

## Intramolecular Oxyselenation of Diolefins <sup>1</sup>

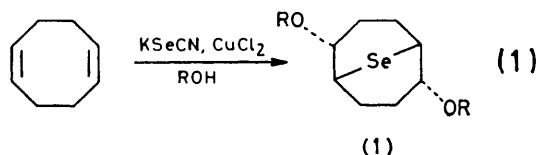
By Akio Toshimitsu, Sakae Uemura,\* and Masaya Okano, Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

Reaction of *cis,cis*-cyclo-octa-1,5-diene, diallyl ether, or hexa-1,5-diene with copper(II) chloride and potassium selenocyanate in methanol gives smoothly 2,6-dimethoxy-9-selenabicyclo[3.3.1]nonane (1), an isomeric mixture of 3,5-bis(methoxymethyl)-1-oxa-4-selenan (2) and 3-methoxymethyl-6-methoxy-1,4-oxaselenepan (3), or an isomeric mixture of 2,5-bis(methoxymethyl)selenolan (4) and 2-methoxymethyl-5-methoxyselenan (5), respectively, in good yield. The <sup>13</sup>C n.m.r. spectra of (2)–(5) revealed the presence of nearly equal amounts of two isomers in each compound, probably *cis* and *trans* with respect to the two substituents on the ring. The reaction has been revealed to proceed through methoxyselenocyanation of one double bond, followed by *in situ* intramolecular oxyselenation of the other in the resulting alkyl selenocyanates. Isomerizations between (2) and (3) and also between (4) and (5) were effected by hydrogen chloride in methanol through an episelenium ion intermediate, the ratios of (2) : (3) and (4) : (5) being 95 : 5 and 41 : 59 respectively at equilibrium.

It has recently been reported <sup>2</sup> that treatment of an olefin with potassium selenocyanate and copper(II) chloride in alcohol resulted in the introduction of both alkoxy and selenocyanate groups into vicinal position of the olefin to afford an alkoxy-selenocyanatoalkane in good yield. When this reaction was applied to certain diolefins, it was found that no such compounds were formed, but instead selenium-containing ring compounds were obtained in high yield. In some cases the products consisted of isomeric mixtures, the ratio of the isomers depending very much on the reaction conditions because of isomerization. We now report details of this novel reaction and discuss the mechanisms for formation and isomerization of the products. The direct synthesis of selenacycloalkanes from diolefins has so far been known only for one case, the reaction with selenium monochloride.<sup>3</sup>

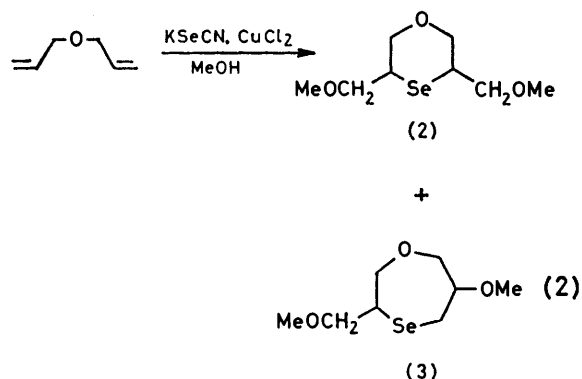
### RESULTS AND DISCUSSION

The reaction was generally carried out by adding a methanol solution of the diolefin to a methanol suspension of copper(II) chloride and potassium selenocyanate (molar ratio 2 : 1) at room temperature and by heating the resulting mixture at reflux for appropriate times. From *cis,cis*-cyclo-octa-1,5-diene(1,5-COD), a single stereoisomer of 2,6-dimethoxy-9-selenabicyclo[3.3.1]nonane (1; R = Me) was obtained as the sole product [equation (1)]. The reaction also proceeded in

