with a substance obtained by oxidation of 2,5-dihydrothiophene with hydrogen peroxide[19] by infrared analysis.

**Reaction of a Sulfur Dichloride Addition Product of 1,3-Butadiene with Potassium Cyanide (8).**—To a suspension of 195.3 g (3 mol) of potassium cyanide in 200 ml of glycerol, which was heated to 120°, 105.5 g (0.5 mol) of a sulfur dichloride addition product of 1,3-butadiene[12] was added with vigorous stirring. The system was maintained at a pressure of 10 mm during the addition, and volatile portions were collected in a liquid nitrogen cooled trap. Gas chromatographic analysis of the resulting product (1.5 g) showed the presence of both **9** and **10** in a proportion of 12:1.

**Reaction of 8 with Sodium Iodide. A. In Acetone.**—To a solution of 2.2 g (0.01 mol) of **8** in 15 ml of acetone, 4.6 g (0.031 mol) of sodium iodide was added. The suspension was heated to reflux temperature for 10 min, which led to the elimination of iodine, evidenced by discoloration of a sample by thiosulfate. Quantitative gas chromatographic analysis showed the formation of 0.63 g (72%) of dihydrothiophene (**10**) as well as a trace amount of vinyl thiirane (**9**). Separation of the insoluble reaction products by filtration yielded 0.225 g of polymeric product after exhaustive extraction with water.

**B. In Glycerol.**—Into a suspension of 50 ml of glycerol and 23 g (0.153 mol) of sodium iodide in a three-necked flask equipped with stirrer, dropping funnel, and internal thermometer, 10.55 g (0.05 mol) of the sulfur dichloride addition product of 1,3-butadiene (**8**) was added. The addition was carried out over a period of 5 min at an internal temperature of 90–105° with stirring. Frothing indicated the formation of gaseous product, which was collected in two Dry Ice–acetone traps and identified by its boiling point (−4.5°) and infrared spectrum as 1,3-butadiene, yield 1.3 g (48%).

The remaining reaction product was then further degassed at a pressure of 100–120 mm, which led to the isolation of 1.5 g (35%) of crude **10**, identified by its gas chromatographic retention time and its infrared spectrum.

**Registry No.**—**1a**, 22061-72-9; **2**, 22061-73-0; **4**, 22061-74-1; **5**, 22061-75-2.

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# The Reaction of Selenium Monochloride with Diolefins

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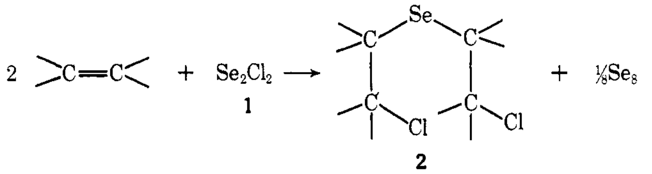
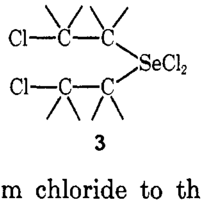
The addition of selenium monochloride to olefins is known to lead to bis(β-chloroalkyl) selenides and free selenium. This reaction has now been studied on a variety of diolefins. Thus, cyclic selenides were obtained from linear diolefins, whereas bi- and tricyclic products were isolated from cyclic and bicyclic diolefins. Significant differences between the addition of selenium monochloride and sulfur dichloride were only apparent in reactions with conjugated olefins. The isolated products represent novel selenium-containing ring structures. The reaction provides a convenient synthesis of β,β′-substituted selenides for which, in most cases, no alternative synthesis is conceivable.

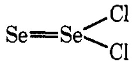
Attempts to add selenium monochloride **1** to olefinic hydrocarbons have been reported [1–5] to lead to the separation of free selenium and the formation of bis(β-chloroalkyl) selenides of the general structure **2**. By-products of the type **3** resulted from the chlorination of the initial addition products. The proportion of **2** and **3** depends on the mode of addition, whereby the addition of the selenium chloride to the olefin favors the formation of **2**. The separation of one of the two selenium atoms of the reagent was interpreted to result from the existence of selenium monochloride in the unsymmetrical structure **4a** in preference to the linear structure **4b**. This is in contrast to recent reports, which favor the linear structure for the homologous sulfur monochloride.[6] Furthermore, in earlier investigations yields of the isolated addition products were not reported and products were only identified by determination of their chlorine content.



