

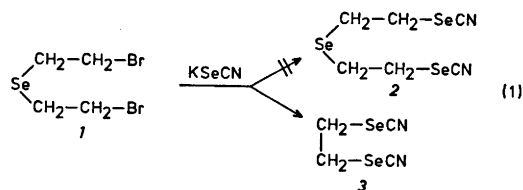
## 2-Halogen Substituted Selenides and their Reactions with Nucleophilic Reagents

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The reactions between bis(2-bromoethyl) selenide (*1*) and a variety of nucleophiles have been studied. Normal substitution products as well as different types of abnormal products have been obtained. A mechanism for these reactions has been proposed which accounts for the formation of all the various products. The reactions of bis(2-haloethyl) selenide dihalides and bis(2-haloethyl) selenoxides with potassium selenocyanate have also been studied. In all cases 1-halo-2-selenocyanatoethanes were isolated as products.

The selenium containing compounds corresponding to mustard gas and its bromine analogue (*1*) were first synthesized by Gibson *et al.*<sup>1,2</sup> These substances were later studied by Smedslund in efforts to elucidate their chemical properties.<sup>3</sup> This investigation was initiated by an unsuccessful attempt to prepare bis(2-selenocyanatoethyl) selenide (*2*). Instead of *2*, diselenocyanatoethane (*3*) was isolated from the reaction mixture (eqn. 1).



This behaviour justified a closer study of the action of various nucleophiles on 2-halogen substituted selenides.<sup>4</sup>

### RESULTS

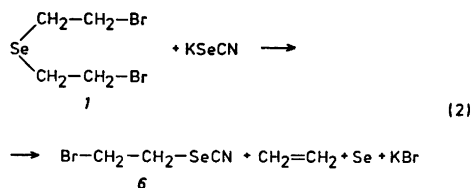
When reacting bis(2-bromoethyl) selenide (*1*) with potassium selenocyanate, ethylene and selenium were produced together with diseleno-

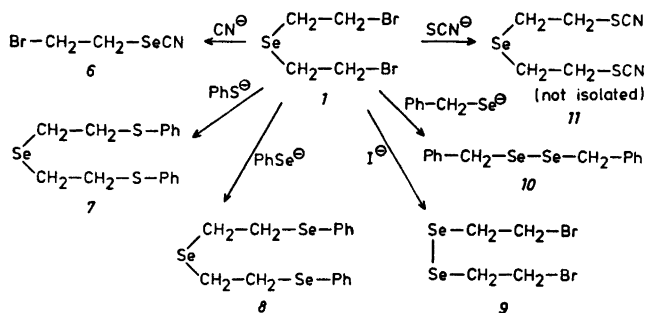
cyanatoethane (*3*). The reaction was easily followed with <sup>1</sup>H NMR spectroscopy using acetone-*d*<sub>6</sub> as solvent. In the spectrum of *1*, which was of the A<sub>2</sub>B<sub>2</sub> type ( $\delta$  3.4), peaks at  $\delta$  5.35 and 3.6 corresponding to ethylene and *3* were obtained on addition of potassium selenocyanate. The formation of ethylene was also qualitatively demonstrated by passing the gaseous products through a solution of selenium tetrabromide in benzene. Bis(2-bromoethyl) selenide dibromide (*4*) was isolated from the mixture.

A number of solvents, such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, ethyl acetate, and ethanol were used as media for the substitution reaction between *1* and potassium selenocyanate. No change of reaction path was, however, observed when using the different solvents. When the reaction was performed in ethanol a competing solvolysis giving bis(2-ethoxyethyl) selenide was noted, in agreement with Smedslund's observations.<sup>5</sup>

When bis(2-chloroethyl) selenide (*5*) was treated with potassium selenocyanate the same reaction as with *1* was observed.

The molar ratio of starting materials in the reaction between potassium selenocyanate and *1* was 2:1. However, when equimolar amounts of the starting materials were used it was possible to isolate 1-bromo-2-selenocyanatoethane (*6*) (eqn. 2). Formation of ethylene was also observed.





Scheme 1.

A number of different nucleophilic reagents were allowed to react with 1 (Scheme 1).

When using benzenethiolate as well as benzeneselenolate ion as nucleophiles the normal substitution products, 7 and 8 respectively, were obtained. The reaction between 1 and thiocyanate ion gave no isolable product. On following the reaction by <sup>1</sup>H NMR spectroscopy an A<sub>2</sub>B<sub>2</sub> spectrum was obtained consisting of two groups of peaks centred around a δ value of 3.3. The product formed is most probably the normal substitution product (11) since only a minute amount of ethylene was produced during the reaction.

