The Reaction of Alkyl Halides with Mercury(II) and Potassium Thioacetates and Selenocyanates

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The reactions of alkyl halides with mercury(II) and potassium thioacetates afford alkyl thioacetates (RSCOMe), $S_{\rm N}1$ and $S_{\rm N}2$ type reactions taking place. In neither case is ROCSMe formed. Reactions with mercury(II) selenocyanate usually give only small amounts of alkyl selenocyanates and/or isoselenocyanates as isolated products except the case of benzyl bromide from which benzyl selenocyanate was obtained almost quantitatively. The ambident reactivity of this salt was revealed to be not so strong as that of mercury(II) thiocyanate. The reaction with potassium selenocyanate is also reported for comparison.

Mercury(II) thiocyanate reacts with alkyl halides in less-polar solvents to afford both alkyl isothiocyanates and thiocyanates, the former being predominant, in contrast to the reaction with the corresponding potassium salt in *N,N*-dimethylformamide (DMF), where alkyl thiocyanates are the main products.1) We have carried out a similar reaction using mercury(II) thioacetate and selenocyanate to confirm the ambident reactivity of mercury(II) salt. The results are given herewith. For the sake of comparison reactions with the corresponding potassium salts were also carried out. It should be noted that the ambident character of potassium selenocyanate in the reaction with alkyl halide is known to some extent.2)

Results and Discussion

Reaction with Mercury(II) or Potassium Thioacetate. The reaction was carried out by stirring equimolar amounts of alkyl halide and mercury(II) thioacetate in hexane at room or refluxing temperature as in the case of the reaction with mercury(II) thiocyanate.1) It was found to be heterogeneous. The products were only alkyl thioacetates (**1**)3) (Scheme 1), their formation being restricted to the cases of *t*-butyl and arylalkyl halides which can form the stable carbonium ions, all the starting alkyl halides being recovered unreacted in the other cases.

$$\mathrm{RX} + \mathrm{Hg(SCOMe)_2} \xrightarrow{\text{hexane}} \underset{(\mathbf{1})}{\mathrm{RSCOMe}} + \mathrm{Hg(X)SCOMe} \qquad (1)$$

The results show that the $S_{\rm N}1$ type reaction might be involved, but when the homogeneous reactions of alkyl halides with potassium thioacetate were carried out in DMF, **1** was obtained in almost all cases except *t*-butyl halide (Scheme 2), suggesting the occurrence of $S_{\rm N}2$ type reaction. In all cases no ROCSMe were obtained. This indicates that mercury(II) thioacetate shows no ambident character, reflecting the significant difference in nucleophilic reactivity toward carbocation between sulfur and oxygen.4) The attack by only S-site in the case of potassium thiocarboxylate is known in several cases such as the reaction of potassium thioacetate with alkyl tosylate5) and that of potassium thiobenzoate with butyl halides.6) Typical results are given in Table 1. An appreciable amount of thioacetic anhydride was also formed in the reaction of *t*-butyl bromide with the mercury(II) salts. Although the exact pathway for this anhydride is still ambiguous, it could not be formed by stirring mercury(II) thioacetate in hexane at room temperature for 24 h in the presence or absence of **1** (R=*t*-Bu).

$$\mathrm{RX} + \mathrm{KSCOMe} \xrightarrow{\text{DMF}} (\mathbf{1}) + \mathrm{KX} \qquad (2)$$

Table 1. Reaction of alkyl halides with $\mathrm{Hg(SCOMe)_2}$ or KSCOMea)

Alkyl Halide (RX)	Yield of **1**b) From Hg salt (%)	(°C, h)	From K salt (%)	(°C, h)
n-BuBr	0	(65, 10)c,d)	80	(25, 2)
i-PrBr	0	(65, 10)c,d)	72	(25, 6)
t-BuBr	45	(25, 4)e)	0	(75, 3)d)
$\mathrm{PhCH_2Br}$	53	(70, 8)	81	(75, 1)
PhCH(Me)Br	91	(25, 3)f)	78	(75, 1)
$\mathrm{Ph_2CHCl}$	99	(60, 1)	95	(70, 1)
c-$\mathrm{C_6H_{11}Br}$	0	(68, 20)d)	40	(75, 5)g)

a) RX and metal thioacetate, each of 15 mmol. Solvent 20 ml; hexane in the case of Hg salt and DMF in the case of K salt. b) Isolated yield. c) Corresponding alkyl iodide was used. d) All alkyl halide was recovered unreacted. e) Other product; $\mathrm{(MeCO)_2S}$ 42%. f) Other product; $\mathrm{(MeCO)_2S}$ 7%. g) Other product; cyclohexane 28% (by GLC).

