BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1925—1928 (1975)

Selenocyanatodethallation in Organothallium(III) Compounds

Sakae Uemura,* Akio Toshimitsu, Masaya Okano, and Katsuhiko Ichikawa**

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

***Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606*

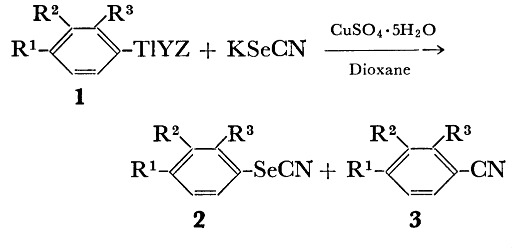
(Received March 3, 1975)

Substitution of thallium moiety in organothallium(III) compounds by selenocyanate is reported. Arylthallium (III) compounds react with KSeCN and $CuSO_4\cdot5H_2O$ or with $Cu(SeCN)_2$ in dioxane to give aryl selenocyanates in good yields. Alkoxythallates of styrene react smoothly with KSeCN in methanol to afford 1-alkoxy-1-phenyl-2-selenocyanatoethanes almost quantitatively. The oxyselenocyanation of terminal olefins is conducted by the *in situ* oxythallation of olefins, followed by the reaction with KSeCN.

Substitution of thallium moiety in organothallium(III) compounds, such as aryl-,[1)] vinyl-,[2)] and alkylthallium(III) compounds,[3,4)] by halogen (I, Br, and Cl) or pseudohalogen (CN and SCN) by use of copper and/or potassium salts has been reported. As another example of such substitution reactions we now wish to report the result of selenocyanatodethallation in aryl- and alkyl-thallium(III) compounds. This reaction would be a convenient method for the preparation of aryl and alkyl selenocyanates.

Results and Discussion

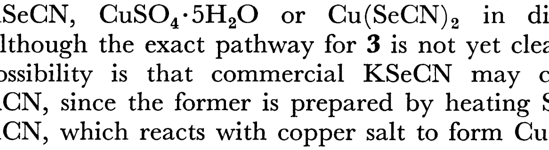
Reaction of Arylthallium(III) Compounds with Copper and/or Potassium Selenocyanates. When a mixture of arylthallium(III) compound (**1**), potassium selenocyanate and copper(II) sulfate hydrate was stirred in such solvents as dioxane, acetonitrile, methanol, and pyridine under reflux for 0.5 hr, aryl selenocyanate (**2**) was obtained in a good yield together with a small amount of aryl cyanide (**3**) (Scheme 1). Dioxane was revealed to be a solvent of choice for the preparation of **2**.



(1)

As in the case of the previously reported halogeno- and pseudohalogeno-dethallation,[1)] the replacement of thallium moiety by SeCN occurred at the position where thallium was attached previously to aromatic ring. In contrast to thiocyanatodethallation which was accompanied by protodethallation forming aromatic hydrocarbon,[1d)] almost no protodethallation occurred in this case. Sandmeyer reaction for preparing **2** has been known to be accompanied by the formation of diaryl selenide,[5)] while none of such product was detected in the reaction products in this case. Typical results are summarized in Table 1.

The reaction proceeded even in the absence of copper(II) sulfate, but the yield of **2** was low. Since the preparation of copper(II) thiocyanate from copper(II) sulfate and potassium thiocyanate has been known,[6)] it seems to be reasonable to assume that **2** was mainly formed by the interaction of **1** with copper(II) selenocyanate which may be formed in a reaction mixture. In order to ascertain this possibility, we prepared copper(II) selenocyanate separately and examined the reaction of some arylthallium(III) compounds with this salt in dioxane. As a result, **2** was obtained in a good yield irrespective of the presence or absence of KSeCN, the formation of **3** being minimized (Table 1). Thus it is highly probable that the reaction affording **2** essentially involves the attack of $Cu(SeCN)_2$, formed *in situ*, on **1**. The reaction is ionic in nature since no effect was observed by the introduction of oxygen into the reaction mixture and no acrylonitrile polymer or phenylated acrylonitrile was obtained from the reaction in the presence of acrylonitrile.[1b)] Reaction scheme seems to be a concerted nucleophilic substitution after coordination of copper to a ligand on thallium as proposed in the cases of halogeno- and pseudohalogenodethallation (Scheme 2).[1b–d)]