When 1 was allowed to react with potassium cyanide, sodium iodide or sodium phenylmethaneselenolate, the expected substitution products could not be isolated. Cyanide ion reacted with 1 giving 6 as the product when DMF was used as solvent. No reaction was obtained in acetone solution. The reaction between iodide ion and 1 gave bis(2-bromoethyl) diselenide (9), ethylene and iodine. Dibenzyl diselenide (10) and ethylene were formed in the reaction between phenylmethaneselenolate ion and 1.

To substantiate the above results the reactions between 2-bromoethyl phenyl selenide (17)<sup>6</sup> and iodide and phenylmethaneselenolate ion were studied. When iodide ion was used as the nucleophile diphenyl diselenide (18), ethylene and iodine were produced. The reaction between 17 and phenylmethaneselenolate ion gave a mixture of products, which was shown by mass and <sup>1</sup>H NMR spectroscopy to consist of four compounds, 18, benzyl phenyl diselenide (20), 10, and 1,5-diphenyl-1,4-diselenapentane (19).

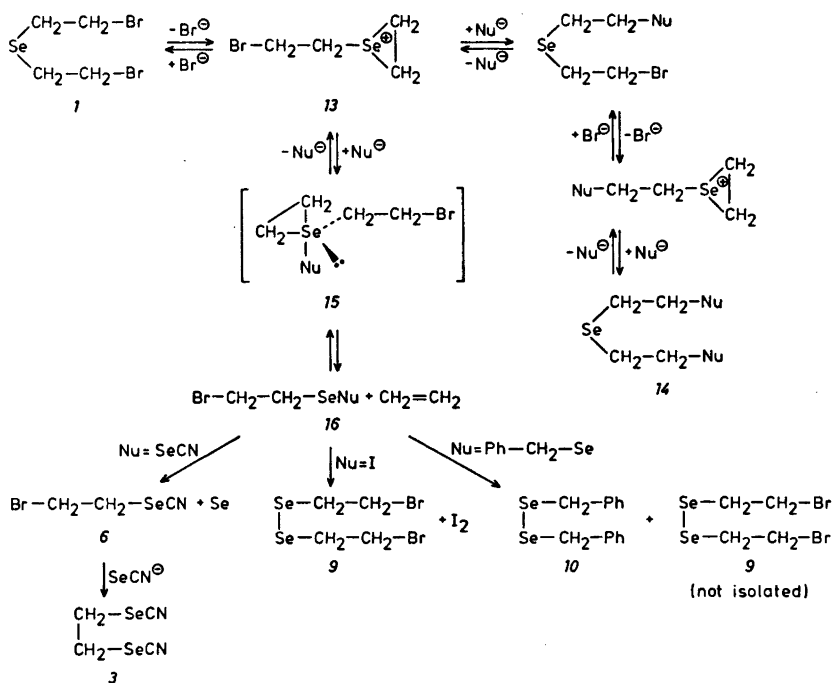
For comparison, thiocyanate<sup>7</sup> and selenocyanate ion were allowed to react with bis(2-

bromoethyl) sulfide (12); normal substitution products were obtained in both cases.

## DISCUSSION

The question arose as to whether it is possible to explain the reaction between bis(2-bromoethyl) selenide (1) and different nucleophiles by a common mechanism. The action of various nucleophiles on mustard gas, which is the sulfur analogue to 5, has been kinetically studied and the formation of an episulfonium ion intermediate in the rate determining step has been proposed.<sup>8,9</sup> A number of relatively stable episulfonium salts have been generated in non-nucleophilic solvents and these when subjected to nucleophilic reactions give varying amounts of Markownikov and *anti*-Markownikov products.<sup>10</sup> It has also been possible to isolate some stable episulfonium salts.<sup>11,12</sup> One of these has been allowed to react with nucleophiles and a competitive attack on sulfur and on carbon has been obtained.<sup>11</sup> Thus in studies on reactions of 2-halogen substituted sulfides it has been possible to confirm the intermediacy of episulfonium ions.

