

was electrolyzed as described for 3. After ca. 1 h of electrolysis, HPLC analysis, using methanol-water (92:8) as the eluent at a flow rate of 1 mL/min and monitored at 312 nm, showed a 71% conversion of 5 and a 28% yield of 6.

The solvent was removed in vacuo. The residue was dissolved in a minimum amount of  $\text{CHCl}_3$  and chromatographed on silica gel using hexane- $\text{CCl}_4$  (60:40) as the eluent. Several recrystallizations from  $\text{CCl}_4$ -hexane gave a pure sample of 6: mp 169-170 °C (lit.<sup>13</sup> mp 167-168 °C); IR (KBr)  $\text{cm}^{-1}$ , 3390, 3140, 1590, 1495, 1410, 1290, 810, 750, 690; UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  308 nm;  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 142.69, 140.58, 134.09, 129.56, 129.42, 129.26, 128.26, 127.07, 124.53, 123.50, 122.25, 120.14, 117.96, 116.59; high-resolution mass spectrum, calcd for  $\text{C}_{32}\text{H}_{24}\text{N}_2$  436.1941, found 436.1962.

**Electrochemical Oxidation of *N,N*-Dimethyl-1-naphthylamine (7).** A solution of 27.3 g (0.159 mol) of 7 in 500 mL of 0.2 M  $\text{NaClO}_4$  in acetonitrile was electrolyzed, using a carbon cloth anode and a platinum cathode. After 1 h of electrolysis, HPLC analysis, with methanol as the eluent, monitored at 320 nm, showed the formation of six products.

**Electrochemical Oxidation of 6-*p*-Toluidino-2-naphthalenesulfonate (8).** A solution of 0.903 g (2.73 mmol) of the ammonium salt of 8 in 0.1 M aqueous  $\text{NaClO}_4$  solution was electrolyzed in a double cell by using a graphite rod anode and a copper cathode. After electrolysis for 1 h, HPLC analysis, using 70% methanol, 30% water containing 7 g/L of cetyltrimethylammonium bromide as the eluent, monitored at 390 nm, showed the presence of five products.

**Electrochemical Oxidation of *N,N*-Dimethyl-5-aminonaphthalene-1-sulfonic Acid (9).** A solution of 0.343 g (1.37 mmol) of 9 in 100 mL of 0.2 M aqueous  $\text{NaClO}_4$  solution was electrolyzed by using a carbon cloth anode and a copper cathode. Periodic analysis by HPLC, using various percentages of methanol in water containing 7 g/L of cetyltrimethylammonium bromide as the eluent, monitored at 320 nm showed a decrease in the peak due to 9 without the appearance of a new peak.

**Chemical Oxidations of Ammonium 8-Anilino-1-naphthalenesulfonate (1). With Sodium Nitrite.** This reaction was patterned after the procedure of Farris et al.<sup>3</sup> A solution of 1.02 g (3.23 mmol) of 1 and 1.6 mL of 0.2 M aqueous  $\text{NaNO}_2$  in 20 mL of glacial acetic acid and 20 mL of concentrated hydrochloric acid was stirred at room temperature for 4 h. After removal of the solvent, the residue was quantitatively dissolved in methanol. Analysis by HPLC showed a 98% conversion of 1 and an 18% yield of 2.

**With Potassium Permanganate.** The reaction was patterned after the procedure of Bridger et al.<sup>13</sup> A solution of 1.02 g (3.23 mmol) of 1 in 10 mL of acetone was cooled to 0 °C. To this stirring solution was added, over a 6-h period, a solution of 0.166 g (1.05 mmol) of  $\text{KMnO}_4$  dissolved in a minimum amount of acetone. After the addition was completed, the solution was allowed to warm to room temperature and an excess of 2-propanol was added to destroy any remaining  $\text{KMnO}_4$ . After removal of the solvent, the residue was dissolved in water. Analysis by HPLC showed a 20% conversion of 1 and a 20% yield of 2.

