

11.32, 11.50; NMR 7.25 (br s, 2, aromatic), 6.6 (s, 1, C₃ H), 6.4 (s, 1, C₅ H), 4.80 and 4.10 (AB q, 2, $J = 17$ Hz, C₁ H), 1.95 (s, 3, CH₃CO), 1.3 (s, 9, (CH₃)₃C); UV max (EtOH) 220 nm (ϵ 28700), 270 (25700). Anal. Calcd for C₁₆H₁₈Cl₃NO₂: C, 52.99; H, 5.00; N, 3.86. Found: C, 52.88; H, 5.02; N, 3.79.

Preparation of Dichloro-2,3,4,5-tetrahydro-1H-2-benzazepines 10. A solution of the dihydro-2-benzazepines 7 (1.0 g, 2.7 mmol) in 80 mL of MeOH was hydrogenated at atmospheric pressure and room temperature with 200 mg of PtO₂. When uptake of hydrogen ceased, the solution was filtered, and the filtrate was concentrated to an oil. The crude 2-acetyltetrahydro-2-benzazepines thus obtained were covered with 50 mL of 4 M aqueous HCl and were refluxed overnight. This acidic hydrolysate was filtered and cooled overnight in the refrigerator, whereupon it deposited white crystalline hydrochlorides of the desired 2-benzazepines.

8,9-Dichloro-2,3,4,5-tetrahydro-1H-2-benzazepine hydrochloride (10e): 80%; mp 268–270 °C (MeOH–Et₂O). The product was identical spectroscopically with a sample prepared by an independent sequence (mp 268–271.5 °C):⁷ IR 6.4, 7.25, 8.4, 8.8, 11.7, 12.1; NMR (Me₂SO-*d*₆) 9.8 (br s, 2, NH₂, D₂O exchanged), 7.64 and 7.30 (AB q, 2, $J = 8$ Hz, aromatic), 4.58 (s, 2, C₁ H), 3.2 (m, 4, C₃ H and C₅ H), 1.9 (m, 2, C₄ H).

7,8-Dichloro-2,3,4,5-tetrahydro-1H-2-benzazepine hydrochloride (10f): 70%; mp 308–310 °C (MeOH–Et₂O). Spectroscopically, the product was identical with a sample prepared by

an independent sequence (mp 315–317 °C):⁸ IR 6.15, 8.8, 10.1, 10.35; NMR (free base) 7.2 (m, 2, aromatic), 3.85 (s, 2, C₁ H), 3.05 (m, 4, C₃ H and C₅ H), 1.7 (m, 3, NH (D₂O exchanged) and C₄ H). Anal. Calcd for C₁₀H₁₁Cl₂N·HCl: C, 47.55; H, 4.79; N, 5.55. Found: C, 47.24; H, 4.86; N, 5.58.

Acknowledgment. We express our appreciation to David Staiger and Gary Zuber for some of the NMR and IR spectra, Gerald Roberts for the mass spectra, and Edith Reich, Gail Johnson, and Suzanne Jancsik for the combustion analyses.

Registry No. 1a, 89-98-5; 1b, 587-04-2; 1c, 456-48-4; 1d, 104-88-1; 1e, 6334-18-5; 1f, 6287-38-3; 2a, 73261-75-3; 2b, 73261-76-4; 2c, 73261-77-5; 2d, 73261-78-6; 2e, 73261-79-7; 2f, 73261-80-0; 3a, 73261-81-1; 3b, 73261-82-2; 3c, 73261-83-3; 3d, 73261-84-4; 3e, 73261-85-5; 3f, 73261-86-6; 4e, 61563-45-9; 4f, 73261-87-7; 5e, 57987-77-6; 5f, 73075-49-7; 6e, 73261-88-8; 6f, 73261-89-9; 7e, 73261-90-2; 7f, 73261-91-3; 9e, 73261-92-4; 9f, 73261-93-5; 10e, 69739-51-1; 10f, 69239-59-4; aminoacetaldehyde dimethyl acetal, 22483-09-6; *N*-[(2-chlorophenyl)methylene]-2,2-dimethoxyethanamine, 62882-12-6; *N*-[(3-chlorophenyl)methylene]-2,2-dimethoxyethanamine, 62882-13-7; *N*-[(3-fluorophenyl)methylene]-2,2-dimethoxyethanamine, 73261-94-6; *N*-[(4-chlorophenyl)methylene]-2,2-dimethoxyethanamine, 54879-73-1; *N*-[(2,3-dichlorophenyl)methylene]-2,2-dimethoxyethanamine, 57987-75-4; *N*-[(3,4-dichlorophenyl)methylene]-2,2-dimethoxyethanamine, 73274-27-8.

Facile Oxyselenation of Olefins in the Presence of Copper(II) or Copper(I) Chloride as Catalyst

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Treatment of olefinic hydrocarbons with phenyl selenocyanate in alcohol in the presence of copper(II) or copper(I) chloride affords β -alkoxyalkyl phenyl selenide in good yield. Similar reactions in aqueous tetrahydrofuran or acetic acid–chloroform give the corresponding selenide. The reaction is trans stereospecific in the cases of *trans*-2-butene, *cis*-2-butene, and cyclohexene and regioselective in the cases of styrene, acrylaldehyde, crotonaldehyde, and vinyl acetate, respectively. The reaction proceeds even with a catalytic amount of copper(II) chloride. Of the various transition-metal salts examined, nickel(II) halides are similar to copper(II) or copper(I) halides as catalyst; the chlorides of Cr(III) and Co(II) are moderately effective, while the chlorides of Mn(II), Fe(III), Fe(II), Zn(II), Ag(I), Cd(II), Hg(II), Hg(I), Tl(III), and Tl(I) are almost ineffective. The use of the pyridine complex of copper or nickel halides suppresses the reaction. The reaction is presumed to proceed via (i) the polarization of the Se–CN bond by coordination of the effective metal salt to the cyano group and (ii) a nucleophilic attack of olefin on the polarized selenium. The substituent parameters of phenylseleno and selenocyanato groups for ¹³C NMR have been found to be +13 and +15 to ~16 ppm for the α carbon and +6 and +6 to ~7 ppm for the β carbon, respectively.

