

The Reaction of Alkyl Halides with Mercuric Thiocyanate in Tetrahydrofuran. The Solvent Incorporation and the Intermediacy of *O*-Alkyltetrahydrofuranium Ions.

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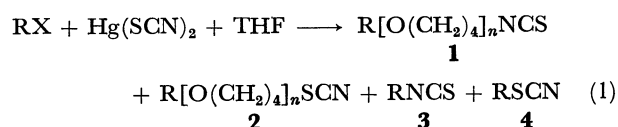
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The reaction of alkyl halides with mercuric thiocyanate in tetrahydrofuran (THF) affords mainly the THF-incorporated products, $R[O(CH_2)_4]_nNCS$ and $R[O(CH_2)_4]_nSCN$ (mostly $n=1$ and 2), where the isomer ratios (N/S ratios) are nearly 1. The reaction of $EtO(CH_2)_mBr$ ($m=2-5$) with mercuric thiocyanate in THF or n -Bu₂O proceeds rapidly only in the case of $m=4$ to give $EtO(CH_2)_4NCS$ and $EtO(CH_2)_4SCN$, the N/S ratio being also nearly 1, and gives $EtNCS$ and $EtSCN$ when $m=5$, while the reaction with potassium thiocyanate in DMF affords a good yield of $EtO(CH_2)_mSCN$ ($m=2-5$) as nearly the only product. It is suggested that the titled reaction involves the initial formation of a five-membered oxonium ion, *O*-alkyltetrahydrofuranium ion, and a subsequent attack by $XHg(SCN)_2^-$.

Previously, we reported that alkyl halides react with $Hg(SCN)_2$ in less polar solvents such as di-*n*-butyl ether and *n*-hexane to afford predominantly alkyl isothiocyanates (RNCS), in contrast to the reaction with the potassium salt in DMF, where alkyl thiocyanates (RSCN) are the main products.¹⁾ When the former reaction was carried out in tetrahydrofuran (THF) as a solvent, it was found that the THF-incorporated products, $R[O(CH_2)_4]_nNCS(-SCN)$ ($n=1$ and 2), were mainly obtained instead of the expected substitution products, $RNCS(-SCN)$. Here, the ratios of isothiocyanates to thiocyanates (hereinafter abbreviated as the N/S ratio) in the THF-incorporated products were nearly 1, regardless of the structure of the alkyl halides. In the present paper we wish to describe the results of the reaction and discuss its reaction mechanism.

Results and Discussion

When the reaction of various alkyl halides with $Hg(SCN)_2$ was carried out in THF at 65—70 °C (in the case of MeI, at 35—40 °C) for several hours, the THF-incorporated products (**1** and **2**) were mainly obtained, together with small amounts of the expected products (**3** and **4**), as shown in scheme 1. Typical results are summarized in Table 1. Besides the products listed in Table



1, small amounts of high-boiling substances which seemed to be **1** and **2** ($n=3$) were always detected in glc analysis. As can be seen from Table 1, the N/S ratios in **3** plus **4** increased upon changing from primary halides to secondary ones; this is in good agreement with the reported result of the reaction in *n*-Bu₂O.¹⁾ On the other hand, the N/S ratios in **1** plus **2** were generally *ca.* 1, regardless of the structure of alkyl halides used. The reactions using $Cu(NCS)_2$ and $AgSCN$ instead of Hg salt gave mainly 4-alkoxybutyl halide and a mixture of **3** and **4**, respectively, whereas the yields of **1** and **2** were very low even for a longer reaction time (see Experimental). Here the N/S ratio in **1** plus **2** was *ca.* 0.1, in sharp contrast to that in the Hg case. Therefore, the formation of nearly equal amounts of **1** and **2** as main products is a characteristic of the reaction with $Hg(SCN)_2$. Similar phenomena were also observed in reactions of EtI with metal bromides in THF, where the bromide analogue of **1** and **2** ($n=1$ and 2) was obtained in good yields by using $HgBr_2$, while the reaction occurred only slightly by using $Cu(II)$ and $Ag(I)$ bromides.²⁾

