g (39%) of yellow crystals: mp 202–204 °C; IR (Nujol) 1635 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.98 and 2.01 (2 t, $J = 7.4$ Hz, 2, pyrrole CH_2), 3.99 (t, $J = 7.4$ Hz, 2, NCH_2), 3.96 and 4.04 (2 s, 3, OCH_3), 7.35–7.75 (complex m, 5, ArH); mass spectrum, *m/e* (relative intensity) 307 (100, M$^+$), 292 (30, M$^+$ − CH_3). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.55. Found: C, 73.98; H, 5.49; N, 4.38.

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Registry No. 1a, 72726-02-4; **1b**, 72749-06-5; **1c**, 72726-03-5; **1d**, 72726-04-6; **1e**, 72726-05-7; **1f**, 72726-06-8; **1g**, 72726-07-9; **1h**, 72726-08-0; **1i**, 72749-07-6; **1j**, 72726-09-1; **2a**, 13712-75-9; **2b**, 72726-10-4; **2c**, 72726-11-5; **3a**, 28544-45-8; **3b**, 2392-54-3; **3c**, 5874-58-8; **4a**, 106-51-4; **4b**, 130-15-4; **4c**, 553-97-9; **4d**, 2207-57-0; **5**, 65022-42-6; **6a**, 72726-12-6; **6b**, 72726-13-7; **6c**, 72726-14-8.

Addition of Selenium Tetrachloride to (*E*)- and (*Z*)-2-Butenes[1]

Dennis G. Garratt* and Mark Ujjainwalla

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

George H. Schmid*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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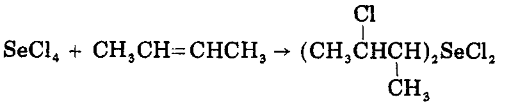
The addition of $SeCl_4$ to (*Z*)-2-butene in methylene chloride at 25 °C forms bis((2*RS*,3*RS*)-3-chloro-2-butyl) and (2*R*,2′*S*,3*R*,3′*S*)-3-chloro-2-butyl 3′-chloro-2′-butyl selenide dichloride. Similarly, addition of $SeCl_4$ to (*E*)-2-butene yields a mixture of bis((2*SR*,3*RS*)-3-chloro-2-butyl) selenide dichloride and (2*S*,2′*R*,3*R*,3′*S*)-3-chloro-2-butyl 3′-chloro-2′-butyl selenide dichloride. Their relative configurations were assigned from their ^{13}C and ^{1}H magnetic resonance spectra. A mechanism involving a stepwise addition of two molecules of alkene to $SeCl_4$ is proposed. Both steps of the addition process involve stereospecific anti addition.

Selenium tetrachloride, $SeCl_4$, reacts with carbon–carbon double bonds in a facile manner.[2-5] For example, 2 mol of an alkene such as 2-butene reacts per mole of $SeCl_4$ to yield bis(3-chloro-2-butyl) selenide dichlorides (eq 1).



$$SeCl_4 + CH_3CH{=}CHCH_3 \rightarrow (CH_3\overset{Cl}{C}H\underset{CH_3}{C}H)_2SeCl_2 \qquad (1)$$

Little is known about the mechanism or the stereochemistry of this reaction. In fact there are a number of abnormalities with respect to reaction conditions and yields in the earlier literature. This is probably due to the incomplete characterization of the selenium reagent.[6-12]

As part of a continuing study of the mechanism and stereochemistry of the additions of selenium reagents to alkenes and alkynes, we wish to report the stereochemistry of this addition reaction.

Results and Discussions

The addition of $SeCl_4$ to 2 equiv of 2-butene can form 10 stereoisomers: two meso isomers and four *dl* pairs. We have found that the reaction of $SeCl_4$ with 2 equiv of (*Z*)-2-butene at 25 °C in anhydrous methylene chloride gives only two products, **1** and **2**, in approximately 90 and 10% yields, respectively. Addition of $SeCl_4$ to (*E*)-2-butene under the same conditions gives two different products, **3** and **4**, in 90 and 10% yields, respectively. The product ratios are based upon integration of nonoverlapping resonances in the ^{1}H NMR spectra. Elemental analyses, obtained for each product mixture, are in agreement with the formation of bis(3-chloro-2-butyl) selenide dichlorides.

The identity and stereochemistry of these four adducts are assigned from their ^{1}H and ^{13}C NMR spectra. The NMR assignments are based upon the observation that, in general, the $SeCl_2R$ group deshields both carbons and protons relative to the effect of a chlorine atom. The exception is a nucleus situated geminal to the selenium, where one observes a shielding interaction. Assignments in Table I were aided by the observation of $^{77}Se^{13}C$ and $^{77}SeC^1H$ spin–spin coupling interactions.