The chemistry of organoselenium compounds is of current interest from the viewpoint of organic synthesis.¹ One of the key reactions in this chemistry is the introduction of selenium into organic compounds. Oxyselenation of olefins is an effective method for this purpose, and so far several methods have been described in the literature² which use aryl- or alkylselenenyl carboxylate or halide or dimethyl selenoxide. We have now found a new facile oxyselenation reaction of olefins by aryl or alkyl

selenocyanate with various metal halides, especially copper or nickel chloride and bromide, in alcohol, acetic acid, or water.³ This provides another method for organic synthesis using the easily accessible aryl^{4,5} or alkyl selenocyanates.^{6,7a} We describe here the details of this reaction,

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(7) (a) A. Toshimitsu, Y. Kozawa, S. Uemura, and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1273 (1978); (b) A. Toshimitsu, S. Uemura, and M. Okano, *ibid.*, 1206 (1979); (c) N. Esaki, H. Tanaka, S. Uemura, T. Suzuki, and K. Soda, *Biochemistry*, 18, 407 (1979); (d) S. Uemura, A. Toshimitsu, T. Aoi, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 610 (1979).

(1) D. L. J. Clive, *Tetrahedron*, 34, 1049 (1978), and references therein.

(2) G. Hölzle and W. Jenny, *Helv. Chim. Acta*, 41, 593 (1958); H. J. Reich, *J. Org. Chem.*, 39, 428 (1974); H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *ibid.*, 43, 1947 (1978); K. B. Sharpless and R. F. Lauer, *ibid.*, 39, 429 (1974); T. Hori and K. B. Sharpless, *ibid.*, 43, 1689 (1978); D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 100 (1974); N. Miyoshi, S. Furui, S. Murai, and N. Sonoda, *ibid.*, 293 (1973); N. Miyoshi, S. Murai, and N. Sonoda, *Tetrahedron Lett.*, 851 (1977); N. Miyoshi, Y. Takai, S. Murai, and N. Sonoda, *Bull. Chem. Soc. Jpn.*, 51, 1265 (1978).

Table I. Reaction of Olefins with PhSeCN^a

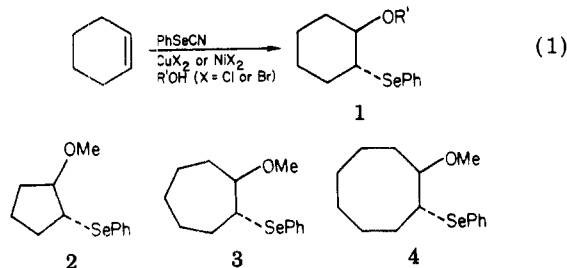
olefin (10 mmol)	temp, °C	time, h	products	yield, % ^b (isomer ratio)
cyclohexene	65	0.5	1 (R' = Me)	100
cyclohexene	25	5	1 (R' = Me)	90
cyclopentene	25	5	2	100
cycloheptene	25	5	3	93
cyclooctene	65	3	4	66
styrene	65	0.5	5 (R = Ph)	87
styrene	25	5	5 (R = Ph)	87
1-hexene	65	0.5	5 + 6 (R = <i>n</i> -Bu)	95 (5:6 = 83:18)
1-hexene	65	3	5 + 6 (R = <i>n</i> -Bu)	94 (5:6 = 90:10)
1-octene	25	15	5 + 6 (R = <i>n</i> -Hex)	88 (5:6 = 83:17)
1-octene	65	0.5	5 + 6 (R = <i>n</i> -Hex)	94 (5:6 = 83:17)
1-octene	65	10	5 + 6 (R = <i>n</i> -Hex)	93 (5:6 = 93:7)
<i>cis</i> -2-butene ^c	15	12	7	78 (>95% threo)
<i>trans</i> -2-butene ^c	15	12	7	82 (>95% erythro)

^a PhSeCN (5 mmol), CuCl₂ (5 mmol), and MeOH (10 mL). ^b Determined by GLC analysis. ^c Butenes were used in a large excess (~25 mmol).

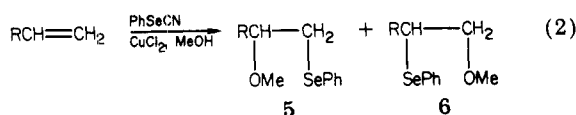
as part of our current studies on organoselenium chemistry.^{6,7}

Results and Discussion

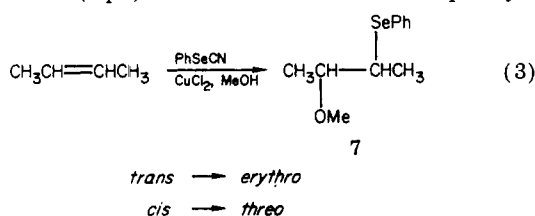
In a typical reaction, solid copper(II) chloride was added to a methanol solution of cyclohexene and phenyl selenocyanate at 65 °C, and the resulting homogeneous solution was kept at this temperature for 0.5 h to give *trans*-2-methoxycyclohexyl phenyl selenide (1, R' = Me) quantitatively (eq 1). From other cyclic olefins such as cy-



clopente, cycloheptene, and cyclooctene, similar selenides (2-4) were obtained in good yields. Application to styrene, 1-hexene, and 1-octene afforded the corresponding β -methoxyalkyl phenyl selenides 5 and 6 in high yield (eq 2).



