

Alkoxy- and Halogeno-selenocyanation of Olefins with Copper(II) Chloride or Bromide and Potassium Selenocyanate

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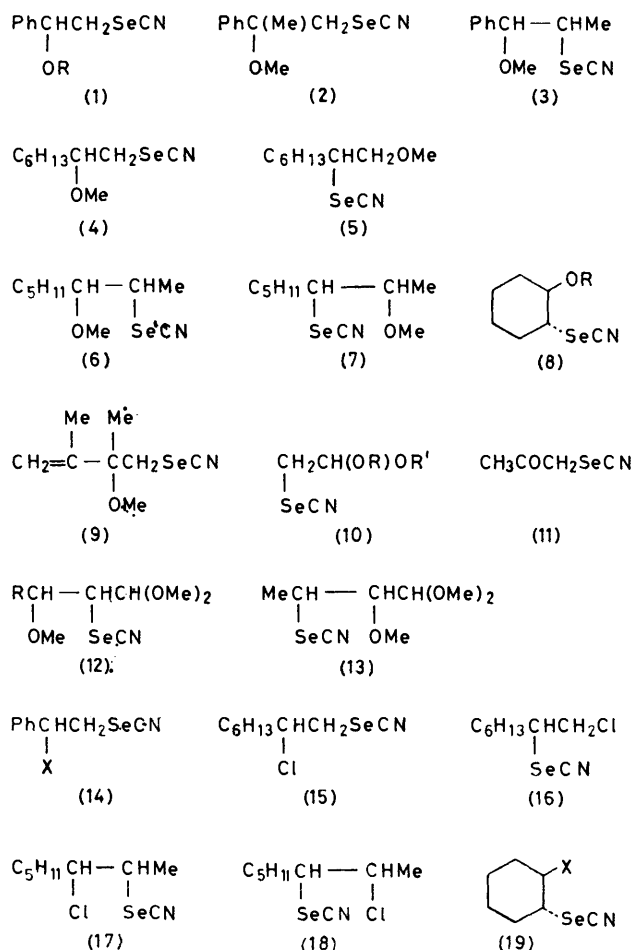
Treatment of olefinic hydrocarbons with copper(II) chloride or bromide and potassium selenocyanate in alcohols readily affords the corresponding vicinal alkoxy-selenocyanatoalkanes (A) in good yields, while in acetonitrile vicinal halogeno-selenocyanatoalkanes (B) are formed in satisfactory yields. In the cases of cyclohexene and octenes, the formation of (B) together with (A) was observed in alcohol when the reaction was stopped after a short time, (B) being converted into (A) by prolonging the reaction. The reaction proceeds through oxidation of selenocyanate anion to the corresponding cation and its electrophilic attack on the olefin, followed by competitive addition of alcohol and complexed halide anion, such as Cu_2X_3^- . The route of the substitution of halogen in (B) by an alkoxy group giving (A) has also been elucidated. The conversion of (B) obtained from cyclohexene into (A) occurs with complete retention of configuration (*trans* \rightarrow *trans*), suggesting the intervention of an epi-selenonium ion intermediate.

A SIMPLE and convenient method for the preparation of vicinal alkoxythiocyanato- or alkoxyiodo-alkanes from olefins by use of a copper(II) salt, potassium thiocyanate or iodide, and alcohols has been reported.¹ We now report that a similar reaction using potassium selenocyanate gives vicinal alkoxy-selenocyanatoalkanes in alcohols and vicinal halogeno-selenocyanatoalkanes in acetonitrile as solvent. Although some of the former compounds have been prepared through alkoxythallation of olefins followed by treatment with potassium selenocyanate,² the method could not be applied to olefins which are readily oxidized by thallium(III) acetate. Our new finding therefore can be used as an alternative and/or complementary method for alkoxy-selenocyanation of olefins and also as a new synthetic method for halogeno-selenocyanatoalkanes.

