ring opening of tricyclic aziridinium ions,[22] and molecular rearrangement of other bycyclic systems.[4,23]

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Thermal Decomposition of Bis(diphenylmethyl) Diselenide

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The thermal decomposition of bis(diphenylmethyl) diselenide (1) has been investigated in the melt and in chlorobenzene solution. In the melt, 1 decomposes readily at 210 °C under reduced pressure with quantitative formation of 1,1,2,2-tetraphenylethane (3) and elemental selenium. The decomposition products at 140 °C are 3 (87%), Se (86.4%), bis(diphenylmethyl) selenide (6.5%), and 6.5% of starting material. In chlorobenzene solution, the decomposition follows first-order kinetics over the temperature range 100–120 °C and polyselenides are produced as additional products. The results are consistent with a radical mechanism involving C–Se and Se–Se bond scissions.

The thermal instability of organic diselenides has often been cited in the literature, but little is known about the kinetics and mechanisms of these thermal decomposition reactions. Morgan and Burstall[1-3] reported that cyclic diselenides, e.g., 1,2-diselenacyclohexane, 1,2-diselenacycloheptane, and 1,2-diselenacyclooctane, lose one selenium atom with concomitant ring contraction when they were heated. Similarly, bis(chloromethyl) diselenide thermally decomposed to give elemental selenium and bis(chloromethyl) selenide.[4] Recently, Lardon[5] has shown that benzyl diselenide undergoes rapid thermal decomposition in the melt or in solution at 150–170 °C to produce a complex mixture of products, including dibenzyl selenide, selenium, and several dibenzyl polyselenides. Substantial quantities of toluene and some 1,2-diphenylethane were formed after heating the melt to 225 °C for about 1 h.

Apart from these studies little else has appeared in the literature. Previously, the thermal instability of bis(diphenylmethyl) diselenide (1) was noted,[6] but its thermal chemistry has not been reported. As part of our continuing studies on the chemistry of organochalcogens,[7-9] we initiated a detailed study of thermal chemistry of this diselenide 1. In the present work, we have investigated the thermal decomposition of 1 in the melt and in solution over the temperature range 100–210 °C. The decomposition products were identified. The kinetics of decomposition were determined and the reaction mechanism is discussed.

Results and Discussion

Diselenide 1 was conveniently prepared in 78% yield by the reaction of sodium diselenide[10] with benzhydryl chloride in ethanol. Bis(diphenylmethyl) selenide (2) was synthesized by treating benzhydryl chloride with an ethanolic solution of sodium hydrogen selenide[9] and sodium ethoxide.

Thermolysis of 1 neat under reduced pressure at 210 °C was completed within 20 min and yielded 1,1,2,2-tetraphenyl-

ethane (3) and elemental selenium as the only products (eq 1). In contrast to benzyl diselenide,[5] formation of monoselenide and polyselenides was not observed. It appears that 1 is much less stable than benzyl diselenide and the former has weaker C–Se bonds. At 140 °C, heating 1 for 23 h resulted in a decreased yield of 3 (87%) and selenium (86.4%) with formation now of monoselenide 2 (6.5%) and recovery of 1 in 6.5% yield. Monoselenide 2, when heated at 140 °C for 23 h, converted to diselenide 1 (15.8%), selenium (16%), 3 (55.2%), and polyselenides 4 (13.8%), with some 2 (15.2%) remaining. This suggests that 2 is one of the major initial products in the thermolysis of 1 at lower temperatures (140 °C) and that it further decomposes under prolonged conditions.