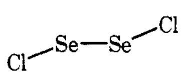
**2**



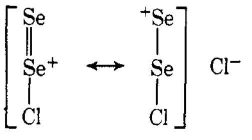
**3**



**4a**



**4b**



**5a** **5b**

Investigations of the reactions of selenium tetrachloride **6** with chlorinated olefins[7a] in the presence of selenium showed that products can be obtained which correspond to the addition products obtained from selenium monochloride. It was therefore concluded that selenium dichloride would exist in equilibrium with selenium tetrachloride and selenium (eq 1). However,

$$SeCl_4 + Se \rightleftharpoons 2SeCl_2 \qquad (1)$$

in the absence of free selenium, the addition of selenium tetrachloride to olefins leads to β, β′-dichloroalkylselenium dichlorides **3**.[7a] Applying the combination of selenium tetrachloride and selenium, the addition of the elements of selenium dichloride was achieved to vinyl chloride. However, the presence of aluminum chloride was required to affect the addition to halogen substituted olefins. Significantly, attempts to carry out substitution reactions on these addition products with methanolic potassium hydroxide have led to dehydro-

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(1) C. E. Boord and F. F. Cope, *J. Amer. Chem. Soc.*, **44**, 395 (1922).

(2) E. S. Gould and J. D. McCullough, *ibid.*, **73**, 1105 (1951).

(3) F. H. Heath and W. L. Semon, *J. Ind. Eng. Chem.*, **12**, 1101 (1920).

(4) H. W. Bausor, C. S. Gibson, and W. J. Pope, *J. Chem. Soc.*, **117**, 1453 (1920).

(5) E. H. Harvey and H. A. Schuette, *J. Amer. Chem. Soc.*, **50**, 2837 (1928).

(6) (a) E. Hirota, *Bull. Chem. Soc., Jap.*, **31**, 130 (1958); (b) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

(7) (a) H. Brintzinger, K. Pfannstiel, and H. Vogel, *Z. Anorg. Chem.*, **256**, 75 (1948); (b) D. M. Yost and C. E. Kircher, *J. Amer. Chem. Soc.*, **52**, 4680 (1930).

halogenation and vinyl selenides were isolated. Thus, the question remains whether substitution could occur on β-chloroalkyl selenides in analogy to substitution reactions on β-chloroalkyl sulfides, by which a large number of derivatives can be obtained through anchimerically assisted displacements.

Later investigations[7b] provided an explanation for the formation of alkyl selenides in the reaction of selenium monochloride with olefins. It was observed that the vapor above liquid selenium monochloride consists in part of selenium dichloride, since on evaporation no increase in the number of molecules in the gas phase was observed, even though a residue of selenium was left behind. Thus, the formation of selenium dichloride according to eq 2 was suggested.

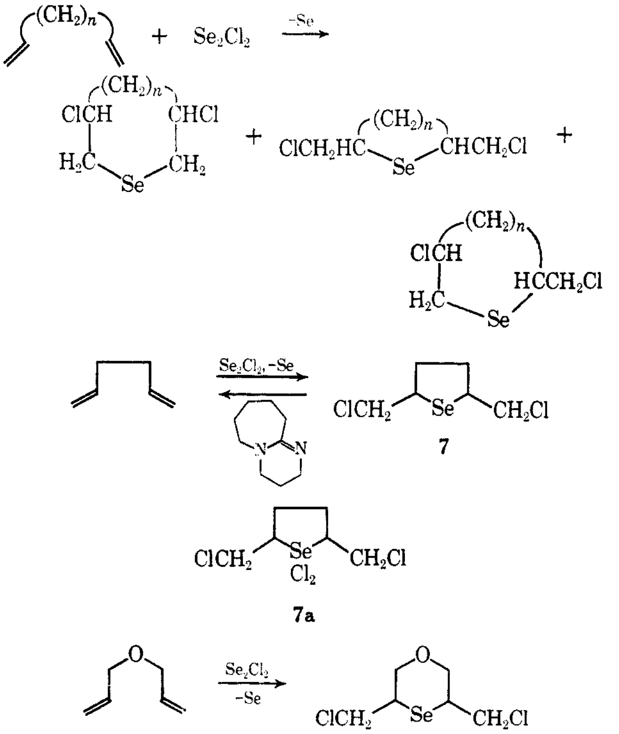
$$Se_2Cl_2 \rightleftharpoons SeCl_2 + Se \qquad (2)$$

## Results and Discussion

It was assumed that the behavior of selenium monochloride in its reactions with olefins should provide a route to cyclic, bicyclic, and tricyclic bis(β-chloroalkyl) selenides in analogy to the reactions of sulfur dichloride with diolefins.[8-14] We have observed that these intramolecular additions of selenium monochloride to diolefins occur readily and that the cyclic products are isolated in good yields.

