

## Photochemical Dimerization of a Benzoselenete Derivative

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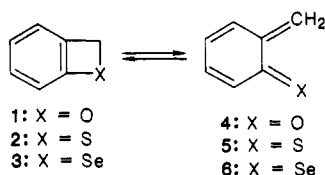
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A synthetic approach to a benzoselenete derivative is examined. Photolysis of 2-diazobenzo[*b*]selenophen-3(2*H*)-one (7) in methanol gave mainly 2-methoxybenzo[*b*]selenophen-3(2*H*)-one (11). Photolysis of 3-diazobenzo[*b*]selenophen-2(3*H*)-one (8) in methanol gave dimethyl 1,5-diazo[*b,f*]diselenocin-2,6-dicarboxylate (14) instead of methyl 2*H*-1-benzoselenete-2-carboxylate (9). 14 is generated presumably by dimerization of the benzoselenete derivative. A theoretical comparative study of the benzothiete and benzoselenete is made on their parent compounds. An STO-3G *ab initio* MO calculation reveals that the *o*-quinoid forms of both compounds are absent in the ground state. The dimerization is suggested to take place in the lowest ( $n,\pi^*$ ) type excited state.

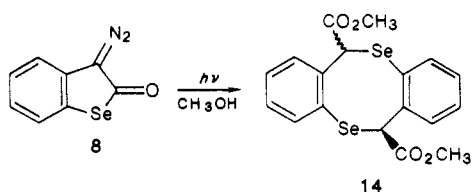
## I. Introduction

Benzo-condensed four-membered heterocyclic ring systems are of special theoretical and synthetic interest because of their valence isomerization between the strained benzenoid form (1-3) and the *o*-quinoid form (4-6).<sup>1</sup>



Benzoxetes 1 are hitherto unknown. All the published benzoxetes 1 have been found to have different structures.<sup>2</sup> Benzothiete (2) and its derivative were synthesized successfully.<sup>3</sup> No synthetic approach to benzoselenetes 3 is known. We now report synthetic efforts to generate the benzoselenete derivative.

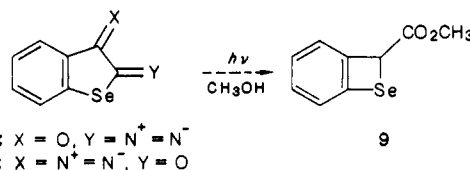
Here we describe that photolysis of 3-diazobenzo[*b*]selenophen-2(3*H*)-one (8) in methanol gave dimethyl 1,5-diazo[*b,f*]diselenocin-2,6-dicarboxylate (14) instead of methyl 2*H*-1-benzoselenete-2-carboxylate (9). 14 is generated presumably by dimerization of the benzoselenete derivative.



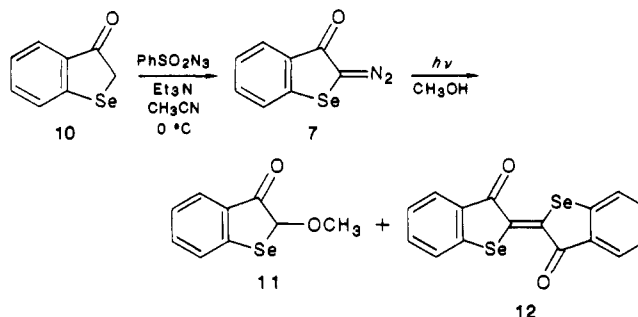
We compare the propensities of benzothiete and benzoselenete for the ring opening with the aid of *ab initio* molecular orbital calculations.

## II. Synthetic Results

2-Diazobenzo[*b*]selenophen-3(2*H*)-one (7) and 3-diazobenzo[*b*]selenophen-2(3*H*)-one (8) are expected to form methyl 2*H*-1-benzoselenete-2-carboxylate (9) via the photo-Wolff rearrangement. We attempted synthesis and photoreaction of 7 and 8.