TABLE 1. REACTION OF RX WITH $Hg(SCN)_2$ IN THF^{a)}

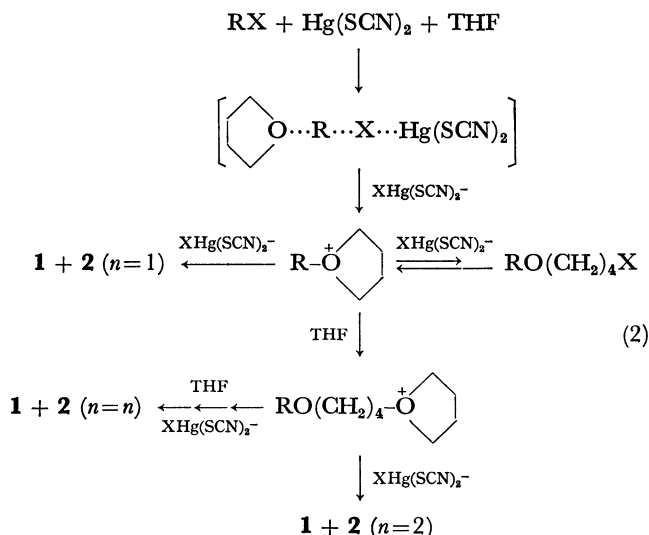
RX (40 mmol)		React. temp (°C)	React. time (hr)	Products Yields (%), ^{b)} (N/S ratios) ^{c)}		
R	X			1 + 2 ($n=1$)	1 + 2 ($n=2$)	3 + 4
Me	I	35—40	28	15 (47/53)	10 (48/52)	1 (8/92)
Et	I	65—70	3	32 (49/51)	13 (52/48)	2 (30/70)
<i>n</i> -Pr	I	65—70	3	36 (49/51)	12 (53/47)	6 (34/66)
<i>n</i> -Bu	I	65—70	3	32 (51/49)	— ^{d)}	4 (33/67)
<i>i</i> -Pr	I	65—70	2	30 (50/50)	17 (50/50)	5 (77/23)
<i>c</i> -C ₆ H ₁₁	I ^{e)}	65—70	5	1 (53/47)	— ^{d)}	1 (75/25)
<i>n</i> -Bu	Br	65—70	4	3 (47/53)	2 (45/55)	1 (38/62)
<i>i</i> -Pr	Br	65—70	6.5	34 (49/51)	15 (50/50)	2 (70/30)

a) $Hg(SCN)_2$, 40 mmol. THF, 30 ml. b) Isolated yield. c) Determined by glc. d) Not determined. e) Other product: cyclohexene, 64%.

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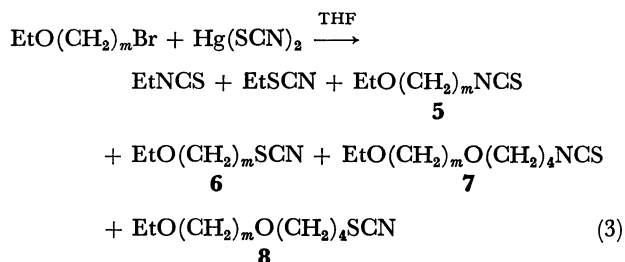
Considering the well-clarified mechanism of the polymerization of THF under the influence of trialkyl-oxonium salts,³⁾ together with the finding that no reaction proceeded between THF and a mixture of ethyl thiocyanate and isothiocyanate by heating at 65–70 °C for 3 hr in the presence of $\text{Hg}(\text{SCN})_2$, we propose a pathway for the formation of **1** and **2** such as that shown in scheme 2, where the *O*-alkyltetrahydrofuranium ion is formed as an initial intermediate from RX and THF.



