photochemical reaction of 2-aryl-1,2-benzisothiazolinones.²⁾ Another report was made by Tezuka et al.⁴⁾ The photooxidized product **8** was formed in spite of the fact that the photoreaction was carried out under argon gas. This means that a slight amount of oxygen was still present in *t*-butyl alcohol, and it oxidized **1** directly by irradiation, affording the peroxy radical **15**. The intermediate **15** oxidized the solvent *t*-butyl alcohol and afforded selenoxide **7** and *t*-butoxyl radical. The *t*-butoxyl radical decomposed to a methyl radical and acetone, and the methyl radical attacked either the selenium atom of compound **1** to give a radical **16** or compound **2** to give a radical **17**. Either of these could abstract a hydrogen atom from *t*-butyl alcohol to give the final product **7**.



Experimental

Measurement. All melting points were uncorrected. IR and UV spectra were determined on a Hitachi EPI-G2 and a Hitachi 220A spectrometer. ¹H NMR spectra were recorded at 60 and 400 MHz using a JEOL JNM-PMX 60SI and a JEOL JNM-GX 400 spectrometer, respectively, using tetramethylsilane as an internal standard. Mass spectra were determined with a JEOL JMS-DX 300 high-resolution mass spectrometer with a JEOL JMA 5000 mass-data system with an ionization energy of 70 eV. Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer.

Preparation of 2-Aryl-1,2-benzisoselenazol-3(2H)-ones (1). To a stirred solution containing 14.0 g of *o*-aminobenzoic acid and 20 cm³ of concd hydrochloric acid in 20 cm³ of water cooled with an ice bath under 5 °C was added dropwise to 9.0 g of sodium nitrite in 20 cm³ of water. A solution of 2-carboxybenzenediazonium chloride resulted; this was added dropwise to a stirred solution containing sodium diselenide which was prepared in advance by the reaction of 8.8 g of selenium powder, 8.8 g of rongalite, and 4.4 g of sodium hydroxide in 60 cm³ of water. The mixture was stirred for an additional 2 h after an initial evolution of nitrogen gas had been completed. It was confirmed that the solution was basic using litmus paper. The reaction mixture was acidified with hydrochloric acid and the precipitated solid was collected by filtration, washed with water, and dried in a desiccator to give 20.0 g (90% yield) of a crude solid of 2,2'-diselenobis[benzoic acid]; mp 293 °C (lit.⁵⁾ mp 295 °C).

A mixture of 3.0 g of 2,2'-diselenobis[benzoic acid] and 15 cm³ of thionyl chloride was heated at reflux for 3 h. The excess thionyl chloride was removed under reduced pressure and the residual solid was recrystallized from hexane to give 3.1 g (81% yield) of pale-yellow crystals of pure 2-(chloroseleno)benzoyl chloride; mp 63–64 °C (lit.⁶⁾ mp 65 °C).

To a stirred solution containing 32 mmol of appropriate arylamine in 30 cm³ of ether was added dropwise 3.0 g of 2-(chloroseleno)benzoyl chloride in 40 cm³ of ether over a 30 min period, and the mixture was stirred for an additional 3 h. The solvent was removed under reduced pressure and the residue was subjected to chromatography on silica-gel using a 4:1 mixture of dichloromethane–ethyl acetate as the eluent to give pure **1**. The following compounds were prepared by this procedure.

2-(4-Methoxyphenyl)-1,2-benzisoselenazol-3(2H)-one (1a). Yield, 65%; mp 178–179 °C; IR (KBr) 1600 cm⁻¹ (s, amide C=O); ¹H NMR (CDCl₃) δ=3.80 (3H, s), 6.90 (2H, d, *J*=8.4 Hz), 7.35 (2H, d, *J*=8.4 Hz), and 7.3–8.1 (4H, m); UV (methanol) 265 (log ε=4.57) and 325 nm (4.19); MS, *m/z* 305 (M⁺), 274, 225, and 184; HRMS, *m/z* 304.9924 (C₁₄H₁₁NO₂Se requires 304.9954).

2-(*p*-Tolyl)-1,2-benzisoselenazol-3(2H)-one (1b). Yield, 65%; mp 169–170 °C; IR (KBr) 1620 cm⁻¹ (s, amide C=O); ¹H NMR (CDCl₃) δ=2.37 (3H, s), 7.20 (2H, d, *J*=8.4 Hz), 7.52 (2H, d, *J*=8.4 Hz), and 7.3–8.2 (4H, m); UV (methanol) 265 (log ε=3.61) 325 nm (3.25); MS, *m/z* 289 (M⁺), 274, and 209; HRMS, *m/z* 289.0017 (C₁₄H₁₁NOSe requires 289.0005).