In the reaction of selenium monochloride with terminal diolefins three different ring systems are conceivable, as was discussed in the investigation of the reaction of sulfur dichloride[13] with these olefins (Chart I).

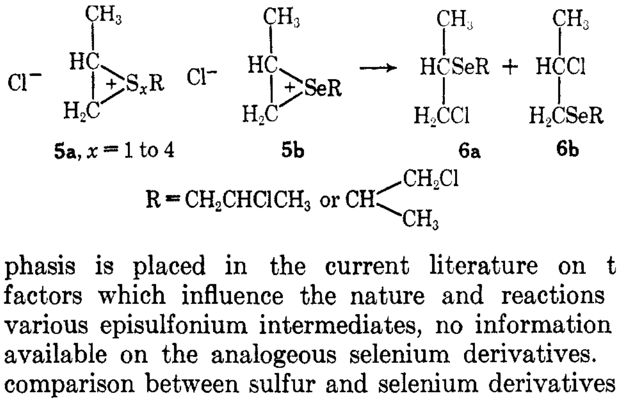
CHART I



In analogy to the formation of Markovnikov products in the reaction of sulfenyl chlorides with terminal olefins,[15] the Markovnikov product from the reaction of selenium monochloride with terminal diolefins would correspond to the isomer of the largest ring structure. If this represents the thermodynamically less stable ring systems, anti-Markovnikov products are expected. Furthermore, two stereoisomers could result from this addition reaction.

The structure of the addition products was assigned on the basis of their nuclear magnetic resonance (nmr) spectra. The relative proportion of $CH_2Cl$ and CHCl *vs.* $CH_2Se$ and CHSe protons distinguishes the various isomeric ring systems obtained from **1** with linear diolefins.

One example of a monoolefin was investigated. The previously reported[1] reaction with propylene was repeated to establish the yield of bis(β-chloroalkyl) selenide as well as the distribution of isomers which may be formed in this reaction. Although considerable emphasis is placed in the current literature on the factors which influence the nature and reactions of various episulfonium intermediates, no information is available on the analogeous selenium derivatives. A comparison between sulfur and selenium derivatives is therefore of interest. In our recent investigation of the influence of the number of sulfur atoms in an episulfonium intermediate such as **5a** on the isomer distribution in the subsequent product,[16] a remarkably small difference was observed. We now observe that, if sulfur is formally substituted by selenium as shown in **5b**, the isomer distribution **5a** and **6b** remains essentially identical within experimental limits. The addition of selenium monochloride to propylene was found to lead to an equal proportion of the isomeric structures **6a** and **6b**. This is evidenced by an identical intensity of CHCl and CHSe protons in the nmr spectrum of that addition product, which is isolated in a yield of 43%. The isomer distribution remains unchanged on distillation of the crude reaction product under reduced pressure. Secondary rearrangements of the nature observed on the addition products of terminal olefins with sulfenyl halides therefore seem to be of little consequence in β-substituted chloro selenides, although no attempts have been made to affect such an isomerization.



Addition of **1** to hexadiene-1,5 leads to a single product as far as can be determined by gas chromatographic analysis. The nmr spectrum suggests structure **7** for that addition product, in agreement with the structure of the product of sulfur dichloride and hexadiene-1,5.[13] Attempted dehydrohalogenation of **7** with 1,5-diazobicyclo[5.4.0]undec-5-ene[17] leads to hexadiene-1,5 in a

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[8] E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1669 (1966).

[9] F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966).

[10] E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

[11] F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).

[12] P. Y. Blanc, P. Diehl, H. Fritz, and P. Schläpfer, *Experientia*, **23**, 896 (1967).

[13] F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620 (1968).

[14] F. Lautenschlaeger, *ibid.*, **33**, 2627 (1968).

[15] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

[16] F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969).

[17] H. Oediger and F. Moeller, *Angew. Chem.*, **79**, 53 (1967); *Angew. Chem., Intern. Ed. Engl.*, **6** (1), 76 (1967).