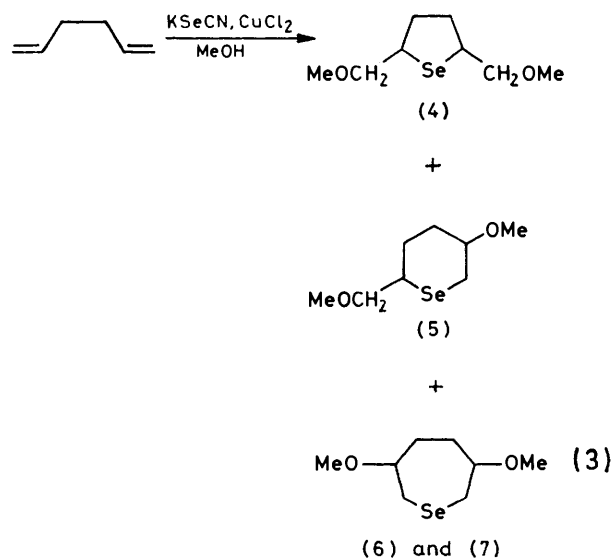


ethanol and propan-2-ol to give (1; R = Et and Pr<sup>i</sup>) respectively. From diallyl ether an isomeric mixture of 3,5-bis(methoxymethyl)-1-oxa-4-selenan (2) and 3-methoxymethyl-6-methoxy-1,4-oxaselenepan (3) was obtained, (2) being the main product [equation (2)]. The ratio of (2) to (3) which is more than unity even for short reaction times increased with longer reaction times, suggesting that (3) isomerizes to the thermodynamically more stable (2) under these conditions. Similarly, from

hexa-1,5-diene, an isomeric mixture of 2,5-bis(methoxymethyl)selenolan (4) and 2-methoxymethyl-5-methoxy-

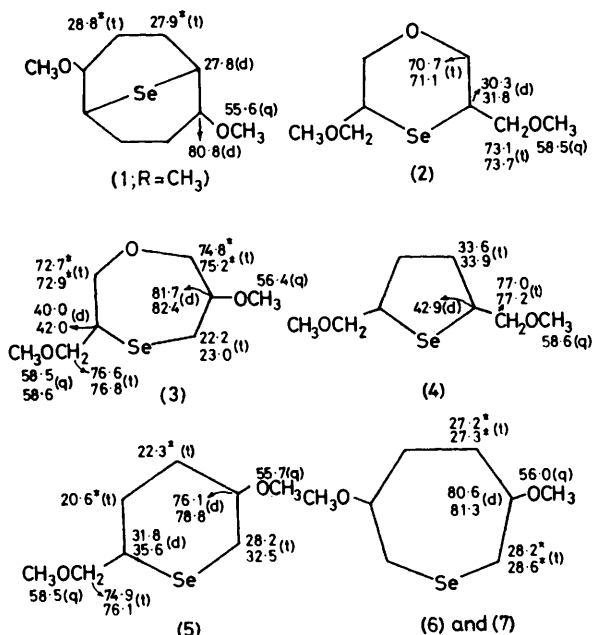


selenan (5) was obtained, (5) being the main product [equation (3)]. In this case the ratio of (5) to (4) which is also more than unity at short reaction times did not fall to less than unity, showing that (5) is thermo-



dynamically more stable than (4), but the kinetically controlled ratio (5) : (4) is much higher than the thermo-

dynamically one in contrast to the case of (2) and (3). When the reaction was carried out at room temperature,



<sup>13</sup>C N.m.r. data for compounds (1)—(7). Tentative assignments are denoted by asterisks

small amounts of stereoisomeric 3,6-dimethoxyselenepans [(6) and (7)] were also formed together with (4) and (5)

each compound except (1) consisted of nearly equal amounts of two stereoisomers, probably *cis* and *trans* with respect to the two substituents on the ring.\* Chemical shifts and coupling patterns in <sup>13</sup>C n.m.r. spectra are shown in the Figure together with those of (6) and (7). The chemical shift of carbon bound to selenium appeared at *ca.* δ 30 p.p.m. which agrees with shifts reported for some organoselenium compounds.<sup>4</sup>