RESULTS AND DISCUSSION

The reaction was generally carried out by adding the olefinic hydrocarbon to a heterogeneous mixture of copper(II) chloride and potassium selenocyanate in the alcohol at room temperature and keeping the resulting mixture at an appropriate temperature for 0.5–10 h with stirring. Typical results of alkoxy-selenocyanation of simple alkenes are summarized in Table 1. In the reaction of styrene both copper(II) chloride and bromide were effective, whereas copper(II) nitrate, sulphate, and fluoride, and iron(III) ammonium sulphate were not. The reaction proceeded with decreasing ease through the following series of alcohols; methyl > ethyl > n-propyl > isopropyl > t-butyl, reflecting both steric and polar factors. In the cases of oct-1-ene, *cis*-oct-2-ene, and cyclohexene, vicinal halogeno-selenocyanatoalkanes (B) were produced together with the expected vicinal alkoxy-selenocyanatoalkanes (A) despite the reaction being carried out in alcohol, the conversion of the former into the latter being observed on prolonging the reaction or raising the temperature. From 2,3-dimethylbuta-1,3-diene only the 1,2-addition product was isolated, though the yield was not high, the 1,4-addition product being

formed only in very limited amount if at all. The reactions of styrene and α - and β -methylstyrene were completely regiospecific, whereas those of oct-1-ene and



oct-2-ene were non-regiospecific. All products obtained from cyclohexene were revealed to be *trans* by n.m.r. spectra and by comparison with authentic samples

¹ A. Onoe, S. Uemura, and M. Okano, *Bull. Chem. Soc. Japan*, 1974, **47**, 2818.

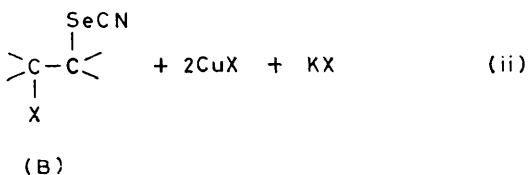
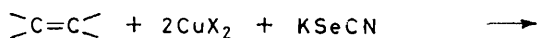
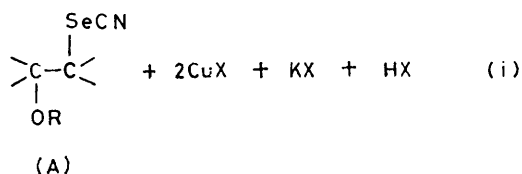
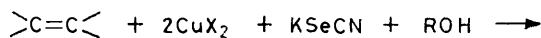
² S. Uemura, A. Toshimitsu, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Japan*, 1975, **48**, 1925.

TABLE 1

Alkoxyselecenylation of simple alkenes in alcohols							
Alkene (15 mmol)	Cu salt (30 mmol)	KSeCN (mmol)	Alcohol (30 ml)	Temp. (°C)	Time (h)	Products	Yield ^a (%)
Styrene	CuCl ₂	30	MeOH	65	0.5	(1; R = Me)	99
Styrene	CuCl ₂	15	MeOH	65	0.5	(1; R = Me)	93
Styrene	CuCl ₂	30	MeOH	25	10	(1; R = Me)	74
Styrene	CuCl ₂	30	EtOH	78	0.5	(1; R = Et)	67
Styrene	CuCl ₂	30	Pr ⁿ OH	75	0.5	(1; R = Pr ⁿ)	57
Styrene	CuCl ₂	30	Pr ⁱ OH	75	1	(1; R = Pr ⁱ)	43
Styrene	CuCl ₂	30	Bu ^t OH	75	0.5	(1; R = Bu ^t)	15
Styrene	CuBr ₂	30	MeOH	65	0.5	(1; R = Me)	100
α -Methylstyrene	CuCl ₂	30	MeOH	65	0.5	(2)	88
<i>trans</i> - β -Methylstyrene	CuCl ₂	30	MeOH	65	0.5	(3) ^b	69
β -Methylstyrene ^c	CuCl ₂	30	MeOH	25	10	(3) ^d	60
Oct-1-ene	CuCl ₂	30	MeOH	65	5	(4)	56 ^e
						(5)	18
<i>cis</i> -Oct-2-ene	CuCl ₂	30	MeOH	65	0.5	(6) + (7) ^f	37
						(17) + (18) ^f	33
<i>cis</i> -Oct-2-ene	CuCl ₂	30	MeOH	65	5	(6) + (7) ^f	76
Cyclohexene	CuCl ₂	30	MeOH	65	0.5	(8; R = Me)	69
						(19; X = Cl)	23
Cyclohexene	CuCl ₂	15	MeOH	65	0.5	(8; R = Me)	64
						(19; X = Cl)	2
Cyclohexene	CuCl ₂	30	MeOH	65	5	(8; R = Me)	93
						(19; X = Cl)	2
Cyclohexene	CuCl ₂	30	MeOH	25	5	(8; R = Me)	21
						(19; X = Cl)	48
Cyclohexene	CuCl ₂	30	EtOH	78	5	(8; R = Et)	74
						(19; X = Cl)	1
Cyclohexene	CuBr ₂	30	MeOH	65	0.5	(8; R = Me)	17
						(19; X = Br)	45
Cyclohexene	CuBr ₂	30	MeOH	65	5	(8; R = Me)	43
						(19; X = Br)	24
Cyclohexene	CuBr ₂	15	MeOH	65	5	(8; R = Me)	60
						(19; X = Br)	3
2,3-Dimethylbuta-1,3-diene	CuCl ₂	30	MeOH	25	5	(9)	23