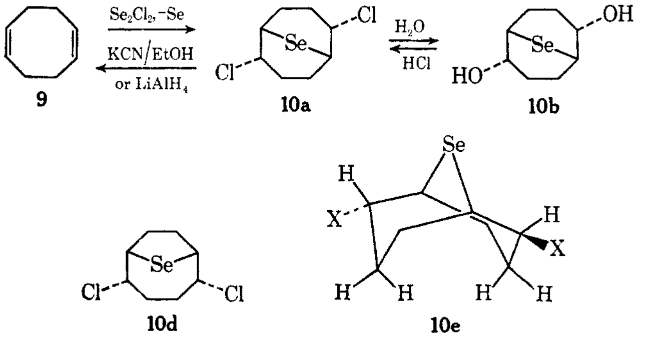
yield of 47.5% as the only isolated volatile reaction product.

Addition of **1** to diallyl ether leads to 2,6-dichloromethyl-1,4-selenoxane **8** in a yield of 39%. Gas chromatographic analysis indicates the absence of isomeric cyclic structures and possibly the absence of stereoisomers, since only a single signal was obtained for the crude reaction product on various columns. The formation of predominantly one stereoisomer suggests that product **8** is of the *cis* configuration, which would be the thermodynamically preferred product, since this configuration permits both chloromethylene groups to be located in an equatorial position. On the basis of this argument, a *cis* configuration may also be assumed for product **7**.

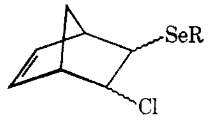
The isolation of **7** and **8**, which may be considered to be anti-Markovnikov products, indicates a steric influence on the product formation, since, in contrast to this, predominatly Markovnikov products were isolated in the reaction of sulfenyl halides with terminal olefins.[15] In the analogous reaction of sulfur dichloride with hexadiene-1,5 and diallyl ether, the anti-Markovnikov product and predominantly one isomer were formed in strict analogy to the reaction of selenium monochloride. Considerations discussed in that addition reaction,[13] therefore, appear equally relevant to the formation of the corresponding selenium compounds.

The analogy of the addition of both selenium monochloride and sulfur dichloride is further evidenced in reactions with cyclic diolefins. Addition of **1** to *cis,cis*-cyclooctadiene-1,5 (**9**) at $-20°$ in methylene chloride leads to an intramolecular addition product in nearly quantitative yield. Two bicyclic ring systems are conceivable for that addition product. The assignment of the 2,6-dichloro-9-selenobicyclo[3.3.1]nonane (**10a**) in preference to the isomeric [4.2.1] ring system **10d** follows from considerations of the anlogy of this product with its sulfur analog.[8–10] The [4.2.1] ring system would lead to severe eclipsing of hydrogen atoms and, therefore, the isomeric [3.3.1] ring system is considered to be the preferred thermodynamic product. The twin-chair conformation **10e** would be the preferred conformation if the chlorine groups are *trans* with respect to selenium, which would permit these substituents to be located in an equatorial position. This twin-chair conformation is indeed evident from the observation of a high methylene deformation mode in the infrared spectrum of **10a** and **10b** at 1480 $cm^{-1}$. Such high frequencies were shown to result from transannular interaction of methylene groups in bicyclic ring systems.[8]

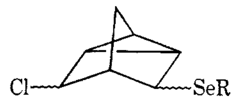
It was of considerable interest whether nucleophilic displacements on β-substituted selenides would occur as readily as similar substitutions on the corresponding sulfides. This was indeed observed. Reactions of **10a** with aqueous sodium bicarbonate or excess of water leads to the dihydroxy selenide **10b**. Conversely, treatment of **10b** with hydrochloric acid leads to the original dichloroalkyl selenide **10a**. The corresponding dicyanide was not isolated from the reaction of **10a** with potassium cyanide in ethanol. Instead, cyclooctadiene-1,5 was formed in a yield of 56%.



Attempts to isolate a transannular addition product of selenium dichloride and bicycloheptadiene failed, as evidenced by gas chromatographic analysis. Instead, a 1:2 addition product was isolated. The nmr spectrum of this product indicates the presence of only 1.4 olefinic protons and suggests, therefore, that, in addition to **11a**, products resulting from a rearrangement of the carbon skeleton (**11b**) are present among the reaction products. This result is in contrast to the addition of sulfur dichloride to this diolefin,[9] but has an analogy in the addition product of sulfur monochloride to bicycloheptadiene[16] and also in the heteropolar additions to bicycloheptadiene, which are accompanied by Wagner–Meerwein rearrangement.[18]