It should be noted here that the chloro analogue of (1), 2,6-dichloro-9-selenabicyclo[3.3.1]nonane, and also several sulphur analogues exhibit sharp absorptions at 1480—1490 cm<sup>-1</sup> in the i.r. spectra,<sup>3,5</sup> these bands being attributed to C-H bending vibrations of the methylene group of the ring system which has a twin-chair conformation. The i.r. spectrum of (1) shows a sharp absorption at 1481—1483 cm<sup>-1</sup>, supporting the presence of a [3.3.1] ring system. In the light of the fact that both <sup>13</sup>C n.m.r. and g.l.c. analyses revealed the presence of only one isomer in (1) together with the assumed configuration of 2,6-dichloro-9-selenabicyclo[3.3.1]nonane,<sup>3</sup> we assign the structure of (1) as shown in equation (1), *i.e.* both alkoxy groups are *trans* to selenium.

It has already been shown that mono-olefins gave vicinal alkoxy-selenocyanatoalkanes under the same conditions [equation (4)].<sup>2</sup> This compound therefore seems to be the intermediate also in the reaction with diolefins. In order to investigate this possibility we prepared separately the corresponding alkoxy-seleno-

TABLE 1

Reactions of several diolefins with CuCl <sub>2</sub> and KSeCN in alcohols at reflux temperature						
Diolefin (mmol)	CuCl <sub>2</sub> (mmol)	KSeCN <sup>a</sup> (mmol)	ROH (ml) R	t/h	Products (isomer ratio) and yield (%) <sup>b</sup>	
Cyclo-octa-1,5-diene						
1	2	1	Me 20	4	(1; R = Me)	84
10	20	10	Me 40	0.25	(1; R = Me)	73
1	2	1	Et 20	4	(1; R = Et)	86
1	2	1	Pr <sup>t</sup> 20	4	(1; R = Pr <sup>t</sup> )	87
Diallyl ether						
1	2	1	Me 10	0.5	(2) + (3) (80:20)	36
1	2	1	Me 10	25	(2) + (3) (95:5)	74
15	20	10	Me 40	0.25	(2) + (3) (81:19)	63
Hexa-1,5-diene						
2	2	2	Me 20	0.5	(4) + (5) (27:73)	62
1	2	1	Me 20	10	(4) + (5) (41:59)	59
2	2	2	Me 20	10	(4) + (5) (40:60)	88
20	20	10	Me 40	0.25	(4) + (5) (32:68)	72

<sup>a</sup> Since the purity of commercial KSeCN was *ca.* 80%, 1.25 times the theoretical amount was weighed out. <sup>b</sup> Determined by g.l.c. analysis. Yield is based on the stoichiometry of equation (4).

[*e.g.* at 20° for 7 h, 40% (4) + (5) and 3% (6) + (7) (42:58)]. It was generally necessary to use the dilute alcoholic solution of reagents in order to obtain good yields and to reduce intermolecular addition which leads to polymer formation. Typical results are shown in Table 1.

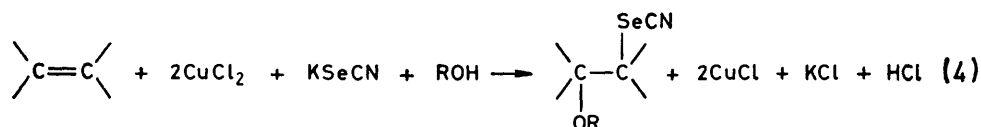
Each of (1)—(5) was purely isolated by distillation or preparative g.l.c. and its structure was assigned by <sup>1</sup>H and <sup>13</sup>C n.m.r., i.r., and mass spectra, and elemental analyses, <sup>13</sup>C n.m.r. spectroscopy being a useful method for determining the structures. Although only a single signal was obtained for each of (1)—(5) on various columns by g.l.c. analyses, <sup>13</sup>C n.m.r. data showed that

cyanatoalkanes (8) and (9) by methoxythallation of diallyl ether and hexa-1,5-diene followed by *in situ* substitution of thallium by selenocyanato<sup>6</sup> and treated these under various conditions in methanol [equations (5) and (6)]. A mixture of (2) and (3) and of (4)—(7) were obtained from (8) and (9), respectively, by stirring each in the presence of copper(II) or hydrogen chloride, the isomer ratios depending on the conditions. Typical results are shown in Table 2. The following facts are clear from Table 2 (1). Compound (8) is thermally stable

\* A mixture of (6) and (7) which appeared as separate peaks on g.l.c. was isolated from the products of intramolecular oxy-selenation of (9) by preparative g.l.c.