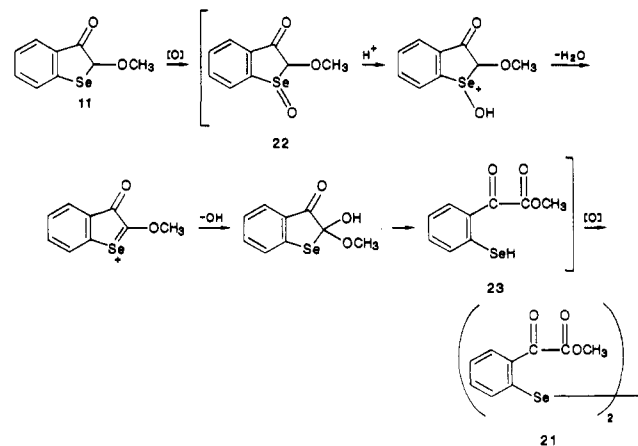


Benzo[*b*]selenophen-3(2*H*)-one (10)<sup>4</sup> was treated with benzenesulfonyl azide<sup>5</sup> at 0 °C in acetonitrile with Et<sub>3</sub>N to give 7 (47%). When the diazo ketone 7 was photolyzed



(5) When *p*-toluenesulfonyl azide was used alternatively, 7 was obtained in 36% yield.

(6) 11 is sensitive to air oxidation to give mainly diselenide 21 (18-70% yield). 21 is characterized by elemental analysis and NMR, IR, and MS spectra. For 21, see: Lesser, R.; Schoeller, A. *Chem. Ber.* 1914, 47, 2292. A possible mechanism from 11 to 21 can be assumed as follows. 11 is oxidized by atmospheric oxygen to form the selenoxide 22 initially. 22 is transformed to 23 via a seleno-Pummerer rearrangement. 23 is oxidized readily to give the stable diselenide 21. For examples of seleno-Pummerer rearrangement, see: (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* 1975, 97, 5434. (b) Norcross, B. E.; Lansinger, J. M.; Martin, R. L. *J. Org. Chem.* 1977, 42, 369.



(7) Evers, M.; Weber, R.; Thibaut, P.; Christiaens, L.; Renson, M.; Croisy, A.; Jacquignon, P. *J. Chem. Soc., Perkin Trans. I* 1976, 2452.

(1) Kanakarajan, K.; Meier, H. *J. Org. Chem.* 1983, 48, 881 and references cited therein.

(2) (a) Meier, H.; Issa, A.; Merkle, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, 34B, 290. (b) Meier, H.; Schneider, H.-P.; Rieker, A.; Hitchcock, P. B. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 121.

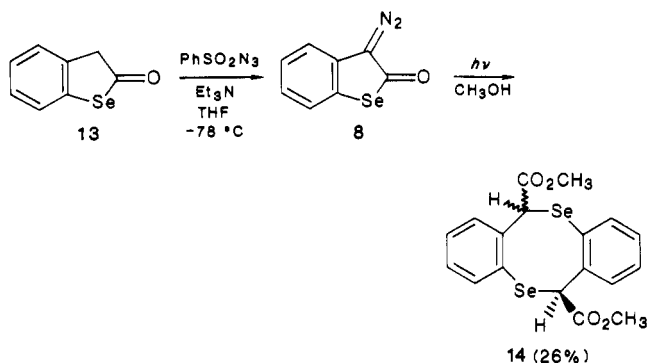
(3) (a) Van Tilborg, W. J. M.; Plomp, R. *J. Chem. Soc., Chem. Commun.* 1977, 130. (b) Voigt, E.; Meier, H. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 117.

(4) (a) Lesser, R.; Weiss, R. *Chem. Ber.* 1912, 45, 1835. (b) Cagniant, P.; Kirsch, G. *Compt. Rend., Ser. C* 1972, 274, 711.

in methanol with a 100-W high pressure mercury lamp (Pyrex filter) for 1 h at  $-20\text{ }^{\circ}\text{C}$ , the photolysate product consisted mainly of 2-methoxybenzo[*b*]selenophen-3-(2*H*)-one (11)<sup>6</sup> on the basis of  $^1\text{H}$  NMR. The minor product 12<sup>4a</sup> (5%) was also obtained from the photolysate.

Irradiation of 7 in methanol leads, by nitrogen elimination, via the carbene intermediate to the major product 11 and the minor product 12. The photo-Wolff rearrangement did not occur.