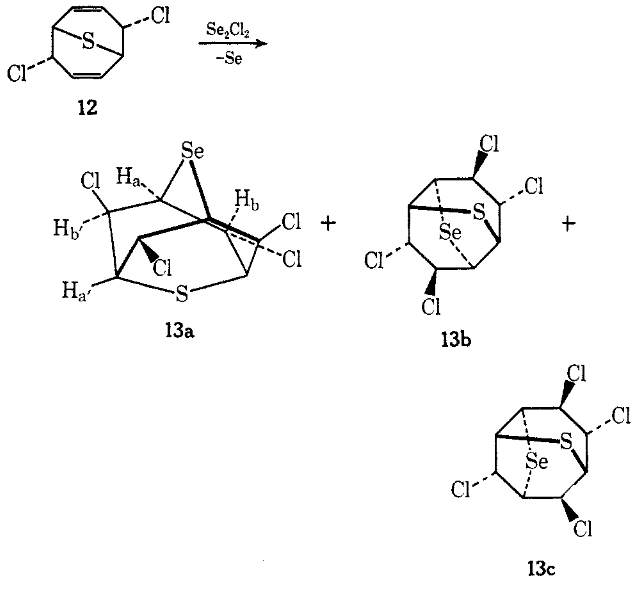


**11a**



**11b**

Transannular addition of selenium dichloride can be extended to bicyclic diolefinic sulfides. Addition to the dichlorosulfide **12**, obtained from cyclooctatetraene and sulfur dichloride[12,14] leads to the selenothiaadamantane ring system **13a** in a yield of 35%. Three different tricyclic ring systems could be formed in this addition reaction, since the transannular addition could proceed either symmetrically across the ring system **12**, involving carbon atoms 3 and 7 (**13a**) or 2 and 6 (**13b**), or unsymmetrically, to form bridge heads at carbon atoms 2 and 7 (**13c**). The configuration of the chloride groups in the resulting product would depend on the question whether the addition of selenium dichloride proceeds *via trans* addition. In case of the addition of sulfur



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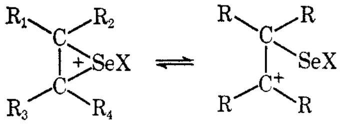
(18) See, for example, P. de Mayo, "Molecular Rearrangements," Vol. I., Interscience, New York, N. Y., 1963, p 198.

dichloride to **12**, this mode of addition was indeed observed and can readily be confirmed for the product **13a**.

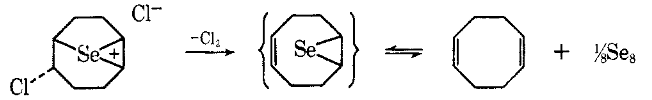
The symmetric structure **13a** is evident from its nmr spectrum. Both pairs of protons CH$_a$Se and CH$_{a'}$S are represented by single peaks at 3.24 and 3.08 ppm, respectively, if recorded on a Varian HA-100 spectrophotometer in deuteriochloroform. The position of the latter is in good agreement with the chemical shift of that proton in 4,8,9,10-tetrachloro-2,6-dithiaadamantane (3.04 ppm).[12,14] The absence of coupling between both H$_a$ and H$_{a'}$ suggests that these protons either form a dihedral angle of nearly 90° or are nonadjacent. Neither of these conditions is satisfied in the bicyclic system **13b**. The ring system **13c** is excluded for symmetry reasons, since the protons within the group HCSeCH would be expected to be nonidentical. For the assignment of the configuration of the addition product, the presence of only two signals for protons CHCl, which are 12.5 cps apart, confirms the configuration as shown in **13a** with two of these protons in the deshielding range of the sulfur atom and the remaining two in the deshielding range of the selenium atom. Molecular models demonstrate that an alternative configuration, in which two pairs of signals for the groups CHCl would result, requires the nonidentity of the protons within one pair of either CHSe or CHS. This is not observed. The spectrum, therefore, agrees with the postulated structure **13a**, which is also anticipated in view of the addition of selenium dichloride to cyclooctadiene, where two consecutive *trans* additions occur in such a mode that the [3.3.1] ring system is formed.