Since the yields of **1** plus **2** from primary alkyl iodides were generally comparable to that from *i*-PrI (see Table 1), it seems unlikely that free R^+ plays a part in the oxonium ion formation. When more polar 1,2-dichloroethane ($\epsilon=10.36$) was used as a solvent instead of THF ($\epsilon=7.58$) (a favorable condition for the $\text{S}_{\text{N}}1$ process), the conversion in the reaction of *i*-PrBr with $\text{Hg}(\text{SCN})_2$ was only 0.5% at 65 °C for 7 hr. On the contrary, the reaction in THF showed a high conversion (see Table 1), suggesting a nucleophilic participation of the solvent. Therefore it seems to be reasonable to assume that both the push by THF and the pull by the Hg salt are involved in the formation of *O*-alkyltetrahydrofuranium ion. The resulting cation reacts with $\text{XHg}(\text{SCN})_2^{-1)}$ to afford a mixture of **1** and **2** ($n=1$) and 4-alkoxybutyl halide, or with another THF molecule with ring opening to give a new tetrahydrofuranium ion, which in turn can

react with $\text{XHg}(\text{SCN})_2^{-}$ to afford **1** and **2** ($n=2$) or can add to another THF molecule. Although the formation of 4-alkoxybutyl halide was only slightly observed in this reaction, the halide became the main product in the reaction of EtI and $\text{Hg}(\text{CN})_2$, instead of $\text{Hg}(\text{SCN})_2$, in THF (see Experimental). Furthermore, we found that 4-butoxybutyl bromide reacted very rapidly with $\text{Hg}(\text{SCN})_2$ in THF to afford **1** and **2** (*i.e.*, almost all of the bromide disappeared after 20 min at 65–70 °C), the N/S ratio in **1** plus **2** being *ca.* 1. Therefore it seems very likely that even if 4-alkoxybutyl halide is formed, the equilibrium is quite unfavorable to this halide in the presence of $\text{Hg}(\text{SCN})_2$.

In the solvolysis of ω -methoxy-*n*-alkyl brosylates, $\text{CH}_3\text{O}(\text{CH}_2)_m\text{OBs}$, a considerable rate enhancement has been observed in the cases of $m=4$ and 5, as compared to those of $m=2$ and 3, and this has been attributed to the formation of a cyclic oxonium ion intermediate.⁴⁾ Furthermore, a favorable nucleophilic attack occurs at the *O*-methylene C atoms of the ring for a five-membered oxonium ion ($m=4$), while it occurs at the methyl C atom of the side chain for a six-membered one ($m=5$).⁵⁾ In order to obtain further evidence for scheme 2, namely the participation of *O*-alkyltetrahydrofuranium ion as an intermediate, we carried out the reaction of $\text{EtO}(\text{CH}_2)_m\text{Br}$ with $\text{Hg}(\text{SCN})_2$ in THF and *n*-Bu₂O and obtained results similar to those described above. Thus the reaction proceeded rapidly when $m=4$, while ethyl thiocyanate and isothiocyanate were obtained only in the case of $m=5$ (Scheme 3, Table 2). The extent of rate



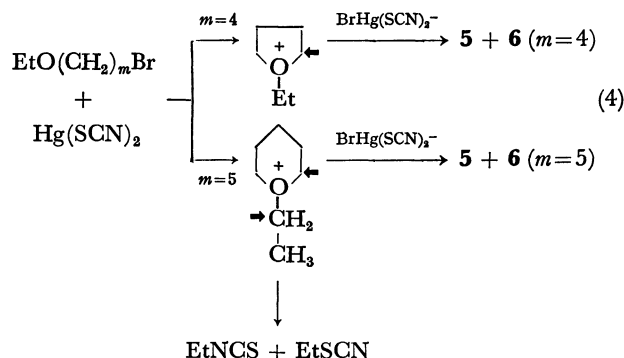
enhancement by the introduction of an alkoxy group at 4-position in *n*-BuBr is such that the reaction of 4-ethoxy-*n*-butyl bromide with $\text{Hg}(\text{SCN})_2$ in *n*-Bu₂O gave a 77% yield of a mixture of **5** and **6** ($m=4$) at 65–70 °C for 1 hr (see Table 2), while only a 23% yield of *n*-BuN-

TABLE 2. REACTION OF $\text{EtO}(\text{CH}_2)_m\text{Br}$ WITH $\text{Hg}(\text{SCN})_2$ IN THF AND *n*-Bu₂O^{a)}