The ^{1}H NMR spectra of adducts **1** and **2** show doublets of quartets with vicinal proton–proton coupling constants of 4.2 and 3.7 Hz, respectively. In contrast, the spectra of adducts **3** and **4**, derived from (*E*)-2-butene, show asymmetric "quintets" with $^3J_{H,H}$ couplings of 6.7 Hz each. The relative configurations were assigned by observing the variations of $^3J_{H,H}$ with solvent dielectric as shown in Table II.[13-15] For the bis-threo compounds $^3J_{H,H}$ should increase with increasing solvent dielectric, whereas for the bis-erythro species a decrease should be observed. Further, $^3J_{H,H}$(threo) is generally less than $^3J_{H,H}$(erythro).

Configurational assignments distinguishing between the *dl*-racemate and meso forms of the bis-threo and bis-erythro adducts were based on the ^{13}C NMR parameters of the methyl carbons geminal to the $SeCl_2R$ moiety and the known δ-syn-1,5 interaction with regard to ^{13}C NMR chemical shifts.[16,17]

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Table I. The Observed ^{1}H and ^{13}C Nuclear Magnetic Resonance Parameters of 1–4 in CD_2Cl_2[a]

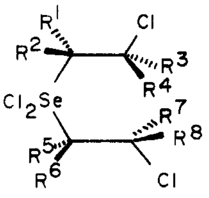
compd	CH_3CCl	CHCl	CHSe	CH_3CSe	$^2J_{Se,CH}$	$^3J_{Se,H}$
			^{1}H Parameters			
1, δ	1.66, d	4.83, dq	4.13, dq	1.83, d	12.2	7
^3J	6.8	6.8, 4.2	6.7, 4.2	6.7		
2, δ	1.64, d	4.87, dq	4.29, dq	1.81, d	12	6
^3J	7.0	7.0, 3.7	5.8, 3.7	6.8		
3, δ	1.73, d	4.94, q^1	4.22, q^1	1.84, d	8.8	5
^3J	6.9	6.9, 6.7	7.1, 6.7	7.1		
4, δ	1.70, d	4.97, q^1	4.20, q^1	1.93, 9	9	6
^3J	6.8	6.8, 6.7	6.8, 6.7	6.8		
			^{13}C Parameters			
1, δ	21.43	56.30	74.47	12.94		
$^1J_{CH}$	130.3	156.2	149.6	131.7		
$J_{Se.C}$		21.5	−62.6	22.0		
2, δ	21.40	56.78	76.03	13.82		
$^1J_{CH}$	128.5	156.2	151.9	130.9		
$J_{Se.C}$		22.3	−60.1			
3, δ	23.77	56.67	73.88	13.92		
$^1J_{CH}$	129.6	154.9	149.9	130.8		
$J_{Se,C}$		19.7	−66.5	21.2		
4, δ	22.89	58.45	74.76	14.04		
$^1J_{CH}$	126.6	155.2	150.5	130.1		
$J_{Se.C}$		20.1	−64.1			

[a] Chemical shifts in δ and coupling constants in hertz.

Table II. Solvent Dependence of Vicinal Proton–Proton Coupling Constants (Hz)

solvent	dielectric constant	1	2	3	4
CCl_4	2.33	3.2	3.0	6.8	6.8
$CDCl_3$	4.70	3.9	3.6	6.7	6.8
CD_2Cl_2	8.9	4.2	3.7	6.7	6.7
CD_3CO_2D	6.19	4.1	3.7	6.6	6.7
$(CD_3)_2CO$	20.7	4.3	3.8	6.5	6.4
CD_3NO_2	38.6	4.5	4.0	6.3	6.0
$(CD_3)_2SO$	49.0	4.5	4.1	6.1	5.9

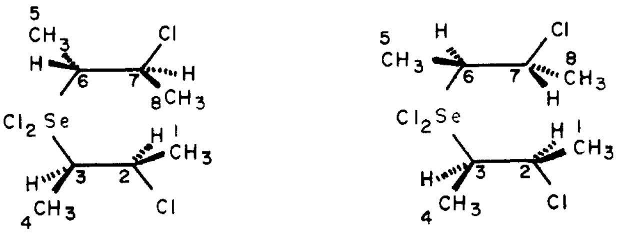
On this basis it is possible to assign **1** and **3** as the *dl* racemates: bis((2*RS*,3*RS*)-3-chloro-2-butyl) and bis((2*RS*,3*SR*)-3-chloro-2-butyl) selenide dichloride, respectively. **2** and **4** are thus the corresponding meso adducts: (2*R*,2′*S*,3*R*,3′*S*)-3-chloro-2-butyl 3′-chloro-2′-butyl and (2*R*,2′*S*,3*S*,3′*R*)-3-chloro-2-butyl 3′-chloro-2′-butyl selenide dichloride, respectively.