For a mechanistic interpretation of the observed formation of bis($\beta$-chloroalkyl) selenides in the addition reaction of **1**, several alternatives must be considered. Firstly, tautomerism could exist between the branched and linear structure of selenium monochloride, **4a**, and **4b**, with the branched structure **4a** undergoing the addition reaction under elimination of selenium. Although dipole moment measurements on **1**[19] have left its structure undecided, infrared and Raman spectra[20,21] support the unbranched structures of sulfur monochloride and selenium monochloride. Secondly, mesomerism of the two ionic forms **5a** and **5b** could be assumed. It is not obvious, however, why a fundamental difference in the addition reaction of sulfur monochloride and selenium monochloride should be observed on the basis of these assumptions. A third alternative, the dissociation of **1** into selenium dichloride and selenium (eq 2) satisfactorily explains the formation of the observed products. The more reactive selenium dichloride undergoes preferential reaction with the olefinic site. For an assumption that initial addition of **1** proceeds to form a bis($\beta$-chloroalkyl) diselenide and that elimination of selenium occurs in a secondary step, no evidence is available. The different behavior of sulfur monochloride and selenium monochloride with respect to their tendency to disproportionate reflects the increased stability of the zero oxidation state of elements of higher atomic number within one family of the periodic table.

The formation of *trans*-addition products and the reactivity of bis($\beta$-chloroalkyl) selenides suggests the involvement of an episelenium ion of the type **14a** in both addition and replacement reactions. Contributions of the open ion **14b** would lead to rearrangements in the addition reaction, for example, with bicyclohepta[2.2.1]diene-1,5.


**14a** **14b**

The elimination of selenium and the formation of diolefin in the reaction of **10a** could result from an equilibrium of the episelenium intermediate **15** with the episelenide **16**, which on elimination of selenium is converted into diolefin. This reaction has an analogy in the formation of an olefinic episulfide from a tricyclic bis($\beta$-chloroalkyl) sulfide,[22] but, whereas in the latter case the resulting episulfide can be isolated, the intermediate episelenide is not expected to be observed on account of its extremely low thermal stability.[23]


**15** **16**

## Experimental Section

Melting points were obtained in a Gallenkamp block and are corrected. Infrared (ir) spectra were recorded on a Perkin-Elmer 421 grating instrument and nmr spectra were recorded on a Varian A-60 spectrophotometer, except otherwise specified. Selenium monochloride was obtained from K & K Laboratories and City Chemical Corp. and was not further purified.

**The Reaction of Selenium Monochloride with Propylene.**—Into a 100-ml round-bottom flask was condensed 42 g (1 mol) of propylene at −60° and a precooled solution of 22.9 g (0.1 mol) of selenium monochloride in 20 ml of methylene chloride was added. The solution was kept at −40° for 4 hr, after which time it was allowed to warm to ambient temperature over a period of 1 hr. Filtration of 10.9 g of selenium and evaporation of volatile portions at 40° (20 mm) gave 17 g of crude product (73%) which was distilled at 62–63° (0.005 mm) to give 10 g (43%) of **6a** and **6b**, $n^{20}$D 1.5366.

*Anal.* Calcd for $C_6H_{12}Cl_2Se$: C, 30.58; H, 5.16. Found: C, 30.78; H, 5.25.

The nmr spectrum ($CDCl_3$) of the distilled product showed two multiplets for protons CHCl and CHSe centered at 4.2 and 3.0 ppm, respectively, each corresponding to 1.5 protons. Overlapping doublets of the $CH_3$ groups were centered at 1.6 ppm.

The ir spectrum showed major absorption bands at 1370, 1260, 1165, 1003, 890, 670, and 610 cm$^{-1}$ in the region from 2000 to 600 cm$^{-1}$.

**2,5-Chloromethylselenacyclopentane (7).**—To 150 ml of methylene chloride, maintained at −20°, were added solutions of 27.5 g (0.12 mol) of selenium monochloride and 9.84 g (0.12 mol) of hexadiene-1,5, each in 75 ml of methylene chloride. On addition, an immediate precipitation of selenium and **7a** occurred. After the suspension was maintained at −20° for 8 hr, the red precipitate was filtered off (14.0 g) and the volatile components of the filtrate were evaporated to give 12.6 g of product, from which on treatment with diethyl ether 5.4 g of **7a** was filtered off.

*Anal.* Calcd for $C_6H_{10}Cl_4Se$: C, 23.79; H, 3.33; Cl, 46.81. Found: C, 23.94; H, 3.25; Cl, 46.84.

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(19) C. P. Smyth, G. L. Lewis, A. J. Grossman, and E. B. Jennings, *J. Amer. Chem. Soc.*, **62**, 1219 (1940).

(20) H. Stammreich and R. Forneris, *Spectrochim. Acta*, **8**, 46 (1956).

(21) S. G. Frankiss, *J. Mol. Struct.*, **2**, 271 (1968).

(22) F. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969).