+ TlY + CuSeCN·Z (2)

As to the formation of a side-product **3**, we confirmed in separate experiments that **3** was not derived from **2** under the present reaction conditions; *i.e.*, no deselenation from **2** occurred by heating **2** in the presence of KSeCN, $CuSO_4\cdot5H_2O$ or $Cu(SeCN)_2$ in dioxane. Although the exact pathway for **3** is not yet clear, one possibility is that commercial KSeCN may contain KCN, since the former is prepared by heating Se and KCN, which reacts with copper salt to form CuCN or $Cu(CN)_2$ in the reaction mixture. Cyanodethallation of arylthallium(III) compounds by these salts has been reported.[1d)]

Reaction of the Alkoxythallate of Styrene with KSeCN. When a mixture of the alkoxythallate of styrene and KSeCN was stirred in methanol under reflux for 15—30 min, 1-alkoxy-1-phenyl-2-selenocyanatoethane (**5**) was obtained almost quantitatively (100% yield when $R=CH_3$, C_2H_5, and n-C_3H_7; 80—83% yield when $R=$ i-C_3H_7, n-C_4H_9, and i-C_4H_9) (Scheme 3). The reaction did not occur at 25 °C for 2 hr. An elongation of the reaction time at refluxing temperature decreased the yield of **5**, because of the secondary reaction of **5** giving unidentified resinous products. When the reaction was applied to the alkoxythallate of α-methylstyrene and the acetoxythallate of norbornene, the compounds corresponding to **5** were scarcely obtained

---

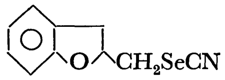
* To whom correspondence should be addressed.

TABLE 1. PREPARATION OF ARYL SELENOCYANATE

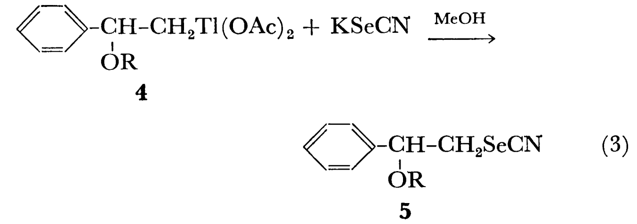
1 (5 mmol)					Cu^{2+} salt (mmol)	KSeCN (mmol)	Solvent (25 ml)	React. temp. (°C)	React. time (hr)	Products and yields(%)$^{a)}$	
R^1	R^2	R^3	Y	Z						**2**	**3**
					$CuSO_4 \cdot 5H_2O$						
H	H	H	OAc	ClO_4	0	20	Dioxane	101	4	24	0
H	H	H	OAc	ClO_4	10	40	Dioxane	101	0.5	78	6
H	H	H	OAc	ClO_4	10	40	Dioxane	101	2	76	6
H	H	H	OAc	ClO_4	10	20	Dioxane	101	2	59	8
H	H	H	OAc	ClO_4	10	40	MeCN	86	0.5	57	5
H	H	H	OAc	ClO_4	10	40	MeOH	65	0.5	22	2
H	H	H	OAc	ClO_4	10	40	Pyridine	115	0.5	28	2
H	H	H	$OCOCF_3$	$OCOCF_3$	10	40	Dioxane	101	0.5	38	1
Me	H	H	OAc	ClO_4	10	40	Dioxane	101	0.5	68	3
Me	Me	H	OAc	ClO_4	10	40	Dioxane	101	0.5	70	5
Me	Me	H	$OCOCF_3$	$OCOCF_3$	10	40	Dioxane	101	0.5	79	1
Me	H	Me	OAc	ClO_4	10	40	Dioxane	101	0.5	79	13
Me	H	Me	$OCOCF_3$	$OCOCF_3$	10	40	Dioxane	101	0.5	89	2
MeO	H	H	OAc	ClO_4	10	40	Dioxane	101	0.5	95	1
Cl H	H	H$^{b)}$ Cl	$OCOCF_3$	$OCOCF_3$	10	40	Dioxane	101	0.5	60$^{b)}$	1
					$Cu(SeCN)_2$						
H	H	H	OAc	ClO_4	10	0	Dioxane	101	0.5	94	trace
H	H	H	OAc	ClO_4	10	20	Dioxane	101	0.5	89	1
H	H	H	NO_3	OH	10	0	Dioxane	101	0.5	50	1
Me	H	H	OAc	ClO_4	10	0	Dioxane	101	0.5	77	trace
Me	H	H	NO_3	OH	10	0	Dioxane	101	0.5	53	trace
Me	Me	H	$OCOCF_3$	$OCOCF_3$	10	0	Dioxane	101	0.5	78	1
Me	H	Me	$OCOCF_3$	$OCOCF_3$	10	0	Dioxane	101	0.5	83	4