EtO(CH ₂) _m Br (20 mmol) <i>m</i>	Solvent (15 ml)	React. time (hr)	Products Yields (%), ^{b)} (N/S ratios) ^{b)}		
			EtNCS+EtSCN	5 + 6	7 + 8
2	THF	4	0	0.2 (15/85)	1 ^{c)} (51/49)
2	<i>n</i> -Bu ₂ O	20	0	0	0
3	THF	4	0	1 (23/77)	2 ^{c)} (47/53)
3	<i>n</i> -Bu ₂ O	20	0	0	0
4	THF	1.5	0	42 ^{d)} (48/52)	17 ^{d)} (50/50)
4	<i>n</i> -Bu ₂ O	1	0	77 ^{d)} (64/36)	0
5	THF	4	12 (53/47)	4 ^{e)} (43/57)	— ^{f)}
5	<i>n</i> -Bu ₂ O	24	12 (55/45)	7 (48/52)	0

a) $\text{Hg}(\text{SCN})_2$, 20 mmol. React. Temp., 65–70 °C. b) Determined by glc. c) Not characterized. d) Isolated yield. Here **5**+**6** and **7**+**8** correspond to **1**+**2** ($\text{R}=\text{Et}$, $n=1$) and **1**+**2** ($\text{R}=\text{Et}$, $n=2$), respectively. e) Other products: $\text{EtO}(\text{CH}_2)_4\text{NCS}(-\text{SCN})$ 5.7%, N/S ratio=44/56. f) Not determined.

CS(-SCN) was obtained from the reaction with *n*-BuBr, even at 80–90 °C for 50 hr.¹⁾ Considering these findings it is obvious that the reaction proceeds through a cyclic oxonium ion intermediate when *m*=4 and 5 (Scheme 4). It should be noted here that the N/S ratio



in **5** plus **6** (*m*=4) was nearly 1 in THF solvent, which is in good agreement with that in **1** plus **2** shown in Table 1. This fact clearly supports scheme 2, where the reaction of RX with Hg(SCN)₂ in THF is supposed to involve an *O*-alkyltetrahydrofuranium ion as an intermediate.

In separate experiments we confirmed that almost no isomerization occurs between the produced alkyl isothiocyanate and thiocyanate under the conditions shown in Tables 1 and 2. Therefore, it can be concluded that the N/S ratios in both Tables are kinetically controlled.

In contrast to the reaction of RO(CH₂)_{*m*}Br with Hg(SCN)₂ described above, the reaction with KSCN in DMF proceeded smoothly with all kinds of RO(CH₂)_{*m*}Br; alkoxyalkyl thiocyanate was nearly the only product (Table 3). Here, the presence of alkoxy groups showed almost no significant effects on either the reaction rate or the yield of the products. In the reaction using THF as a solvent, where the rate was slow compared to that in DMF, none of the THF-incorporated products was formed and alkoxyalkyl thiocyanate was also nearly the only product. These results clearly indicate that the

TABLE 3. REACTION OF RO(CH₂)_{*m*}Br WITH KSCN IN DMF AND THF^{a)}

RO(CH ₂) _{<i>m</i>} Br (20 mmol)		Solvent (15 ml)	React. temp. (°C)	React. time (hr)	Yield of product (%) ^{b)} RO(CH ₂) _{<i>m</i>} - SCN
R	<i>m</i>				
Et	2	DMF	65—70	1	78
Et	3	DMF	65—70	1	86
Et	4	DMF	65—70	1	89
<i>n</i> -Bu	4	DMF	65—70	1	93
<i>n</i> -Bu	4	THF	65—70	24	38
Et	5	DMF	65—70	1	92

a) KSCN, 40 mmol. b) Isolated yield. Each product contained 0.6–0.8% of RO(CH₂)_{*m*}NCS (by glc).

reaction of alkoxyalkyl bromide with KSCN is S_N2 type in either solvent, as expected.¹⁾