In the case of styrene, the phenylseleno group was introduced at the terminal carbon atom to give 5 selectively. In the case of other terminal olefins a small amount of regioisomer 6 was also obtained. Here, it was found that the ratio of 5 to 6 increased with longer reaction time, indicating that 6 isomerized to 5 at reflux temperature. We investigated the stereochemical course of this reaction using *cis*- and *trans*-2-butenes as starting materials. From *trans*-2-butene, 3-methoxy-2-butyl phenyl selenide (7) was obtained in 82% yield; this contained more than 95% of the erythro isomer (by GLC and ¹³C NMR). Similarly, the product obtained from *cis*-2-butene consisted of more than 95% of *threo*-7 (eq 3). These results show that phenyl-

Table II. Effect of the Amount of CuCl₂ on the Yield of 1 (R' = Me)^a

CuCl ₂ , mmol	time, h	yield of 1 (R' = Me) ^b	
		mmol	% ^c
2	0.5	2.0	100
1	0.5	2.0	200
0.5	0.5	1.5	300
0.5	2	2.0	400
0.25	2	1.6	640
0.025	2	0.32	1280
0	2	<i>d</i>	

^a Reaction conditions: cyclohexene (4 mmol), PhSeCN (2 mmol), methanol (4 mL), at refluxing temperature.

^b Determined by GLC analysis. ^c Based on the amount of copper(II) chloride charged. ^d 1 (R' = Me) was not detected by GLC analysis (less than 0.01 mmol)

seleno and methoxy groups add to the olefin in a *trans* fashion. Typical results are shown in Table I.

The effect of copper(II) chloride is remarkable in these reactions. As Table II shows, the reaction proceeds at a slower rate even when the amount of copper(II) chloride is reduced to a catalytic amount, while no reaction occurs in the absence of copper(II) chloride. Since there is no reason to save the cheap reagent at the expense of reaction time, we have used it in a stoichiometric amount in almost all other reactions.

Similar treatment of cyclohexene in other alcohols, acetic acid-chloroform, and aqueous tetrahydrofuran gave the corresponding β -oxy selenides 1 (R' = Et, *i*-Pr, MeCO, and H) in 50-100% yield. The last compound, 2-hydroxycyclohexyl phenyl selenide, was identical with an authentic sample (*trans*) prepared from cyclohexene oxide, phenyl selenocyanate, and sodium borohydride,^{4,8} again confirming the *trans* stereospecificity of this reaction. The reaction also proceeded with alkyl selenocyanates such as *n*-hexyl and benzyl selenocyanates in methanol to afford the corresponding β -methoxy selenide in good yield. Typical results are shown in Table III.

Of the many transition-metal salts other than copper(II) chloride examined with cyclohexene as substrate, copper(II) bromide, copper(I) chloride, and nickel(II) bromide and chloride showed similar activity to copper(II) chloride, while the chlorides of Mn(II), Fe(III), Fe(II), Zn(II), Ag(I), Cd(II), Hg(II), Hg(I), Tl(III), and Tl(I) were almost ineffective. The chlorides of Cr(III) and Co(II) showed in-

Table III. Reaction of Cyclohexene with Various RSeCN and in Various Solvents^a

RSeCN, R	R'OH (mL)	time, h	yield of 1 ^b , %
Ph	MeOH (10)	0.5	100
<i>n</i> -Hex	MeOH (10)	0.5	76 ^c
PhCH ₂	MeOH (10)	0.5	80 ^d
Ph	EtOH (10)	0.5	80
Ph	<i>i</i> -PrOH (10)	0.5	88
Ph	AcOH (3)	5	48
Ph	CHCl ₃ (9)		
Ph	H ₂ O (5)	19	51
	THF (55)		

^a Cyclohexene (10 mL), RSeCN (5 mmol), CuCl₂ (5 mmol), at 65–68 °C. ^b Determined by GLC analysis. ^c *n*-Hex instead of Ph in 1. ^d PhCH₂ instead of Ph in 1.

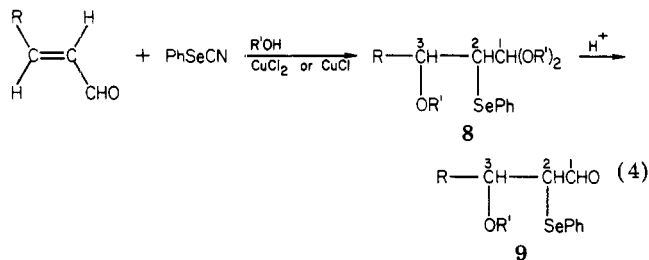
Table IV. Effect of Various Transition-Metal Salts on the Yield of 1 (R' = Me)^a

metal salt ^b	yield of 1 (R' = Me), ^c %	recovered PhSeCN, %
CuCl ₂	100	0
Cu ₂ Cl ₂	94	0
CuBr ₂	99	0
CuF ₂ ·2H ₂ O	18	82
Cu ₂ (CN) ₂	58	42
Cu(OAc) ₂ ·H ₂ O	23	77
CuCl ₂ (py) ₂	14	86
CuBr ₂ (py) ₂	80	20
Cu ₂ (CN) ₂ (py) ₂	16	84
[Cu(OAc) ₂] ₂ (py) ₂	14	73
NiCl ₂	90	0
NiCl ₂ (py) ₄	52	4
NiBr ₂	96	0
CrCl ₃ ·6H ₂ O	81	19
CoCl ₂	20	2

^a Cyclohexene (4 mmol), PhSeCN (2 mmol), metal salt (2 mmol), MeOH (4 mL), at 65 °C for 0.5 h. ^b py denotes pyridine. ^c Determined by GLC analysis.

intermediate activity (Table IV). The reason copper and nickel halides are effective is not yet known.