2-Phenyl-1,2-benzisoselenazol-3(2H)-one (1c). Yield, 86%; mp 179–180 °C; IR (KBr) 1600 cm⁻¹ (s, amide C=O);

^1H NMR (CDCl_3) δ =7.20–8.13 (9H, m); UV (methanol) 260 (log ϵ =3.37) and 325 nm (3.30); MS, m/z 275 (M^+) and 195; HRMS, m/z 274.9845 ($\text{C}_{13}\text{H}_9\text{NOSe}$ requires 274.9849).

Photolysis of 2-Aryl-1,2-benzisoselenazol-3(2H)-one (1) in Benzene. A solution containing 0.65 mmol of 2-aryl-1,2-benzisoselenazol-3(2H)-one (**1**) in 230 cm^3 of benzene was irradiated under argon through a Pyrex filter sleeve using a 450-W Hanovia medium-pressure mercury lamp for 10 h. A removal of the solvent left a light-brown residue which was purified by silica-gel chromatography using chloroform as the eluent. Photoproduct **2** was isolated with the recovered starting material **1**. The physical, spectral data, and analyses of the photoproducts **2** are as follows:

7-Methoxydibenzo[*b,f*][1,4]selenazepin-11(10H)-one (2a). Mp 213 °C (from chloroform–hexane); IR (KBr) 2950–3200 (w, amide N–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR ($\text{DMSO}-d_6$) 400 MHz, δ =3.73 (3H, s), 6.92 (1H, dd, J =8.8 and 2.6 Hz), 7.14 (1H, d, J =8.4 Hz), 7.23 (1H, d, J =2.6 Hz), 7.37–7.64 (4H, m), and 10.39 (1H, s); MS, m/z 305 (M^+), 274, 225, and 210; HRMS, m/z 304.9951 ($\text{C}_{14}\text{H}_{11}\text{NO}_2\text{Se}$ requires 304.9954).

7-Methyldibenzo[*b,f*][1,4]selenazepin-11(10H)-one (2b). Mp 268–269 °C (from chloroform–hexane); IR (KBr) 2900–3200 (w, amide N–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR ($\text{DMSO}-d_6$) 400 MHz, δ =2.23 (3H, s), 7.12 (1H, d, J =8.4 Hz), 7.14 (1H, d, J =8.4 Hz), 7.39–7.41 (2H, m), 7.50 (1H, s), 7.59–7.62 (2H, m), and 10.48 (1H, s); MS, m/z 289 (M^+) and 209; HRMS, m/z 288.9991 ($\text{C}_{14}\text{H}_{11}\text{NOSe}$ requires 289.0005).

Dibenzo[*b,f*][1,4]selenazepin-11(10H)-one (2c). Mp 273.5 °C (from chloroform–hexane); IR (KBr) 2950–3200 (w, amide N–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR ($\text{DMSO}-d_6$) 400 MHz, δ =7.11 (1H, t, J =7.7 Hz), 7.22 (1H, d, J =7.7 Hz), 7.34 (1H, t, J =7.7 Hz), 7.40–7.43 (2H, m), 7.60–7.65 (2H, m), 7.68 (1H, d, J =7.7 Hz), and 10.59 (1H, s); MS, m/z 275 (M^+) and 195; HRMS, m/z 274.9854 ($\text{C}_{13}\text{H}_9\text{NOSe}$ requires 274.9849).

Photolysis of 2-Aryl-1,2-benzisoselenazol-3(2H)-one (1) in *t*-Butyl Alcohol. A solution containing 0.65 mmol of 2-aryl-1,2-benzisoselenazol-3(2H)-one (**1**) in 230 cm^3 of *t*-butyl alcohol was irradiated under argon through a Pyrex filter sleeve using a 450-W Hanovia medium-pressure mercury lamp for 10 h. A TLC analysis showed that four photoreaction products were formed. The solvent was removed under reduced pressure to give a light-brown residue which was purified by preparative TLC using chloroform as the eluent. Photoproducts **2**, **6**, **7**, and **8** were isolated, and the physical and spectral data of these products are as follows:

4'-Methoxy-2-(2-hydroxy-2-methylpropylseleno)benzanilide (6a). IR (neat) 2900–3000 (w, amide N–H and O–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =1.33 (6H, s), 1.55 (1H, s), 3.21 (2H, s), 3.81 (3H, s), 6.90 (2H, d, J =9.0 Hz), 7.57 (2H, d, J =9.0 Hz), 7.2–8.3 (4H, m), and 8.13 (1H, s); MS, m/z 379 (M^+) and 306; HRMS, m/z 379.0700 ($\text{C}_{18}\text{H}_{21}\text{NO}_3\text{Se}$ requires 379.0684).