^a Based on equations (i) and (ii) and determined by g.l.c. analysis. ^b Only *erythro*-isomer. ^c *trans*:*cis* ca. 4:1 by n.m.r. ^d *erythro*:*threo* 80–82:20–18 by g.l.c. ^e Formation of two unidentified products was also observed by g.l.c. analysis. In a 0.5 h reaction, the formation of small amounts of halogenoselenoalkanes (15) and (16) was observed. ^f Isomer ratio not known.

prepared independently (see Experimental section). The general scheme for these reactions is as follows:



The reaction was applied to various other olefinic hydrocarbons in methanol or ethanol with use of copper(II) chloride. It was found that vinyl acetate, ethyl

vinyl ether, acrylaldehyde, and crotonaldehyde gave the expected products in the form of dialkyl acetals. In the former three cases the formation of the product was completely regiospecific, whereas from crotonaldehyde were obtained two products which were tentatively identified as the regioisomers (12; R = Me) and (13). From isopropenyl acetate was obtained selenocyanatoacetone, which may be derived from the first-produced alkoxyselecenylation product. The results are shown in Table 2. Although acrylaldehyde and crotonaldehyde reacted smoothly, almost no reaction occurred with β -bromostyrene, acrylonitrile, methyl acrylate, and methyl vinyl ketone, each of which also has an electron-withdrawing substituent. The reason for the high reactivity of acrylaldehyde and crotonaldehyde seems to be their ready acetalization; indeed we confirmed separately that acetalization of acrylaldehyde occurred smoothly in methanol in the presence of a catalytic amount of copper(II) chloride and that the dimethyl acetal produced is susceptible to alkoxyselecenylation (see Experimental section). On the other hand, the acetalization of methyl vinyl ketone was slow under similar conditions, consistent with its low reactivity in alkoxyselecenylation.

In the cases of octenes and cyclohexene, (B) was formed as a side-product in alcohols as described above. When the reaction was carried out in acetonitrile, (B) was the sole product. Typical results are shown in Table 3.

From octenes mixtures of regioisomeric products were obtained. The product from styrene was identified as (1; R = Me) by its ready methanolysis in the presence of a copper(II) salt and hydrogen chloride, since it was hard to isolate in a pure form because of its instability

the scheme represented by equations (iv)–(vi) for this reaction.

The first step is the formation of halogenoselenocyanogen [equation (iv)]. This is activated by complexation with copper(I) salt [equation (v)] and attacks olefin

TABLE 2

Alkoxyseleocyanation of vinyl esters, a vinyl ether, and $\alpha\beta$ -unsaturated aldehydes in alcohols^a

Alkene (15 mmol)	Alcohol (30 ml)	Temp. (°C)	Time (h)	Products	Yield ^b (%)
Vinyl acetate	MeOH	65	0.5	(10; R = R' = Me)	67
Vinyl acetate	EtOH	78	0.5	(10; R = R' = Et)	66
Isopropenyl acetate	MeOH	25	5	(11)	41
Ethyl vinyl ether	MeOH	25	1	(10; R = Me, R' = Et)	11
Ethyl vinyl ether	MeOH	65	0.5	(10; R = R' = Me)	6
Ethyl vinyl ether	MeOH	65	5	(10; R = Me, R' = Et)	14
Ethyl vinyl ether	MeOH	65	5	(10; R = R' = Me)	20
Ethyl vinyl ether	MeOH	65	5	(10; R = Me, R' = Et)	5
Ethyl vinyl ether	EtOH	78	0.5	(10; R = R' = Et)	82
Acrylaldehyde	MeOH	65	0.5	(12; R = H)	64
Crotonaldehyde	MeOH	65	0.5	(12; R = Me) + (13)	75 ^c
Crotonaldehyde	MeOH	25	5	(12; R = Me) + (13)	52 ^c

^a KSeCN and CuCl₂ (both 30 mmol) were used. ^b Based on equation (i) and determined by g.l.c. analysis. ^c A 54 : 46 mixture (by g.l.c.).

(see Experimental section). In this case, when an excess of potassium selenocyanate was present, the diselenocyanato-compound (14; X = SeCN) was obtained as the main product. This may be formed by substitution of halogen in (14; X = Cl or Br) with selenocyanate anion.