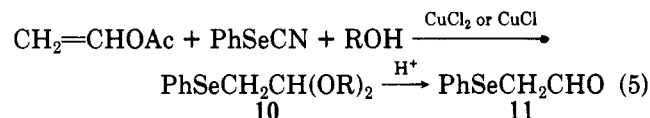
Although no oxyselenation products were obtained from olefins bearing electron-withdrawing groups such as methyl vinyl ketone, acrylonitrile, and methyl acrylate, the reaction proceeded rather smoothly with acrylaldehyde and crotonaldehyde to give the products in the form of dialkyl acetal 8 (R = H or Me) (eq 4). As has been clarified in



oxyselenocyanation of these aldehydes,^{7a} their acetalization occurs under the conditions employed. Therefore, it is very likely that the dialkyl acetals of the starting aldehydes were initially formed and then oxyselenation of them took place. In fact, we have confirmed that the dimethyl acetal of acrylaldehyde, prepared separately, reacts with phenyl selenocyanate and alcohol in the presence of copper(I) chloride under conditions similar to those for oxyselenation of acrylaldehyde. Typical results are shown in Table V. Although GLC analyses on several different columns could not separate 8 (R = R' = Me) at all, ¹³C NMR measure-

ment revealed that 8 (R = R' = Me) consisted of two isomers. As shown in Table VI, the carbon (C-2) attached to the phenylseleno group appeared at 55.2 and 56.0 ppm as doublets and the carbon (C-3) attached to one methoxy group appeared at 76.0 and 76.9 ppm also as doublets, for all other carbons two different signals being observed, respectively. The chemical shifts of the two carbon atoms calculated from substituent parameters of the methoxy group (+61.5 ppm for the α carbon and ca. +8 ppm for the β carbon)⁹ and phenylseleno group (+13 ppm for the α carbon and +6 ppm for the β carbon)^{10,11} for di-*n*-butyl ether as a reference compound are ca. 58 and ca. 83 ppm, respectively, and would be ca. 108 and ca. 36 ppm if the methoxy and phenylseleno groups were on the reverse position. These results indicate that crotonaldehyde reacts regioselectively to give a mixture of stereoisomers (erythro and threo, ca. 1:1). After deacetalization of 8 (R = R' = Me) to give 9 (R = R' = Me), ¹³C NMR measurement of 9 (R = R' = Me) showed the signal of the C-2 carbon shifted to lower field (58.1 and 59.4 ppm) and that of the C-3 carbon shifted to higher field (73.8 and 75.5 ppm). The chemical shifts of 9 (R = R' = Me) were also quite consistent with the calculated ones for butanal as a reference compound.¹² The ¹³C NMR data of 8 (R = R' = Me), 9 (R = R' = Me), and methoxyselenocyanation products of crotonaldehyde 8'^{13,14} are summarized in Table VI together with those of the reference compounds.

Application to vinyl acetate resulted in the formation of a dialkyl acetal of (phenylseleno)acetaldehyde (10) which was readily acid hydrolyzed to the aldehyde 11 (see Table V and eq 5).



Since the regioselectivity of the products shows an electrophilic addition of the phenylseleno group to the olefins, the role of the effective metal salts seems to be the polarization of the Se–CN bond in phenyl or alkyl selenocyanate by coordination on the CN moiety to give a positive selenium. In fact, the yield of selenide was always lower when the pyridine complex of these metal salts was used, probably because the coordination site is blocked (see Table IV). Here, the assistance of nucleophilic attack of olefin on the polarized selenium atom also provides a driving force for the reaction, since almost all phenyl selenocyanate was recovered from the mixture of phenyl selenocyanate and copper(II) or copper(I) chloride after heating it at refluxing temperature for 1–2 h. Consider-

(9) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, pp 56 and 144.

(10) These substituent parameters were obtained by comparing the chemical shifts of 3-(phenylseleno)propyl chloride with those of *n*-propyl chloride,¹¹ the former being prepared from 1-bromo-3-chloropropane, phenyl selenocyanate, and NaBH₄ in ethanol.

(11) Reference 9, p 133.

(12) Reference 9, pp 145 and 282.

(13) Although we have tentatively assigned in the previous paper^{7a} two products of methoxyselenocyanation of crotonaldehyde as regioisomers [CH₂CH(OMe)CH(SeCN)CH(OMe)₂ (8') + CH₂CH(SeCN)CH(OMe)CH(OMe)₂], it has now been clarified from ¹³C NMR spectral data that the products should be stereoisomers of 8' (erythro and threo). Thus, the carbon attached to the selenocyanato group appeared at 55.9 and 57.3 ppm as doublets, and the carbon attached to one methoxy group appeared at 74.6 and 76.3 ppm also as doublets. Since substituent parameters of the selenocyanato group (+15 to ~16 ppm for the α carbon and +6 to ~7 ppm for the β carbon)¹⁴ are very similar to those of the phenylseleno group (see text), these products could be assigned as stereoisomers of 8' and not as its regioisomer.