4'-Methoxy-2-(methylseleno)benzanilide (7a). Mp 266–267 °C (from benzene–hexane); IR (KBr) 3300 (s, amide N–H) and 1635 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =2.27 (3H, s), 3.73 (3H, s), 6.82 (2H, d, J =8.4 Hz), 7.42 (2H, d, J =8.4 Hz), 7.0–8.1 (4H, m); MS, m/z 321 (M^+), 306, 225, 199, and 122. Found: C, 56.24; H, 4.76; N, 3.99%. Calcd for

$\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Se}$: C, 56.25; H, 4.72; N, 4.37%.

2-(4-Methoxyphenyl)-1,2-benzisoselenazol-3(2H)-one 1-Oxide (8a). Mp 212–213 °C (from benzene); IR (KBr) 1690 (s, C=O) and 820 cm^{-1} (s, Se=O); ^1H NMR (CDCl_3) δ =3.80 (3H, s), 7.37 (2H, d, J =8.8 Hz), 7.50 (2H, d, J =8.8 Hz), 7.80–7.95 (3H, m), and 8.24 (1H, d, J =7.7 Hz); MS, m/z 321 (M^+), 305, 290, and 225; HRMS, m/z 320.9828 ($\text{C}_{14}\text{H}_{11}\text{NO}_3\text{Se}$ requires 320.9903).

4'-Methyl-2-(2-hydroxy-2-methylpropylseleno)benzanilide (6b). IR (neat) 3000–3500 (w, amide N–H and O–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =2.00 (1H, s), 2.15 (1H, s), 2.36 (3H, s), 3.10 (2H, s), 7.12–7.95 (8H, m); MS, m/z 363 (M^+); HRMS, m/z 363.0031 ($\text{C}_{18}\text{H}_{21}\text{NO}_2\text{Se}$ requires 363.0681).

4'-Methyl-2-(methylseleno)benzanilide (7b). Mp 252.5–253.5 °C; IR (KBr) 3300 (s, amide N–H) and 1620 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =2.30 (3H, s), 2.74 (3H, s), 7.67–8.11 (8H, m), and 8.20 (1H, s); MS, m/z 305 (M^+) and 209; HRMS, m/z 305.0281 ($\text{C}_{15}\text{H}_{15}\text{NOSe}$ requires 305.0318).

2-(4-Methylphenyl)-1,2-benzisoselenazol-3(2H)-one 1-Oxide (8b). Mp 182–183 °C; IR (KBr) 1680 (s, C=O) and 810 cm^{-1} (s, S=O); ^1H NMR (CDCl_3) δ =2.26 (3H, s), 7.10–7.52 (8H, m); MS, m/z 305 (M^+); HRMS, m/z 305.0037 ($\text{C}_{14}\text{H}_{11}\text{NO}_2\text{Se}$ requires 304.9954).

2-(2-Hydroxy-2-methylpropylseleno)benzanilide (6c). IR (neat) 3000 (w, amide N–H and O–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =1.31 (1H, s), 1.33 (6H, s), 3.13 (2H, s), 7.20–7.69 (9H, m), and 8.20 (1H, s); MS, m/z 349 (M^+); HRMS, m/z 349.0602 ($\text{C}_{17}\text{H}_{19}\text{NO}_2\text{Se}$ requires 349.0580).

2-(Methylseleno)benzanilide (7c). Mp 169–170 °C; IR (KBr) 3300 (s, amide N–H) and 1640 cm^{-1} (s, amide C=O); ^1H NMR (CDCl_3) δ =2.23 (3H, s), 7.00–7.79 (9H, m), and 7.97 (1H, s); MS, m/z 291 (M^+), 276, and 199; HRMS, m/z 291.0123 ($\text{C}_{14}\text{H}_{13}\text{NOSe}$ requires 291.0161).

2-Phenyl-1,2-benzisoselenazol-3(2H)-one 1-Oxide (8c). Mp 180–181 °C; IR (KBr) 1680 (s, C=O) and 810 cm^{-1} (s, Se=O); ^1H NMR (CDCl_3) δ =7.20–7.87 (10H, m); MS, m/z 291 (M^+); HRMS, m/z 291.0081 ($\text{C}_{13}\text{H}_9\text{NO}_2\text{Se}$ requires 290.9798).

Photolysis of 7-Methoxydibenzo[*b,f*][1,4]selenazepin-11-(10H)-one (2a). A solution containing 14 mg of 7-methoxydibenzo[*b,f*][1,4]selenazepin-11(10H)-one (**2a**) in 20 cm^3 of *t*-butyl alcohol was irradiated in a degassed sealed tube using a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter sleeve for 10 h. The solvent was removed under reduced pressure to give a residue which was subjected to the silica-gel preparative TLC using chloroform as the eluent. 4'-Methoxy-2-(2-hydroxy-2-methylpropylseleno)benzanilide (**6a**) 6.6 mg (47% yield) was isolated.

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