3-Diazobenzo[*b*]selenophen-2(3*H*)-one (8) was also obtained by treatment of benzo[*b*]selenophen-2(3*H*)-one (13)<sup>7</sup> with benzenesulfonyl azide<sup>8</sup> ( $-78\text{ }^{\circ}\text{C}$ , THF/ $\text{Et}_3\text{N}$ ) in 24% yield.

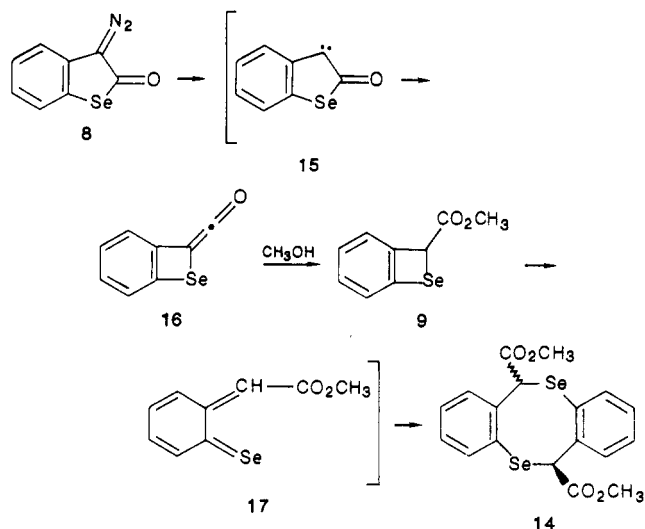


Photochemical reaction of 8 (with Pyrex filter) in methanol (1 h,  $-20$  to  $-60\text{ }^{\circ}\text{C}$ ) gave 14 having the molecular formula  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Se}_2$  (26%) as the major isolable product. Its IR spectrum ( $1724\text{ cm}^{-1}$ ) shows the presence of ester groups. The  $^1\text{H}$  NMR spectrum of 14 exhibited a 6 H singlet assignable to  $\text{CO}_2\text{CH}_3$  groups at  $\delta$  3.83 and a 2 H singlet at  $\delta$  6.62 together with 2 H triplet at  $\delta$  6.81, 4 H multiplet at  $\delta$  7.14–7.22, and 2 H doublet at  $\delta$  7.36. The  $^{13}\text{C}$  NMR spectrum of 14 exhibited two  $\text{sp}^3$  carbons ( $\delta$  45.05 (d), 53.10 (q)), six aromatic carbons ( $\delta$  127.4 (d), 128.4 (d), 129.8 (d), 130.0 (s), 136.4 (d), 140.0 (s)), and a carbonyl carbon (170.4 (s)). By  $^{13}\text{C}$ - $^1\text{H}$  selective decoupling, a singlet ( $^1\text{H}$  NMR  $\delta$  6.62 ppm) is assigned to the methine protons adjacent to the  $\text{sp}^3$  carbons ( $^{13}\text{C}$  NMR  $\delta$  45.05 ppm). The protons of 6.62 ppm are located at extremely low field, which suggests that selenium atoms are adjacent to the methine carbons. From these spectral features, the structure of 14 may be assigned as dimethyl 1,5-dibenzo[*b,f*]diselenocin-2,6-dicarboxylate, resulting from the dimerization of 9. The configuration will be discussed in section III.

Together with 14 a small amount of minor products was obtained in this reaction. Because of the small quantity, the difficult separation, and their instability, the mixture could not be purified (see Experimental Section).

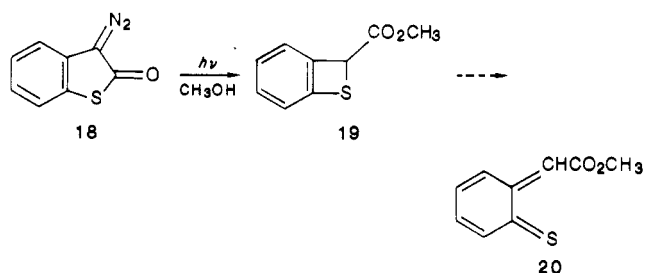
The formation of 14 could be interpreted as follows.<sup>10</sup> The photochemical primary step affords the carbene 15, which subsequently rearranges to the ketene 16. Addition of methanol to 16 is followed by ring opening of 9. After 9 is converted to 17, the latter dimerizes to give 14.