In a previous paper¹⁾ we reported that the N/S ratios of the products in the reaction of alkyl halides with Hg(SCN)₂ are 21/79–34/66 for primary alkyl halides (S_N2 type) and 85/15–99/1 for secondary and tertiary ones (S_N1 type). A high selectivity for N attack was ascribed to the structure of Hg(SCN)₂, where Hg is S-bonded. As described above, the N/S ratio in **1** plus **2** was nearly 50/50 (more precisely 47/53–53/47) regardless of the structure of alkyl halides used; this ratio was thought to be determined by the step of the attack on the intermediate oxonium ion. In order to confirm this point we prepared Et₃O⁺BF₄[–] separately and carried out the reaction of this oxonium ion with a mixture of KBr and Hg(SCN)₂ in 1,2-dichloroethane. As a result, although the yield was low, a mixture of EtNCS and EtSCN was obtained, with a N/S ratio of 66/34 (see Experimental). Here, neither THF nor *n*-Bu₂O could be used as a solvent because of the polymerization of the solvent or an alkyl exchange reaction. For comparison, when the reaction of EtO(CH₂)₅Br with Hg(SCN)₂ was carried out in 1,2-dichloroethane at 65–70 °C for 4 hr, a mixture of EtNCS and EtSCN was obtained in 38% yield, with a N/S ratio of 61/39, together with **5** and **6** (*m*=5)

TABLE 4. BOILING POINTS AND ANALYTICAL DATA OF NEW COMPOUNDS

Compounds ^{a)}	Bp(°C/mmHg)	Found (Calcd)		
		C (%)	H (%)	N (%)
1 + 2 (R=Me, <i>n</i> =1)	70–75 /5	49.19 (49.63)	8.07 (7.64)	9.34 (9.65)
1 + 2 (R=Et, <i>n</i> =1)	77–85 /5	52.44 (52.80)	8.64 (8.23)	8.55 (8.80)
1 + 2 (R= <i>n</i> -Pr, <i>n</i> =1)	81–88 /2	54.88 (55.45)	8.98 (8.73)	7.89 (8.08)
1 + 2 (R= <i>i</i> -Pr, <i>n</i> =1)	91–102/6	55.16 (55.45)	9.05 (8.73)	7.96 (8.08)
1 + 2 (R= <i>n</i> -Bu, <i>n</i> =1)	93–104/3	57.68 (57.71)	9.38 (9.15)	7.58 (7.48)
1 + 2 (R=Me, <i>n</i> =2)	119–126/2	55.53 (55.27)	9.32 (8.81)	6.29 (6.45)
1 + 2 (R=Et, <i>n</i> =2)	145–157/4	56.70 (57.11)	9.51 (9.15)	5.78 (6.05)
1 + 2 (R= <i>n</i> -Pr, <i>n</i> =2)	131–137/2	58.22 (58.74)	9.72 (9.45)	5.68 (5.71)
1 + 2 (R= <i>i</i> -Pr, <i>n</i> =2)	127–132/2	58.44 (58.74)	9.97 (9.45)	5.66 (5.71)
EtO(CH ₂) ₂ SCN	99–101/22	45.27 (45.78)	7.12 (6.92)	10.56 (10.68)
EtO(CH ₂) ₃ SCN	75–76 /6.5	49.01 (49.63)	7.95 (7.64)	9.47 (9.65)
EtO(CH ₂) ₄ SCN ^{b)}	95–96 /6			
EtO(CH ₂) ₅ SCN	109–111/5.5	55.22 (55.45)	9.01 (8.73)	8.04 (8.08)
<i>n</i> -BuO(CH ₂) ₄ SCN ^{c)}	120–121/6.5			

a) The N/S ratios in **1** plus **2** are shown in Table 1. RO(CH₂)_{*m*}SCN contains 0.6–0.8% of RO(CH₂)_{*m*}NCS. b) Corresponds to **2** (R=Et, *n*=1). c) Corresponds to **2** (R=*n*-Bu, *n*=1).