In alkoxyiodination or alkoxythiocyanation, the oxidation of iodide or thiocyanate anion by a copper(II) salt to molecular iodine or thiocyanogen has been proposed as the initial step of the reaction.¹ On the contrary, the formation of halogenoselenocyanogen (XSeCN) seems to be the key step in this alkoxyseleocyanation for the following reasons.* First, copper(II) nitrate and sulphate and iron(III) ammonium sulphate, which have strong oxidizing ability, were almost completely ineffective. Thus selenocyanogen [(SeCN)₂] cannot be involved in the main reaction step, since the above metal salts should also produce it. Secondly, selenocyanogen has been shown to be very unstable and its reactions have only been studied previously *in situ* at very low temperature.³ Furthermore, although the stoichiometry involving selenocyanogen should be as shown in equation (iii), nearly twice as much product as expected from this was obtained in methoxyseleocyanation of styrene by use of 15 mmol of potassium selenocyanate (see Table 1). Lastly, in the reactions of cyclohexene and octenes in

electrophilically. Competitive addition of halide of copper complex (path *a*) and alcohol (path *b*) then occurs to give (B) and (A), respectively [equation (vi)]. The conversion of (B) into the corresponding (A) cannot be excluded for the formation of (A) in view of the results

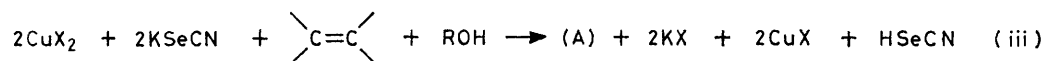
TABLE 3

Halogenoselenocyanation of alkenes in acetonitrile^a

Alkene (15 mmol)	Cu ^{II} salt (30 mmol)	KSeCN (mmol)	Products	Yield ^b (%)
Styrene	CuCl ₂	12	(14; X = Cl)	83 ^c
Styrene	CuBr ₂	12	(14; X = Br)	58 ^c
Styrene	CuBr ₂	30	(14; X = SeCN)	40 ^d
Oct-1-ene	CuCl ₂	15	(15) + (16)	82 ^e
<i>cis</i> -Oct-2-ene	CuCl ₂	15	(17) + (18)	60 ^e
Cyclohexene	CuCl ₂	30	(19; X = Cl)	69
Cyclohexene	CuBr ₂	30	(19; X = Br)	54

^a At 82 °C for 0.5 h; MeCN (30 ml). ^b Based on equation (ii) and determined by g.l.c. analysis. ^c Based on the initial amount of KSeCN. Determined as (1; R = Me) after methanolysis. ^d Isolated yield. Other product (14; X = Br) (*ca.* 10%). ^e Isomer ratio not known.

for the cases of cyclohexene and octenes. The reason why (B) could not be obtained from other alkenes examined (in alcohols) seems to be that these products suffer very rapid alcoholysis under the conditions employed, the halogens being on labile positions (benzylic, -COCHX-, and ROCHX-). The proposed episelenonium ion intermediate in equation (vi) can explain why



alcohols appreciable amounts of (B) were formed as by-products, and furthermore halogenoselenocyanation is the sole reaction in acetonitrile. We therefore propose

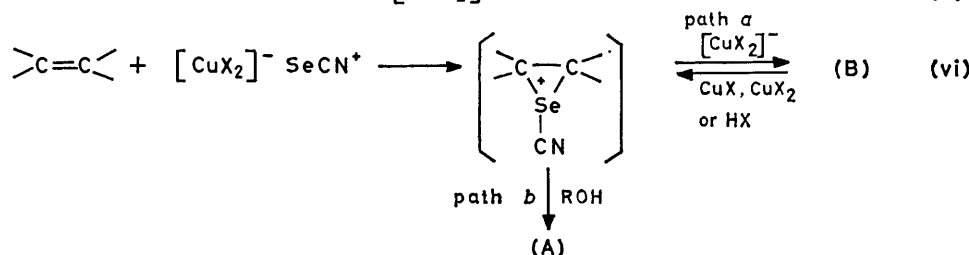
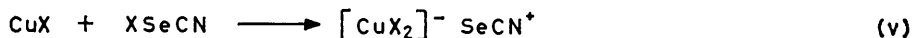
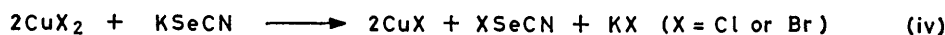
* Another possibility is that copper(II) selenocyanate is formed from copper(II) halide and potassium selenocyanate, and reacts with olefin, attack of alcohol then giving the product. We confirmed separately, however, that no reaction occurs on refluxing styrene (15 mmol) and copper(II) selenocyanate (15 mmol) in methanol (30 ml) for 0.5 h.