(23) W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strauz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 4277 (1966).

The filtrate of **7a** was distilled to give 6.3 g (23%) of **7**, bp 75–8° (0.001 mm), $n^{20}{}_D$ 1.5796, leaving only traces of a distillation residue.

*Anal.* Calcd for $C_6H_{10}Cl_2Se$: C, 31.06; H, 4.34; Cl, 30.56. Found: C, 31.53; H, 4.16; Cl, 30.81.

The nmr spectrum of 7 ($CDCl_3$) showed the four protons of the $CH_2Cl$ groups between 3.5 and 4.1 ppm, the two protons CHSe were centered at 3.05 ppm, and the four methylenic ring protons were observed between 1.7 and 2.5 ppm in agreement with the proposed structure.

The ir spectrum of 7 showed major absorption peaks at 1435, 1260, 1170, 1145, 806, 745, 708, and 635 $cm^{-1}$ in the region from 2000 to 600 $cm^{-1}$.

**The Reaction of 7 with 1,5-Diazobicyclo[5.4.0]undec-5-ene.**—To a solution of 4.64 g (0.02 mol) of **7** in 25 ml of chloroform was added 9.2 g (0.06 mol) of 1,5-diazobicyclo[5.4.0]undecene. An exothermal reaction proceeded and moderate refluxing of the solution was observed. Gas chromatographic analysis indicated the absence of starting material 5 min after the addition of the reagents and showed the formation of hexadiene-1,5 as the only detectable product in a yield of 47.5%. The diene was identified by its gas chromatographic retention time and by the ir absorption spectrum of the distillable reaction products, consisting of both hexadiene-1,5 and chloroform.

**2,6-Dichloromethyl-1,4-selenoxane** (**8**).—Solutions of 10.7 g (0.11 mol) of diallyl ether and 22.9 g (0.10 mol) of selenium monochloride, each in 50 ml of methylene chloride, were added at an equivalent rate over a period of 30 min to 50 ml of methylene chloride, which was maintained at −20°. The suspension was kept at this temperature for 24 hr and was then filtered, and the volatile portions were evaporated to give 20.3 g of a partially crystallized material, which was exhaustively extracted with hexane. Evaporation of the extract and recrystallization of the product gave 3.9 g of **8**, mp 61–71°, and 1.2 g of product, mp 40–60° (21%). Recrystallization by chilling a methanol solution of the product to −20° produced an analytical sample, mp 75–77.5°.

*Anal.* Calcd for $C_6H_{10}Cl_2OSe$: C, 29.05; H, 4.06; Cl, 28.59. Found: C, 29.43; H, 4.23; Cl, 28.75.

The nmr spectrum ($CDCl_3$) could not be resolved in detail but supports the structure **8** by a proportion of $CH_2O/CH_2Cl/CHSe$ of 2:2:1.

**2,6-Dichloro-9-selenobicyclo[3.3.1]nonane** (**10a**). **A.**—Equimolar solutions of selenium monochloride (30 g, 0.131 mol), and *cis,cis*-cyclooctadiene-1,5 (14.1 g, 0.131 mol), each made up to 75 ml in methylene chloride, were added to 150 ml of methylene chloride at an internal temperature of −20° over a period of 15 min. After 12 hr, 12.1 g of insoluble product was filtered off and the filtrate was evaporated to give 25.9 g (76%) of a colorless crystalline material, mp 80–88°; recrystallization from benzene raised the melting point to 99.5–102°.

*Anal.* Calcd for $C_8H_{12}Cl_2Se$: C, 37.24; H, 4.68; Cl, 27.48. Found: C, 37.55; H, 4.69; Cl, 27.72.

The ir spectrum showed major absorption peaks at 1480, 1444, 1135, 797, 690, 592, and 556 $cm^{-1}$. The nmr spectrum ($CDCl_3$) showed a multiplet for the protons CHCl at 4.90 ppm, whereas the 10 remaining protons are poorly resolved in the range from 3.2 to 2.1 ppm.

B.—To 20 ml of concentrated hydrochloric acid was added 0.4 g (0.0018 mol) of the dihydroxy selenide **10b**. A crystalline material separated from the solution within several minutes, and, after heating to 60° for 3 hr, the suspension was filtered and the residue was air dried to give 0.38 g of **10a**. Exhaustive sublimation at 70° (0.2 mm) and recrystallization from benzene gave 0.2 g (43%) of **10a**, mp 99–102°. The product was identified by its ir spectrum and its mixture melting point as being identical with the product obtained from selenium monochloride and cyclooctadiene.