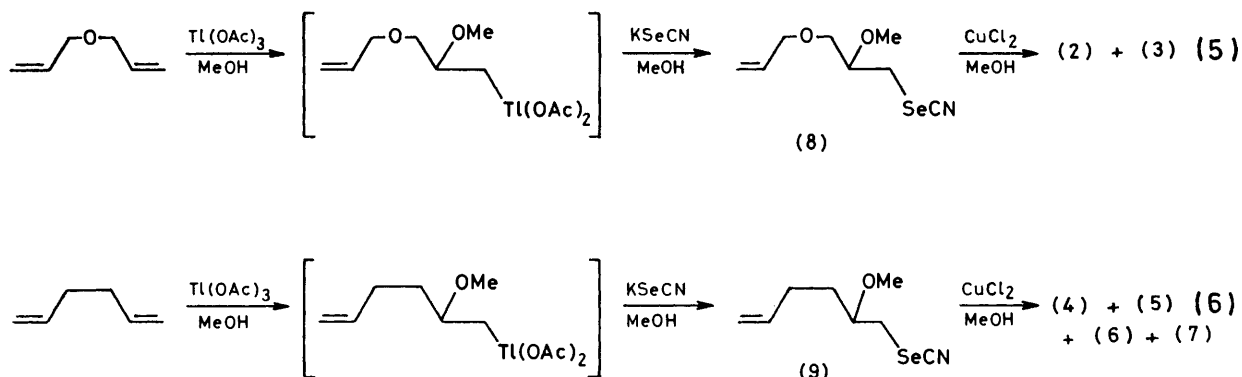
in refluxing methanol, while (9) is slowly converted into a mixture of (5)—(7) under the same conditions. (2) In contrast to the ready formation of six- and seven-

(1)—(7) can be formed by alkoxy-selenocyanation of one double bond, followed by *in situ* intramolecular alkoxy-selenation of the other in the resulting alky-seleno-



membered cyclic selenides, *i.e.* (3) from (8), and (5)—(7) from (9), no eight-membered ring compound is formed from (8) under any conditions. (3) Copper(II) chloride

cyanates [equation (7); 1,5-COD as diolefin].\* For diallyl ether and hexa-1,5-diene, the formation of regioisomers of (8) and (9), namely allyl 2-selenocyanato-



and hydrogen chloride accelerate the conversion rate profoundly. (4) Compound (3) and a mixture of (5)—(7) are the initial products from (8) and (9), respectively,

3-methoxypropyl ether and 5-selenocyanato-6-methoxyhex-1-ene, and their conversion into cyclic selenium compounds are also quite plausible.

TABLE 2

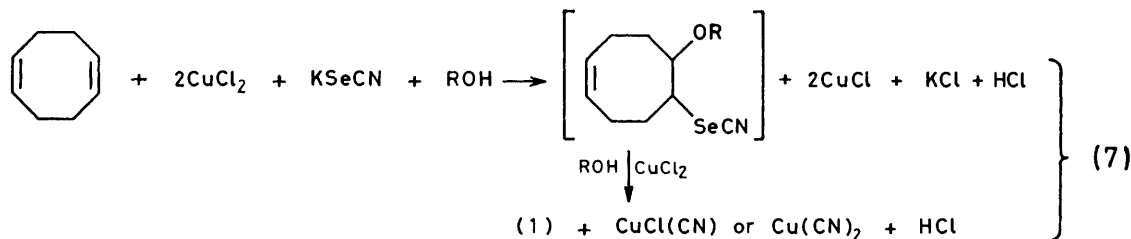
Intramolecular oxy-selenation of (8) and (9)

