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Aromatic Thiocyanation by a Mixture of Antimony(V) Chloride and Lead(II) Thiocyanate

Sakae UEMURA,* Akira ONOE, Hajime OKAZAKI, and Masaya OKANO
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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Alkyl- and halobenzenes give thiocyano-derivatives when treated with a mixture of $SbCl_5$ and $Pb(SCN)_2$ in CCl_4. The reaction proceeds *via in situ* formation of ClSCN from $SbCl_5$ and $Pb(SCN)_2$ followed by its attack on aromatic compounds catalyzed by $SbCl_5$, the reaction species being $SCN^+SbCl_6^-$.

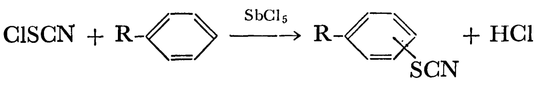
Nuclear thiocyanation of aryl ethers and amines and polymethylbenzenes has been carried out with thiocyanogen[1] or thiocyanogen chloride.[2] However, thiocyanation of less reactive aromatic compounds requires a Lewis-acid catalyst such as $AlCl_3$.[3] Other methods for the preparation of aromatic thiocyano-derivatives involve the Gattermann and Sandmeyer reaction[1] and the reaction of arylthallium compounds with copper thiocyanates[4] or with KSCN under irradiation of light.[5] We report here another simple method of nuclear thiocyanation of less reactive aromatic compounds such as alkyl- and halobenzenes by a mixture of $SbCl_5$ and $Pb(SCN)_2$.

Results and Discussion

To a heterogeneous mixture of antimony (V) chloride and lead (II) thiocyanate in carbon tetrachloride was added aromatic compound, and the mixture was then heated under reflux for 3 hr to give aryl thiocyanate occasionally together with aryl chloride. Aryl thiocyanate was generally obtained predominantly and in good yield when aromatic compound was added drop by drop at 58—62 °C where the color of the mixture is yellow-orange owing to the formaion of ClSCN, and when the molar ratio of $SbCl_5$ to $Pb(SCN)_2$ is 1—1.67. No isomeric aryl isothiocyanate was found in the reaction products. When more $SbCl_5$ was used, the formation of aryl chloride became predominant as expected.[6] Only in the case of benzene, the best yield of phenyl thiocyanate was obtained when benzene was added at room temperature (20—25 °C) and the mixture was then rapidly heated to reflux. The results are summarized in the Table. Reactions in other solvents such as chloroform and 1,2-dichloroethane did not give the satisfactory results.

The reaction is clearly electrophilic, and no reaction occurred with compounds having strong deactivating substituent, such as nitrobenzene, acetophenone, and ethyl benzoate. The reaction seems to proceed by the following schemes 1 and 2.

$$2SbCl_5 + Pb(SCN)_2 \rightarrow 2SbCl_3 + PbCl_2 + 2ClSCN \qquad (1)$$



(2)

Namely, thiocyanogen chloride is formed by the interaction of antimony(V) chloride with lead (II) thiocyanate and then it attacks aromatic compound. When cyclohexene instead of aromatic compound was added as substrate in this reaction system ($SbCl_5/Pb(SCN)_2=1-1.67$), *trans*-1-chloro-2-thiocyanocyclohexane was formed in 60—80% yield together with *cis*- and *trans*-1,2-dichlorocyclohexanes (10—40%), showing clearly the presence of ClSCN in the reaction mixture. The addition of ClSCN to olefin has already been known.[2a] Here, any trace of 1,2-dithiocyanocyclohexane was not detected in the reaction products. Further, it is clear that $SbCl_5$ activates ClSCN in the succeeding thiocyanation as in the case of the $SbCl_5$-catalyzed halogenation,[7] since only a trace amount and 13% yield of aryl thiocyanate was obtained respectively from the reaction of benzene and toluene with ClSCN formed *in situ* from a mixture of $Pb(SCN)_2$ (10 mmol) and $PhICl_2$ (20 mmol) instead of $SbCl_5$ in CCl_4 (50 ml). The k_T/k_B value of 150—160 and *o*-/*p*- ratio of 0.40—0.46 observed in competitive reaction between toluene and benzene suggest that the attacking species is not molecular ClSCN but slightly activated species. If molecular ClSCN is the reaction species, larger k_T/k_B value should be obtained since the reactivity of ClSCN is known to be nearly the same as ICl[2a] which is less reactive than Br_2. Taking into account the Lewis-acidity of $SbCl_5$, the reaction species seems to be $SCN^+SbCl_6^-$. The above facts mean that $SbCl_5$ acts as both the source of thiocyanogen chloride and a Lewis-acid catalyst for the thiocyanation.

By use of other metal thiocyanates such as AgSCN, CuSCN or $Hg(SCN)_2$ in place of $Pb(SCN)_2$, phenyl thiocyanate was formed from benzene in 41%, 26% or 21% yield respectively under the conditions where 32% yield was obtained by use of the lead salt. Reactions with $Cu(NCS)_2$, $Zn(SCN)_2$, $Cd(SCN)_2$, and KSCN did not give the satisfactory results.

