Alkoxythiocyanation and Alkoxyiodination of Olefins with Copper(II) Salts

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A simple and convenient method for the preparation of vicinal alkoxythiocyano- and alkoxyiodoalkanes is described. The reaction of olefins with copper(II) salts, such as chloride, bromide and sulfate, and potassium thiocyanate or iodide in alcohols readily affords the compounds in good yields. From vinyl acetates, alkyl vinyl ethers and α,β-unsaturated aldehydes, the products are obtained in the form of dialkyl acetals. The reaction mechanism is discussed.

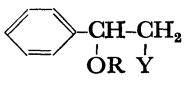
Baird *et al.*[1] reported the preparation of chloroiodoalkanes with the use of copper(II) chloride, metal iodide and olefins in acetonitrile. We found that when the reaction was carried out in alcohol, the main products were alkoxyiodoalkanes instead of chloroiodoalkanes, and that when KSCN was used, alkoxythiocyanoalkanes were obtained. Since the preparation of alkoxyiodo- and alkoxythiocyanoalkanes has so far been restricted to the reaction of olefin with iodine in alcohol in the presence of catalysts such as HgO[2] and $AgClO_4$[3] for the former, and to that with $Tl(OAc)_3$ and KSCN in alcohol for the latter,[4] we wish to report a simple and efficient synthetic method for these compounds using copper(II) salts.

Results and Discussion

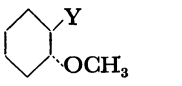
The reaction was carried out by adding olefinic hydrocarbons to a homogeneous alcoholic solution of copper(II) chloride and KSCN or KI at an appropriate temperature, the mixture being kept for 0.3—5 hr. Styrene, cyclohexene, vinyl esters, vinyl ethers and α,β-unsaturated aldehydes were chosen as the olefinic substrates. The products were vicinal alkoxythiocyano- (**1a**—**5a**) or alkoxyiodoalkanes (**1b**—**5b**). The general reaction is illustrated by the following scheme.

$$\text{C=C} + 2CuCl_2 + KY + ROH \longrightarrow \text{C(OR)—C(Y)} + 2CuCl + KCl + HCl \quad (1)$$

(Y=SCN, I)



1 (**a**, Y=SCN; **b**, Y=I)



2 (**a**, Y=SCN; **b**, Y=I)

Some typical results with the former two and last three olefins are summarized in Tables 1 and 2, respectively. Copper(II) bromide, sulfate, nitrate and iron(III) chloride could also be used in the reaction, although these salts were less effective than copper(II) chloride. All the products obtained from the reaction of cyclohexene were found to be *trans*.

In the reactions of vinyl and isopropenyl acetates, the products (**3a** and **3b**) were isolated in the form of dialkyl acetals, no compounds containing acetoxy group being obtained.

$$CH_2=C(R)(OAc) \xrightarrow[R'OH]{CuCl_2,\ KY} YCH_2C(OR')_2-R \quad (2)$$

3 (**a**, Y=SCN; **b**, Y=I)