(16% yield, N/S=55/45). The fact that the N/S ratios of the products, EtNCS and EtSCN, are nearly the same in both reactions shows that the latter reaction proceeds through an ethyloxonium ion, and also supports the reaction mechanism shown in schemes 2 and 4. The reason why the attack by N is more preferred in the reaction with the oxonium ion (N/S=47/53—53/47) than in that with primary halides (N/S=21/79—34/66) seems to be explained by the symbiotic effect in the HSAB principle proposed by Pearson,⁶⁾ since both reactions are supposed to be of the S_N2 type. This effect states that in an S_N2 reaction a grouping of either several hard ligands or several soft ligands on the central carbon atom should stabilize the transition state and cause an increased rate of reaction. Namely, the carbon bearing a harder ligand as the leaving group is apt to be attacked more preferably by a harder atom in an ambident ion. In our case, R_2O in R_3O^+ is harder than X^- in RX as the leaving group, and the N atom in the attacking species, $XHg-(SCN)_2^-$, is harder than the S atom.⁷⁾

Experimental

The N/S ratios in mixtures of alkyl thiocyanates and isothiocyanates were determined by gas chromatography (glc). Glc analyses were carried out on a Shimadzu 5APTF apparatus using EGSS-X (1 m), Apz-L (1 m), and PEG-6000 (3 m) columns (carrier gas, N_2). The retention time of RSCN was longer than that of RNCS in EGSS-X and PEG-6000 columns, while the reverse was observed by using Apz-L column. The NMR spectra were recorded with a Varian A-60 spectrometer in CCl_4 , using TMS as an internal standard. The IR spectra were taken with a Hitachi EPI-S2 spectrometer.

Materials. All the organic substances, including the solvents, were used after distillation, while commercial inorganic salts were used without further purification. $Cu(NCS)_2$ was prepared from $CuSO_4 \cdot 5H_2O$ and KSCN by the reported method.⁸⁾ Alkoxyalkyl bromides, $RO(CH_2)_mBr$, were prepared by PBr_3 bromination of the corresponding alcohols which were synthesized from RBr and $NaO(CH_2)_mOH$:⁹⁾ R=Et and $m=2$, bp 126—127 °C (lit.¹⁰⁾ bp 126—127 °C); R=Et and $m=3$, bp 147—148 °C (lit.⁹⁾ bp 147—150 °C); R=Et and $m=4$, bp 78—80 °C/30 mmHg (lit.¹¹⁾ bp 69 °C/15 mmHg); R=Et and $m=5$, bp 91—92 °C/20 mmHg (lit.¹¹⁾ bp 185—192 °C/741 mmHg); R=*n*-Bu and $m=4$, bp 105—108 °C/25 mmHg (lit.¹²⁾ bp 57 °C/1.5 mmHg).

Reaction of Alkyl Halides with Mercuric Thiocyanate in THF.

The following example shows a typical procedure. To a suspension of $Hg(SCN)_2$ (12.7 g, 40 mmol) in THF (30 ml) was added *i*-PrI (6.8 g, 40 mmol) drop by drop at 65—70 °C; the resulting yellowish-green homogeneous solution was kept for 2 hr under stirring while orange precipitates gradually came out. After being cooled down to room temperature, Et_2O (200 ml) was added and the precipitated inorganic salt was filtered off. The filtrate was washed several times with aqueous KI in order to remove a small amount of dissolved mercuric salt and then dried over $MgSO_4$. Distillation afforded the following products: **3+4** (R=*i*-Pr), bp 45—50 °C/40 mmHg, 0.2 g (5% yield); **1+2** ($n=1$, R=*i*-Pr), bp 91—102 °C/6 mmHg, 2.1 g (30% yield); **1+2** ($n=2$, R=*i*-Pr), bp 127—132 °C/2 mmHg, 1.7 g (17% yield).

Reaction of $RO(CH_2)_mBr$ with KSCN in DMF. The following example shows a typical procedure. To a homogeneous solution of KSCN (7.8 g, 80 mmol) in DMF (30 ml) was added $EtO(CH_2)_3Br$ (6.1 g, 40 mmol) at 65—70 °C. After being

kept for 1 hr under stirring, the mixture was cooled down to room temperature, poured into water, and then extracted with Et_2O (200 ml). Distillation of the ether extract gave 4.1 g (78% yield) of $EtO(CH_2)_3SCN$, which contains a small amount of isothiocyanate (N/S=0.7/99.3); bp 99—101 °C/22 mmHg. IR 2150 (ν_{SCN}), 1120 (ν_{C-O}) cm^{-1} . NMR δ 1.21 (t. 3H, $J=7$ Hz, methyl), 3.1 (t. 2H, $J=5.5$ Hz, $-OCH_2-CH_2S-$), 3.53 (q. 2H, $J=7$ Hz, CH_3CH_2O-), 3.7 (t. 2H, $J=5.5$ Hz, $-OCH_2CH_2S-$).