Cyclic selenonium ions as intermediates have until recently been proposed only a few times.<sup>13-15</sup> However, a number of episelenonium salts have now been prepared.<sup>16</sup> In one of the methods of preparation, 2-halogen substituted selenides were used as the starting material. The products obtained have been subjected to nucleophilic substitution by chloride, bromide, and acetate ion. In all cases nucleophilic attack was at the carbon atom and competitive attack at selenium was not observed.



Scheme 2.

The formation of an episelenonium ion (**13**) as a common intermediate in the reactions between **1** and various nucleophiles is thus very probable<sup>4</sup> (Scheme 2). The cyclic selenonium ion formed can be attacked at carbon or selenium. Attack on carbon gives rise to the normal substitution product (**14**). When the positive selenium atom of the selenonium ion is attacked by a nucleophile, the intermediate formation of an episelenurane (**15**), in analogy with episulfonium compounds,<sup>17</sup> can be proposed. The episelenurane decomposes to give ethylene and a selenenyl compound (**16**). A stable episelenurane has recently been isolated in the reaction between an arylselenenyl halide and ethylene.<sup>18</sup> The identity of this compound has, however, been questioned.<sup>19</sup>

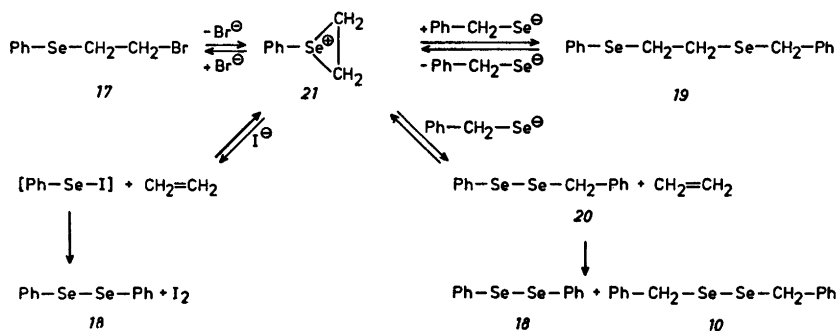
The selenenyl compound **16** can undergo further reaction depending on the nature of the nucleophile. When the nucleophile is the selenocyanate ion, **16** corresponds to 1-bromo-2-(selenenylselenocyanato)ethane. Stable aliphatic selenenyl selenocyanates have not been isolated. The aromatic representatives of this type of compound decompose at higher tem-

perature to give the corresponding selenocyanate and selenium.<sup>20</sup> In the reaction between **1** and potassium selenocyanate, selenium is formed and 1-bromo-2-selenocyanatoethane (**6**) is trapped as an intermediate. Intermediate **6** then reacts with another molecule of potassium selenocyanate to give **3**.

The nucleophilic attack of cyanide ion on **13** gives rise to compound **16** which corresponds to **6**. (Scheme 2).

The isolation of bis(2-bromoethyl) diselenide (**9**), iodine and ethylene when sodium iodide and **1** are allowed to react is explained by the formation of an intermediate **16** corresponding to a selenenyl iodide, which decomposes to give **9** and iodine (Scheme 2).

In the reaction between **1** and phenylmethaneselenolate ion, the formation of ethylene and dibenzyl diselenide (**10**) is explained in accordance with the mechanism in Scheme 2. The intermediate selenenyl compound **16** corresponds to an unsymmetrical diselenide, benzyl 2-bromoethyl diselenide. The isolation of **10** from the reaction mixture can be explained by a disproportionation of the unsymmetrical



Scheme 3.

diselenide to give 10 and 9. Bis(2-bromoethyl) diselenide (9) has, however, not been isolated from the reaction mixture. The analogous reactions between 17 and iodide and phenylmethaneselenolate ion were mechanistically explained in analogy with the results obtained above for 1 (Scheme 3). An intermediate episelenonium ion 21 is formed from 17 and then attacked by iodide ion to give a selenenyl iodide, which decomposes to give 18 and iodine. When phenylmethaneselenolate ion is used as nucleophile 21 is attacked on carbon as well as on selenium giving the normal substitution product 19 and the unsymmetrical diselenide 20, respectively. The unsymmetrical diselenide then partially disproportionates to give 10 and 18 (Scheme 3).