**The Reaction of 10a with Potassium Cyanide and Lithium Aluminum Hydride.**—To a solution of 1.3 g (0.02 mol) of potassium cyanide in 40 ml of 95% aqueous ethanol was added 1.29 g (0.005 mol) of **10a** at 60°. The reaction proceeded instantaneously and the gas chromatographic spectrum showed the formation of 56% cyclooctadiene-1,5 after the reaction mixture was maintained at 60° for 12 hr.

Only cyclooctadiene-1,5 was observed in the gas chromatogram of a mixture obtained by the reduction of 0.9 g (0.0035 mol) of **10a** with 0.19 g (0.005 mol) of lithium aluminum hydride in tetrahydrofuran, after the suspension was refluxed for 3 hr.

**2,6-Dihydroxy-9-selenobicyclo[3.3.1]nonane** (**10b**).—To 50 ml of boiling water was added 2.0 g (0.007 mol) of the dichloro selenide **10a** with rapid stirring over a period of 5 min. The clear solution was cooled to 25°, 0.5 g of polymeric product was filtered off, and the filtrate was continuously extracted with diethyl ether. On partial evaporation of the ether extract, 0.6 g of **11b** was obtained: mp 183–186°; total yield 70%. Recrystallization of the crude product from diethyl ether and drying over phosphorus pentoxide provided an analytical sample, mp 188° dec.

*Anal.* Calcd for $C_8H_{14}O_2Se$: C, 43.55; H, 6.37. Found: C, 43.28; H, 6.45.

The ir spectrum (KBr) showed very intense peaks at 1015 and 3300 $cm^{-1}$ and medium absorptions at 2890, 1480, 1445, 1428, 1350, 978, 870, and 645 $cm^{-1}$.

**The Reaction of Selenium Monochloride with Bicyclo[2.2.1]-heptadiene-1,5** (**11a and 11b**).—To a solution of 12.97 g (0.141 mol) of bicycloheptadiene was added 32.3 g (0.141 mol) of selenium monochloride in 100 ml of methylene chloride at an internal temperature of −20°. After complete addition of the chloride, another 18.4 g (0.2 mol) of bicycloheptadiene was added, after which a negative test with potassium iodide was obtained. After filtration of 12.3 g of selenium and the removal of volatile portions under vacuum at 30° (1 mm), 47.2 g (100%) of crude product was obtained.

*Anal.* Calcd for $C_{14}H_{16}Cl_2Se$: C, 50.32; H, 4.83. Found: C, 50.04; H, 4.84.

No attempt was made to purify the reaction product. The nmr spectrum ($CDCl_3$) showed signals for 1.4 olefinic protons centered at 6.2 ppm and 2.6 protons between 2.0 and 1.0 ppm, probably representing $CH_2$ and nortricyclene protons. Protons of the group CHCl (1.0) and CHSe (2.0) are represented by complex patterns in the ranges from 3.5 to 4.2 and from 2.9 to 3.5 ppm, respectively.

**The Reaction of Selenium Monochloride with 2,6-Dichloro-9-thiabicyclo[3.3.1]nonadiene-2,7** (**13a**).—A solution of 3.1 g (0.015 mol) of **12** and 3.5 g (0.015 mol) of selenium monochloride in 25 ml of benzene was refluxed for 5 days, after which time gas chromatographic analysis indicated the absence of **12**. Evaporation of the reaction mixture and exhaustive extractions with boiling heptane gave 2.2 g (42%) of **13a**, mp 225–228°.

*Anal.* Calcd for $C_8H_8SSeCl_4$: C, 26.92; H, 2.26; Cl, 39.73; S, 8.98. Found: C, 27.12; H, 2.36; Cl, 39.57; S, 9.22.

The ir spectrum of **13a** showed major absorption bands at 1320, 1225, 798, 782, and 663 $cm^{-1}$.

The nmr spectrum (0.15 g in 2.0 g of $CDCl_3$) at 60° showed protons for CHCl at 5.67 and 5.55 ppm and protons for CHSe at 3.24 and CHS at 3.08 ppm, respectively, in agreement with the assigned structure.

**Registry No.**—Selenium monochloride, 21317-32-8; **7**, 21321-60-8; **8**, 21321-61-9; **10a**, 21321-62-0; **10b**, 21321-63-1; **11a**, 21321-64-2; **11b**, 21321-65-3; **13a**, 21339-84-4.

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