(14) These substituent parameters were obtained by comparing the chemical shifts of *n*-hexyl selenocyanate with those of *n*-hexane.⁹

Table V. Oxyseleation of Acrylaldehyde, Crotonaldehyde, and Vinyl Acetate^a

olefin (mmol)	metal halide (mmol)	solvent (mL)	time, h	product (% yield) ^b	recovered PhSeCN, %
acrylaldehyde (1.2)	CuCl (1)	MeOH (2)	24	8 (R = H, R' = Me) (93)	7
acrylaldehyde (1.2)	CuCl (0.2)	MeOH (2)	24	8 (R = H, R' = Me) (88)	12
acrylaldehyde (1.2)	CuCl ₂ (1)	MeOH (2)	24	8 (R = H, R' = Me) (61)	39
acrylaldehyde (1.2)	NiCl ₂ (1)	MeOH (2)	24	8 (R = H, R' = Me) (60)	25
acrylaldehyde (2)	CuCl (0.5)	EtOH (3)	24	8 (R = H, R' = Et) (74)	19
crotonaldehyde (2)	CuCl (1)	MeOH (4)	48	8 (R = R' = Me) (84)	16
crotonaldehyde (2)	CuCl (0.5)	MeOH (4)	48	8 (R = R' = Me) (67)	33
crotonaldehyde (1.2)	CuCl ₂ (0.5)	MeOH (2)	24	8 (R = R' = Me) (41)	55
crotonaldehyde (2)	CuCl ₂ (1)	MeOH (4)	48	8 (R = R' = Me) (44)	56
CH ₂ =CHCH(OMe) ₂ (2)	CuCl (1)	MeOH (2)	24	8 (R = H, R' = Me) (90)	1
vinyl acetate (2)	CuCl (1)	MeOH (2)	24	10 (R = Me) (84)	12
vinyl acetate (1.2)	CuCl (1)	MeOH (1)	12	10 (R = Me) (74)	17
vinyl acetate (1.2)	CuCl (1)	EtOH (1)	12	10 (R = Et) (75)	25

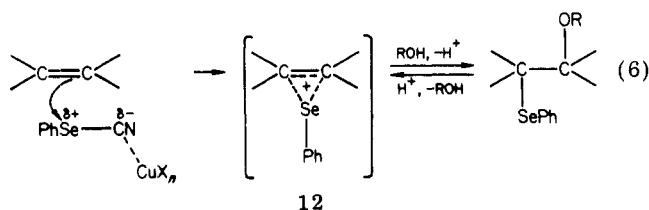
^a At 25 °C, PhSeCN (1 mmol). ^b Determined by GLC analysis.

Table VI. ¹³C NMR Chemical Shifts of 8 (R = R' = Me), 8', 9 (R = R' = Me), and Related Compounds^a

compd	C-1	C-2	C-3	C-4	C-5	C-6	others	ref
8 (R = R' = Me)	105.7 106.0	55.2 56.0	76.0 76.9	17.4 17.7			54.2, 55.3, 55.5, 55.7, 56.2, 56.4 (OMe), 126.9, 127.0 (<i>p</i>), 128.7 (<i>m</i>), 130.7, 131.0 (=CSe), 133.8, 134.1 (<i>o</i>)	this work
8' ^b	102.9 104.3	55.9 57.3	74.6 76.3	17.1 17.6			54.5, 54.9, 55.4, 56.1, 56.7, (OMe), 103.1 (SeCN), phenyl	this work
di- <i>n</i> -butyl ether	71.2	33.1	20.3	14.6				12
9 (R = R' = Me)	192.7 192.8	58.1 59.4	73.8 75.5	17.5			56.5, 56.8 (OMe), phenyl	this work
butanal	201.6	45.7	15.7	13.3				14
3-phenylselenopropyl chloride	44.2	32.5	24.4				phenyl	this work
propyl chloride	46.7	26.5	11.5					13
<i>n</i> -hexyl selenocyanate	28.7 ^c	29.7 ^c	30.8	30.9	22.4	13.9	101.5 (SeCN)	this work
<i>n</i> -hexane	13.9	22.9	32.0	32.0	22.9	13.9		12

^a Given in parts per million downfield from internal Me₄Si. Determined in CDCl₃ as solvent. ^b MeCH(OMe)CH(SeCN)-CH(OMe)₂. ^c Might be reversed.

ation of these results together with the stereochemistry of addition (trans in general) led to the reaction scheme (eq 6) which seems to be most plausible at present. Isom-



erization observed in the cases of the addition products of 1-hexene and 1-octene may occur via an intermediate such as 12 to give the thermodynamically more stable isomers. Nonstereospecificity in the reaction of crotonaldehyde may be attributed to trans \rightleftharpoons cis isomerization of the dimethyl acetal of crotonaldehyde prior to oxyseleation or, more likely, to the effect of two electron-withdrawing methoxy groups preventing the formation of an episelenonium ion intermediate, though the details are not yet known.

Experimental Section

IR spectra were recorded with a Hitachi EPI-S2 spectrometer. ¹H NMR spectra were taken with a Varian EM-360 instrument on solutions in CDCl₃ or CCl₄ with Me₄Si as internal standard (with internal lock). ¹³C NMR spectra were taken at 25.1 MHz with a JEOLCO ¹³C Fourier-transform NMR system (JNM-PFT-100) and were recorded after 350–750 pulses with intervals of 3 s. GLC analyses were carried out with a Shimadzu 5APTF apparatus by using EGSS-X(15%)-Chromosorb W (1-m) and

Silicone DC QF-1(30%)-Chromosorb W (1- and 3-m) columns (N₂ as carrier gas; benzophenone, dibenzyl, or *p*-nitroanisole as internal standard).

Materials. Phenyl selenocyanate was prepared by the reported method from a phenyldiazonium salt and potassium selenocyanate;¹⁵ bp 100–108 °C (8 torr) [lit.¹⁶ bp 134 °C (10 torr)]. *n*-Hexyl and benzyl selenocyanates^{6b,17} were prepared by the reported methods. A pyridine complex of copper or nickel salt was prepared by treating the corresponding metal halide with excess pyridine in methanol under reflux for 1 h or at 20 °C for 10 h. All other organic and inorganic materials were commercial products. Characterization of new compounds is summarized in Table VII. IR spectra of β -alkoxy selenides showed strong absorptions due to the ether group (\sim 1100 cm⁻¹), other absorptions being assigned to alkyl (and phenyl) groups. They are not included in Table VII.