Under the same conditions, benzothiete derivative 19 was obtained (30% yield).<sup>3b</sup> Even if the reaction of 8 was



prematurely interrupted, no benzoselenete derivative 9 could be isolated, and only the starting material 8 and the dimeric products 14 were obtained.

These findings suggest that the photochemical ring opening of  $9 \rightarrow 17$  is more favorable than that of  $19 \rightarrow 20$ .



### III. Mechanistic Consideration

The isolation of the dimeric form of the benzoselenete derivatives is discussed in terms of the molecular orbital (MO) scheme. First, the stabilities of the strained benzenoid form ( $\text{X} = \text{S}$ , 2) and the *o*-quinoid form ( $\text{X} = \text{S}$ , 5) are compared.

With the geometry optimization of the STO-3G basis set,<sup>9</sup> 2 is calculated to be 49.5 kcal/mol more stable than 5 in the ground state,  $\text{S}_0$ .  $E_T$  is the total energy in hartrees (1 hartree = 627.52 kcal/mol). Thus for the benzothiete, the *o*-quinoid form is practically absent (exclusively, 2) in the ground state,  $\text{S}_0$ .  $E_T$  of the lowest excited triplet state  $\text{T}_1$  is calculated with the  $\text{S}_0$  geometry. Noteworthy is the result that  $\text{T}_1(n, \pi^*)$  is energetically more stable (20.3 kcal/mol) than  $\text{S}_0$  in 5. In the lowest excited state, only the isomer 5 is likely (no 2). Thus, the stability order of 2 and 5 is opposite in  $\text{S}_0$  and  $\text{T}_1$  states.

Geometries and total energies of 3 and 6 are shown below. The trend of the energetic contrast (in  $\text{S}_0$  3 only, and in  $\text{T}_1$  6 only) is similar to that of 2 and 5. We could not find any significant differences of computed data between S and Se compounds. In the photochemical route, the carboxylate *o*-quinoid form 17 ( $\text{T}_1$ ) predominates. There is a choice of whether 17 is deactivated to give the benzoselenete 9 ( $\text{S}_0$ ) or its proceeds to photodimerization to give 14. The choice seems to hold also for the sulfur compound.

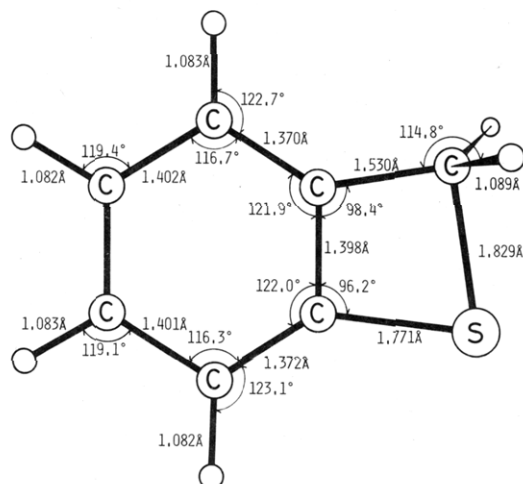
The pattern of the photodimerization is discussed in 6 (without the  $\text{CH}_3\text{COO}$  group). In the  $\text{T}_1$  state,  $6^*$ , the singly occupied MO's,  $\pi$  and  $\pi^*$ , are frontier orbitals to give the adduct. The following two dominant orbital interactions are "in-phase" (symmetry allowed) in the exciplex,  $6^* \cdots 6$ . According to this dimerization path, the following

(8) When *p*-toluenesulfonyl azide was used alternatively, 8 was obtained in 9% yield.

(9) Ab initio MO calculations were made by using the GAUSSIAN 82 program. J. S. Brinkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, and J. A. Pople, Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, PA, 1984. The lowest excited state was approximated by the UHF triplet state.

(10) For references of the Wolff rearrangement of  $\alpha$ -diazo carbonyl compounds, see: Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 32 and ref 3b.

