The Reaction of Arylthallium(III) Compounds with Copper(II) and (I) Thiocyanates[1)]

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Arylthallium(III) acetate perchlorates reacted with copper(II) thiocyanate to afford aryl thiocyanates in various solvents. The Cu(I) salt was found to be less effective for the thiocyanation. The choice of solvent and the addition of potassium thiocyanate had a significant effect on the yield of aryl thiocyanates. The reaction with the mixture of copper(II) and potassium thiocyanates (1: 1) in dioxane showed the best result. Electron-releasing groups in the aromatic ring accelerated hydrodethallation, yielding aromatic hydrocarbons with a depression of the thiocyanate formation.

In previous papers we showed that the thallium in arylthallium(III) compounds can be replaced by the cyano group[2)] or halogen[3)] by a reaction with copper(II) and (I) cyanides or with halides respectively. As another example of such replacement reactions, we will describe here how arylthallium(III) acetate perchlorate monohydrates (**1**), $ArTl(OAc)ClO_4 \cdot H_2O$, react with $Cu(SCN)_2$ in the presence of KSCN, mainly in a dioxane solvent, to afford aryl thiocyanates, sometimes along with aromatic hydrocarbons. In this connection, Taylor and McKillop have recently reported that the thiocyanation of arylthallium(III) bis(trifluoroacetates) with KSCN proceeds under UV irradiation.[4)]

Results and Discussion

Phenylthallium(III) acetate perchlorate monohydrate (**1a**) and $Cu(SCN)_2$ were added to an appropriate solvent, such as water, alcohols, cyclic ethers, pyridine, or acetonitrile, and the stirred mixture was then heated under reflux to afford phenyl thiocyanate. Isomeric phenyl isothiocyanate could not be found in the products. The formation of $TlClO_4$ and a Cu (II) salt containing an acetoxy group, probably Cu(OAc)(SCN), was supposed on the basis of a study of the IR spectra. The reaction mixtures were generally heterogeneous, except in the cases of pyridine and acetonitrile solvents, because of the poor solubilities of $Cu(SCN)_2$ in water and the organic solvents used. Among the various solvents, dioxane was found to be the best solvent for preparing phenyl thiocyanate; with it the reaction proceeded even at 70 °C and was almost complete within 1 hr under reflux. However, most reactions including other solvents were carried out under reflux for 5 hr for convenience of comparison. Various results are shown in Table 1.

$$PhTl(OAc)ClO_4 \cdot H_2O + Cu(SCN)_2 \longrightarrow PhSCN + TlClO_4 + Cu(OAc)SCN + H_2O \quad (1)$$

In dioxane, the yield of phenyl thiocyanate was improved by the addition of KSCN; this addition probably caused an increased solubility of $Cu(SCN)_2$ in the solvent, even if to only a slight degree. When an equimolar mixture of $Cu(SCN)_2$ and KSCN was used in dioxane, the yield was more than 80%. A similar additive effect was observed in a homogeneous reaction using a pyridine or acetonitrile solvent, but unexpectedly, whether KSCN was present or absent, the yields of the thiocyanate were less than those in dioxane. On the contrary, when hydroxylic solvents (water, methanol, and ethanol) and tetrahydrofuran were used as solvents (in them KSCN is more soluble than in dioxane),[5)] the addition of KSCN resulted in the formation of diphenylthallium(III) thiocyanate (**2**) and a depression in the yield of phenyl thiocyanate. In addition, separate experiments showed that, in hydroxylic solvents, **1a** readily reacted with KSCN at room temperature to give phenylthallium(III) dithiocyanate (**3**), which was then slowly converted into **2** on heating, while in dioxane no **3** was isolated at room temperature and considerable amounts of **2** were obtained on heating. Such a difference may arise from both the poor solubility of KSCN in dioxane and the high-boiling nature of the solvent, the latter of which is favorable for the transformation of **3** into **2**. A similar disproportionation has already been reported for phenylthallium(III) chloride and cyanide.[6)] All the results are included in Table 1.

Here, let us consider the possibility of thiocyanate formation from **2** or **3**. When **2** was heated in dioxane, in either the presence or the absence of $Cu(SCN)_2$, no appreciable amounts of phenyl thiocyanate were formed. As to **3**, though its decomposition to give phenyl thiocyanate at above 120 °C had been reported,[6)] such transformation was not observed, at least under reflux (65—101 °C) in the usual solvents. However, in the presence of $Cu(SCN)_2$, **3** afforded considerable amounts of phenyl thiocyanate, along with **2** (in dioxane). On the other hand, the reaction of **1a** with $Cu(SCN)_2$ under the same conditions gave only the thiocyanate in a higher yield. Thus, it may be deduced that, in

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1) Presented at the 27th Annual Meeting of the Chemical Society of Japan, Nagoya, October, 1972.