The products of the reaction of alkyl vinyl ethers were

Table 1. Alkoxythiocyanation and alkoxyiodination of styrene and cyclohexene

Olefin (100 mmol)	Cu(II) salt (100 mmol)	K salt (100 mmol)	Solvent (100 ml)	Temp. (°C)	Time (hr)	Products and Yield (%)[a]	
Styrene	$CuCl_2$	KSCN	CH_3OH	65	5	**1a**(R=CH_3)	31
Styrene	$CuSO_4\cdot5H_2O$	KSCN	CH_3OH	65	2	**1a**(R=CH_3)	12
Styrene	$CuCl_2$	KI[b]	CH_3OH	65	2	**1b**(R=CH_3)	91
Styrene	$CuBr_2$	KI	CH_3OH	65	2	**1b**(R=CH_3)	94
Styrene	$CuSO_4\cdot5H_2O$	KI	CH_3OH	65	2	**1b**(R=CH_3)	61
Styrene	$CuCl_2$	KI	C_2H_5OH	78	2	**1b**(R=C_2H_5)	81
Styrene	$CuCl_2$	KI	*n*-C_3H_7OH	97	3	**1b**(R=*n*-C_3H_7)	90
Styrene	$CuCl_2$	KI	*n*-C_4H_9OH	118	3	**1b**(R=*n*-C_4H_9)	91
Styrene	CuCl[c]	I_2[d]	CH_3OH	65	2	**1b**(R=CH_3)	86[e]
Cyclohexene	$CuCl_2$	KSCN	CH_3OH	65	2	**2a**	30[f]
Cyclohexene	$CuSO_4\cdot5H_2O$	KSCN	CH_3OH	65	2	**2a**	10
Cyclohexene	$CuCl_2$	KI	CH_3OH	65	2	**2b**	13[g]
Cyclohexene	$CuSO_4\cdot5H_2O$	KI	CH_3OH	65	2	**2b**	53
Cyclohexene	CuCl[c]	I_2[d]	CH_3OH	65	2	**2b**	64[e]

a) Based on Cu(II) salt charged and scheme 1. b) KI, 50 mmol. When 100 mmol of KI was used, **1b** (R=CH_3) was obtained in 97% yield. c) 10 mmol. d) 50 mmol. e) Based on I_2 charged. f) By-product: *trans*-1-chloro-2-thiocyanocyclohexane, 12%. g) By-product: *trans*-1-chloro-2-iodocyclohexane, 29%.

Table 2. Alkoxythiocyanation and alkoxyiodination of vinyl ester, alkyl vinyl ether, and α,β-unsaturated aldehyde[a)]

Olefin (100 mmol)	K salt (100 mmol)	Solvent (100 ml)	Temp. (°C)	Time (hr)	Products and Yield[b)] (%)	
CH_2=CHOAc	KSCN	CH_3OH	62	3	**3a**(R=H, R′=CH_3)	86
CH_2=CHOAc	KSCN	C_2H_5OH	60	1	**3a**(R=H, R′=C_2H_5)	63
CH_2=CHOAc	KSCN	$HOCH_2CH_2OH$	70	3	**3a**[R=H, (OR′)$_2$=O(CH_2)$_2$O]	77
CH_2=CHOAc	KI	CH_3OH	62	1	**3b**(R=H, R′=CH_3)	86
CH_2=C(CH_3)OAc	KSCN	$HOCH_2CH_2OH$	65	3	**3a**[R=CH_3, (OR′)$_2$=O(CH_2)$_2$O]	93
CH_2=CHOC_2H_5[c)]	KSCN	CH_3OH	30	0.25	**4a**(R=C_2H_5, R′=CH_3)	59
CH_2=CHOC_2H_5[c)]	KSCN	CH_3OH	50	3	**4a**(R=C_2H_5, R′=CH_3) **3a**(R=H, R′=CH_3)	18 47
CH_2=CHOC_2H_5[c)]	KSCN	t-C_4H_9OH	55	3	**4a**(R=C_2H_5, R′=t-C_4H_9)	52
CH_2=CHOC_2H_5[c)]	KSCN	$HOCH_2CH_2OH$	35	1	**4a**(R=C_2H_5, R′=CH_2CH_2OH) **3a**[R=H, (OR′)$_2$=O(CH_2)$_2$O]	54 2
CH_2=CHOC_2H_5[c)]	KSCN	$HOCH_2CH_2OH$	60	5	**3a**[R=H, (OR′)$_2$=O(CH_2)$_2$O]	77
CH_2=CHOC_2H_5[c)]	KI	CH_3OH	35	0.25	**4b**(R=C_2H_5, R′=CH_3) **3b**(R=H, R′=CH_3)	58 19
CH_2=CHO-n-C_4H_9	KSCN	t-C_4H_9OH	70	3	**4a**(R=n-C_4H_9, R′=t-C_4H_9)	69
CH_2=CHO-n-C_4H_9	KI	i-C_3H_7OH	62	3	**3b**(R=H, R′=i-C_3H_7)	54
CH_2=CHCHO	KSCN	CH_3OH	63	1	**5a**(R=H, R′=CH_3)	72
CH_2=CHCHO	KI	CH_3OH	62	1	**5b**(R=H, R′=CH_3)	83
CH_3CH=CHCHO	KSCN	CH_3OH	35	1	**5a**(R=R′=CH_3)	89
CH_3CH=CHCHO	KI	CH_3OH	30	1	**5b**(R=R′=CH_3)	97

a) $CuCl_2$, 100 mmol. b) Based on $CuCl_2$ charged. c) 200 mmol.