The formation of a cyclic selenonium ion as the first step in the reaction between 2-halogen substituted selenides and different nucleophiles has been discussed above. The question arises as to whether it is possible, by blocking the selenium atom by certain substituents, to prevent the formation of an episelenonium ion and thereby obtain exclusive formation of normal substitution product. Selenide dihalides and selenoxides obtained from the corresponding bis(2-haloethyl) selenides were therefore allowed to react with potassium selenocyanate. The reaction between 4 and potassium selenocyanate gave 6 as product. Potassium selenocyanate and bis(2-chloroethyl) selenide dichloride gave 1-chloro-2-selenocyanatoethane (22) as product. When bis(2-bromoethyl) selenoxide and bis(2-chloroethyl) selenoxide, respectively, were allowed to react with potassium selenocyanate, 6 and 22

were isolated. Normal substitution products were not observed.

### EXPERIMENTAL

The selenium analyses were performed by a microanalytical method developed by Bengtsson<sup>21</sup> and very similar to that of Gould.<sup>22</sup> The melting points are uncorrected.

*The reaction between bis(2-bromoethyl) selenide (1) and potassium selenocyanate (molar ratio 1:2).* To a solution of 8.85 g (0.03 mol) of 1<sup>3</sup> in 150 ml of acetone were added 9.50 g (0.066 mol) of potassium selenocyanate<sup>23</sup> dissolved in 75 ml of acetone. The mixture was refluxed for 2 h, filtered, the residue washed with acetone and the filtrate evaporated. The product was recrystallized from benzene. Yield: 5.3 g (74 %) of 3<sup>24</sup> m.p. 136–137.5 °C. Elemental selenium [2.0 g (84 %)] was regained. During the reaction ethylene is evolved. This can qualitatively be shown by letting all volatile fumes formed pass through a trap containing selenium tetrabromide in benzene. Theoretically 0.03 mol of ethylene is evolved. Thus, by adding 1.65 ml [2.93 g/cm<sup>3</sup>; 4.8 g (0.03 mol)] of bromine to a suspension of 1.2 g (0.015 mol) of selenium in 25 ml of benzene, a solution containing 0.015 mol of selenium tetrabromide was obtained. When the reaction is complete 1.1 g of the trapping product 4 is obtained, m.p. 124–125 °C. (Analysis for 3: Found: C 20.23; H 1.76; Se 66.35. Calc. for C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>Se<sub>2</sub>: C 20.18; H 1.70; Se 66.35).

*The reaction between 1 and potassium selenocyanate (molar ratio 1:1).* To a solution of 5.9 g (0.02 mol) of 1 in 100 ml of acetone were added 3.2 g (0.022 mol) of potassium selenocyanate dissolved in 50 ml of acetone. The reaction mixture was allowed to stand under stirring at room temperature for 2 h, the solvent was evaporated and a yellow oil obtained. Elemental selenium [1.3 g (82 %)] was regained. The oil was distilled giving 0.6 g (14 %) of product, b.p. 77–78 °C/0.02 mmHg. IR and <sup>1</sup>H NMR spectra of the compound showed it to be 6, though slightly impure.

*The reaction between 1 and potassium cyanide.* To a solution of 5.9 g (0.02 mol) of **1** in 100 ml of DMF a suspension of 2.9 g (0.044 mol) of potassium cyanide in 50 ml of DMF were added. The reaction mixture was allowed to stand at room temperature for 5 h, then filtered, poured into water and the mixture extracted with ether. From the mother liquor 0.1 g of diselenocyanatoethane was obtained. Evaporation of the dried ether gave an oil which was distilled, b.p. 80–88 °C/0.1 mmHg. Yield: 1.3 g (31 %). Redistillation gave 0.35 g of product, b.p. 79–80 °C/0.05 mmHg. The product was shown by IR and <sup>1</sup>H NMR spectroscopy to consist of **6**.

*The reaction between 1 and sodium benzenethiolate.* To a sodium methoxide solution, prepared by reacting 1.01 g (0.044 mol) of sodium with 20 ml of absolute methanol, were added 4.85 g (0.044 mol) of freshly distilled benzenethiol. The solution was evaporated to dryness under stirring at reduced pressure. The residue was dissolved in 25 ml of acetone and a filtered solution of 5.9 g (0.02 mol) of **1** in 50 ml of acetone was added. The mixture was allowed to stand for 5 h with stirring at room temperature and in a nitrogen atmosphere. The reaction mixture was filtered and the filtrate evaporated. The product was recrystallized from ethanol. Yield: 4.3 g (61 %). To obtain the analytically pure compound another recrystallization from cyclohexane and treatment with active carbon was necessary, m.p. 66.5–67 °C. (Found: C 54.52; H 5.06; Se 22.38. Calc. for C<sub>16</sub>H<sub>18</sub>S<sub>2</sub>Se: C 54.37; H 5.14; Se 22.34).