a) Based on **1**. Determined by glc. b) A mixture of *o*- and *p*-isomers (*o*-/*p*-=30/70).

TABLE 2. OXYSELENOCYANATION OF OLEFINS$^{a)}$

Olefin (5 mmol)	Solvent (25 ml)	React. time (hr)		Products, Yield (%)$^{d)}$	
		at 15—20 °C$^{b)}$	at reflux$^{c)}$		
Styrene	MeOH	2	0.5	$PhCH(OMe)CH_2SeCN$	80
Styrene	MeOH	1	0.5	$PhCH(OMe)CH_2SeCN$	68
1-Octene	MeOH	2	0.25	$n\text{-}C_6H_{13}CH(OMe)CH_2SeCN$	80
1-Octene	MeOH	1	0.25	$n\text{-}C_6H_{13}CH(OMe)CH_2SeCN$	70
1-Hexene	MeOH	2	0.5	$n\text{-}C_4H_9CH(OMe)CH_2SeCN$	76
o-Allylphenol	MeOH	2	0.25		50
$EtOCH{=}CH_2$	EtOH	2	0.25	$(EtO)_2CHCH_2SeCN$	83
				$\begin{matrix}EtO\\AcO\end{matrix}\!>\!CHCH_2SeCN$	10
$AcOCH{=}CH_2$	EtOH	2	0.25	$(EtO)_2CHCH_2SeCN$	53
				$\begin{matrix}EtO\\AcO\end{matrix}\!>\!CHCH_2SeCN$	24
$CH_2{=}CH{-}CH{=}CH_2$	MeOH	2	0.25	$CH_2{=}CH{-}\underset{\underset{OMe}{\mid}}{CH}{-}CH_2SeCN$	61

a) Tl(OAc)$_3$ 8 mmol, KSeCN 20 mmol. b) Time for oxythallation. c) Time for Tl-SeCN replacement. d) Based on olefin charged.

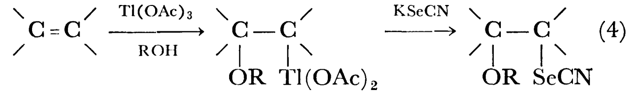

4

5

(3)

under room or refluxing temperature for 0.5 hr, and the oxidation products of olefins and/or the deoxythallation products were obtained. For example, benzyl methyl ketone and α-methylstyrene were obtained in 50% and 32% yields respectively in the former case, while norbornene was mainly formed in the latter.

The in situ Oxyselenocyanation of Olefins. The result of the reaction of the alkoxythallate of styrene with KSeCN described above and the report[3] of the *in situ* oxythiocyanation of olefins by $Tl(OAc)_3$ and KSCN prompt us to examine the *in situ* oxyselenocyanation of olefins. After a mixture of olefin and thallium(III) acetate was stirred in alcohol at 15—20 °C for 1—2 hr (oxythallation), an alcoholic solution of KSeCN was added and the mixture was then heated under reflux for 15—30 min to afford oxyselenocyanated compound, **6** (Scheme 4). Typical results are summarized in Table 2. Terminal olefins reacted smoothly to give **6**, while internal olefins such as cyclohexene and 2-octene gave only the oxidation products. This may be due to the difference of the stability between the intermediate alkoxythallates of olefins. From isoprene, two oxyselenocyanated compounds which seem to be 1,2- and 3,4-addition products were obtained, but the yield was very low (<10% yield) compared to the case of butadiene. Application of the reaction to isopropenyl acetate and α-methylstyrene resulted in only a slight formation of **6**, while methyl vinyl ketone and β-methylstyrene did not react at all under the conditions described above. The reaction with allyl chloride as a substrate afforded only allyl selenocyanate (bp 80 °C/20 mmHg; lit,[7] bp 75 °C/12 mmHg) quantitatively, irrespective of the presence or absence of thallium(III) acetate. The reaction of alkyl halide with KSeCN affording alkyl selenocyanate is well-known.[8]