**With Potassium Dichromate.** A solution of 1.00 g (3.16 mmol) of 1 in 10 mL of acetone was cooled to 0 °C and a solution of 0.528 g (1.79 mmol) of  $\text{K}_2\text{Cr}_2\text{O}_7$  in a minimum amount of water was added over a 6 h-period. After removal of the solvent, the residue was dissolved in water. Analysis by HPLC showed an 81% conversion of 1 and a 1% yield of 2.

**With Chromium Trioxide.** A solution of 0.599 g (1.90 mmol) of 1 and 0.096 g (0.96 mmol) of  $\text{CrO}_3$  in 100 mL of DMF was heated to reflux for 4 h. Analysis by HPLC showed a 46% conversion of 1 and a 4% yield of 2.

**With Lead Tetraacetate.** The reaction was patterned after the procedure of Taylor et al.<sup>7</sup> To a solution of 0.500 g (1.58 mmol) of 1 in 40 mL of glacial acetic acid was added 2 mL of boron trifluoride diethyl etherate and 0.461 g (1.04 mmol) of lead tetraacetate. The solution was stirred at room temperature for 4 h. After addition of 10 mL of 50% hydrochloric acid and 5 mL

of methanol, the solvent was removed. The residue was dissolved in 10 mL of concentrated ammonium hydroxide solution. To this was added 10 mL of methanol and 10 mL of water. The lead dioxide was removed by filtration. Analysis by HPLC showed a 69% conversion of 1 and a 14% yield of 2.

**With Cobalt(III) Fluoride.** This reaction was patterned after the procedure of Taylor et al.<sup>7</sup> To a solution of 0.558 g (1.77 mmol) of 1 in 100 mL of  $\text{Me}_2\text{SO}$  was added 0.654 g (5.63 mmol) of  $\text{CoF}_3$ . The solution was heated to 80 °C for 12 h. The solvent was removed in vacuo and the residue was dissolved in methanol. Analysis by HPLC showed a 73% conversion of 1 and an 11% yield of 2.

**With Thallium Trifluoroacetate.** The reaction was patterned after the procedure of Taylor et al.<sup>7</sup> To a refluxing solution of 0.214 g (0.678 mmol) of 1 in 20 mL of glacial acetic acid was added, over a 4-h period, a solution of 0.202 g (0.372 mmol) of thallium trifluoroacetate in 20 mL of glacial acetic acid. Analysis by HPLC showed a 71% conversion of 1 and a 31% yield of 2.

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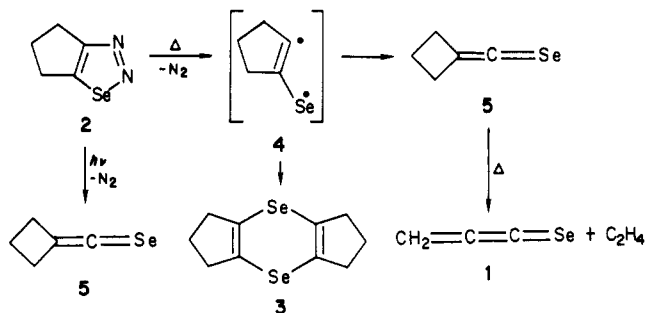
## Propadieneselone

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Propadienone and its derivatives have been the subject of recent investigations.<sup>1,2</sup> Nothing is known of the analogous thio- and selenocumulenes. We report the preparation, spectroscopic characterization, and photochemistry of propadieneselone (1).



Meier and Voigt<sup>3</sup> showed that cyclopenteno-1,2,3-selenadiazole (2) gives dicyclopenteno-1,4-diselenine (3) in 27% yield when heated to 140 °C and suggested that 3 is formed by dimerization of diradical 4. No products derived from loss of selenium were found.