Compound	Amount (mmol)	Additive (mmol)	MeOH (ml)	T/°C	t/h	Products and yield (%) (isomer ratio) <sup>a</sup>	
						(8)	100
(8)	1		10	65	20	(8)	100
(8)	1	HCl 0.5	10	65	10	(2) + (3) <sup>b</sup>	86 (75 : 25)
(8)	1	CuCl <sub>2</sub> 1	2.5	25	10	(2) + (3) <sup>b</sup>	36 (4 : 96)
(8)	2	CuCl <sub>2</sub> 2	5	65	0.5	(2) + (3) <sup>b</sup>	60 (24 : 76)
(9)	1		5	65	20	(5) + (6) + (7) <sup>c</sup>	100 (76 : 11 : 13)
(9)	1	CuCl <sub>2</sub> 1	2.5	25	10	(4) + (5) + (6) + (7) <sup>c</sup>	79 (2 : 91 : 3 : 4)
(9)	2	CuCl <sub>2</sub> 2	5	65	0.5	(4) + (5) <sup>c</sup>	68 (35 : 65)

<sup>a</sup> Determined by g.l.c. analysis. <sup>b</sup> No (8) was detected after the reaction. <sup>c</sup> No (9) was detected after the reaction.

and then isomerization to (2) and to (4) occurs in the presence of copper(II) chloride or hydrogen chloride at higher temperatures.

Lastly, in order to obtain more information on the isomerizations of the selenium-containing cyclic products, each of (2)—(7) or a mixture of known components was



These results clearly show that (8) and (9) are intermediates in these reactions. Since it has already been shown that olefins react with alkyl or phenyl selenocyanate and alcohol in the presence of copper(II) chloride to give  $\beta$ -alkoxyalkyl selenides (oxy-selenation of olefin),<sup>7</sup> the conversions observed here may be regarded as intramolecular oxy-selenations. That is, compounds

heated in methanol in the presence of hydrogen chloride and/or copper(II) chloride. Copper(II) chloride had almost no effect on isomerization, while hydrogen

\* We could isolate 5-methoxy-6-thiocyanatocyclo-octene from the reaction of 1,5-COD with copper(II) chloride and potassium thiocyanate in methanol. This compound was quite stable and did not give any sulphur analogue of (1) under the conditions we employed.

chloride had a marked effect. In the presence of hydrogen chloride a nearly equilibrium mixture was obtained from isomeric mixtures of any composition

can be formed in the reaction system [see equation (4) or (7)]. One plausible mechanism for this conversion may be protonation on the oxygen of the methoxy group

TABLE 3

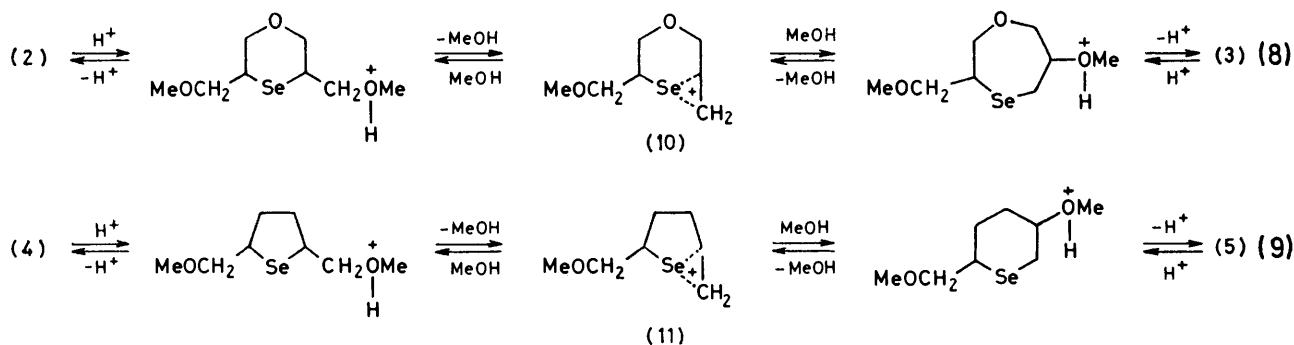
Isomerization of (2)—(7) in methanol at reflux temperature in the presence of hydrogen chloride