$$Ph_2CHSeSeCHPh_2 \xrightarrow{\Delta} Ph_2CHCHPh_2 + Se \quad (1)$$
$$\underset{1}{} \qquad \underset{3\,(99.4\%)}{} \quad \underset{(99.8\%)}{}$$
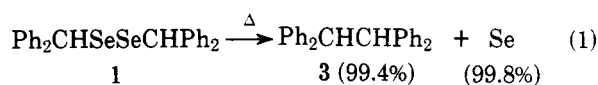
The kinetics of decomposition of 1 were studied in purified and degassed chlorobenzene at temperatures of 100–120 °C. The rate of disappearance of 1 was determined spectrometrically by following the decrease in peak area of the methine proton with a chemical shift of δ 4.95 in the NMR spectrum. In all cases, the decomposition reactions obeyed a first-order rate law. Figure 1 shows typical first-order plots. The rate constants determined from the slopes of the first-order plots for the thermal decomposition of 1 in chlorobenzene in the temperature range 100–120 °C are listed in Table I. The lack of rate constant change with variation in initial concentration of 1 listed in Table I further supports a first-order kinetic scheme for this decomposition reaction. Nonlinear first-order plots were obtained at reaction temperatures exceeding 120 °C. The control reactions showed that monoselenide 2, one of the initial decomposition products, is not stable at temperatures above 120 °C and further decomposed to re-form diselenide 1 along with other products. The deviation from the first-order kinetics is apparently due to the secondary
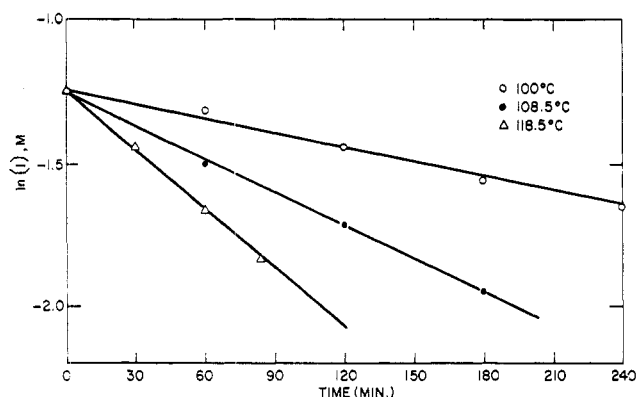
Figure 1. First-order plots for the decomposition of bis(diphenylmethyl) diselenide (1) in chlorobenzene.

Table I. Rate Constants for the Thermal Decomposition of Bis(diphenylmethyl) Diselenide in Chlorobenzene

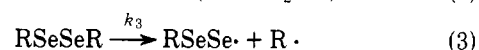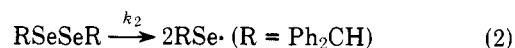| Temp, °C	M^a	10^4k, s^{-1}
100	0.286	0.294 ± 0.023^b
108.5	0.286	0.637 ± 0.017
118.5	0.286	1.117 ± 0.040
118.5	0.285	1.119 ± 0.036
118.5	0.199	1.108 ± 0.184
118.5	0.119	1.120 ± 0.062

^{a} Initial diselenide concentration. ^{b} Standard deviation.

thermolysis of **2**. An Arrhenius plot of the rate constants given in Table I yielded a straight line from which the energy of activation for the decomposition of **1** in chlorobenzene was calculated to be 20.9 kcal mol^{-1}.
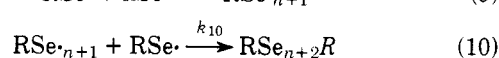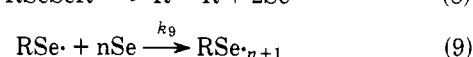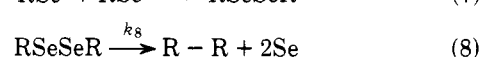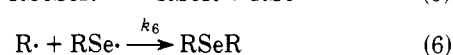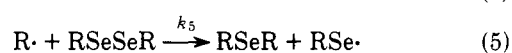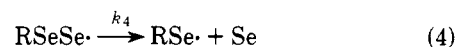
Table II gives the products formed and their yields as determined by NMR analyses for the thermal decomposition of **1** in chlorobenzene at various temperatures. The ratios of the products were judged on the basis of the integration of the various methine proton peaks observed in the NMR spectrum. It is noteworthy that at the temperature range 100–120 °C, precipitation of elemental selenium was not observed and the formation of polyselenides **4** was detected by NMR analysis.[5] Attempts at isolating polyselenides failed, since they slowly decomposed in chlorobenzene at room temperature and upon prolonged heating. They were also unstable under TLC conditions in a variety of solvents. The reduction in the concentration of polyselenides is accompanied by the precipitation of elemental selenium. Krafft and Lyons[11] reported that aromatic polyselenides split off selenium under a variety of conditions, such as dissolving in any solvent or mild heating. Diphenyl triselenide readily decomposed to selenium and the diselenide upon treatment with solvents.[12] The precipitation of elemental selenium and the absence of polyselenides **4** in the product mixture at higher reaction temperature or by

prolonged heating (Table II) confirm the instability of the polyselenides.