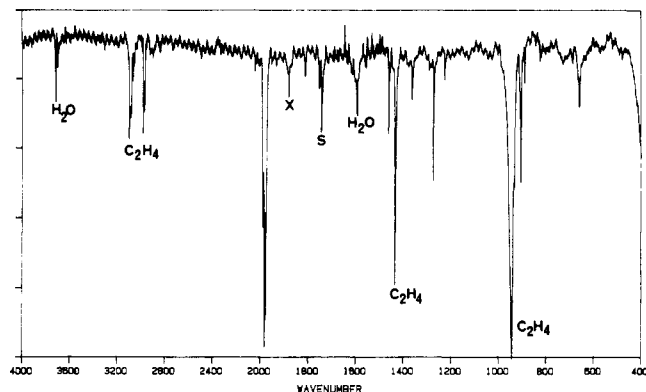
Flash vacuum thermolysis of 2 (500 °C,  $10^{-6}$  torr) with trapping of the products in argon at 12 K gave trimethyleneselenoketene (5) in high yield. Intermolecular reactions are excluded under these conditions, and dimer 3 is not formed. Selenoketene 5 was characterized by its infrared spectrum. The intense band at  $1746\text{ cm}^{-1}$  is assigned to the  $\text{C}=\text{C}=\text{Se}$  stretching mode. This assignment is in good agreement with selenoketene ( $1695\text{ cm}^{-1}$ )<sup>4</sup> and bis(trimethylsilyl)selenoketene ( $1730\text{ cm}^{-1}$ ).<sup>5</sup> Other bands of trimethyleneselenoketene (5) appear at 2967 (s), 2863

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(17) The yield was very poor if a small amount of aqueous ferric nitrate was not added. Addition of larger amounts did not further increase the yield. We are unsure why the ferric nitrate is needed. It is possible that the iron is acting as an electron-transfer mediator or is acting as a catalyst in a chemical step.



**Figure 1.** Infrared spectrum of propadieneselone (1) prepared by flash vacuum pyrolysis of 2 at 700 °C with trapping in argon at 12 K. S = selenoketene 4, X = unknown contamination.

**Table I. Infrared Spectroscopic Data of Propadieneselone (1), Propadienone,<sup>2</sup> and Dimethylallene<sup>7</sup>**

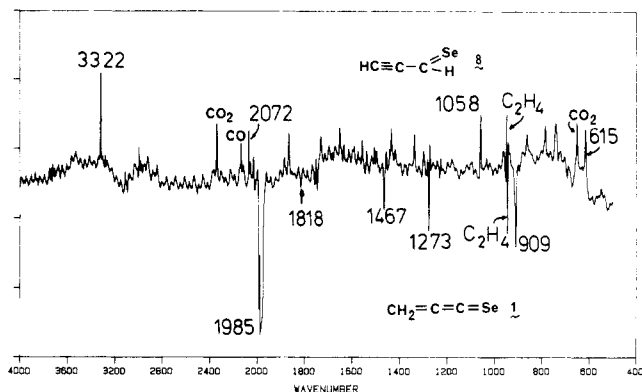
1	propadienone <sup>2</sup>	dimethylallene <sup>7</sup>	assignment
1993 s			
1985 vs	2171 s	1970 m	asym C=C=C str
	2127 vs		
1981 s			
1467 m	1446 m	1438 m	=CH <sub>2</sub> in-plane def
1279 s	?	1286 m	sym C=C=C str
909 s	907 m	848 s	=CH <sub>2</sub> out-of-plane def

(s), 1757 (m), 1432 (w), and 1232 (m) cm<sup>-1</sup>. Irradiation (>300 nm) of 2 matrix isolated in argon at 12 K gave only trimethyleneselenoketene (5). The chemistry of 2 thus parallels that of the parent selenadiazole which gives selenoketene on thermolysis<sup>6</sup> or photolysis.<sup>4</sup>

Flash vacuum thermolysis of 2 (700 °C, 10<sup>-6</sup> torr) with trapping of the products in argon at 12 K gave ethylene (identified by infrared comparison), propadieneselone (1), and a trace of trimethyleneselenoketene (5). The infrared bands due to propadieneselone were identified by their appearance as a function of thermolysis temperature and by their simultaneous disappearance on irradiation. Comparison of the infrared spectra of propadieneselone (1), propadienone, and 1,1-dimethylallene (Table I) reveals a striking similarity.