2) S. Uemura, Y. Ikeda, and K. Ichikawa, *Tetrahedron*, **28**, 3025 (1972).

3) S. Uemura, Y. Ikeda, and K. Ichikawa, *ibid.*, **28**, 5499 (1972).

4) E. C. Taylor, F. Kienzle, and A. McKillop, *Synthesis*, **1972**, 38.

5) Though the solubility of KSCN in tetrahydrofuran was not so large as that in alcohols, a clear difference in its solubility between tetrahydrofuran and dioxane solvents was observed.

6) F. Challenger and O. V. Richards, *J. Chem. Soc.*, **1934**, 405.

Table 1. Results of the reaction of PhTlYZ with $Cu(SCN)_2$

PhTlYZ mmol		$Cu(SCN)_2$ mmol	KSCN mmol	Solvent 50ml	Temp. °C	Time hr	Products, yield(%)[a) PhSCN	**3**	**2**
1a	10	10	0	H_2O	100	5	40	0	0
	10	10	10	H_2O	100	5	30	0	15
	10	0	20	H_2O	20	0.05	0	57	0
	10	0	20	H_2O	100	5	0	0	36
	10	10	0	MeOH	65	5	44	0	0
	10	10	20	MeOH	65	5	7	0	25
	10	0	20	MeOH	20	0.05	0	49	0
	10	0	20	MeOH	65	5	0	0	29
	10	10	0	EtOH	78	5	46	0	0
	10	10	20	EtOH	78	5	18	0	22
	10	10	0	THF	65	5	42	0	0
	10	10	20	THF	65	5	13	0	13
	10	10	0	Dioxane	101	5	58	0	0
	10	10	10	Dioxane	101	5	82	0	0
	10	10	20	Dioxane	101	5	75	0	0
	10	10	40	Dioxane	101	5	56	0	11
	10	0	20	Dioxane	101	5	0	0	50
	10	10	20	Dioxane	101	1	75	0	0
	10	10	20	Dioxane	70	5	62	0	0
	10	10	20	Dioxane-H_2O[b)	89	5	33	0	11
	10	10	0	MeCN	82	5	8	0	0
	10	10	20	MeCN	82	5	27	0	0
	10	10	0	Pyridine	115	5	38	0	0
	10	10	10	Pyridine	115	5	45	0	0
3	5	0	5	MeOH[c)	65	5	0	0	48
	5	5	10	Dioxane[c)	101	5	27	0	27
4a	5	5	10	Dioxane[c)	101	5	trace	0	0
5	5	5	0	Dioxane[c)	101	5	trace	0	0
	5	5	10	Dioxane[c)	101	5	trace	0	0

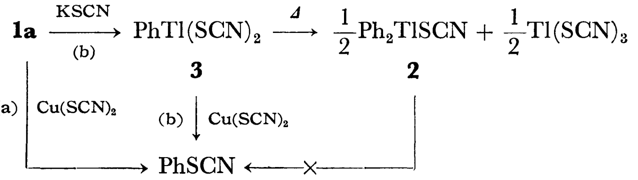
1a: $PhTl(OAc)ClO_4 \cdot H_2O$, **2**: $Ph_2Tl(SCN)$, **3**: $PhTl(SCN)_2$, **4a**: $PhTl(OCOCF_3)_2$, **5**: $PhTlCl_2$.

a) Based on Tl compound charged (Glc determination).

b) Dioxane: H_2O=7: 3.

c) Solvent 25 ml.

dioxane, thiocyanation using a mixture of $Cu(SCN)_2$ and KSCN occurs directly by Path (a) mainly and *via* **3** by Path (b) partly, while in hydroxylic solvents it is accompanied by a significant formation of **3**, which may be responsible for the facile disproportionation. In connection with the reactivity of **3**, it is worthwhile to note that phenylthallium(III) dichloride and bis(trifluoroacetate) were almost unreactive toward $Cu(SCN)_2$, even in the presence of KSCN in dioxane (see Table 1).



Although $Cu_2(CN)_2$ and CuCl could be used as reagents for cyano- and chlorodethallation respectively,[2,3) CuSCN was found to be not so effective for thiocyanodethallation. For example, the reaction of **1a** (10 mmol) with CuSCN (20 mmol) in dioxane gave a 12% yield of phenyl thiocyanate under reflux for 5 hr; the addition of KSCN (40 mmol) improved the yield to 22%. In the cases of tetrahydrofuran and pyridine solvents, only trace amounts of the thiocyanate were formed.