The kinetic information makes it reasonably certain that the thermal decomposition of **1** in chlorobenzene is a unimolecular process at temperatures of 100–120 °C. It has been shown that both Se–Se bond and C–Se bond cleavages are the important processes for photolysis of benzyl diselenide.[7] Based on the luminescence bands of diphenylmethyl radical, the scission of the C–S bond by UV radiation of bis(diphenylmethyl) disulfide has been confirmed.[13] If a similar reaction mechanism is assumed for the thermal decomposition of **1**, then the primary processes are undoubtedly the homolysis of the Se–Se bond (eq 2) and the cleavage of C–Se bond (eq 3).

$$\text{RSeSeR} \xrightarrow{k_2} 2\text{RSe} \cdot \ (\text{R} = \text{Ph}_2\text{CH}) \tag{2}$$

$$\text{RSeSeR} \xrightarrow{k_3} \text{RSeSe} \cdot + \text{R} \cdot \tag{3}$$

The control experiments showed that monoselenide **2** is stable at 100–120 °C and decomposes to diselenide **1** and other products at 140 °C. Therefore, it is reasonable to assume that diphenylmethylselenyl radicals (RSe·) do not decompose to elemental selenium and diphenylmethyl radicals. Initially formed diphenylmethylselenyl radicals (eq 2) could either recombine or attack the weak Se–Se linkage leading to radical displacement and re-formation of **1**. These reactions, of course, give no decomposition products to be observed. The following reactions are proposed to account for the experimental observations:

$$\text{RSeSe} \cdot \xrightarrow{k_4} \text{RSe} \cdot + \text{Se} \tag{4}$$

$$\text{R} \cdot + \text{RSeSeR} \xrightarrow{k_5} \text{RSeR} + \text{RSe} \cdot \tag{5}$$

$$\text{R} \cdot + \text{RSe} \cdot \xrightarrow{k_6} \text{RSeR} \tag{6}$$

$$\text{RSe} \cdot + \text{RSe} \cdot \xrightarrow{k_7} \text{RSeSeR} \tag{7}$$

$$\text{RSeSeR} \xrightarrow{k_8} \text{R} - \text{R} + 2\text{Se} \tag{8}$$

$$\text{RSe} \cdot + n\text{Se} \xrightarrow{k_9} \text{RSe} \cdot_{n+1} \tag{9}$$

$$\text{RSe} \cdot_{n+1} + \text{RSe} \cdot \xrightarrow{k_{10}} \text{RSe}_{n+2}R \tag{10}$$

The thermally produced diphenylmethyl radicals (eq 3) may diffuse away from the formation cage, undergoing secondary reaction with **1** to yield monoselenide **2** (eq 5). Recombination of R· and RSe· radicals would also produce **2** (eq 6). Since the concentration of R· is very low during the thermal decomposition and the radical coupling reaction (i.e., R· + R· → R–R) is a second-order radical reaction, we may simplify the reaction kinetics by assuming that all the R· diffused out of the solvent "cage" are consumed in either eq 5 or 6. The formation of **3** may be rationalized by the recombination of diphenylmethyl radicals within a solvent cage, or possibly by a molecular mechanism (eq 8).

Table II. Reaction Products from the Thermal Decomposition of Bis(diphenylmethyl) Diselenide in Chlorobenzene^a

Temp, °C	Time, h	1^c	2	3	4	Se^d
100	4	67.4	9.8	6.5	16.3	e
108.5	4	41.7	12.9	6.9	38.5	
118.5	2	51.6	20.3	19.6	8.5	
118.5	20	29.7	16.7	53.6		57.6
150	2	9.7	8.0	82.3		83.1

(Header: Product composition, %^{b} spans columns 1^c, 2, 3, 4)

^{a} Reactions were carried out in sealed tubes (<10^{-4} Torr). ^{b} Determined by NMR analysis of the reaction mixture. ^{c} Unreacted diselenide. ^{d} Isolated yield. ^{e} Not observed.

The presence of polyselenides **4** may be attributed to recombination reactions such as 9 and 10. This would be consistent with the results of Lardon,[5] who reported that dibenzyl polyselenides are the thermal reaction products of benzyl diselenide. Assuming steady-state conditions for all reaction intermediates, the following rate expression may be derived.

$$-d[RSeSeR]/dt = (k_3 + k_8)[RSeSeR]$$

The result is in agreement with the first-order dependence for 1 found experimentally.

The decomposition mechanism proposed (eq 2–10) adequately accounts for all the products and kinetic results. The present study shows, therefore, that the thermal decomposition of bis(diphenylmethyl) diselenide (1) in chlorobenzene proceeds by a radical mechanism and follows first-order kinetics over the temperature range 100–120 °C.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are not corrected. NMR spectra were determined on a JEOL C6OH instrument with $CDCl_3$ or C_6H_5Cl as solvent and tetramethylsilane as internal standard. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Chlorobenzene. Baker reagent grade chlorobenzene was vigorously stirred with three portions of reagent sulfuric acid and washed successively with distilled water, sodium bicarbonate solution, and distilled water. After successive 24-h periods of drying with calcium chloride and phosphorus pentoxide, the chlorobenzene was distilled from phosphorus pentoxide. A middle fraction, bp 131.8–132.5 °C, was collected.