(4)

6

Experimental

The IR spectra were taken with a Hitachi EPI-S2 spectrometer in paraffin mull and KBr disc. The NMR spectra were recorded with a Varian A-60 spectrometer in CCl_4, using TMS as an internal standard. Glc analyses were carried out on a Shimadzu 5APTF apparatus, using DEGS (25%)-Shimalite(1m) column (N_2 as carrier gas).

Materials. Arylthallium (III) acetate perchlorate monohydrate[9] and ditrifluoroacetates,[10] and the alkoxythallates of styrene and α-methylstyrene[4] were prepared by the reported methods. Arylthallium(III) nitrate hydroxide was prepared by heating aromatics with $Tl(NO_3)_3\cdot 3H_2O$ in CCl_4.[11] Commercial butadiene, $CuSO_4\cdot 5H_2O$, and KSeCN were used without purification. Other organic materials were purified before use by distillation.

$Cu(SeCN)_2$: An aqueous (20 ml) solution of KSeCN (10.8 g, 70 mmol) was added to an aqueous (50 ml) solution of $CuSO_4\cdot 5H_2O$ (12.5 g, 50 mmol) at room temperature to afford the black precipitates immediately. After the mixture was stirred vigorously for 0.5 hr, the black precipitates were filtered off and washed with water and methanol to afford pure $Cu(SeCN)_2$. Yield, 9 g (94% yield based on KSeCN). It turns to pale brown at 200—210 °C and decomposes at about 260—280 °C. Found: C, 8.69; N, 9.77%. Calcd for $C_2CuN_2Se_2$: C, 8.79; N, 10.25%. IR 2150 cm^{-1}.

Reaction of Arylthallium(III) Compounds with KSeCN in the Presence of $CuSO_4\cdot 5H_2O$. The following preparation of **2** ($R^1=CH_3$, $R^2=R^3=H$), *p*-tolyl selenocyanate, shows a typical procedure. To a brown heterogeneous solution of KSeCN (5.76 g, 40 mmol) and $CuSO_4\cdot 5H_2O$ (2.50 g, 10 mmol) in dioxane (15 ml) was added a dioxane (10 ml) solution of **1**($R^1=CH_3$, $R^2=R^3=H$, X=OAc, $Y=ClO_4\cdot H_2O$) (2.36 g, 5 mmol) at 15—20 °C. The mixture was then refluxed for 30 min under stirring to give a black heterogeneous solution. The solution was cooled down and filtered from the dark-grey precipitates. The filtrate was added by water (150 ml) and extracted with benzene. The extract was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. Glc analysis with dibenzyl as an internal standard showed the presence of 3.4 mmol of **2** ($R^1=CH_3$, $R^2=R^3=H$) (68% yield) and 0.2 mmol of *p*-tolunitrile (4% yield). Distillation gave pure *p*-tolyl selenocyanate; bp 86 °C/2 mmHg, mp 52—53 °C (lit,[12] mp 55—56 °C). IR 2140 (ν_{SeCN}) and 804(1,4-substituted phenyl) cm^{-1}. NMR δ 2.38 (s. 3H), 7.17 (d. 2H, $J=8.5$ Hz), and 7.50 (d. 2H, $J=8.5$ Hz).