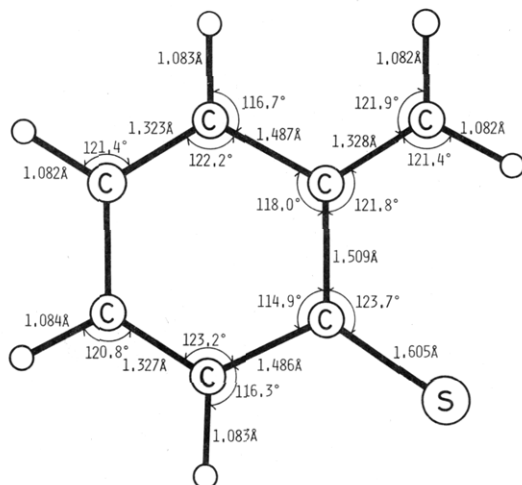
molecular model (with the  $C_2$  symmetry) may be constructed. Therefore, it is thought stereochemically that the diastereomer of 14, 14' is unstable due to the exchange repulsion between the benzene  $\pi$  electronic cloud and the methoxy group, X.



$$E_T = -658.47146 (S_0)$$

$$E_T = -658.32963 (T_1)$$

2



$$E_T = -658.39253 (S_0)$$

$$E_T = -658.42486 (T_1)$$

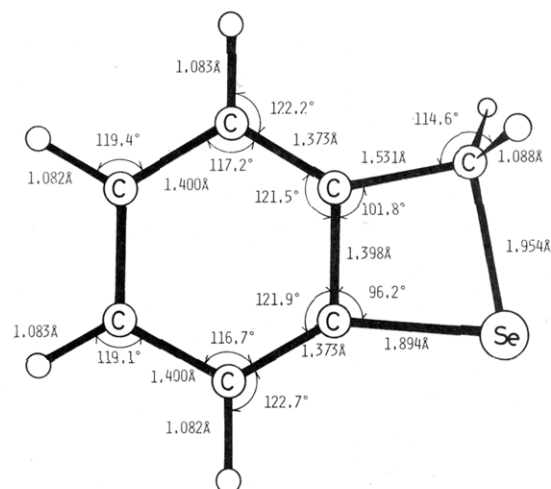
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#### IV. Concluding Remarks

In this work, the synthesis of the benzoselenetes was attempted. However, the photochemical product is not the strained benzoselenete derivative but its dimeric form. Photolysis of 3-diazobenzo[*b*]selenophen-2(3*H*)-one (8) in methanol gave dimethyl 1,5-dibenzo[*b,f*]diselenocin-2,6-dicarboxylate (14).

According to a theoretical calculation, the *o*-quinoid form (5 and 6) needed to initiate the dimerization is absent in the ground state,  $S_0$ . The dimerization of 5 and 6 should occur photochemically. In the lowest excited triplet state  $^3(n, \pi^*)$ , the *o*-quinoid form is much more stable than the strained benzenoid form. The stability provides the condition of the dimerization for the  $\pi$ - $\pi$  and  $\pi^*$ - $\pi^*$  frontier-orbital interactions.

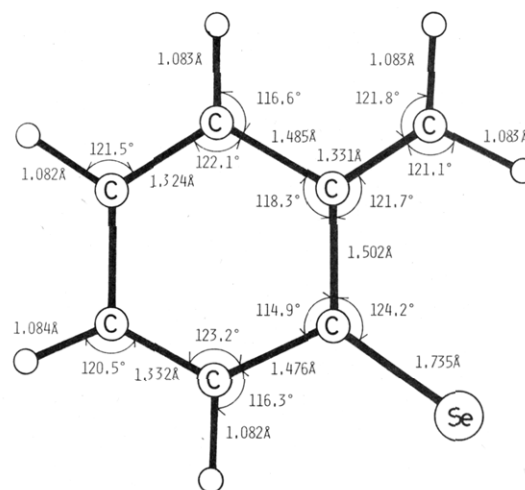
Two reaction channels from 5 and 6 of the lowest excited state are likely. One is the deactivation with the ring closure to the ground-state product (5  $\rightarrow$  2 and 6  $\rightarrow$  3, respectively). The other is the above-mentioned photo-dimerization.