the reaction proceeds with complete *trans*-stereospecificity and also why the 1,2-addition product was obtained almost exclusively from 2,3-dimethylbuta-1,3-diene. The presence of such episelenonium ions has been confirmed by n.m.r. in the reactions of *cis*- and

³ See for example, 'Organic Selenium Compounds: their Chemistry and Biology,' ed. D. L. Klaymann and W. H. H. Günther, Wiley-Interscience, New York, 1973, pp. 43, 44.

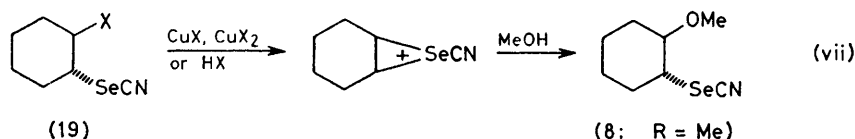
trans-octadec-9-ene with phenylselenyl hexafluoroantimonate⁴ and proposed in several other instances.^{5,6}

In order to obtain more information on the conversion



of (B) into (A) in equation (vi), its rate and stereochemistry were studied in more detail using cyclohexane

Typical results are illustrated in Figure 1. In methoxy-selenocyanation of cyclohexene (Table 1), the ratio of



derivatives (19; X = Cl or Br). When each compound was dissolved in refluxing methanol in the presence or

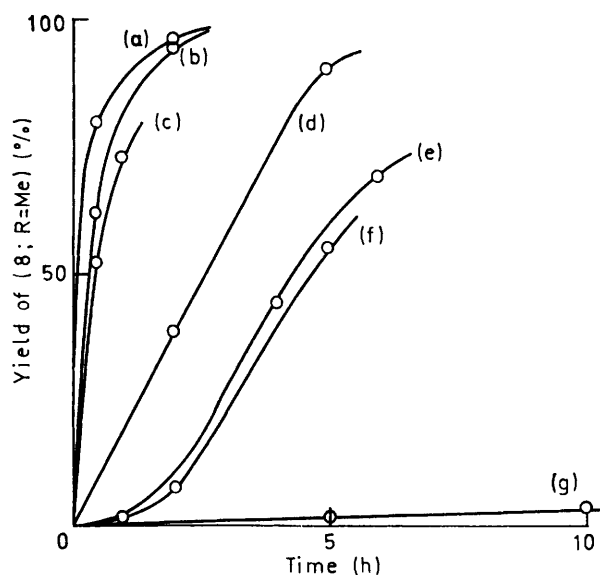


FIGURE 1 Methanolysis of (19) to give (8; R = Me) under various conditions at reflux: (a) (19; X = Cl) (1 mmol), CuCl (1 mmol), MeOH (2 ml); (b) (19; X = Br) (1 mmol), CuBr (1 mmol), MeOH (2 ml); (c) (19; X = Br) (1 mmol), CuBr₂ (1 mmol), MeOH (2 ml); (d) (19; X = Cl) (1 mmol), HCl (0.5 mmol), MeOH (2 ml); (e) (19; X = Br) (1 mmol), MeOH (10 ml); (f) (19; X = Cl) (1 mmol), CuCl₂ (1 mmol), MeOH (2 ml); (g) (19; X = Cl) (1 mmol), MeOH (10 ml)

absence of either copper(II) or copper(I) halide or hydrogen chloride, it was converted into (8; R = Me) in

* The employed conditions are as similar as possible to those after 0.5 h duration of methoxyselenocyanation of cyclohexene.

⁴ J. Rémon and A. Krief, *Tetrahedron Letters*, 1976, 3743.

⁵ K. C. Nicolaou and Z. Lysenko, *Tetrahedron Letters*, 1977, 1257; *J. Amer. Chem. Soc.*, 1977, **99**, 3185.

EXPERIMENTAL

All organic and inorganic materials were commercial products. Potassium selenocyanate (purity *ca.* 80%) was obtained from Wako Pure Chemicals Ltd. I.r. spectra were recorded with a Hitachi EPI-S2 spectrometer. ¹H N.m.r. spectra were taken with a Varian EM-360 and a JEOL MH-100 instrument for solutions in CDCl₃ with Me₄Si as internal standard (with internal and external lock, respectively). G.l.c. analyses were carried out with a Shimadzu 5AETF apparatus [DEGS (25%)–Shimalite (1 m) and EGSS-X (15%)–Chromosorb W (1 m) columns; N₂ as carrier gas; benzophenone, bibenzyl, *p*-nitrotoluene, or ethyl cinnamate as internal standard]; (A) has a shorter retention time than the corresponding (B) in all cases.