Starting material (isomer ratio)	Amount (mmol)	HCl (mmol)	MeOH (ml)	t/h	Products (isomer ratio) <sup>a</sup>
(2)	1	0.5	10	25	(2) + (3) (95 : 5)
(3)	1	0.5	10	0.5	(2) + (3) (20 : 80)
(3)	1	0.5	10	25	(2) + (3) (95 : 5)
(4)	0.2	0.1	2	0.5	(4) + (5) (64 : 36)
(4)	0.2	0.1	2	12.5	(4) + (5) (41 : 59)
(5) + (6) + (7) (76 : 11 : 13)	0.8	0.4	8	0.5	(4) + (5) (28 : 72)
(4) + (5) (28 : 72)	1	0.5	10	12.5	(4) + (5) (41 : 59)
(6) + (7) (34 : 66)	0.5	0.25	5	0.5	(4) + (5) (21 : 79)

<sup>a</sup> Determined by g.l.c. analysis. Yields are almost quantitative in all cases.

after 12.5 or 25 h in refluxing methanol. The ratios of (2) : (3) and (4) : (5) at equilibrium were 95 : 5 and 41 : 59, respectively; (2) and (5), both of which are six-membered

intermediate which can be stabilized by selenium participation in the form of an episelenium ion [(10) and



compounds, are thermodynamically more stable in each case. Typical results are shown in Table 3. The isomerization of the products in equations (1)—(3) therefore occurs by the action of hydrogen chloride which

(11)] as shown in equations (8) and (9). Then attack of solvent methanol on this intermediate leads to both products, the formation of the thermodynamically more stable one being favoured. The participation of an

TABLE 4  
Characterization of new compounds

Compound	B.p. (°C) [ <i>p</i> /Torr]	Chemical shift $\delta^a$	Found (required) (%)			$\nu_{\max.}/\text{cm}^{-1}$
			C	H	N	
(1; R = Me)	137—139 [9]	1.6—2.5 (6 H, m), 2.5—2.9 (2 H, m), 3.0—3.2 (2 H, m), 3.44 (6 H, s), 3.8—4.2 (2 H, m)	48.1 (48.2)	7.4 (7.3)		1 482 ( $\delta_{\text{CH}_2}$ )
(1; R = Et)	115—117 [4]	1.22 (6 H, t, <i>J</i> 7 Hz), 1.7—2.4 (6 H, m), 2.5—2.9 (2 H, m), 2.95—3.15 (2 H, m), 3.57 (2 H, q, <i>J</i> 7 Hz), 3.66 (2 H, q, <i>J</i> 7 Hz), 3.95—4.25 (2 H, m)	52.3 (52.0)	8.1 (8.0)		1 483 ( $\delta_{\text{CH}_2}$ )
(1; R = Pr <sup>i</sup> )	122—124 [4]	1.13 (3 H, d, <i>J</i> 6 Hz), 1.15 (3 H, d, <i>J</i> 6 Hz), 1.7—3.1 (10 H, m), 3.75 (2 H, septet, <i>J</i> 6 Hz), 4.10 (2 H, dt, <i>J</i> 3.5 and 9 Hz)	54.9 (55.1)	8.6 (8.6)		1 481 ( $\delta_{\text{CH}_2}$ )
(2)	115—120 [7] <sup>b</sup>	3.24 (6 H, s), 2.9—4.0 (10 H, m)	40.3 (40.2)	6.7 (6.8)		
(3)		3.42 (6 H, s), 3.45—4.25 (10 H, m)	40.35 (40.2)	6.7 (6.8)		
(4)	112 [8] <sup>c</sup>	1.6—2.2 (4 H, m), 3.30 (6 H, s), 3.2—3.8 (6 H, m)	43.1 (43.1)	7.4 <sup>d</sup> (7.2)		
(5)		1.1—2.9 (7 H, m), 3.36br (3 H, s), 3.39 (3 H, s), 3.1—3.7 (3 H, m)				
(6) + (7)	<sup>e</sup>	1.4—2.2 (4 H, m), 2.5—3.1 (4 H, m), 3.36 (6 H, s), 3.4—3.6 (2 H, m)	43.5 (43.1)	7.0 (7.2)		
(8)	108—110 [4]	3.46 (3 H, s), 3.2—3.9 (5 H, m), 4.01br (2 H, d, <i>J</i> 6 Hz), 5.0—5.4 (2 H, m), 5.6—6.3 (1 H, m)	41.4 (41.0)	5.6 (5.6)	6.2 (6.0)	2 150 ( $\nu_{\text{SeCN}}$ )
(9)	112—115 [6]	1.4—2.3 (4 H, m), 3.37 (3 H, s), 3.0—3.6 (3 H, m), 4.8—5.2 (2 H, m), 5.5—6.1 (1 H, m)	43.9 (44.0)	6.2 (6.0)	6.3 (6.4)	2 150 ( $\nu_{\text{SeCN}}$ )