*The reaction between 1 and sodium benzeneselenolate.* To a sodium methoxide solution prepared by reacting 1.01 g (0.044 mol) of sodium with 20 ml of absolute methanol, was added 6.91 g (0.044 mol) of newly distilled benzeneselenol. The solution was evaporated to dryness under stirring at reduced pressure. The residue was dissolved in 25 ml of acetone and a filtered solution of 5.9 g (0.02 mol) of **1** in 50 ml of acetone was added. The mixture was allowed to stand for 2 h at room temperature in a nitrogen atmosphere. The reaction mixture was filtered and the filtrate evaporated. The product was recrystallized from ethanol. Yield: 5.1 g (57 %). The analytical specimen was obtained by repeated recrystallization from ethanol and cyclohexane (active carbon), m.p. 78–79 °C. (Found: C 42.92; H 4.06; Se 52.97. Calc. for C<sub>16</sub>H<sub>18</sub>Se<sub>3</sub>: C 42.97; H 4.07; Se 52.97).

*The reaction between 1 and sodium iodide.* To a solution of 2.9 g (0.01 mol) of **1** in 50 ml of acetone was added 1.65 g (0.011 mol) of sodium iodide dissolved in 25 ml of acetone. Immediate formation of iodine was observed. The reaction was performed at room temperature and was considered complete after 15 min. Ethylene was shown to be evolved by isolating **4**, m.p. 122–124 °C as mentioned before. The reaction mixture was filtered and the filtrate was evaporated to give a solid

residue which was dissolved in ether. The ether solution was washed with aqueous sodium pyrosulfite and dried with calcium chloride. The residue after evaporation was recrystallized from a mixture of light petroleum and ethyl ether (19/1) at –60 °C. From the reaction mixture 0.1 g of elemental selenium was recovered. The product was unstable and decomposed at room temperature. <sup>1</sup>H NMR and mass spectra of the compound were consistent with the spectra of **9**.

Unsuccessful efforts were made to trap the intermediate selenenyl iodide as 2-bromoethyl 2'-iodocyclohexyl selenide by adding an excess of cyclohexene to the reaction mixture.

*Bis(2-bromoethyl) diselenide (9).* A solution of 4.0 g (0.016 mol) of bis(2-hydroxyethyl) diselenide<sup>6</sup> in dry chloroform was cooled in ice while dry hydrogen bromide gas was passed through the solution. After a few minutes a heavy oil<sup>8</sup> separated and after some further time formation of red selenium started. The introduction of gas was stopped, the reaction mixture filtered through a bed of calcium chloride and the solvent evaporated. The residue was extracted with ether, the ether extract washed with an aqueous sodium hydrogen carbonate solution and dried. After evaporation, the product was recrystallized from a mixture of light petroleum and ethyl ether (19/1) at –60 °C. The yellow product, which melted at about 25–30 °C, was unstable and decomposed rapidly even below room temperature. When recording the <sup>1</sup>H NMR spectrum in deuteriochloroform and acetone-*d*<sub>6</sub>, the product decomposed with formation of free selenium. The <sup>1</sup>H NMR spectrum changed gradually to that of **1**. Presumably **9**, when dissolved in the above solvents, decomposes to give elemental selenium and **1**.

*The reaction between 2-bromoethyl phenyl selenide (17) and sodium iodide.* To a solution of 2.65 g (0.01 mol) of **17** in 50 ml of acetone was added 1.65 g (0.011 mol) of sodium iodide dissolved in 25 ml of acetone. On addition the reaction mixture became brownish owing to the formation of free iodine. The reaction mixture was allowed to stand at room temperature for 3 h. A small amount of **4** was isolated as described earlier. After filtering the reaction mixture, the solvent was evaporated and the residue dissolved in ether. The ether solution was washed with an aqueous sodium pyrosulfite solution and dried. After evaporation, a solid residue was obtained which was recrystallized from ethanol to give 0.5 g (32 %), m.p. 60.5–61.5 °C, of **18**.