Characterization of other aryl selenocyanates is as follows. **2**($R^1=R^2=R^3=H$); bp 111 °C/8 mmHg (lit,[13] 134 °C/10 mmHg). **2**($R^1=MeO$, $R^2=R^3=H$); bp 115 °C/3 mmHg, mp 61—63 °C (lit,[14] mp 65 °C). IR 2140 (ν_{SeCN}) and 823 (4-substituted phenyl cm^{-1}. NMR δ 3.77 (s. 3H), 6.85 (d. 2H, $J=9$ Hz), and 7.53 (d. 2H, $J=9$ Hz). **2** (R^1 or $R^3=$ Cl, $R^2=H$), chlorophenyl selenocyanate (*o*-/*p*-=3/7); bp 92 °C/2 mmHg (lit,[15] *o*-isomer; bp 152-153 °C/20 mmHg, *p*-isomer; mp 55 °C). **2** ($R^1=R^2=Me$, $R^3=H$); bp 105 °C/4 mmHg. IR 2150 (ν_{SeCN}) and 802 (phenyl)cm^{-1}. NMR δ 2.24 (s. 6H) and 7.0—7.35 (m. 3H). Found: C, 51.92; H, 4.49; N, 6.67%. Calcd for C_9H_9NSe: C, 51.47; H, 4.32; N, 6.67%. **2** ($R^1=R^3=Me$, $R^2=H$); bp 96—100 °C/3.5 mmHg (lit,[16] bp 138—139 °C/5 mmHg).

Reaction of the Alkoxythallates of Styrene with KSeCN. A methanol solution (25 ml) of KSeCN (2.88 g, 20 mmol) was added to **4**($R^1=CH_3$) (2.28 g, 5 mmol) and the mixture was heated under reflux for 30 min during which period the yellow solids formed at first turned to white precipitates. The solution was cooled down and filtered from white precipitates (1.51 g, TlSeCN). The filtrate was treated as described above. Glc analysis with benzophenone as an internal standard showed the presence of 5 mmol of **5** ($R^1=CH_3$), 1-methoxy-1-phenyl-2-selenocyanatoethane (100% yield). Distillation gave pure compound; bp 150—151 °C/6.5 mmHg. IR 2150(ν_{SeCN}), 1103(ν_{C-O}), 761(phenyl), and 698(phenyl)cm^{-1}. NMR δ 3.25 (s. 3H, methoxy), 3.27 (d. 1H, $J=5.5$ Hz, methylene), 3.29 (d. 1H, $J=7.5$ Hz, methylene), 4.42 (q. 1H, $J=5.5$ and 7.5 Hz, methine), and 7.30 (s. 5H, phenyl). Found: C, 50.04; H, 4.76; N, 5.52%. Clacd for $C_{10}H_{11}NOSe$: C, 50.02; H, 4.62; N, 5.83%.

Characterization of the products obtained by a similar treatment with other oxythallates is as follows. **5**($R^1=Et$): bp 133 °C/5 mmHg. IR 2150 (ν_{SeCN}), 1095 (ν_{C-O}), 760 (phenyl), and 700 (phenyl) cm^{-1}. NMR δ 1.17 (t. 3H, J=7 Hz), 3.31—3.45 (m. 4H), 4.53 (q. 1H, J=5.5 and 7.5 Hz), 7.28 (s. 5H). Found: C, 52.20; H, 5.26; N, 5.38%. Calcd for $C_{11}H_{13}NOSe$; C, 52.00; H, 5.16; N, 5.51%. **5**(R^1=n-Pr): bp 120 °C/3 mmHg. IR 2150 (ν_{SeCN}), 1097 (ν_{C-O}), 762 (phenyl) and 700 (phenyl) cm^{-1}. NMR δ 0.92 (t. 3H, J=7 Hz), 1.57 (sex. 2H, J=7 Hz), 3.2—3.4 (m. 4H), 4.52 (q. 1H, J=5.5 and 8 Hz), and 7.30 (s. 5H). Found: C, 53.46; H, 5.86; N, 5.05%. Calcd for $C_{12}H_{15}NOSe$: C, 53.75; H, 5.64; N, 5.22%. **5** (R^1=i-Pr): bp 115 °C/2.5 mmHg. IR 2150 (ν_{SeCN}), 1120 (ν_{C-O}), 1088 (ν_{C-O}), 762 (phenyl) and 700(phenyl) cm^{-1}. NMR δ 1.07 (d. 3H, J=6 Hz), 1.20(d. 3H, J=6 Hz), 3.25(d. 1H, J=5.5 Hz), 3.27 (d. 1H, J=8 Hz), 3.55 (sep. 1H, J=6 Hz), 4.66 (q. 1H, J=5.5 and 8 Hz), and 7.30 (s. 5H). Found: C, 53.72; H, 5.75; N, 5.18%. **5** (R^1=n-Bu): bp 121 °C/3 mmHg. IR 2150 (ν_{SeCN}), 1100 (ν_{C-O}), 762 (phenyl), and 701(phenyl) cm^{-1}. NMR δ 0.8—1.7 (m. 7H), 3.25—3.40 (m. 4H), 4.52 (q. 1H, J=5.5 and 8 Hz), and 7.30 (s. 5H). Found: C, 55.54; H, 6.25; N, 5.16%. Calcd for $C_{13}H_{17}NOSe$: C, 55.33; H, 6.07; N, 4.96%. **5**(R^1=i-Bu): bp 128 °C/3 mmHg. IR 2150(ν_{SeCN}), 1100(ν_{C-O}), 762(phenyl), and 700(phenyl) cm^{-1}. NMR δ 0.90 (d. 6H, J=6.5 Hz), 1.4—2.2 (m. 1H), 3.10 (d. 1H, J=5.5 Hz), 3.11 (d. 1H, J=6.5 Hz), 3.29 (d. 1H, J=5.5 Hz), 3.32 (d. 1H, J=8 Hz), 4.50 (q. 1H, J=5.5 and 8 Hz), and 7.29 (s. 5H). Found: C, 55.33; H, 6.21; N, 4.97%.