<sup>a</sup> Determined by 100 MHz n.m.r. The spectra of (8) and (9) were determined by 60 MHz n.m.r. <sup>b</sup> B.p. of a mixture of (2) and (3) [(2) : (3) 8 : 2]. <sup>c</sup> B.p. of a mixture of (4) and (5) [(4) : (5) 4 : 6]. <sup>d</sup> Analysis of a mixture of (4) and (5) [(4) : (5) 4 : 6]. <sup>e</sup> Not determined.

analogous episulphonium ion intermediate has been proposed in the reaction of sulphur dichloride with diolefins affording cyclic sulphides.<sup>8</sup>

#### EXPERIMENTAL

All organic and inorganic materials were commercial products. Potassium selenocyanate (purity *ca.* 80%) was from Wako Pure Chemicals Ltd. I.r. spectra were recorded with Hitachi EPI-S2 and Perkin-Elmer 521 spectrometers. <sup>1</sup>H N.m.r. spectra were taken with Varian EM-360 and JEOL MH-100 instruments for solution in CDCl<sub>3</sub> or CCl<sub>4</sub> with Me<sub>4</sub>Si as internal standard (with internal and external lock respectively). <sup>13</sup>C N.m.r. spectra were taken at 25.1 MHz with a JEOLCO <sup>13</sup>C Fourier transform n.m.r. system (JNM-PFT-100) and were recorded after 50–100 pulses with intervals of 3 s. An internal deuterium lock was employed and Me<sub>4</sub>Si used as internal standard. G.l.c. analyses were carried out with a Shimadzu 5APTF apparatus generally using an EGSS-X (15%)–Chromosorb W (1 m) column [N<sub>2</sub> as carrier gas; diphenyl or benzophenone as internal standard]; in some cases DEGS (25%)–Shimalite (1 m), Apiezon L (25%)–Shimalite (1 m), and PEG-6000 (25%)–Shimalite (1 m) columns were used. A Varian 920 apparatus was used for preparative g.l.c. [He as carrier gas; EGSS-X (15%)–Chromosorb W (1 m × 3/8 in) column]. Properties of all new compounds are summarized in Table 4.

**Preparation of Compounds (1)–(5).**—A typical experimental procedure is as follows. *cis,cis*-Cyclo-octa-1,5-diene (1.08 g, 10 mmol) was added to methanol (40 ml) containing copper(II) chloride (2.68 g, 20 mmol) and potassium selenocyanate (1.80 g, 10 mmol as pure KSeCN) at room temperature with vigorous stirring, and the mixture heated at reflux temperature for 0.25 h during which period the colour turned from red to black. After cooling, the red-brown precipitates were filtered off and the filtrate added to water (*ca.* 200 ml) and extracted with benzene (70 ml × 3). The extract was concentrated to *ca.* 10 ml, then analysed by g.l.c. (diphenyl as internal standard) giving compound (1; R = Me) (7.26 mmol, 73%).