Experimental

The NMR spectra were measured with a Varian A-60 spectrometer in CCl_4, using TMS as an internal standard. The IR spectra were taken with a Perkin-Elmer Model 521 spectrometer. Glc analyses were carried out on Shimadzu 5APTF apparatus, using PEG 6000 (25%)-Chromosorb W (3m) and Apiezon L (30%)-Celite (1 m) columns (N_2 as carrier gas), phenyl isothiocyanate being used as an internal standard for the determination of aryl thiocyanate. Commercial organic materials, $SbCl_5$, and metal thiocyanates were used without purification. The identification of phenyl, tolyl and 3,4-dimethylphenyl thiocyanates[4] and *trans*-1-chloro-2-thiocyanocyclohexane[8] was reported previously. Competitive reaction was carried out by rapid addition of a mixture of benzene (0.2 mol) and toluene (0.1 mol) to a CCl_4 solution of $Pb(SCN)_2$ (10 mmol) and $SbCl_5$ (16.7 mmol)

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* To whom all correspondences should be addressed.

Table. Thiocyanation of alkyl- and halobenzenes in CCl_4 (50 ml)

Aromatics (100 mmol)	$SbCl_5$ (mmol)	$Pb(SCN)_2$ (mmol)	Products		
			ArSCN(%)[a]	(*p*/*o*)	ArCl(%)[a]
Benzene	25	15	32		11
Benzene[b]	25	15	64		13
Toluene	10	10	41	(2.50)	0
Toluene	16.7	10	42	(2.50)	1
Ethylbenzene	10	10	41	(2.74)	0
Cumene	10	10	36	(5.79)	0
t-Butylbenzene	10	10	45[c]		—[d]
o-Xylene	10	10	55[e]		3
m-Xylene	10	10	69[f]		trace
p-Xylene	10	10	62[g]		trace
Mesitylene	10	10	68[h]		0
Fluorobenzene	16.7	10	25[i]		1
Chlorobenzene	16.7	10	15	(4.70)	1
Bromobenzene	10	10	14	(2.46)	3

a) Based on $SbCl_5$ charged. b) Only in this case benzene was added at 25 °C and the mixture was then rapidly heated to reflux. c) Almost *p*-isomer. d) Not determined. e) 2,3- and 3,4-Dimethylphenyl thiocyanates (1 : 9). f) 2,4-Dimethylphenyl thiocyanate. g) 1,4-Dimethylphenyl thiocyanate. h) 2,4,6-Trimethyl phenyl thiocyanate. i) Only *p*-isomer.

at 62 °C and then by stirring at reflux for 1 hr.

Preparation of 2,5-Dimethylphenyl Thiocyanate. The following is a typical procedure for the thiocyanation. *p*-Xylene (10.6 g, 0.1 mol) was added drop by drop (*ca.* in 5 min) at 58—60 °C under vigorous stirring to a yellow-orange heterogeneous solution of $SbCl_5$ (3 g, 10 mmol) and $Pb(SCN)_2$ (3.23 g, 10 mmol) in CCl_4 (50 ml). The mixture was then heated to 79 °C (reflux) and stirred for 3 hr. After being cooled down to room temperature, 300 ml of water was added to the solution and the precipitated white solid of SbOCl (1.6 g, 9.25 mmol) was filtered off. Organic layer of the filtrate was washed with water, dried over Na_2SO_4, and concentrated to *ca.* 25 ml which contained 6.2 mmol (62% yield) of 2,5-dimethylphenyl thiocyanate and a trace amount of chlorinated *p*-xylene. Distillation gave 0.82 g (5 mmol) of 2,5-dimethylphenyl thiocyanate; bp 136—138 °C/20 mmHg. IR 2162 cm^{-1} (ν_{SCN}). NMR δ 2.31 (s. 3H), 2.37 (s. 3H), 7.0—7.1 (m, 2H), 7.34 (s. 1H). Found: C, 65.68; H, 5.67; N, 8.28%. Calcd for C_9H_9NS: C, 66.22; H, 5.56; N, 8.58%.

Characterization of other aryl thiocyanate is as follows. NMR and IR spectra of all compounds were consistent with the structure. IR 2126 cm^{-1} (ν_{SCN}). Ethylphenyl(*p*/*o*=2.7), bp 137—139 °C/19 mmHg; Found: C, 66.47; H, 5.61; N, 8.58%. Calcd for C_9H_9NS: C, 66.22; H, 5.56; N, 8.58. Isopropylphenyl(*p*/*o*=5.8), bp 140—142 °C/20 mmHg; Found: C, 67.49; H, 6.27; N, 7.75%. Calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.25; N, 7.90%. 4-*t*-Butylphenyl, bp 152—154 °C/20 mmHg; Found: C, 69.21; H, 7.00; N, 7.19%. Calcd for $C_{11}H_{13}NS$: C, 69.06; H, 6.85; N, 7.32%. 2,4-Dimethylphenyl, bp 141—143 °C/26 mmHg (lit,[2c] bp 133—134 °C/12 mmHg). 2,4,6-Trimethylphenyl, bp 135—137 °C/28 mmHg, mp 70—72 °C (lit,[3] 71—72 °C). 4-Fluorophenyl, bp 89—91 °C/6 mmHg (lit,[9] bp 103—105 °C/10 mmHg). Chlorophenyl(*p*/*o*=4.7), bp 96.5—97 °C/4 mmHg (lit, *o*-isomer,[9] bp 120—123 °C/9 mmHg; *p*-isomer,[10] mp 35—36 °C. Bromophenyl(*p*/*o*=2.4), bp 130—132 °C/21 mmHg; *p*-isomer, mp 52—53.5 °C (lit,[9] *p*-isomer, mp 53—54 °C).

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