Bis(diphenylmethyl) Diselenide (1). Ethanolic sodium diselenide solution was prepared by reaction of 6.0 g (76 mmol) of selenium powder and 2.0 g (54 mmol) of sodium borohydride in absolute ethanol according to the procedure of Klayman and Griffin.[10] To ethanolic sodium diselenide solution was added 10.54 g (52 mmol) of benzhydryl chloride with stirring, and the solution was heated at reflux under nitrogen for 30 min. The yellow reaction mixture was cooled to room temperature and stirred overnight. The resulting mixture was acidified with glacial acetic acid and purged with N_2 to remove hydrogen selenide by trapping it into an aqueous lead acetate solution. The ethanol was then removed on a rotatory evaporator and the residue was extracted with hot chloroform. The crude product, obtained by removal of chloroform from the extracts, was recrystallized from ethanol to yield 9.98 g (78%) of 1 as pale yellow needles: mp 123–124 °C (lit.[6] 120–123 °C); NMR ($CDCl_3$) δ 4.95 (2 H, s), 7.17 (20 H, s).

Anal. Calcd for $C_{26}H_{22}Se_2$: C, 63.42; H, 4.50; Se, 32.07. Found: C, 63.52; H, 4.37; Se, 31.89.

Bis(diphenylmethyl) Selenide (2). Benzhydryl chloride (30.96 g, 152 mmol) and sodium ethoxide (5.2 g, 76 mmol) were added with stirring to an ethanolic solution of sodium hydrogen selenide (76 mmol) prepared by adapting the method of Klayman and Griffin,[10] and the mixture was stirred under nitrogen at room temperature for 18 h. After purging with nitrogen to remove H_2Se, the reaction mixture was filtered. The filtrate was concentrated in vacuo and the residue was extracted with hot petroleum ether to give 12.82 g (41%) of 2. Recrystallization from petroleum ether (bp 20–40 °C) yielded the analytical sample: mp 65–66 °C; NMR ($CDCl_3$) δ 4.84 (2 H, s), 7.16 (20 H, s).

Anal. Calcd for $C_{26}H_{22}Se$: C, 75.54; H, 5.36; Se, 19.09. Found: C, 75.70; H, 5.27; Se, 18.94.

Thermolysis of 1. Thermolysis was conducted in a bulb-to-bulb distillation apparatus. 1 (0.545 g) was placed in a reaction bulb at one end of the apparatus and the system was evacuated with a vacuum pump. After the pressure was about 2 mmHg, the reaction bulb was heated at 210 °C for 20 min in a microdistillation oven; the receiving bulb was cooled in liquid nitrogen. The black solid residue in the reaction bulb was washed with organic solvents and dried to yield 0.169 g of elemental selenium. The slightly pink-colored solids in the receiving bulb were dissolved in chloroform and the resulting mixture was filtered to remove selenium (0.005 g). The filtrate was concentrated in vacuo to give 0.365 g (99.4%) of 1,1,2,2-tetraphenylethane: mp 208–209 °C; NMR ($CDCl_3$) δ 4.63 (2 H, s), 7.04 (2 0 H, s). The total yield of elemental selenium was 0.174 g (99.8%).

General Procedure for Thermal Decomposition Study. Solid samples or solutions of organic selenides in chlorobenzene were placed inside Pyrex ampules which were sealed under high vacuum ($<1 \times 10^{-4}$ Torr) after being degassed at liquid nitrogen temperature. In the case of the solutions, a four degassing cycle "freeze–degas–thaw" procedure was used. The ampules were placed in a thermostat-bath (Thermocal Model TH-050 Fluidized solids constant temperature bath) at the desired temperature, withdrawn at various times, and rapidly quenched in ice water. The bath temperature did not vary by more than 0.5 °C during an experiment. The ampules were cleaned and cracked open with a hot glass rod. The content of each ampule was analyzed by NMR. In the case of the solid samples, the decomposition products were extracted with chloroform. The solid selenium was dried and weighed, and the extracts were concentrated and analyzed by NMR.

Kinetic Measurements. The decomposition of organic diselenide (1) was followed by the disappearance of its methine protons chemical shift (δ 4.95) in the NMR spectrum. The chemical shifts of the methine protons for bis(diphenylmethyl) selenide (δ 4.84), diselenide (δ 4.95), and 1,1,2,2-tetraphenylethane (δ 4.63) are sufficiently different to allow spectral peak areas to be compared. The NMR data at each time interval for each complete run were then used to construct a first-order plot. The first-order rate constant was calculated from the slope of the plot. The activation energy was calculated from the slope of a plot of ln k vs. $1/T$. Least-squares treatments were used to calculate the slopes.

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