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1	CH_3	H	CH_3	H	H	CH_3	H	CH_3
2	CH_3	H	CH_3	H	CH_3	H	CH_3	H
3	H	CH_3	CH_3	H	H	CH_3	CH_3	H
4	H	CH_3	CH_3	H	CH_3	H	H	CH_3

The final two *dl* racemates, **5** and **6**, were prepared by the addition of $SeCl_4$ to 2 equiv of a 1:10 mixture of (*Z*)- and (*E*)-2-butenes in anhydrous methylene chloride at 25 °C. **1**, **2**, **3**, and **4** were formed as well.

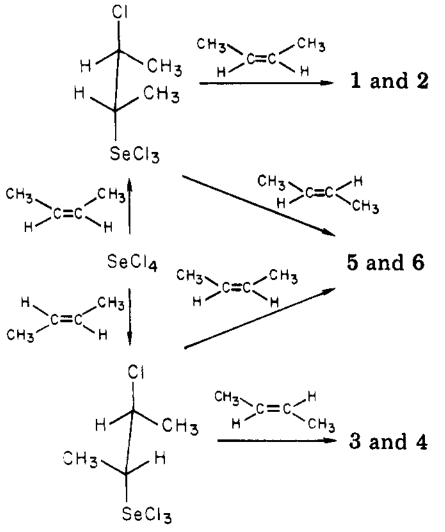
Table III. Observed ^{13}C Nuclear Magnetic Resonance Parameters of 5 and 6



5 **6**

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
5	21.75	56.14	74.35	12.69	13.68	75.13	56.03	22.78
6	21.19	56.88	73.76	13.32	14.23	74.82	57.87	23.44

Scheme I. Stepwise Addition of Two Molecules of Alkene to One Molecule of $SeCl_4$



Their ^{13}C NMR spectra are given in Table III. The major feature of the spectra of **5** and **6** is the lack of symmetry consistent with the proposed structure. The observation that a mixture of **1** and **2** reacts after a period of 1 month with a large excess (40–60-fold) of (*E*)-3-butene to form a mixture of **5** and **6** is further support for their structure.

The absence of a common product from the addition to (*Z*)- and (*E*)-2-butene as well as the stereochemistry of the adducts is consistent with the antistereospecific addition

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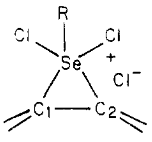
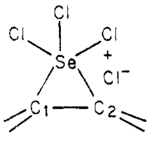
of $SeCl_4$ to both alkenes. This addition could be a synchronous or a stepwise addition. We favor the stepwise mechanism shown in Scheme I. Both steps are electrophilic additions.

Support for this hypothesis is found in the work of Brintzinger and co-workers[3] who treated $SeCl_4$ with vinyl chloride and 1,2-dichloroethylene in chloroform solution. The reaction with vinyl chloride was slow, but reportedly forms bis(2,2-dichloroethyl) selenide dichloride. In contrast, 1,2-dichloroethylene did *not* react even in the presence of aluminum chloride. Furthermore Riley and co-workers[2] reported that $SeCl_4$ reacts in a facile manner with terminal olefins even at low temperatures. Thus the electron-withdrawing nature of the halogens decreases the nucleophilicity of the carbon–carbon double bond, which either retards the rate of addition or does not allow addition to occur at all.

The observation of anti-stereospecific addition in the second step has a precedent in the reported anti additions of β-methylselenium trichloride[18] and 2,4-dinitrophenylselenium trichloride[19] to related alkenes. In view of these apparently similar product-determining steps, one may propose analogous structures for the product-determining transition-state species in the form of a perseleniranium ion, 7. Nucleophilic attack by chloride ion at either C_1 or C_2 of the perseleniranium ion might then be expected to be governed by factors, such as "steric approach control", which are believed to be of importance with respect to collapse of the corresponding seleniranium and thiiranium ions.[20-23] A similar species, 8, may also be proposed to account for the observed anti-stereospecific addition of $SeCl_4$ to the first molecule of olefin to yield the β-chloroalkylselenium trichloride intermediate.



7



8

Although species such as the perseleniranium ions 7 and 8 are able to account for the observed product distributions, it must be emphasized that these species have been proposed in the absence of kinetic data and therefore may not reflect the true stoichiometry of the transition states. For example, our hypothesis does not account for the known trimeric and tetrameric states of aggregation of solvated selenium tetrachloride. That the state of aggregation is of importance has been demonstrated for the related reactions of α- and β-methylselenium trichloride (monomeric and dimeric, respectively) where different reactivities and product distributions have been reported.[18] We therefore feel that until such time as the kinetics may be unambiguously established, our data do not warrant further mechanistic speculation.