⁶ D. G. Garratt and G. H. Schmid, *J. Org. Chem.*, 1977, **42**, 1776.

⁷ K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1974, **39**, 429.

TABLE 4
Characterization of new alkoxy- and halogeno-selenocyanatoalkanes

Compound	B.p. (°C) [Torr]	¹ H N.m.r. (δ) (J in Hz)	Found (reqd.) (%)		
			C	H	N
(1; R = Bu ^t)	129—131 [5]	1.10 (9 H, s), 3.24 (2 H, d, J 7), 4.79 (1 H, t, J 7), 7.30 (5 H, s)	55.6 (55.3)	6.3 (6.05)	4.7 (4.95)
(3) ^a	124—127 [5]	1.51 (3 H, d, J 7), 3.29 (3 H, s), 3.86 (1 H, dq, J 5 and 7), 4.52 (1 H, d, J 5), 7.33 (5 H, s)	51.9 (52.0)	5.15 (5.15)	5.4 (5.5)
(3) ^b	118—120 [5]	1.51 (3 H, d, J 7), 3.16 and 3.29 (3 H, s), 3.6—4.2 (1 H, m), 4.52 (1 H, d, J 5), 7.33 and 7.38 (5 H, s)	51.5 (52.0)	4.95 (5.15)	5.75 (5.5)
(4) + (5)	130—133 [6]	0.7—2.0 (13 H, m), 3.40 (3 H, s), 3.1—3.7 (3 H, m)	48.7 (48.4)	8.0 (7.7)	5.8 (5.65)
(6) + (7)	101—105 [5]	0.8—2.0 (11 H, m), 1.68 (3 H, d, J 7), 3.30 and 3.34 (3 H, s), 3.1—3.9 (3 H, m)	48.7 (48.4)	7.8 (7.7)	5.35 (5.65)
(8; R = Me)	107—109 [5]	1.1—2.7 (8 H, m), 3.35 (3 H, s), 2.9—3.5 (2 H, m)	43.9 (44.0)	6.1 (6.0)	6.5 (6.4)
(8; R = Et)	109—110 [6]	1.16 (3 H, t, J 7), 1.0—2.4 (8 H, m), 3.1—3.8 (4 H, m)	46.6 (46.6)	6.8 (6.5)	6.1 (6.05)
(9)	82—86 [4]	1.50 (3 H, s), 1.77 (3 H, s), 3.13 (3 H, s), 3.33 (2 H, s), 5.0—5.2 (2 H, m)	44.4 (44.0)	6.1 (6.0)	6.0 (6.4)
(10; R = R' = Me)	100 [5]	3.37 (2 H, d, J 5), 3.51 (6 H, s), 4.76 (1 H, t, J 5)	31.0 (31.0)	4.8 (4.7)	7.3 (7.2)
(10; R = Me, R' = Et)	89 [4]	1.23 (3 H, t, J 7), 3.26 (2 H, d, J 5), 3.39 (3 H, s), 3.61 (1 H, q, J 7), 3.66 (1 H, q, J 5), 4.69 (1 H, t, J 5)	34.2 (34.6)	5.15 (5.35)	7.1 (6.75)
(11) ^c	100—102 [5]	2.33 (3 H, s), 4.21 (2 H, s)	30.5 (29.7)	3.4 (3.1)	8.2 (8.65)
(12; R = H)	97—98 [4]	3.48 (3 H, s), 3.49 (3 H, s), 3.54 (3 H, s), 3.8—4.2 (2 H, m), 4.72 (1 H, d, J 5)	35.5 (35.3)	5.7 (5.5)	6.15 (5.9)
(12; R = Me) + (13) ^d	142 [10]	1.34 and 1.35 (3 H, d, J 6), 3.30, 3.37, 3.44, ^e 3.45 and 3.47 (9 H, s), 3.5—4.0 (2 H, m), 4.60 (1 H, d, J 6)	38.3 (38.1)	5.95 (6.0)	5.8 (5.55)
(14; X = SeCN) ^f	(m.p. 140—141) ^g	4.00 (1 H, d, J 11), 4.04 (1 H, d, J 6), 5.05 (1 H, dd, J 11 and 6), 7.42 (5 H, s)	38.3 (38.2)	2.45 (2.55)	9.2 (8.9)
(15) + (16)	130—132 [5]	0.6—2.2 (13 H, m), 3.2—4.4 (3 H, m)	43.2 (42.8)	6.5 (6.4)	5.55 (5.55)
(17) + (18)	113—116 [5]	0.8—2.3 (11 H, m), 1.65 and 1.75 (3 H, d, J 6), 3.5—4.6 (2 H, m)	43.3 (42.8)	6.4 (6.4)	5.45 (5.55)
(19; X = Cl) ^h	137—139 [9]	1.2—2.15 (6 H, m), 2.3—2.7 (2 H, m), 3.70 (1 H, dt, J 4 and 10), 4.12 (1 H, dt, J 4 and 10)	38.0 (37.8)	4.5 (4.55)	6.6 (6.3)
(19; X = Br) ^h	118—122 [5]	1.2—2.2 (6 H, m), 2.35—2.8 (2 H, m), 3.92 (1 H, dt, J 4 and 10), 4.34 (1 H, dt, J 4 and 10)	31.4 (31.5)	3.8 (3.75)	4.8 (5.25)