4 and/or **3**, the amounts of both products depending on the reaction conditions. Higher temperature and longer time favored the exchange of alkoxy group, giving **3** as the main product.

$$CH_2{=}C(H)(OR) \xrightarrow[R'OH]{CuCl_2,\ KY} YCH_2C(OR')H \xrightarrow{R'OH} \textbf{3a or 3b}\ (R{=}H) \qquad (3)$$

4 (**a**, Y=SCN; **b**, Y=I)

Under the same or even more drastic conditions, the reaction of diethyl or di-*n*-butyl acetal of acetaldehyde with copper(II) chloride and KSCN or KI gave none or only trace amounts of **3** and/or **4**. The result excludes such reaction schemes as one in which alcohol adds to the double bond at first, followed by the attack of Y. The reaction of acrolein and crotonaldehyde under similar conditions gave the products also in the form of dialkyl acetal. According to Castro *et al.*[5)]

$$RCH{=}CHCHO \xrightarrow[R'OH]{CuCl_2,\ KY} RCH(OR')CH(Y)CH(OR')_2 \qquad (4)$$

5 (**a**, Y=SCN; **b**, Y=I)

the reaction of acrolein with copper(II) chloride or bromide in methanol gave **5** (R=H, R′=CH_3, Y=Cl, or Br) in 12—39% yield. They proposed that the reaction proceeds through the addition of methanol to acrolein affording β-methoxypropionaldehyde followed by the attack of chlorine or bromine of copper(II) salt on the α-position of the saturated aldehyde thus formed. In order to see whether the same reaction scheme is operative in our case, the reaction of butyraldehyde with copper(II) chloride was carried out in the presence of KSCN in refluxing methanol for 1 hr. The yield of 1,1-dimethoxy-2-thiocyanobutane,[6)] however, was quite low (19%) as compared with the 89% yield for **5** obtained from crotonaldehyde. This indicates that the reaction scheme proposed by Castro *et al.*[5)] is partly operative, but not important in our case. Thus the main route for the formation of **5** would be the attack of Y on double bond followed by addition of the alkoxy group.

The reaction scheme for the formation of **1**—**5** can be described as follows.

$$2CuX_2 + 2Y^- \longrightarrow 2CuX + Y_2 + 2X^- \qquad (5a)$$

$$CuX + Y_2 \rightleftharpoons [CuXY]^-Y^+ \qquad (5b)$$

$$\text{>C=C<} + [CuXY]^-Y^+ \longrightarrow \left[\text{>C(Y)}-\text{C<}\right]^+[CuXY]^- \xrightarrow{ROH} \text{>C(OR)}-\text{C(Y)<} \qquad (5c)$$

The first step is the oxidation of thiocyanate or iodide anion by copper(II) salt to form a molecular thiocyanogen or iodine (Scheme 5a, Y=SCN or I). These molecules are activated by complexation with copper(I) salt (Scheme 5b), the electrophilic attack to olefin being followed by addition of the alkoxy group (Scheme 5c). The fact that **1**—**5** are all Markownikov addition products and that the products obtained in the reaction of cyclohexene are *trans*, supports the reaction shceme. In connection with this, the following observations are worth noting. **1** (R=CH_3, Y=I) was obtained in a good yield by refluxing styrene and iodine in methanol in the presence of copper(I) chloride (Table 1). In the absence of copper(I) salt, however, the reaction did not give **1** under similar conditions. Similar phenomena were observed with cyclohexene as a substrate. The reaction of cyclohexene with a mixture of silver(I) thiocyanate and bromine in methanol, which has been known to evolve thiocyanogen,[7)] at 20 °C for 2 hr afforded 19% yield or a trace amount of *trans*-1-

methoxy-2-thiocyanocyclohexane, **2a**, in the presence or absence of copper(I) chloride, respectively.