The boiling points and analytical data of all new compounds in Tables 1—3 are summarized in Table 4. All IR and NMR spectra were reasonably explained.

Reaction of Isopropyl Iodide with $Cu(NCS)_2$ or $AgSCN$ in THF. When the heterogeneous mixture of $Cu(NCS)_2$ (7.2 g, 40 mmol) and *i*-PrI (6.8 g, 40 mmol) in THF (30 ml) was heated at 65—70 °C for 10 hr, the following compounds were obtained: *i*-PrNCS($-SCN$) 0.24 g (6% yield, N/S=6/94), **1+2** (R=*i*-Pr, $n=1$) 0.52 g (7.5% yield, N/S=11/89), *i*-PrO(CH_2)₄I 1.65 g (17% yield), a small amount of unidentified product, and a residue (1.1 g). *i*-PrO(CH_2)₄I: bp 96—97 °C/20 mmHg, IR 1130 (ν_{C-O}) cm^{-1} . NMR δ 1.08 (d. 6H), 1.4—2.2 (m. 4H), 3.0—3.7 (m. 5H). Found: C, 34.93; H, 6.57%. Calcd for $C_7H_{15}OI$: C, 34.73; H, 6.25%.

A similar reaction using $AgSCN$ at 65—70 °C for 24 hr afforded 0.6 g (14% yield) of *i*-PrNCS($-SCN$) (N/S=24/76) and 0.35 g (5% yield) of **1+2** (N/S=14/86). Almost no reaction occurred at 65—70 °C for 1 hr in either case.

Reaction of Ethyl Iodide with $Hg(CN)_2$ in THF. A homogeneous solution of EtI (6.3 g, 40 mmol) and $Hg(CN)_2$ (10 g, 40 mmol) in THF (20 ml) was heated at 70 °C for 24 hr. The products were 4-ethoxybutyl iodide (1.1 g, 12% yield) and 0.86 g of an unidentified compound, probably $EtO(CH_2)_4O(CH_2)_4I$. Almost no reaction occurred by heating for 1.5 hr. 4-Ethoxybutyl iodide: bp 87—89 °C/23 mmHg, IR 1130 (ν_{C-O}) cm^{-1} . NMR δ 1.15 (t. 3H), 1.4—2.25 (m. 4H), 3.1—3.6 (m. 6H).

Reaction of $Et_3O^+BF_4^-$ with $Hg(SCN)_2$ and KBr in 1,2-Dichloroethane.

To 1,2-dichloroethane (5 ml) solution of $AgBF_4$ (1.0 g, 5 mmol) was added Et_2O (1 ml) and then EtBr (1 ml) at 15—20 °C under N_2 atmosphere.¹³⁾ After stirring for 1 hr the resulting $AgBr$ was filtered off and washed with 1,2-dichloroethane (5 ml). A solid mixture of KBr (1.1 g, 5 mmol) and $Hg(SCN)_2$ (1.6 g, 5 mmol) was added to the combined 1,2-dichloroethane solution and the resulted heterogeneous mixture was stirred at 40 °C for 4 hr under N_2 . Glc analysis of the mixture using *n*-BuNCS as an internal standard showed the presence of 5 mg (0.06 mmol, 1.2% yield based on $AgBF_4$) of a mixture of EtNCS and EtSCN (N/S=66/34). The reaction with KSCN was similarly carried out to give 11.6% yield of a mixture of EtNCS and EtSCN (N/S=2/98). Although it was conceivable that excess EtBr instead of $Et_3O^+BF_4^-$ reacted to give the product, we confirmed that EtBr did not react at all with $Hg(SCN)_2$ or KSCN under similar conditions.

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