Methoxyseleation of Cyclopentene (General Procedure).

To a solution of cyclopentene (0.14 g, 2 mmol) and phenyl selenocyanate (0.18 g, 1 mmol) in methanol (2 mL) was added anhydrous copper(II) chloride (0.14 g, 1 mmol) to give a deep green solution which was stirred at 25 °C for 5 h. The resulting black mixture was added to water (50 mL), and the white precipitate thus formed was filtered off. The filtrate was extracted with benzene (3 \times 20 mL) and the organic layer was washed with water and dried over MgSO₄. Evaporation of solvent in vacuo left a pale yellow oil, which was analyzed by GLC using dibenzyl as an internal standard to show the presence of 2 (1.0 mmol, 100%). Pure 2 was isolated by distillation of this oil obtained from the reaction carried out in 5-times scale (0.87 g, 3.4 mmol; 68% isolated

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Table VII. Characterization of New Compounds

compd	bp, °C (torr)	chemical shifts, δ (J, Hz)	found (calcd)	
			% C	% H
1 (R' = Me)	151-153 (8)	1.0-2.1 (8 H, m), 3.0-3.3 (2 H, m), 3.27 (3 H, s), 7.0-7.6 (5 H, m)	57.95 (57.99)	6.67 (6.74)
1 (R' = Et)	161-162 (9)	1.16 (3 H, t, $J = 7$), 1.0-2.4 (8 H, m), 3.1-3.5 (2 H, m), 3.46 (1 H, q, $J = 7$), 3.66 (1 H, q, $J = 7$), 7.0-7.7 (5 H, m)	58.53 (58.50)	7.01 (7.01)
1 (R' = <i>i</i> -Pr)	158-159 (7)	1.07 (6 H, d, $J = 6$), 1.0-2.3 (8 H, m), 3.1-3.5 (2 H, m), 3.63 (1 H, septet, $J = 6$), 7.1-7.7 (5 H, m)	60.08 (60.60)	7.38 (7.46)
1 (R' = Me; Ph \rightarrow <i>n</i> -Hex) ^a	142-144 (9)	0.7-2.3 (19 H, m), 2.60 (2 H, t, $J = 7$), 2.8-3.3 (2 H, m), 3.30 (3 H, s)	56.01 (56.31)	9.46 (9.45)
1 (R' = Me; Ph \rightarrow PhCH ₂) ^b	177 (10)	1.1-2.3 (8 H, m), 3.26 (3 H, s), 2.8-3.3 (2 H, m), 3.83 (2 H, s), 7.20 (5 H, s)	59.55 (59.36)	7.46 (7.12)
2	129-130 (3)	1.6-2.3 (6 H, m), 3.14 (3 H, s), 3.4-3.9 (2 H, m), 7.1-7.7 (5 H, m)	56.63 (56.47)	6.09 (6.32)
3	156-157 (3)	1.3-2.2 (10 H, m), 3.26 (3 H, s), 3.2-3.6 (2 H, m), 7.0-7.7 (5 H, m)	59.52 (59.36)	7.21 (7.12)
4	<i>e</i>	1.2-2.3 (12 H, m), 3.27 (3 H, s), 3.3-3.6 (2 H, m), 7.1-7.7 (5 H, m)	60.08 (60.60)	7.13 (7.46)
5 (R = Ph)	181-182 (8)	2.8-3.5 (2 H, m), 3.21 (3 H, s), 4.33 (1 H, dd, $J = 6, 8$), 7.0-7.6 (10 H, m)	61.70 (61.86)	5.62 (5.54)
5 + 6 (R = <i>n</i> -Bu) ^c	118 (7)	0.7-1.9 (9 H, m), 2.9-3.5 (3 H, m), 3.29 (3 H, s), 7.1-7.7 (5 H, m)	57.42 (57.56)	7.58 (7.43)
5 + 6 (R = <i>n</i> -Hex) ^d	160-161 (7)	0.7-1.9 (13 H, m), 2.9-3.6 (3 H, m), 3.30 (3 H, s), 7.1-7.7 (5 H, m)	60.20 (60.19)	8.33 (8.08)
7 (<i>threo</i>)	93-95 (3)	1.24 (3 H, d, $J = 7$), 1.39 (3 H, d, $J = 7$), 3.29 (3 H, s), 3.3-3.6 (2 H, m), 7.2-7.7 (5 H, m)	53.84 (54.32)	6.20 (6.63)
7 (<i>erythro</i>)	105-107 (6)	1.21 (3 H, d, $J = 7$), 1.41 (3 H, d, $J = 7$), 3.31 (3 H, s), 3.3-3.6 (2 H, m), 7.2-7.7 (5 H, m)	54.11 (54.32)	6.47 (6.63)
8 (R = H, R' = Me)	143-151 (5)	3.28 (3 H, s), 3.40 (3 H, s), 3.42 (3 H, s), 3.3-3.8 (3 H, m), 4.56 (1 H, d, $J = 4$), 7.1-7.7 (5 H, m)	49.93 (49.83)	6.06 (6.27)
8 (R = H, R' = Et)	151-160 (3)	1.13, 1.16, and 1.21 (9 H, t, $J = 7$), 3.2-4.0 (8 H, m), 4.73 (1 H, d, $J = 4$), 7.1-7.7 (5 H, m)	54.18 (54.38)	7.00 (7.30)
8 (R = R' = Me)	140-143 (5)	1.26 and 1.34 (3 H, d, $J = 6, 7$), 3.28, ^f 3.33, 3.38, 3.39, and 3.41 (9 H, s), 3.0-3.8 (2 H, m), 4.58 and 4.60 (1 H, d, $J = 5, 7$), 7.0-7.7 (5 H, m)	51.51 (51.49)	6.49 (6.65)
10 (R = Me)	118-121 (5)	3.06 (2 H, d, $J = 6$), 3.33 (6 H, s), 4.57 (1 H, d, $J = 6$), 7.1-7.7 (5 H, m)	48.99 (48.99)	5.78 (5.76)
10 (R = Et)	124-132 (5)	1.19 (6 H, t, $J = 7$), 3.12 (2 H, d, $J = 6$), 3.59 (2 H, q, $J = 7$), 3.64 (2 H, q, $J = 7$), 4.75 (1 H, t, $J = 6$), 7.2-7.8 (5 H, m)	52.44 (52.75)	6.38 (6.64)
11	<i>e</i>	3.50 (2 H, d, $J = 4$), 7.2-7.7 (5 H, m), 9.60 (1 H, t, $J = 4$)	48.50 (48.26)	4.15 (4.05)