Nuclear thiocyanation at a *para* position occurred with reactive aromatic compounds such as phenol or *N,N*-dimethylaniline by this reaction system. Thus, *p*-thiocyanophenol [mp 52 °C (recrystallized from H_2O), lit,[8] mp 52—53 °C] was obtained in 51% yield by refluxing phenol, copper(II) chloride and potassium thiocyanate in methanol for 2 hr.

Experimental

The NMR spectra were measured with a Varian A-60 spectrometer in $CDCl_3$, using TMS as an internal standard. The IR and mass spectra were measured with Hitachi EPI-S2 and JEOL JMS-01SG spectrometers, respectively. Glc analysis was carried out on Shimadzu 5APTF and 4BMPF apparatus, using PEG 6000(25%)-Chromosorb W(3 m) and Apiezon L(30%)-Celite(1 m) columns(carrier gas, N_2).

Materials. All the organic materials were distilled before use. Commercial anhydrous $CuCl_2$ and $CuBr_2$ and other inorganic salts were used without further purification.

Preparation of 3a(R=H, R'=CH$_3$) from Vinyl Acetate. The following is a typical experimental procedure for alkoxythiocyanation, alkoxyiodination being similarly carried out. Vinyl acetate(8.6 g, 0.1 mol) was added at 62 °C under stirring to a greenish-black homogeneous solution of anhydrous $CuCl_2$ (13.4 g, 0.1 mol) and KSCN(9.7 g, 0.1 mol) in methanol(100 ml). In 20 min the color of the reaction mixture turned to pale yellow and a large amount of white precipitate of CuCl was formed. After 3 hr, 400 ml of water was added and then CuCl(8.9 g, 0.09 mol) was filtered. The filtrate was extracted with diethyl ether and the extract was evaporated by a rotary evaporator to *ca.* 20 ml which contained 0.043mol (86% yield) of 1,1-dimethoxy-2-thiocyanoethane **3a**(R=H, R'=CH_3). Distillation gave 4.41 g (0.03 pure compound; bp 106—107 °C/19 mmHg. IR, 2160 (s) mol) of (ν_{SCN}), 1120 (s) (ν_{C-O}) and 1070 (s) (ν_{C-O}) cm^{-1}. NMR, δ 3.12 (d 2H, J=5 Hz), 3.42 (s. 6H), 4.60 (t 1H, J=5 Hz). Found: C, 40.40; H, 6.40; N, 9.47%. Calcd for $C_5H_9NO_2S$: C, 40.80; H, 6.16; N, 9.52%. 2,4-Dinitrophenylhydrazone (2,4-DNP) of **3a**, mp 173—175 °C(yellow crystals, from EtOH).

Identification of the Products. Data on alkoxythiocyanation and alkoxyiodination are given in Tables 1 and 2. **1a**-(R=CH_3), bp 129—130 °C/6 mmHg(lit,[9] 146—147 °C/9 mmHg). **1b**(R=CH_3), bp 94.5 °C/3 mmHg(lit,[2b] 107—108 °C/5 mmHg). **1b**(R=C_2H_5), bp 95.5—96 °C/3 mmHg(lit,[2b] 142—144 °C/14 mmHg). **1b**(R=*n*-C_3H_7), bp 102.5—103 °C/3 mmHg, Found: C, 45.60; H, 5.47%. Calcd for $C_{11}H_{15}IO$: C, 45.53; H, 5.21%. **1b**(R=*n*-C_4H_9), bp 105.5 °C/4 mmHg. Found: C, 47.80; H, 5.87%. Calcd for $C_{12}H_{17}IO$: C, 47.38; H, 5.64%.