^a *erythro*-isomer. ^b A mixture of *erythro*- and *threo*-isomer (4 : 1). ^c Preparation of this compound from chloroacetone and potassium selenocyanate has long been known.⁸ ^d A 55 : 45 mixture (by g.l.c.). ^e Two singlet peaks overlapped. ^f Me₂SO used as solvent for n.m.r. ^g Recryst. from benzene. ^h 100 MHz n.m.r.

Properties of all new compounds are summarized in Table 4. All compounds showed a sharp i.r. absorption at 2 150 cm⁻¹.

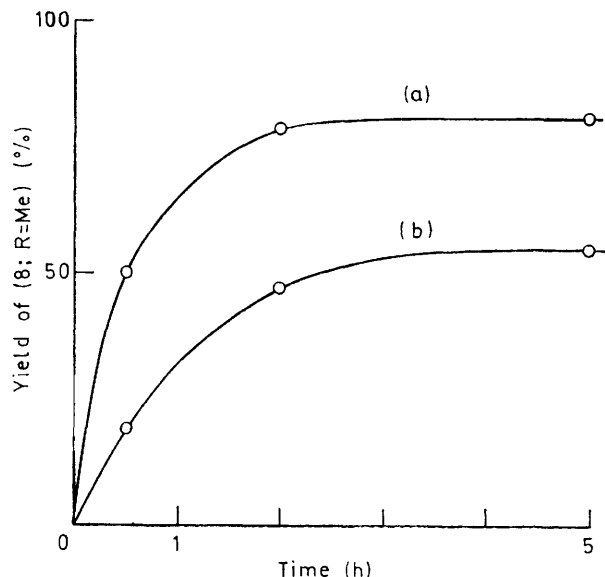


FIGURE 2 Methanolysis of (19) to give (8; R = Me) in the presence of copper(I) salt, KSeCN, and HCl: (a) (19; X = Cl) (1 mmol), CuCl (3 mmol), KSeCN (1.5 mmol), HCl (0.36 mmol), MeOH (3 ml), reflux; (b) (19; X = Br) (1 mmol), CuBr (3 mmol), KSeCN (1.5 mmol), HCl (0.36 mmol), MeOH (3 ml), reflux

Other alkoxy-selenocyanatoalkanes used as authentic samples were prepared as reported previously.²

Alkoxy-selenocyanation of Olefins.—A typical procedure is as follows. Styrene (1.56 g, 15 mmol) was added to methanol (30 ml) containing copper(II) chloride (4.03 g, 15 mmol) and potassium selenocyanate (5.40 g, 30 mmol; as pure KSeCN) at room temperature with vigorous stirring, and the mixture was heated at reflux temperature for 0.5 h during which period the colour turned from red to black. After cooling, the dark grey precipitate was filtered off and the filtrate was 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. (benzophenone as internal standard); yield of (1; R = Me)² 14.8 mmol (99%).

Acetalization of Acrylaldehyde and Methoxy-selenocyanation of the Acetal produced.—A solution of acrylaldehyde (5.6 g, 100 mmol) and copper(II) chloride (0.67 g, 5 mmol) in methanol (100 ml) was refluxed for 0.5 h with stirring. After cooling, the mixture was added to water (ca. 400 ml) and extracted with ether. Distillation of the extract afforded the dimethyl acetal (2.7 g, 26 mmol), b.p. 97—98 °C; δ 3.30 (6 H, s), 4.75 (1 H, d), and 5.1—6.1 (3 H, m).