^a *n*-Hex instead of Ph in 1. ^b PhCH₂ instead of Ph in 1. ^c 5:6 = 90:10 (by GLC). ^d 5:6 = 83:17 (by GLC). ^e Not determined [purified by column chromatography: SiO₂, hexane-ethyl acetate (10:1)]. ^f Two singlet peaks overlapped.

yield); IR (film) 3060, 2950, 2840, 1578, 1472, 1435, 1095, 735, and 690 cm⁻¹.

Hydroxyselenation of Cyclohexene. To a solution of cyclohexene (0.82 g, 10 mmol) and phenyl selenocyanate (0.91 g, 5 mmol) in tetrahydrofuran (THF) (50 mL) were added copper(II) chloride dihydrate (0.85 g, 5 mmol) and then water (5 mL), and the resulting green homogeneous solution was stirred under reflux for 19 h. After the solution was cooled, water (200 mL) was added and the white precipitate thus formed was filtered off. The benzene (3 \times 50 mL) extract of the filtrate was dried over MgSO₄, concentrated to ca. 10 mL, and analyzed by GLC (benzophenone as internal standard); 1 (R' = H), 2.6 mmol (52%). This compound was identical on different GLC columns with an authentic sample prepared^{4,8} from cyclohexene oxide (0.49 g, 5 mmol), phenyl selenocyanate (0.91 g, 5 mmol), and sodium borohydride (0.29 g, 6 mmol) in ethanol (20 mL) (20 °C to reflux, 2.5 h).

Methoxyselenation of *cis*-2-Butene. A solution of phenyl selenocyanate (0.81 g, 5 mmol) and anhydrous copper(II) chloride (0.67 g, 5 mmol) in methanol (10 mL) was placed in a 50-mL pressure bottle (Taiatsu Glass Industry Co. Ltd.). Butene (2.5 mL, ca. 25 mmol) was charged at -78 °C, and after the temperature was raised to 15 °C the solution was stirred under pressure for 12 h. The resulting mixture was added to water (50 mL) and extracted with benzene (3 \times 20 mL). The benzene extract was washed with brine, dried over MgSO₄, and concentrated to ca. 10 mL. GLC analysis of this residue (Silicon DC QF-1, 3 m)

showed that the main product was identical with *threo*-7 (vide infra) and the isomer ratio (*threo*:*erythro*) was >95:<5. The same procedure starting from *trans*-2-butene gave *erythro*-7 containing less than 5% of the *threo* isomer.

Preparation of *threo*- and *erythro*-7. *threo*-3-(Phenylseleno)-2-butanol was prepared by the epoxidation of *cis*-2-butene (>97.5%) using *m*-chloroperbenzoic acid followed by trans ring opening of the epoxide by phenylselenate anion.⁸ Methylation of the alcohol with methyl iodide and sodium hydride¹⁸ afforded *threo*-7: IR (film) 3060, 2970, 2920, 2830, 1575, 1472, 1435, 1370, 1095, 740, and 690 cm⁻¹; ¹³C NMR δ 15.7 (q), 17.0 (q), 43.7 (d), 56.5 (q), 79.8 (d), 127.2 (d), 128.8 (d), 129.6 (s), and 134.3 (d). The same procedure starting from *trans*-2-butene (>99%) gave *erythro*-7: IR (film) 3060, 2980, 2940, 2840, 1575, 1473, 1435, 1370, 1095, 740, and 690 cm⁻¹; ¹³C NMR δ 16.8 (q), 17.4 (q), 45.2 (d), 56.7 (q), 79.9 (d), 127.2 (d), 128.9 (d), 129.6 (s), and 134.6 (d).

Methoxyselenation of Vinyl Acetate and Deacetalization of the Product to (Phenylseleno)acetaldehyde. To a solution of vinyl acetate (0.86 g, 10 mmol) and phenyl selenocyanate (0.91 g, 5 mmol) in methanol (10 mL) was added anhydrous copper(II) chloride (0.67 g, 5 mmol) to give a deep green solution which was stirred at 25 °C for 12 h. The resulting mixture was treated as

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described above; evaporation of solvent from the benzene extract under reduced pressure left crude 10 (R = Me) as a colorless oil: IR (film) 3060, 2950, 2840, 1578, 1475, 1438, 1120, 1075, 1055, 960, 740, and 690 cm⁻¹. This oil was dissolved in THF (14 mL) containing water (5 mL) and hydrogen chloride (36.5% solution, 1 mL), and the solution was stirred at 25 °C for 0.5 h. Water (100 mL) was then added and the product was extracted with benzene (3 × 50 mL). The extract was washed with water (3 × 30 mL) and dried over MgSO₄. Evaporation of the solvent left a pale yellow oil which was purified by column chromatography [silica gel, hexane-dichloromethane (1:1) as eluant] to give pure 11 (0.63 g, 3.1 mmol, 62% total isolated yield): IR (film) 3080, 2950, 2850, 2750, 1710, 1578, 1478, 1437, 1150, 1022, 740, and 690 cm⁻¹.