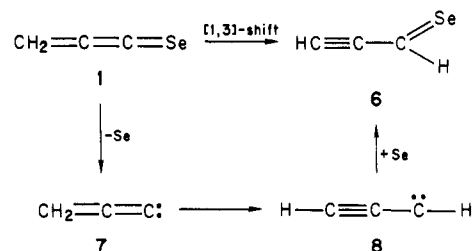
The intense bands at 1993, 1985, and 1981 cm<sup>-1</sup> (Figure 1) are due to the cumulene antisymmetric stretch. It is not clear whether the three components of this mode arise from Fermi resonance or matrix site effects. The effect of selenium isotopes should be smaller than the observed effect. The position of this band is 240 cm<sup>-1</sup> above the highest selenoketene frequency known, and it thus permits facile distinction of selenoketenes and propadieneselone. The symmetric stretch of the cumulene in 1 at 1279 cm<sup>-1</sup> is quite intense as it is in 1,1-dimethylallene. The methylene out-of-plane deformation mode of 1 is observed at 909 cm<sup>-1</sup> with an overtone at 1818 cm<sup>-1</sup>. The in-plane methylene deformation appears at 1467 cm<sup>-1</sup>.

Irradiation (>220 nm) of propadieneselone matrix isolated in argon at 12 K gives propyneselenol (6) (Figure 2). The infrared spectrum of 6 shows a primary acetylene C—H stretch (3322 cm<sup>-1</sup>), C≡C stretch (2072 cm<sup>-1</sup>) and C—H deformation mode (615 cm<sup>-1</sup>). Selenoketenes and



**Figure 2.** Difference spectrum was obtained by subtracting the spectrum of argon matrix isolated propadieneselone (1) and ethylene from that of the same sample after irradiation. The bottom part of the spectrum shows bands assigned to 1, which decreases on irradiation ( $\lambda > 220$  nm). The top part shows bands assigned to 6 coming in. The strongest band of ethylene (947 cm<sup>-1</sup>) does not subtract completely.

thioketones do not exhibit strong diagnostic bands for the C=Se or C=S stretching modes. Thioketones<sup>8</sup> frequently show a medium intensity band near 1200 cm<sup>-1</sup>, and some selenoketenes<sup>9</sup> show bands about 1050 cm<sup>-1</sup>. We tentatively assign the medium intensity band at 1058 cm<sup>-1</sup> to the selenal C=Se stretch. The formation of 6 might involve either a 1,3-hydrogen shift or loss of selenium giving allenylidene (7), rearrangement to propargylene (8), and recombination with selenium.



### Experimental Section

Cyclopenteno-1,2,3-selenadiazole (2) was prepared according to a literature procedure.<sup>3</sup> It was found to be stable at -20 °C but decomposed at room temperature within several days. Infrared spectra were obtained on a Perkin-Elmer Model 580-B spectrometer. The matrix isolation technique used in these laboratories is described elsewhere.<sup>10</sup> In a typical run 2 was sublimed at -10 °C through a quartz tube which was equipped with a heating wire and a thermocouple. The temperature of the quartz tube was varied from room temperature to 800 °C. The products of the pyrolysis were codeposited with 0.3–0.35 L of argon (99.999%) within 150–200 min on a CsI plate kept at 25–28 K. After deposition, the temperature was lowered to 12 K. Irradiation was performed with a 300-W high-pressure Xe lamp (Varian Associates, ELMAC division) and quartz optics. Wavelength control was achieved by a ultraviolet cutoff filter (Corning Glass 0-56, <1% transmission at 220 nm).

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