**Preparation of Compounds (8) and (9).**—A solid thallium(III) acetate (9.55 g, 25 mmol) was added in small portions to a methanolic solution (125 ml) of hexa-1,5-diene (4.10 g, 50 mmol) with stirring to give a pale yellow solution. After the solution was kept at 15–20 °C for 2 h with stirring, a methanolic solution (25 ml) of potassium selenocyanate (9.00 g, 50 mmol as pure KSeCN) was added to give a heavy yellow precipitate. The mixture was then heated at reflux temperature for 0.5 h to give a precipitate of TlSeCN. The cooled mixture was filtered, and the filtrate added to water (500 ml) and then extracted with benzene (100 ml × 3). The extract was washed with aqueous NaHCO<sub>3</sub> and water and then dried over MgSO<sub>4</sub>. Distillation gave pure (9) (2.89 g, 13.2 mmol, 53%).

Similar treatment of diallyl ether with the same scale of reactants afforded pure (8) (2.06 g, 8.8 mmol, 35%).

**Intramolecular Oxyselenation of Compounds (8) and (9).**—A methanolic solution (45 ml) of (9) (1.94 g, 8.90 mmol) was heated at reflux temperature for 20 h. The solution was then poured into water (200 ml) and the product was

extracted with benzene (70 ml × 3). After the benzene extract had been treated as described above, benzene was removed and the residual oil was separated by preparative g.l.c. into two parts [(5) (1.44 g, 6.46 mmol, 73%) and (6) + (7) (0.29 g, 1.30 mmol, 15%)].

A green methanolic suspension (30 ml) of (8) (3.51 g, 15 mmol) and copper(II) chloride (2.00 g, 15 mmol) was stirred at 25 °C for 18 h during which period the colour turned black. The solution was then treated as described above. Distillation of the benzene extract afforded a mixture of (2) and (3) (0.64 g, 2.68 mmol, 18%) [(2) : (3) 8 : 92], b.p. 102–105 °C at 5 Torr.

**Isomerization between Compounds (4) and (5).**—A typical experimental procedure is as follows. A methanolic solution (2 ml) of (4) (45 mg, 0.20 mmol) and hydrogen chloride (36.5% HCl; 0.1 mmol as pure HCl) was heated at reflux temperature for 0.5 h. After cooling, the solution was treated as described above. G.l.c. analysis using diphenyl as an internal standard showed the presence of (4) and (5) [0.195 mmol, 98%, (4) : (5) 64 : 36].

**Preparation of 5-Methoxy-6-thiocyanatocyclo-octene.**—A methanolic solution (80 ml) containing *cis,cis*-cyclo-octa-1,5-diene (4.32 g, 40 mmol), copper(II) sulphate (9.99 g, 40 mmol) and potassium thiocyanate (4.86 g, 50 mmol) was heated at reflux temperature for 0.5 h during which period the colour turned from greenish-brown to white. The cooled mixture was then filtered, and the filtrate treated as described above. Distillation of the benzene extract gave pure 5-methoxy-6-thiocyanatocyclo-octene (0.49 g, 12%), b.p. 117–136 °C at 4 Torr; δ(CDCl<sub>3</sub>) 1.6–2.6 (8 H, m), 3.1–3.9 (2 H, m), 3.37 (3 H, s), and 5.5–5.8 (2 H, m); ν<sub>max.</sub> 2 150 (SCN) and 1 645 (C=C) cm<sup>-1</sup> (Found: C, 61.1; H, 7.9; N, 6.7. C<sub>10</sub>H<sub>15</sub>NSO requires C, 60.9; H, 7.7; N, 7.1%).

This compound (1 mmol) was unaffected by heating in refluxing methanol (3 ml) containing copper(II) chloride (1 mmol) for 0.5 h.

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