2a, bp 108—109.5 °C/18 mmHg. NMR, δ 1.2—2.0(m. 6H), 2.9—3.2 (m. 2H, >CHSCN and >CHOCH$_3$), 3.40(s 3H, OCH$_3$). IR, 2150(s) (ν_{SCN}). **2b**(bp 99.5—101 °C/20 mmHg); identical in glc and NMR with the compounds prepared by the reported method using HgO (red)[2a] or $AgClO_4$[3] as a catalyst, and assigned to *trans*[10] (lit,[2a] bp 114 °C/49 mmHg). *trans*-1-Chloro-2-thiocyanocyclohexane; identical with the compound prepared by the method using $Pb(SCN)_2$ and Cl_2.[8] It was also prepared by the reaction of cyclohexene with $Pb(SCN)_2$ and $SbCl_5$; bp 110—112 °C/4 mmHg(lit,[8] bp 154—156 °C/21 mmHg). *trans*-1-Chloro-2-iodocyclohexane; identical with the compound prepared by the method[1a] from cyclohexene, $CuCl_2$ and I_2 in pentane, bp 66—66.5 °C/4 mmHg (lit,[1a] bp 37 °C/0.2 mmHg).

3a(R=H, R'=C_2H_5), bp 85 °C/5 mmHg. Found: C, 47.62; H, 7.71; N, 7.86%. Calcd for $C_7H_{13}NO_2S$: C, 47.97; H, 7.47; N, 7.99%. **3a**[R=H, (OR')$_2$=O(CH$_2$)$_2$O], bp 97.5—98 °C/5 mmHg, NMR, δ 3.20 (d 2H, J=3 Hz), 4.00 (m 4H), 5.22 (t 1H, J=3 Hz). Found: C, 48.25; H, 7.88; N, 7.66%. Calcd for $C_5H_7NO_2S$: C, 47.97; H, 7.48; N, 7.99%. **3a**[R=CH_3, (OR')$_2$=O(CH$_2$)$_2$O], bp 84 °C/3.5 mmHg. NMR(CCl_4), δ 1.45 (s 3H), 3.17 (s 2H), 4.02 (s 4H). **3b** (R=H, R'=CH_3), bp 37 °C/5 mmHg. Found: C, 22.20; H, 4.37%. Calcd for $C_4H_9IO_2$: C, 22.23; H, 4.20%. 2,4-DNP, mp 145—148 °C (yellow crystals, from EtOH). **3b** (R=H, R'=*i*-C_3H_7), bp 55.5 °C/3 mmHg. Found: C, 35.65; H, 6.63%. Calcd for $C_8H_{17}IO_2$: C, 35.30; H, 6.30%.

4a (R=C_2H_5, R'=CH_3), bp 85 °C/5 mmHg. Found: C, 44.46; H, 7.32; N, 8.64%. Calcd for $C_6H_{11}NO_2S$: C, 44.70; H, 6.88; N, 8.69%. **4a** (R=C_2H_5, R'=*t*-C_4H_9), bp 97.5—98 °C/6 mmHg. Found: C, 52.60; H, 8.80; N, 7.08%. Calcd for $C_9H_{17}NO_2S$: C, 53.17; H, 8.43; N, 6.89%. **4a** (R=C_2H_5, R'=CH_2CH_2OH), bp 135—136 °C/8 mmHg. Found: C, 44.35; H, 7.18; N, 7.25%. Calcd for $C_7H_{13}NO_3S$: C, 43.96; H, 6.85; N, 7.32%. **4a** (R=*n*-C_4H_9, R'=*t*-C_4H_9), bp 105.5—106 °C/4 mmHg. Found: C, 56.20; H, 9.24; N, 6.39%. Calcd for $C_{11}H_{21}NO_2S$: C, 57.10; H, 9.15; N, 6.05%. **4b** (R=C_2H_5, R'=CH_3), bp 38 °C/4 mmHg. Found: C, 26.56; H, 5.08%. Calcd for $C_5H_{11}IO_2$: C, 26.10; H, 4.82%.