Reaction with Mercury(II) or Potassium Selenocyanate. When benzyl bromide was reacted with equimolar amount of mercury(II) selenocyanate in hexane or dibutyl ether at refluxing temperature for 0.5—1 h, benzyl selenocyanate [**2**($\mathrm{R{=}PhCH_2}$)] was obtained almost quantitatively. In the cases of almost all other alkyl or arylalkyl halides, however, the yields of the products, the corresponding selenocyanate (**2**) and isoselenocyanate (**3**) (Scheme 3), were quite low because of the rapid formation of lots of sticky solids containing mercury(II) salt, about 60—80% of the starting alkyl or arylalkyl halides being recovered unreacted. The situation was not improved by changing the

$$\mathrm{RX} + \mathrm{Hg(SeCN)_2} \xrightarrow{\text{hexane}} \underset{(\mathbf{2})}{\mathrm{RSeCN}} + \underset{(\mathbf{3})}{\mathrm{RNCSe}} + \mathrm{Hg(X)SeCN} \qquad (3)$$

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TABLE 2. REACTION OF ALKYL HALIDES WITH $Hg(SeCN)_2$ OR KSeCN

Alkyl halide (10 mmol)	Metal salt[a] (10 mmol)	Solvent (20 ml)	Temp (°C)	Time (h)	Products and yields (%)[b]	
					2	**3**
n-BuI	Hg	hexane	68	20	3[c]	0
n-BuBr	K	acetone	58	4	67	0
i-PrI	Hg	hexane	68	1	10[c]	8[c]
i-PrI	Hg	acetone	58	0.5	0	11[c]
i-PrI	K	acetone	58	4	74	0
t-BuBr	Hg	hexane	68	1	0	4[c]
t-BuBr	Hg	acetone	58	0.25	0	8[c]
t-BuBr	K	acetone	58	4	4[c]	7[c]
t-BuBr	K	EtOH	78	6	8[c]	11[c]
$PhCH_2Br$	Hg	$(n\text{-}Bu)_2O$	70	0.5	99	0
$PhCH_2Br$	Hg	hexane	68	1	99	0
$PhCH_2Br$	K	acetone	58	3	97	0
PhCH(Me)Br	K	acetone	58	4	86	0
PhCH(Me)Br	K	DMF	80	1	64	0
Ph_2CHBr	K	acetone	58	4	80	0
Ph_3CCl	K	acetone	58	4	0	66

a) Hg and K designate $Hg(SeCN)_2$ and KSeCN, respectively. b) Isolated yield. c) By GLC. About 60—80% of alkyl halide was recovered unreacted.

solvent, reaction temperature, and molar ratio of the reactants. Although these solids were found to contain C and N, attempts to identify them were unsuccessful. The reason for the phenomena is not clear, but instability of the products, especially **3**, may be one cause.[7] In fact, when **3** (R=*t*-Bu), prepared separately,[7b] was heated in hexane for 1 h in the presence of an equimolar amount of mercury(II) selenocyanate and/or bromide, only half the amount of the starting material **3** was recovered. In the case of **2** (R=*i*-Pr), 75% of **2** was recovered by a similar treatment.

Formation of **3** from secondary and tertiary alkyl halides, although in low yield, suggests the ambident nature of mercury(II) selenocyanate. However, when the isomer ratio of **3**/**2** obtained from benzyl bromide[0 in hexane and $(n\text{-}Bu)_2O$] is compared with that of $PhCH_2NCS/PhCH_2SCN$[0.56 in $(n\text{-}Bu)_2O$][1] obtained in the reactions with mercury(II) thiocyanate, the ambident nature is clearly not so strong as in the case of mercury(II) thiocyanate. The exclusive formation of **2** ($R=PhCH_2$) indicates the predominant attack of the Se-site despite the fact that mercury is bonded with Se and not with N in mercury(II) selenocyanate.[8] This is probably due to the difference in nucleophilicity of Se and S. In this connection, the former is known to be a much stronger nucleophile than the latter in aliphatic nucleophilic substitution (S_N2).[9] Diphenylmethyl bromide reacts with potassium selenocyanate to give diphenylmethyl selenocyanate, while triphenylmethyl chloride gives only triphenylmethyl isoselenocyanate by a similar treatment.[2] In order to obtain authentic samples for alkyl selenocyanate and clarify the isomer distribution in the products, reactions with potassium selenocyanate were also carried out in acetone or DMF as solvent.[10] All alkyl halides except tertiary ones were found to give only the corresponding **2**, triphenylmethyl chloride affording only **3** and *t*-butyl bromide a small amount of a mixture of **2** and **3**.