When certain arylthallium(III) acetate perchlorate monohydrates (**1b**—**e**) were treated with $Cu(SCN)_2$ in dioxane in the presence of KSCN, the corresponding arylthiocyanates and aromatic hydrocarbons were obtained, showing that both thiocyanation and protonation occurred at the position where the thallium was attached to the aromatic ring. As can be seen in Table 2, hydrodethallation is accelerated by the presence of electron-releasing groups as aromatic substituents and also with an increase in the water content in the reaction mixture. This is the same tendency as was previously observed in the reaction between **1** and $CuCl_2$.[3) Here, the proton clearly comes from water, and **1** may serve as a source of water when no external water was added to the reaction system. In thiocyanation, the reverse substituent effect was observed, indicating a nucleophilic character of the reaction; *e.g.*, the yields of aryl thiocyanates from **1d**

$$\underset{\textbf{1b—e}}{ArTl(OAc)ClO_4 \cdot H_2O} \xrightarrow[KSCN]{Cu(SCN)_2} ArSCN + ArH \qquad (2)$$

b: $4\text{-}CH_3$, **c**: $3,4\text{-}(CH_3)_2$, **d**: $2,4\text{-}(CH_3)_2$, **e**: $4\text{-}OCH_3$

TABLE 2. RESULTS OF THE REACTION OF ArTlYZ WITH $Cu(SCN)_2$ IN DIOXANE

ArTlYZ mmol	$Cu(SCN)_2$ mmol	KSCN mmol	Solvent ml	Temp. °C	Time hr	Products, yield (%)[a) ArSCN	Products, yield (%)[a) ArH
1b 10	10	0	50	101	5	42	0
10	10	10	50	101	5	49	trace
10	10	20	50[b)	89	5	18	19
1c 5	5	5	25	101	5	36	16
1d 5	5	5	25	101	5	13	46
1e 10	10	20	50	101	5	21	55
4b 10	10	20	50	101	5	trace	0

1b: $4\text{-}CH_3C_6H_4Tl(OAc)ClO_4\cdot H_2O$, **1c**: $3,4\text{-}(CH_3)_2C_6H_3Tl(OAc)ClO_4\cdot H_2O$, **1d**: $2,4\text{-}(CH_3)_2C_6H_3Tl(OAc)ClO_4\cdot H_2O$, **1e**: $4\text{-}CH_3OC_6H_4Tl(OAc)ClO_4\cdot H_2O$, **4b**: $4\text{-}ClC_6H_4Tl(OCOCF_3)_2$.

a) Based on Tl compound charged (Glc determination).

b) Dioxane: H_2O=7: 3.

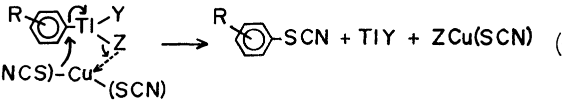
and **1e** were very low (below *ca.* 20%).

The following observations will also serve to make it possible to presume a probable reaction mechanism. In the reactions between equimolar amounts of **1a** and $Cu(SCN)_2$, the yields of phenyl thiocyanate sometimes exceeded 50%. Moreover, the pale green color of a dioxane solution of $Cu(SCN)_2$, though its solubility is very limited, did not change on 5 hrs' refluxing. These facts appear to exclude the possibility of thiocyanogen formation (by Eq. (3)) and its participation as reactive

$$Cu(SCN)_2 \longrightarrow CuSCN + \frac{1}{2}(SCN)_2 \qquad (3)$$

species, at least in dioxane, which has been the subject of several experiments.[7,8)] A route *via* phenyl isothiocyanate was also eliminated by an experiment examining its isomerization. Further, the reaction between **1a** and a mixture of $Cu(OAc)_2$ and KSCN in dioxane afforded no phenyl thiocyanate, indicating that no ligand exchange to form $Cu(SCN)_2$ occurred. Thus, it is clear that the thiocyano group comes from $Cu(SCN)_2$ itself. Since no biphenyl was found in the reaction products from **1a**, the possibility *via* an organocopper compound can also be excluded. In addition, the reaction does not appear to involve a radical path, because when **1a** was treated with a mixture of $Cu(SCN)_2$ and KSCN in dioxane in the presence of acrylonitrile, neither an acrylonitrile polymer nor arylated acrylonitrile was formed and no effect on the yield of phenyl thiocyanate was observed.

After a consideration of all the above results, the most plausible mechanism involving a concerted nucleophilic substitution after coordination is proposed to be as follows:



(4)

In cases where KSCN is added to the reaction system, one might expect the participation of $Cu(SCN)_4^{2-}$ as the attacking species which would be a more powerful nucleophile than $Cu(SCN)_2$, since the formation of the complex anion from $Cu(SCN)_2$ and KSCN in acetonitrile has been established.[8)] However, this seems to be very unlikely; the coordination number of Cu(II) is generally known to be 4, and hence the above anion is thought to be ineffective for such a reaction involving initial coordination.