5a (R=H, R'=CH_3), bp 98—99 °C/5 mmHg. Found: C, 43.43; H, 7.05; N, 7.08%. Calcd for $C_{17}H_{13}NO_3S$: C, 43.96; H, 6.86; N, 7.33%. **5a** (R=R'=CH_3), bp 91.5—93 °C/5 mmHg. Found: C, 46.55; H, 7.65; N, 6.80%. Calcd for $C_8H_{15}NO_3S$: C, 46.80, H, 7.37; N, 6.82%. **5b** (R=H, R'=CH_3), bp 80.5 °C/5 mmHg. Found: C, 27.87; H, 5.43%. Calcd for $C_6H_{13}IO_3$: C, 27.60; H, 5.40%. **5b** (R=R'=CH_3), bp 83.5—84 °C/5 mmHg. Found: C, 30.69; H, 5.76%. Calcd for $C_7H_{15}IO_3$: C, 30.67; H, 5.51%.

Reaction Conditions, Yields and Identification of Products Other than Those Shown in Tables 1 and 2. From styrene: 82 °C, 3 hr, **1b** (R=*i*-C_3H_7) 35%, bp 95.5—96 °C/3 mmHg. Found: C, 46.20; H, 5.39%. Calcd for $C_{11}H_{15}IO$: C, 45.53; H, 5.21%. 82 °C, 2 hr, **1b** (R=*t*=C_4H_9) 32%, bp 100—101.5 °C/3 mmHg, NMR, δ 1.16 (s 9H), 3.24 (d 2H, J=6.5 Hz), 4.62 (t 1H, J=6.5 Hz), 7.27—7.36 (m 5H). From vinyl acetate: 60 °C, 5 hr, **3a** (R=H, R'=*n*-C_3H_7) 36%, bp 105—106.5 °C/5 mmHg. Found: C, 53.16; H, 9.15; N, 6.35%. Calcd for $C_9H_{17}NO_2S$: C, 53.17; H, 8.43; N, 6.89%. 60 °C, 5 hr, **3a** (R=H, R'=*n*-C_4H_9) 52%, bp 124.5—125 °C/5 mmHg. Found: C, 56.50; H, 9.72; N, 6.00%. Calcd for $C_{11}H_{21}NO_2S$: C, 57.10; H, 9.15; N, 6.06%. 60 °C, 1 hr, **3b** (R=H, R'=C_2H_5) 84%, bp 57.5—59 °C/5 mmHg (lit,[11] 100 °C/10 mmHg). 25 °C, 2 hr, **3b** (R=H, R'=*n*-C_3H_7) 39%, bp 74 °C/5 mmHg. Found: C, 34.93; H, 6.42%. Calcd for $C_8H_{17}IO_2$: C, 35.31; H, 6.30%. 60° C, 1 hr, **3b** (R=H, R'=*n*-C_4H_9) 37%, bp 103.5—104 °C/5 mmHg. Found: C, 39.78; H, 7.33%. Calcd for $C_{10}H_{21}IO_2$: C, 40.01; H, 7.05%. 25 °C, 1 hr, **3b** (R=H, R'=*i*-C_4H_9) 38%, bp 89—89.5 °C/5 mmHg. Found: C, 39.06; H, 7.35%. Calcd for $C_{10}H_{21}IO_2$: C, 40.01; H, 7.05%.

cis-*1-Methoxy-2-thiocyanocyclohexane.* **2b** (5.0 g, 20 mmol) was added at 110 °C to a stirred solution of KSCN (3.7 g, 40 mmol) in DMF (50 ml). After 12 hr water was added and extracted with diethyl ether. Distillation of the product gave 1.6 g of pure compound (9.4 mmol, 47% yield); bp 95—97 °C/5 mmHg. The retention time of the compound (t_R=7.7 min) was longer than that of **2a** (t_R=7.1 min) in the glc using Apiezon-L column (1 m) (column temp. 150 °C; N_2 100 ml/min). NMR, δ 1.4—2.1 (m 8H), 3.37 (s 3H, OCH$_3$), 3.4—3.8 (m 2H, >CHSCN and >CHOCH$_3$). IR

2150 (s) (ν_{SCN}). Mass spectrum (*m/e*) 171 (M^+). Attempts to prepare *cis*-1-chloro-2-thiocyanocyclohexane from the reaction of *trans*-1-chloro-2-iodocyclohexane with KSCN were unsuccessful.

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