Experimental

All the organic substrates except the solvents were used without further purification. Mercury(II) thioacetate[11] was prepared as follows. Thioacetic acid (10 g, 130 mmol) was slowly added to a chloroform (40 ml) suspension of mercury(II) oxide (yellow, 13 g, 6 mmol) at 5—10 °C with stirring for 1 h. The precipitated yellowish gray solid was collected and recrystallized from chloroform to give white leaflets; yield, 13.7 g (65%). Potassium thioacetate was prepared from thioacetic acid and $KHCO_3$.[12] Mercury(II) selenocyanate was prepared from mercury(II) nitrate and commercial potassium selenocyanate in water.[8] A sharp absorption at 2150 cm^{-1} ($\nu_{C\equiv N}$) in the IR spectrum (KBr disc) suggests the coordination of mercury with selenium.[8]

Gas chromatography (GLC) was used for detection of the isomer and determination of the isomer ratios, NMR analysis also being used in some cases. GLC analyses were carried out with a Shimadzu 5APTF apparatus using DEGS (1 m), Apiezon-L (1 m), and PEG-6000 (3 m) columns (carrier gas, N_2). The NMR and IR spectra were recorded on Varian EM-360 ($CDCl_3$, TMS, internal lock) and Hitachi EPI-S2 spectrometers, respectively.

All the products except **1** ($R=Ph_2CH$) and **2** (R=PhCHMe) are known compounds and were identified by NMR spectra and by comparison of their bp and mp with those in literature. The authentic samples of thioacetic anhydride,[13] **3** (R=*i*-Pr),[7a] and **3** (R=*t*-Bu)[7b] were prepared according to reported methods for identification of the products on GLC. **1** ($R=Ph_2CH$); bp 120—140 °C/5 mmHg, mp 39—40 °C (from EtOH); NMR δ 2.30 (s, 3H), 5.95 (s, 1H), 7.30 (s, 10H). **2** (R=PhCHMe); bp 120—125 °C/10 mmHg, NMR δ 2.30 (d, 3H), 4.90 (q, 1H), 7.39 (s, 5H).

Reaction of Benzyl Bromide with Mercury(II) Thioacetate in Hexane. Benzyl bromide (2.57 g, 15 mmol) was added to a stirred suspension of $Hg(SCOMe)_2$ (5.25 g, 15 mmol) in hexane (20 ml) at 30 °C, and the mixture was heated to 70 °C and kept for 8 h with stirring. The resulting red-brown suspension was cooled and filtered to remove the red-brown precipitates which were found to contain C, H, and Br by analyses. The pale orange filtrate was washed with water and dried over Na_2SO_4. The GLC analysis of this filtrate showed the presence of one product and the absence of the starting benzyl bromide. Distillation afforded benzyl thioacetate [**1**($R=PhCH_2$), 1.33 g, 53.4% yield, bp 100—102 °C/7 mmHg (lit,[5] bp 54 °C/0.05 mmHg)], leaving 0.14 g of residue. NMR δ 2.32 (s, 3H), 4.12 (s, 2H), 7.28 (s, 5H).

Formation of Bis(diphenylmethyl) Sulfide (4). Diphenylmethyl chloride (2.03 g, 10 mmol) was added to a stirred suspension of $Hg(SCOMe)_2$ (1.75 g, 5 mmol) in hexane (20 ml) at 40 °C and the resulting heterogeneous mixture was heated to 70 °C and kept for 2 h with stirring. After being cooled, the yellow orange precipitates were filtered and the filtrate was treated as above. GLC analysis of the filtrate showed the absence of diphenylmethyl chloride and the presence of **1** ($R=Ph_2CH$). Evaporation of the solvent left 2.10 g of an oil shown by NMR to consist of 1.20 g (5 mmol) of **1** ($R=Ph_2CH$) and 0.90 g (2.5 mmol) of **4**. The residue after distilling **1** ($R=Ph_2CH$) off was solidified and recrystallized from petroleum ether to afford 0.83 g of pure **4**; mp 63—65 °C (lit,[3] mp 66.5 °C), NMR δ 4.72 (s, 2H), 6.85—7.5 (m, 20H).

*Reaction of Benzyl Bromide with Mercury(II) Selenocyanate in (*n*-Bu)$_2$O.* Benzyl bromide (1.11 g, 6.5 mmol) was added to a stirred suspension of $Hg(SeCN)_2$ (2.68 g, 6.5 mmol) in (n-Bu)$_2$O (20 ml) at 85 °C, and the mixture was kept for 0.5 h with stirring. The reaction mixture was cooled and filtered in order to remove the orange sticky precipitates. Removal of (n-Bu)$_2$O from the filtrate gave white solids of crude benzyl selenocyanate [**2** ($R=PhCH_2$), 1.12 g, 94% yield] which were recrystallized from aqueous ethanol; mp 69—70 °C (lit,[10] mp 71.5 °C, 72 °C), NMR δ 4.25 (s, 2H), 7.33 (s, 5H).

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