$$E_T = -2639.59734 (S_0)$$

$$E_T = -2639.47593 (T_1)$$

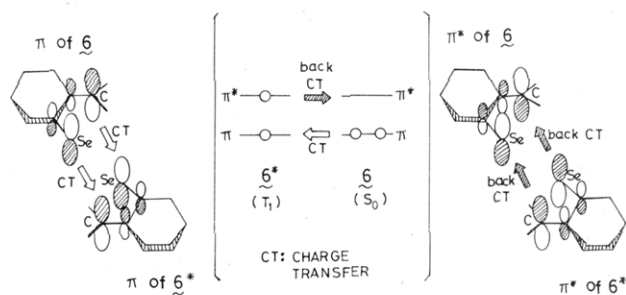
3



$$E_T = -2639.52043 (S_0)$$

$$E_T = -2639.55446 (T_1)$$

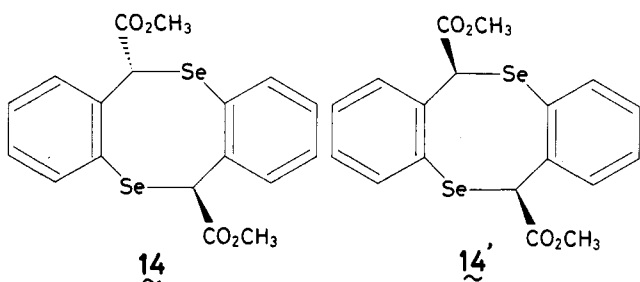
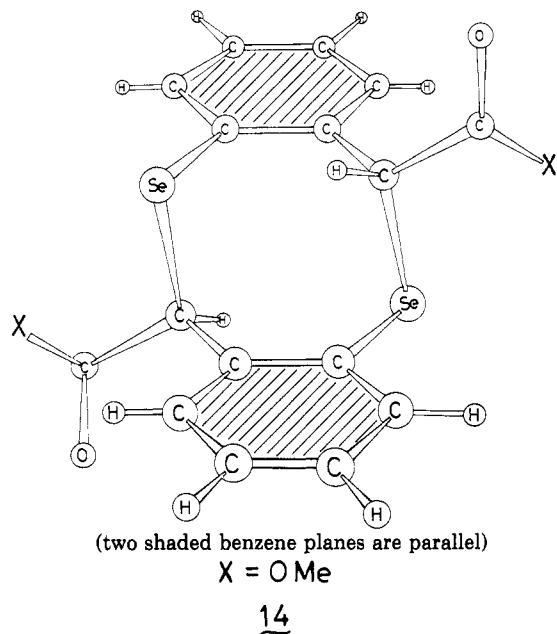
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According to the calculated electronic structure of 5 and 6, we could not find any noticeable difference in the reactivity. The similarity or the difference of the photochemical behavior between S and Se compounds is to be solved by further work.

#### V. Experimental Section

**General Methods.** Melting points are uncorrected. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. NMR spectra were recorded in  $CDCl_3$  on a JEOL FX-200 spectrometer. For the  $^1H$  and  $^{13}C$  NMR spectra,  $Me_4Si$  was used as an internal reference.  $^{13}C$  NMR multiplicities were determined by INEPT experiments. Mass spectra were determined on a JEOL JMS-01SG-2 spectrometer and UV/vis spectra were measured with



a Hitachi 200-20 spectrophotometer. High pressure liquid chromatograph (HPLC) was performed on JASCO Triotar-II instrument. All reactions were carried out under a nitrogen atmosphere.

**2-Diazobenzo[b]selenophen-3(2H)-one (7).** To a mixture of benzo[b]selenophen-3(2H)-one (10) (400 mg, 1.01 mmol) and triethylamine (0.80 ml, 5.74 mmol) in 8 mL of acetonitrile was added benzenesulfonyl azide (1.46 g, 7.38 mmol) at 0 °C. After the addition of water, the mixture was extracted with ether. The extracts were washed with 1 N aqueous NaOH and water and dried. Removal of the solvent and separation by column chromatography on silica gel with benzene ( $R_f = 0.2$ ) gave 7 (199 mg, 47%). 7: orange crystals, mp 92–93 °C (from hexane–benzene);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.36–7.64 (m, 3 H), 7.96 (d,  $J = 8.0$  Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  58.03, 126.1, 126.2, 127.3, 131.9, 134.0, 138.2, 187.0 ppm; IR (KBr) 2070, 1610, 1590, 1580  $\text{cm}^{-1}$ ; UV (methanol)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 257 (4.20), 399 (3.83); MS (70 eV),  $m/z$  (relative intensity) 224 (38), 196 (52), 168 (100); exact mass  $M^+$  223.9602 (calcd for  $\text{C}_8\text{H}_4\text{N}_2\text{OSe}$  223.9488).