Experimental Section

Proton and carbon-13 NMR spectra were run on Varian Associates HA100, T-60, CFT20, and HFT80 spectrometers. Chloroform-*d* was used as an internal lock and reference. All spectra were referenced to Me_4Si. Determination of carbon-13–proton coupling constants was based on first order analysis of the fully coupled naturally abundance carbon-13 spectra and may not, thus, represent true *J* values. Infrared spectra were recorded on a Unicam SPT100 or Perkin-Elmer 237B spectrometer by using CCl_4 solutions in NaCl cavity cells. Melting points were determined on a Fisher-Johns block. Elemental analyses were carried out by A. B. Gygli Microanalysis Laboratory, Toronto.

Selenium tetrachloride was commercially available from Alfa-Ventron and used without further purification.

Alkenes. (*E*)- and (*Z*)-2-butenes were available as the CP gases from Matheson. Isomeric purity was confirmed in all cases via GLC and NMR.

General Procedure. To a freshly prepared solution of $SeCl_4$ (0.221 g, 1.0 mmol) in 25 mL of anhydrous CH_2Cl_2 was added dropwise 2.0 mmol of the appropriate alkene. The solutions turn a clear yellow within a few seconds. Evaporation of solvent leaves yellow-orange oils. Crystallization from pentane or cyclohexane generally gives colorless air and moisture sensitive solids. Specific details are given below for pure species.

Bis(*threo*-3-chloro-2-butyl) Selenide Dichloride (1 + 2): mp 84–85 °C; IR (μm) 3.38, 3.43, 3.50 (sh), 4.14, 4.20, 6.95 (sh), 6.98 (s), 7.25 (vs), 7.28 (s), 7.32 (sh), 7.49 (w), 7.52 (w), 8.79 (w), 8.85 (w), 9.11 (vs), 9.45 (msh), 9.67 (s), 9.96 (m), 10.0 (m), 10.09 (s), 10.55 (vs), 12.3 (bw), 17.9 (bs), 20.42 (s); mass spectrum, (*m*/*e* $[\% \sum_{30}{}^{M+}]$) 297 (2.4), 262 (5.5), 227 (1.7), 199 (5.3), 206 (2.4), 171 (3.6). Anal. Calcd for $C_8H_{16}SeCl_4$: C, 28.86; H, 4.84; Cl, 42.59. Found: C, 29.14; H, 4.79; Cl, 41.63.

Bis(*erythro*-3-chloro-2-butyl) Selenide Dichloride (3 + 4): mp 101–102 °C; IR (μm) 3.39, 3.43, 3.49 (sh), 4.13, 4.19, 6.89 (vs), 7.97 (sh), 7.25 (vs), 7.30 (s), 7.42 (w), 7.52 (m), 7.69 (s), 7.79 (w), 8.72 (m–s), 8.85 (vs), 9.10 (m), 9.23 (m), 9.50 (m), 9.65 (sh, s), 9.75 (bs), 10.0 (vs), 10.25 (s), 10.35 (s), 10.45 (vs), 10.2 (bs), 16.8 (wsh), 17.9 (bs), 19.2 (bm), 19.7 (bs), 20.2 (msh), 20.6 (s), 22.4 (m), 22.85 (ms); mass spectrum, (*m*/*e* $[\% \sum_{30}{}^{M+}]$) 297 (0.8), 262 (5.2), 227 (1.5), 199 (5.0), 206 (2.1), 171 (3.0). Anal. Calcd for $C_8H_{16}SeCl_4$: C, 28.86; H, 4.84; Cl, 42.49. Found: C, 28.65; H, 4.63; Cl, 42.22.

Preparation of Mixed Threo–Erythro Adducts. Procedure i. To a methylene chloride solution, 0.1 M in 2-butenes, prepared from the liquified 2-butenes (*Z*:*E* ratio = 1:10), was added with vigorous stirring, under nitrogen with a Schlenk apparatus, powdered $SeCl_4$ in a portion corresponding to 45% of the theoretical amount required for total conversion of the butenes to adducts. The resultant product mixture contained a preponderance of 1 and 2 and the mixed adducts 5 and 6. 3 and 4 were also present as minor components.

Procedure ii. To a sample of either 1 + 2 or 3 + 4, approximately 1 g in 200 mL of CH_2Cl_2 or ethyl acetate, was added sufficient (*E*)- or (*Z*)-2-butene, respectively, to saturate the solution at 23 °C. After a period of approximately 1 month, workup followed by analysis of resultant oil showed a mixture of the original adducts plus species 5 and 6.

Acknowledgment. Continued financial support from the Natural Science and Engineering Research Council of Canada in the form of annual operating grants to D.G.G. and G.H.S. is gratefully acknowledged.

Registry No. (±)-1, 72852-98-3; *meso*-2, 72904-10-0; (±)-3, 72903-58-3; *meso*-4, 72903-59-4; (±)-5, 72903-60-7; (±)-6, 72903-61-8; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; $SeCl_4$, 10026-03-6.

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