*The reaction between bis(2-bromoethyl) sulfide (12) and potassium selenocyanate.* To a solution of 15 g (0.06 mol) of **12** in 25 ml of acetone 19.0 g (0.132 mol) of potassium selenocyanate dissolved in 50 ml of acetone was added. The mixture was refluxed for 5 h. After the stipulated time the reaction mixture was filtered and the filtrate evaporated, giving an oily residue. By shaking the oil with ethyl ether

a crystalline product was obtained. Recrystallization from ethanol gave 10.3 g (58 %) of product. Repeated recrystallization from ethyl acetate-light petroleum gave the pure bis(2-selenocyanatoethyl) sulfide m.p. 38–39 °C. (Found: C 24.18; H 2.70; S 11.30; Se 53.15. Calc. for  $C_8H_{16}N_2SSe_2$ : C 24.17; H 2.71; S 10.75; Se 52.97).

*The reaction between 1 and sodium phenylmethaneselenolate.* A sodium methoxide solution was prepared by reacting 1.01 g (0.044 mol) of sodium with 20 ml of absolute methanol. To the solution obtained, 7.55 g (0.044 mol) of phenylmethaneselenol was added. The red-brown solution was evaporated under stirring at reduced pressure. The residue was dissolved in 25 ml of DMF and added to a filtered solution of 5.8 g (0.02 mol) of 1 in 50 ml of DMF. The reaction was performed in a nitrogen atmosphere at room temperature with stirring for 3 h. Evolution of ethylene was detected as described earlier by letting the gaseous products pass through a solution of selenium tetrabromide; 2.5 g of 4 was isolated. When the reaction was complete, the reaction mixture was poured into water and the solution extracted with ether. The dried ether solution was evaporated and the residue recrystallized from a mixture of ethanol and water giving 5.0 g (74 %) of 10. The structure of the product was verified using  $^1H$  NMR and IR spectroscopy. The reaction could also be performed in acetone.

*The reaction between 17 and sodium phenylmethaneselenolate.* To a sodium methoxide solution prepared by reacting 0.3 g (0.013 mol) of sodium with 10 ml of absolute methanol, was added 2.0 g (0.012 mol) of phenylmethaneselenol. The red-brown solution was evaporated under stirring at reduced pressure. The residue was dissolved in 25 ml of acetone and the solution obtained added to a filtered solution of 2.65 g (0.01 mol) of 17 in 50 ml of acetone. The reaction mixture was allowed to stand at room temperature with stirring in a nitrogen atmosphere for 3 h. After filtration of the reaction mixture, the filtrate was evaporated giving an oil as residue, which was investigated by  $^1H$  NMR and mass spectroscopy. The  $^1H$  NMR spectrum consisted of three singlets at  $\delta$  3.73, 3.65 and 3.03 and an  $A_2B_2$  spectrum centred around a  $\delta$  value of 2.79. The mass spectrum suggested that the oily product was a mixture of four different compounds. A molecular peak at  $m/e$  356, corresponded to the normal substitution product 19. Peaks were also obtained at  $m/e$  342, 328 and 314, which must be due to the molecular peaks of the diselenides 10, 20 and 18, respectively. The assumption, that the product of the reaction between 17 and phenylmethaneselenolate ion consists of four separate substances, is based on the following reasoning. It is very improbable that the three peaks at  $m/e$  342, 328 and 314 are formed by fragmenta-

tion of 19; as has been described earlier 10 does not fragment to give peaks at  $m/e$  328 and 314.<sup>25</sup> It is also unlikely that the peak at  $m/e$  314 is caused by fragmentation of 20, with its molecular peak at  $m/e$  328. The most probable fragmentation of an unsymmetrical diselenide should be breakage of the diselenide bond. Assignment of the resonances in the  $^1H$  NMR spectrum to various compounds was made as follows. When integrating the spectrum it was possible to relate the singlet at  $\delta$  3.65 to the  $A_2B_2$  spectrum at  $\delta$  2.79, as the integrals were in the proportion 1:2. These resonances are consequently due to 19. To confirm that the  $A_2B_2$  spectrum was not due to starting material, a little 17 was added to the NMR tube and another spectrum was run. A new  $A_2B_2$  spectrum was obtained centred around a  $\delta$  value of 3.29 corresponding to 17. On addition of 10 to the NMR tube and running a spectrum, a distinct increase of the singlet at  $\delta$  3.73 was obtained. All resonances are now identified except that at  $\delta$  3.03, which is tentatively assigned to the methylene group of the unsymmetrical diselenide 20. Efforts were made to separate the four components by preparative TLC using a mixture of methylene chloride and pentane (3/7) as migrating phase. Two slightly impure fractions were obtained, one containing the three diselenides and the other the normal substitution product.

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