**Photolysis of 7 in Methanol.** A solution of 7 (170 mg, 0.76 mmol) in 270 mL of methanol was irradiated with a 100-W high pressure mercury lamp and a Pyrex apparatus for 1 h at –20 °C. Removal of the solvent gave 172 mg of the crude photolysate. The crude photolysate consists of mainly 11<sup>6</sup> on the basis of  $^1\text{H NMR}$ . 11 was purified by distillation of the photolysate. Column chromatography on silica gel (containing 5% water) with benzene of the photolysate gave 12 ( $R_f = 0.7$ , 5% yield) and 21 ( $R_f = 0.4$ , 18% yield). 11: a pale yellow oil, bp 100 °C/1 mmHg;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.49 (s, 3 H), 6.09 (s, 1 H), 7.21–7.29 (m, 1 H), 7.43–7.56 (m, 2 H), 7.78 (d,  $J = 8.3$  Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  57.87, 87.69, 125.9, 128.1, 128.6, 131.3, 136.6, 144.4, 199.6 ppm; IR ( $\text{CHCl}_3$ ) 1690  $\text{cm}^{-1}$ ; MS (70 eV),  $m/z$  (relative intensity) 228 (100), 198 (73), 157 (94); exact mass  $M^+$  227.9628 (calcd for  $\text{C}_9\text{H}_8\text{O}_2\text{Se}$

227.9686). 12: a violet solid, sublimed at about 260 °C; MS (70 eV),  $m/z$  (relative intensity) 392 (100), 390 (86), 388 (54); IR (KBr) 1635  $\text{cm}^{-1}$ . 12 is not sufficiently soluble in organic solvents. These properties of 12 are in agreement with those of known selenoindigo 12.<sup>4a</sup>

21: yellow crystals, mp 147–148 °C (from methanol);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.04 (s, 6 H), 7.31–7.49 (m, 4 H), 7.90 (d,  $J = 7.7$  Hz, 2 H), 7.97 (dd,  $J = 7.7$ , 1.6 Hz, 2 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  53.10, 126.2, 130.6, 131.7, 134.4, 134.9, 137.6, 163.7, 186.8 ppm; IR (KBr) 1735, 1650  $\text{cm}^{-1}$ ; MS (70 eV),  $m/z$  (relative intensity) 486 (2), 484 (9), 482 (9), 242 (100). Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_6\text{Se}_2$ : C, 44.65; H, 2.91. Found: C, 44.56; H, 3.15.

**3-Diazobenzo[b]selenophen-3(2H)-one (8).** To a mixture of benzo[b]selenophen-2(3H)-one (13) (100 mg, 0.507 mmol) and triethylamine (0.071 ml, 0.509 mmol) in 2 mL of THF was added dropwise benzenesulfonyl azide (100 mg, 0.546 mmol) in 0.50 ml of THF at –78 °C. The mixture was stirred for 3 h at –78 °C. After the addition of water the mixture was extracted with ether. The extracts were washed with 1 N aqueous NaOH and water and dried. Removal of the solvent and separation by column chromatography on silica gel with benzene ( $R_f = 0.6$ ) gave 8 (25.3 mg, 24%). 8: pale yellow crystals, mp 64.0–65.0 °C (from methanol);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.14 (dd,  $J = 7.6$ , 1.3 Hz, 1 H), 7.19 (td,  $J = 7.6$ , 1.3 Hz, 1 H), 7.32 (td,  $J = 7.6$ , 1.2 Hz, 1 H), 7.50 (dd,  $J = 7.6$ , 1.2 Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  74.5 (s), 118.7 (d), 126.2 (s), 126.5 (d), 126.9 (d), 127.1 (s), 127.1 (d), 188.6 (s); IR (KBr) 2110, 2080, 1630, 1620  $\text{cm}^{-1}$ ; IR ( $\text{CHCl}_3$ ) 2080, 1650  $\text{cm}^{-1}$ ; UV (methanol)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 224 (4.57), 255 (4.14), 312 (3.58); MS (70 eV),  $m/z$  (relative intensity) 224 (25), 196 (26), 168 (100); exact mass  $M^+$  223.9484 (calcd for  $\text{C}_8\text{H}_4\text{N}_2\text{OSe}$  223.9488). Anal. Calcd for  $\text{C}_8\text{H}_4\text{N}_2\text{OSe}$ : C, 43.07; H, 1.81; N, 12.56. Found: C, 43.05; H, 1.95; N, 12.08.