The in situ *Oxyselenocyanation of Olefins.* The following preparation of α-selenocyanatomethylcoumaran shows a typical procedure. To a suspension of $Tl(OAc)_3$ (3.05 g, 8 mmol) in methanol (10 ml) was added *o*-allylphenol (0.67 g, 5 mmol) at 15—20 °C to give a pale yellow homogeneous solution. After the solution was kept at 15—20 °C for 2 hr under stirring, a methanolic solution (15 ml) of KSeCN (2.88 g, 20 mmol) was added to give the voluminous yellow precipitates. The mixture was then rapidly heated to refluxing temperature and kept for 15 min to give the white precipitates of TlSeCN (2.2 g, 7 mmol). The reaction mixture was cooled down and treated as described above. Glc analysis with benzyl phenyl ketone as an internal standard showed the presence of 2.5 mmol of α-selenocyanatomethylcoumaran (50% yield). Distillation gave pure compound; bp 132 °C/2 mmHg. IR 2150 (ν_{SeCN}), 1480 (δ_{CH_2}), 1229 (ν_{C-O}), and 751(phenyl) cm^{-1}. NMR δ 2.7—3.6 (m. 2H, CH_2Se–), 3.24 (d. 2H, J=5.5 Hz, $ArCH_2$), 4.75—5.2 (m. 1H, methine), and 6.6—7.2 (m. 4H, aryl). Found: C, 50.51; H, 3.92; N, 5.79%. Calcd for $C_{10}H_9NOSe$: C, 50.45; H, 3.81; N, 5.88%.