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Registry No. 1 (R' = Me), 51533-22-3; 1 (R' = Et), 73090-26-3; 1 (R' = *i*-Pr), 73090-27-4; 2, 73090-28-5; 3, 73090-29-6; 4, 73090-30-9; 5 (R = Ph), 63603-28-1; 5 (R = *n*-Bu), 73090-31-0; 5 (R = *n*-Hex), 63603-31-6; 6 (R = *n*-Bu), 73090-32-1; 6 (R = *n*-Hex), 63603-32-7; *erythro*-7, 73090-33-2; *threo*-7, 73090-34-3; 8 (R = H, R' = Me), 73090-35-4; 8 (R = H, R' = Et), 73090-36-5; 8 (R = R' = Me), 73090-37-6; 8', 69310-37-8; 9 (R = R' = Me), 73090-38-7; 10 (R = Me), 73090-39-8; 10 (R = Et), 71338-47-1; cyclohexene, 110-83-8; cyclopentene, 142-29-0; cyclooctene, 931-88-4; styrene, 100-42-5; 1-hexene, 592-41-6; 1-octene, 111-66-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; CH₃(CH₂)₅SeCN, 60669-47-8; PhSeCN, 2179-79-5; PhCH₂SeCN, 4671-93-6; H₂O, 7732-18-5; acrylaldehyde, 107-02-8; crotonaldehyde, 4170-30-3; vinyl acetate, 108-05-4; 3-(phenyl-seleno)propyl chloride, 73090-40-1; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; AcOH, 64-19-7; *trans*-2-methoxycyclohexyl hexyl selenide, 73090-41-2; *trans*-2-methoxycyclohexyl benzyl selenide, 73090-42-3; CuCl, 7758-89-6; CuCl₂, 7447-39-4; CuBr₂, 7789-45-9; NiCl₂, 7718-54-9; NiBr₂, 13462-88-9.

Fluoride Ion Elimination-Addition Reactions. Synthesis of 2,2-Difluoroethenyl Phenyl Selenide and 2,2,2-Trifluoroethyl Phenyl Selenide

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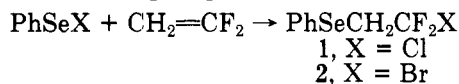
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2-Chloro-2,2-difluoroethyl phenyl selenide (1) reacts with KF and a catalytic amount of 18-crown-6 to give 2,2-difluoroethenyl phenyl selenide (3) and 2,2,2-trifluoroethyl phenyl selenide (4). The latter is formed by an elimination-addition sequence. 2-Bromo-2,2-difluoroethyl phenyl selenide (2) under the same conditions gives only 3. The olefin 3 is highly reactive toward nucleophiles. Sulfide, sulfone, and keto analogues of 1 react with KF/18-crown-6 by a similar elimination-addition sequence, affording the corresponding 2,2,2-trifluoroethyl derivatives.

Organoselenium compounds,¹ including vinyl selenides,² are popular reagents for organic synthesis. It seemed that vinyl selenides having fluorine or fluorinated substituents on the olefinic portion should be highly reactive and have useful properties for the construction of fluorinated organic compounds. In an effort to prepare the previously unknown 2,2-difluoroethenyl phenyl selenide (3), an unusual fluorination process employing "naked fluoride ion"³ which proceeds by elimination-addition was uncovered. In this paper, the synthesis of 3 and the details of this fluorination process are described.

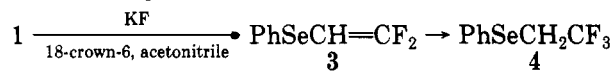
Results

Phenylselenenyl chloride or bromide added cleanly to vinylidene fluoride, giving the adducts 1 and 2, respec-

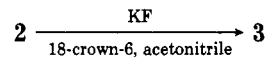


tively, in over 90% yield. A single regioisomer was obtained in both cases. 1 was treated with 7 equiv of an-

hydrous potassium fluoride in acetonitrile containing 0.3 equiv of 18-crown-6 at 60 °C to effect elimination of HCl. The reaction was monitored by GLPC. The data, summarized in Figure 1, showed the disappearance of the peak assigned to 1 and the corresponding appearance of a new peak. This second peak reached a maximum and then began to decrease with the appearance of a third component. The products were subsequently isolated and identified in pure form as the desired olefin 3 and the



trifluoride 4, respectively. In contrast, reaction of 2 with KF under identical conditions gave only 3. No trace of 4 was detected after a 260-min reaction time.



In preparative-scale experiments, both 3 and 4 were isolated in pure form. Reaction of 1 with excess KF and catalytic 18-crown-6 in refluxing acetonitrile gave about 80% 4 and 20% 3. Since 3 and 4 have virtually identical boiling points, pure 4 was isolated by selective destruction of 3. Treatment of the crude product with ethanolic potassium hydroxide for a few minutes at room temperature resulted in conversion of 3 to higher boiling materials. The trifluoride could be distilled from this mixture in 78% isolated yield. Pure 3 was isolated in 85% yield from the reaction of 2. The olefin is a colorless distillable liquid which can be stored for months in a sealed vial in the freezer. It is stable to neutral water and can be briefly

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