**Photolysis of 8 in Methanol.** A solution of 8 (134 mg, 0.60 mmol) in 268 mL of methanol was irradiated with a 100-W high pressure mercury lamp and a Pyrex apparatus for 1 h at –20 to –60 °C. Removal of the solvent and column chromatography on silica gel (containing 5% water) with benzene gave a mixture of 14 and the minor products ( $R_f = 0.4$ ). The ether-soluble component of the mixture is 14 (35 mg, 26%). The ether-insoluble component of the mixture (8.7 mg) could not be purified by crystallization or column chromatography. Analytical HPLC (Chemcosorb 5-ODS-H, 4.6 × 150 mm, 2:1  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  elution) of the ether-insoluble component showed two peaks with retention times of 6.38 min and 7.01 min, respectively, at a detection wavelength of 254 nm. 14: colorless crystals, mp 117–118 °C (from  $\text{CHCl}_3$ –hexane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.83 (s, 6 H), 6.62 (s, 2 H), 6.81 (t,  $J = 7.6$  Hz, 2 H), 7.14–7.22 (m, 4 H), 7.36 (d,  $J = 7.8$  Hz, 2 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  45.05 (d), 53.10 (q), 127.4 (d), 128.4 (d), 129.8 (d), 130.0 (s), 136.4 (d), 140.4 (s), 170.4 (s);  $^{77}\text{Se NMR}$  ( $\text{CDCl}_3$ , relative to  $(\text{CH}_3)_2\text{Se}$ )  $\delta$  477.8 ppm; IR (KBr) 1724  $\text{cm}^{-1}$ ; MS (70 eV),  $m/z$  (relative intensity) 456 (31), 454 (33), 336 (14), 334 (13), 307 (53), 305 (49), 169 (100), 148 (100); exact mass  $M^+$  455.9394 (calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Se}_2$  455.9379). The unseparated products: colorless solid, mp 193–194 °C (from methanol–benzene);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.77 (s, relative intensity 3 H), 3.82 (s, 1.2 H), 5.75 (s, 1 H), 6.81 (m, 0.4 H), 7.10–7.24 (m, 1.4 H), 7.41 (t,  $J = 6.8$  Hz, 1 H), 7.88 (dd,  $J = 6.3$ , 1.2 Hz, 1 H), 7.90 (dd,  $J = 6.3$ , 1.2 Hz, 1 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) the major peaks  $\delta$  46.8, 52.8, 126.8, 127.8, 130.5, 132.4, 137.9, 143.9, 171.8 ppm; IR (KBr) 1724  $\text{cm}^{-1}$ ; MS (70 eV),  $m/z$  (relative intensity) 456 (33), 454 (32), 307 (46), 305 (46), 169 (90), 148 (100); exact mass  $m/z$  455.9386 (calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Se}_2$  455.9379).

**Acknowledgment.** We thank the Institute for Molecular Science for the allotment of CPU time of the HITAC M-680H computer.

**Registry No.** 2, 63559-01-3; 3, 117582-97-5; 5, 59130-11-9; 6, 117582-98-6; 7, 117582-99-7; 8, 117583-00-3; 9, 117583-01-4; 10, 19446-95-8; 11, 117583-02-5; 12, 4388-01-6; 13, 61629-30-9; 14, 117583-03-6; 21, 117582-96-4.