Characterization of other oxyselenocyanatoalkanes in Table 2 is as follows. 1-Selenocyanato-2-methoxyoctane: bp 131 °C/6 mmHg. IR 2150 (ν_{SeCN}) and 1093 (ν_{C-O}) cm^{-1}. NMR δ 0.7—1.7 (m. 13H), 3.15—3.35 [m. 3H, –CH(OR)–CH_2Se–], and 3.35 (s. 3H, methoxy). Found: C, 48.63; H, 8.16; N, 5.60%. Calcd for $C_{10}H_{19}NOSe$: C, 48.40; H, 7.72; N, 5.64%. 1-Selenocyanato-2-methoxyhexane: bp 90 °C/4 mmHg. IR 2150 (ν_{SeCN}) and 1090 (ν_{C-O}) cm^{-1}. NMR δ 0.8—1.7 (m. 9H), 3.1—3.5 [m. 3H, –CH(OR)–CH_2Se–], and 3.36 (s. 3H, methoxy). Found: C, 43.69; H, 7.19; N, 6.38%. Calcd for $C_8H_{15}NOSe$: C, 43.65; H, 6.87; N, 6.36%. 1,1-Diethoxy-2-selenocyanatoethane: bp 81 °C/2.5 mmHg. IR 2150 (ν_{SeCN}), 1120 (ν_{C-O}), and 1060 (ν_{C-O}) cm^{-1}. NMR δ 1.21 (t. 6H, J=7 Hz, methyl), 3.21 (d. 2H, J=5.5 Hz, –CH_2Se–), 3.58 (q. 2H, J=7 Hz, –OCH_2–), 3.62 (q. 2H, J=7 Hz, –OCH_2–), and 4.70 (t. 1H, J=5.5 Hz, methine). Found: C, 37.95; H, 6.13; N, 5.64%. Calcd for $C_7H_{13}NOSe$: C, 37.86; H, 5.90; N, 6.31%. 1-Acetoxy-1-ethoxy-2-selenocyanatoethane: This compound was characterized from a mixture with 1,1-diethoxy-2-selenocyanatoethane. The analysis of each component in the mixture was carried out by glc using PEG 6000(25%)-Chromosorb W(1 m) column. IR 1747($\nu_{C=O}$) cm^{-1}. NMR δ 2.10 (s. 3H, acetoxy) and 5.96 (t. 1H, methine). (CH_3– and CH_2Se– protons were not resolved.) 3-Methoxy-4-selenocyanato-1-butene: bp 83 °C/4 mmHg. IR 2150 (ν_{SeCN}), 1640 ($\nu_{C=C}$), 1100 (ν_{C-O}), 990 (vinyl), and 938 (vinyl)cm^{-1}. NMR δ 3.19 (d. 1H, J=7 Hz, methylene), 3.20 (d. 1H, J=6 Hz, methylene), 3.30 (s. 3H, methoxy), 3.87 (q. 1H, J=6.5 Hz, methine), and 5.1—6.0 (m. 3H, vinyl). Found: C, 37.77; H, 4.89; N, 7.20%. Calcd for C_6H_9NOSe: C, 37.92; H, 4.77; N, 7.37%.

References

1) a) K. Ichikawa, Y. Ikeda, and S. Uemura, *Chem. Commun.*, **1971**, 169. b) S. Uemura, Y. Ikeda, and K. Ichikawa, *Tetrahedron*, **28**, 3025 (1972). c) S. Uemura, Y. Ikeda, and K. Ichikawa, *ibid.*, **28**, 5499 (1972). d) S. Uemura, S. Uchida, M. Okano, and K. Ichikawa, This Bulletin, **46**, 3254 (1973).

2) S. Uemura, H. Tara, M. Okano, and K. Ichikawa, *ibid.*, **47**, 2663 (1974).

3) H. Mitani, T. Ando, and Y. Yukawa, *Chem. Lett.*, **1972**, 455.

4) S. Uemura, K. Zushi, A. Tabata, A. Toshimitsu, and M. Okano, This Bulletin, **47**, 920 (1974).

5) O. Behaghel and H. Seibert, *Ber.*, **65**, 812 (1932).

6) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3095 (1971).

7) H. Brintzinger, K. Pfannstiel, and H. Vogel, *Z. Anorg. Allg. Chem.*, **256**, 85 (1948).

8) "Methoden der Organischen Chemie," (Houben-Weyl), Vol. 9, ed. by E. Müller, Georg Thieme Verlag, Stuttgart (1955), pp. 939—942.

9) K. Ichikawa, S. Uemura, T. Nakano, and E. Uegaki, This Bulletin, **44**, 545 (1971).

10) A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Amer. Chem. Soc.*, **93**, 4841 (1971).

11) S. Uemura, A. Toshimitsu, and M. Okano, unpublished data.

12) F. Challenger, A. T. Peters, and J. Halévy, *J. Chem. Soc.*, **1926**, 1648.

13) F. Challenger and A. T. Peters, *ibid.*, **1928**, 1364.

14) O. Behaghel and M. Rollman, *J. Prakt. Chem.*, **123**, 336 (1929).

15) O. Behaghel and H. Seibert, *Ber.*, **66**, 708 (1933).

16) L. Chierici and R. Passerini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **12**, 131 (1954); *Chem. Abstr.* **49**, 6868h (1955).