Experimental

The IR spectra were taken with Hitachi EPI-2 and EPS-3T spectrometers. The NMR spectra were recorded by a Varian A-60 spectrometer in $CDCl_3$, using TMS as the internal standard. The glc analyses were carried out on a Shimadzu 5APTF apparatus, using PEG 6000(25%)-Chromosorb W (3 m) and Apiezon L (30%)-Celite (3 m) columns (He as the carrier gas).

Materials. All the organic materials except the arylthallium(III) compounds were purified immediately before use by distillation, while commercially-available CuSCN and KSCN were used without further purification. $Cu(SCN)_2$ was preqared by the reported method from $CuSO_4\cdot 5H_2O$ and KSCN.[8)] The prepatation of various arylthallium(III) compounds, except for phenylthallium(III) dithiocyanate, and diphenylthallium(III) thiocyanate, was described in previous papers.[2,3)]

Formation of Phenylthallium(III) Dithiocyanate (3) and Diphenylthallium(III) Thiocyanate (2). Reactions of Phenylthallium(III) Acetate Perchlorate Monohydrate (1a) with KSCN in Hydroxylic Solvents. By the addition of a solution of 1.9 g (20 mmol) of KSCN dissolved in water (25 ml) to an aqueous solution (25 ml) of 4.6 g (10 mmol) of **1a** at room temperature, **3** was readily obtained as a white amorphous precipitate in a 57% yield; mp 130—140 °C (d) [lit,[6)] mp 100—120 °C (d)]. Found: C, 24.07; H, 1.22; N, 7.15%. Calcd for $C_8H_5N_2S_2Tl$: C, 24.16; H, 1.27; N, 7.05%. A similar reaction at the refluxing temperature in water for 5 hr gave a white precipitate, **2** (which is soluble in alcohols and insoluble in water), in a 36% yield; mp 285—287 °C. Found: C, 37.40; H, 2.39; N, 3.28%. Calcd for $C_{13}H_{10}NSTl$: C, 37.41; H, 2.59; N, 3.36%. The preparations of **3** and **2** could be carried out similarly in a methanol solvent. Further, when 2.0 g (5 mmol) of **3** was heated for 5 hr in refluxing methanol (25 ml) containing 0.5 g (5 mmol) of KSCN, 0.5 g (1.2 mmol) of **2** was formed.

Reactions of Arylthallium (III) Acetate Perchlorate Monohydrates (1) with $Cu(SCN)_2$ in Dioxane. The following example shows a typical experimental procedure. A mixture of 4.6 g (10 mmol) of **1a**, 1.8 g (10 mmol) of $Cu(SCN)_2$, and 1.9 g (20 mmol) of KSCN in 50 ml of dioxane was stirred at 101°C for 5 hr, during which period the color of the heterogeneous

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[7)] H. P. Kaufmann and K. Küchler, *Ber.*, **67**, 944 (1934).

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

solution changed from pale black to deep yellow. After the filtration of the yellow precipitate (6.2 g), the yellow filtrate was diluted with aqueous NaCl (sometimes white **2** was precipitated) and extracted with benzene. The benzene extract contained 8.2 mmol (82% yield) of phenyl thiocyanate and no phenyl isothiocyanate (determined by glc; benzyl acetate was used as the internal standard). Phenyl thiocyanate was isolated in a pure form by distillation at 101—102 °C/18 mmHg. IR ν_{SCN} 2150 cm^{-1} (s). The washing of the yellow precipitate with hot water left a greyish-yellow solid (4.3 g), which was shown by IR spectroscopy to contain thiocyano and acetate and no perchlorate groups; it was probably a mixture of CuSCN, Cu(SCN)$_2$, and Cu(SCN)(OAc). The treatment of the water-washing containing perchlorate ion with dil. HCl gave a precipitate (1.5 g) of TlCl.

In similar reactions using other arylthallium(III) salts, the formation of the corresponding aryl thiocyanates and aromatic hydrocarbons was observed. The yields of both compounds were determined by glc (benzyl acetate and ethylbenzene were used respectively as the internal standards). Aromatic thiocyanates were isolated by distillation and identified by means of their IR and NMR spectra. *p*-Tolyl thiocyanate, bp 117—118 °C/20 mmHg; 3,4-dimethylphenyl thiocyanate, bp 140—141 °C/28 mmHg; *p*-Anisyl thiocyanate, bp 159—160 °C/27 mmHg.