A reaction of the dimethyl acetal (1.53 g, 15 mmol) with CuCl₂ (4.9 g, 30 mmol) and KSeCN (5.40 g, 30 mmol; as pure KSeCN) in methanol (30 ml) at reflux for 0.5 h afforded exclusively (12; R = H) (10.6 mmol, 71% yield by g.l.c.).

Halogenoselenocyanation of Olefins.—To a well stirred suspension of copper(II) chloride (4.03 g, 30 mmol) and

⁸ G. Hofmann, *Annalen*, 1889, **250**, 296.

potassium selenocyanate (5.40 g, 30 mmol; as pure KSeCN) in acetonitrile (30 ml), cyclohexene (1.23 g, 15 mmol) was added at room temperature and the mixture was heated at reflux temperature for 0.5 h. After treatment as described above, distillation gave pure (19; X = Cl) (1.52 g, 6.8 mmol) as an oil. N.m.r. analysis (100 MHz) revealed two methine protons having different chemical shifts and the same coupling constants of 10, 10, and 4 Hz. These values correspond to two axial-axial and one axial-equatorial proton coupling, indicating that the two methine protons are on axial positions and therefore that (19; X = Cl) is the *trans*-compound.

Similar treatment of styrene (15 mmol), copper(II) chloride (30 mmol), and potassium selenocyanate (12 mmol) in acetonitrile (30 ml), and concentration of the benzene extract gave crude (14; X = Cl) as a dark red oil (2.52 g, 10.3 mmol, 86%); δ 3.55 (1 H, d, J 8 Hz), 3.60 (1 H, d, J 7 Hz), 5.13 (1 H, t, J 7.5 Hz), and 7.36 (5 H, s). Distillation resulted in decomposition. Column chromatography on Wakogel C-200 with benzene as eluant afforded a small amount (*ca.* 0.2 g) of the *product* (14; X = Cl) (Found: C, 45.35; H, 3.4; N, 5.7. C_9H_8ClNSe requires C, 44.2; H, 3.3; N, 5.7%). Methanolysis of this crude product in methanol (10 ml) containing copper(II) chloride (0.67 g, 5 mmol) and hydrogen chloride (0.55 g of 35% aq. HCl, 5 mmol) at reflux temperature for 2.5 h produced (1; R = Me) (9.93 mmol, 83% yield, by g.l.c. analysis).

cis-1-Methoxy-2-selenocyanatocyclohexane.—To a solution containing *trans*-1-iodo-2-methoxycyclohexane (2.40 g, 10 mmol),¹ in dimethylformamide (25 ml) potassium selenocyanate (2.88 g, 20 mmol) was added in several portions at

room temperature. The resulting yellow solution was stirred at 90 °C for 12 h. After the usual work-up, distillation gave almost pure *cis*-1-methoxy-2-selenocyanatocyclohexane (0.82 g, 3.7 mmol, 37%); b.p. 97–99 °C at 4 Torr. The retention time of this compound (5.4 min) was longer than that of (8; R = Me) (4.9 min) [PEG 6 000 (25%)–Shimalite (1 m); column temp. 190 °C; N_2 95 ml min^{-1}]; δ (100 MHz) 1.12–2.2 (8 H, m), 3.43 (3 H, s), 3.68 (1 H, ddd, J 2.5, 3.5, and 6 Hz), and 4.18 (1 H, ddd, J 3.5, 5, and 8.5 Hz) (Found: C, 45.1; H, 6.1; N, 6.3. $C_8H_{13}NOSe$ requires C, 44.0; H, 6.0; N, 6.4%).

Attempts to prepare *cis*-1-chloro- or bromo-2-selenocyanatocyclohexane from *trans*-1-chloro- or bromo-2-iodocyclohexane¹ and potassium selenocyanate in dimethylformamide or acetone as solvent were unsuccessful.

Methanolysis of Halogenoselenocyanatoalkanes.—A typical procedure is as follows. Copper(I) chloride (0.33 g, 3 mmol) and then potassium selenocyanate (0.22 g, 1.5 mmol) were added to methanol (3 ml) containing (19; X = Cl) and hydrogen chloride (0.037 g of 35% HCl) at room temperature and the resulting orange suspension was stirred at reflux temperature for 5 h. After the usual work-up, g.l.c. analysis of the benzene extract revealed the presence of (8; R = Me) (0.878 mmol, 87.8%) and (19; X = Cl) (0.065 mmol, 6.5%).

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