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The Aromatic Thiocyanation of 1-Alkoxynaphthalene by the Copper(II) Thiocyanate Method

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Synopsis. A facile thiocyanation of 1-alkoxynaphthalene using copper(II) thiocyanate afforded 4-thiocyanato compound. The reaction proceeded at a moderate temperature (80—90 °C) even for 1-alkoxynaphthalene with higher alkyl groups (C_6, C_8, and C_{12}).

During the course of an investigation of the pesticidal activities of aryl ethers it became desirable to prepare thiocyanato compounds of 1-alkoxynaphthalene because of their effected insecticidal and fungicidal activities.[1]

As a means of introducing a thiocyanato group into the aromatic nucleus, thiocyanogen is useful as a reagent for such reactive substrates as amines and phenols.[2] Less reactive substrates, such as phenolic ethers, naphthalene derivatives, and anillides, which are unreactive towards thiocyanogen, give thiocyanates in high yields when treated with thiocyanogen chloride in acetic acid;[3] however, 2-methoxynaphthalene reacts with not only thiocyanogen chloride[3] but also thiocyanogen[2,4] to give the 1-thiocyanato compound. As to the thiocyanation of 1-methoxynaphthalene, it has been thiocyanated at the 4-position in a 10.7% yield by a mixture of KSCN and *N*-chlorourea in acetone.[5] The 4-thiocyanato compounds of 1-ethoxy, 1-propoxy, 1-butoxy, and 1-isopentyloxy naphthalene have also been synthesized in a liquid state in a similar manner.[6] Other methods for the thiocyanation of aryl ethers involve the reaction of arylthallium(III) compounds with copper(II) and (I) thiocyanate[7] or with KSCN under the irradiation of light.[8]

The present paper will deal with the preparation of 1-alkoxy-4-thiocyanatonaphthalene by the copper(II) thiocyanate method[9], which was previously applied to the thiocyanation of 1-naphthol.[2] It is considered that the copper(II) thiocyanate method shows promise of being effective for the thiocyanation of higher alkyl naphthyl ethers, since copper(II) thiocyanate releases thiocyanogen merely by the dissociation of the cupric to cuprous salt (Eq. 1). Moreover, the procedure has the advantage over the others previously described of permitting a higher temperature for thiocyanation.

$$2Cu(SCN)_2 \rightarrow 2CuSCN + (SCN)_2 \quad (1)$$

Thiocyanation with $(SCN)_2$ was less reactive in higher alkyl (C_6–C_{12}) naphthyl ethers due to an electrophilic attack of SCN^+.

To a solution of 1-alkoxynaphthalene in acetic acid we added copper(II) thiocyanate, freshly prepared[10] in advance; the mixture was then warmed while being stirred for 2.0 to 2.5 h. The reaction is accompanied by a color change from black to white[2] (actually from black to a yellowish green or yellow color) due to the formation of copper(I) thiocyanate.

$$ArH + 2Cu(SCN)_2 \rightarrow ArSCN + 2CuSCN + HSCN \quad (2)$$

Usually the 4-thiocyanato compound of 1-alkoxynaphthalene was obtained in a good yield when the molar ratio of $Cu(SCN)_2$ to the 1-alkoxynaphthalene was 4 to 1. The IR and NMR spectra[11] revealed no isomeric naphthyl isothiocyanate or 2-thiocyanato compound in the reaction product. When the molar ratio of $Cu(SCN)_2$ to 1-ethoxynaphthalene was 2 to 1, and when the reaction temperature was raised to the range from 115 to 118 °C, no thiocyanate was produced, but a small amount of the disulfide of 4-ethoxynaphthalene was obtained. The experimental results are summerized in Table 1.

Experimental

The method used in the preparation of 1-alkoxynaphthalene was a modification of the method of Yokoyama *et al.*[12] The IR spectra were recorded on a Hitachi EPI G3 spectrophotometer. The NMR spectra were taken on a Varian A-60 or on a Japan Electron JNM-G-60 or 100 spectrometer in $CDCl_3$, using TMS as the internal standard.

The following is a typical method for the thiocyanation.

Thiocyanation of 1-Methoxynaphthalene. Copper(II) thiocyanate (100 mmol), which has been prepared according to the directions of Jenkins and Kochi,[10] was suspended in a solution of 1-methoxyanphthalene (25 mmol) in glacial acetic acid (30 ml). The mixture was then warmed while being stirred until the solid of copper(II) thiocyanate turned brownish yellow. After cooling, the solid, which was extracted with ether if necessary, was filtered off. The filtrate was cooled or poured into 300 ml of ice water, and the resulting solid was extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, thus giving a crystalline residue. In the course of a number of preparations, both low-melting (95—97 °C; yellow plates) and high-melting (102—102.5 °C; colorless plates) forms were obtained. (The reported value is 105—105.5 °C.[5]) The former was converted to the high-melting variety upon numerous recrystallizations from methanol. The IR and NMR spectra of the yellow plates were exactly the same as those of the colorless ones. IR ($CHCl_3$) 2145 cm^{-1} (SCN). NMR ($CDCl_3$) δ=3.91 (3H, s, OCH_3), 6.72 (1H, d, J=7.5 Hz, aromatic proton of the 2-position[11]), 7.74 (1H, d, J=7.5 Hz), 7.4—7.7 (2H, m), 8.1—8.4 (2H, m, aromatic proton of the 5 and 8 positions[11]) Found: C, 67.13; H, 3.91; N, 6.55; S, 14.91%; M^+, 215. Calcd for $C_{12}H_9NOS$: C, 66.95; H, 4.21; N, 6.51; S, 14.89%; M, 215.

The characterization of other alkoxynaphthyl thiocyanates is as follows. R=C_2H_5, mp 73.5—75 °C). (recrystallization solvent; ethanol. Lit,[6] bp/7 Torr 105 °C). IR ($CHCl_3$) 2140 cm^{-1}. NMR ($CDCl_3$) δ=1.52 (3H, t, J=7 Hz), 4.16 (2H, q, J=7 Hz), 6.64 (1H, d, J=8 Hz), 7.69 (1H, d, J=8 Hz), 7.3—7.7 (2H, m), 8.1—8.3 (2H, m). Found: C, 67.95; H, 4.68; N, 6.23; S, 13.92%: M^+, 229. Calcd for $C_{13}H_{11}NOS$; C, 68.10; H, 4.84; N, 6.11; S, 13.98%; M, 229. R=*n*-C_3H_7, mp 82.2—83.5 °C (isopropanol, lit,[6] bp/4 Torr

Table 1. Thiocyanation of 1-alkoxynaphthalene

R	Alkoxynaphthalene : $Cu(SCN)_2$ (molar ratio)		Temp (°C)	Time (h)	Yield (%)
CH_3	1	4	67—70	2.5	79.2
C_2H_5	1	4	64—69	2.0	80.8
C_2H_5[a)]	1	2	115—118	5.0	—
n-C_3H_7	1	4	70—76	2.8	67.8
n-C_4H_9	1	4	65—70	2.5	60.3
i-C_5H_{11}	1	4	72—76	6.0	50.8
	1	4	75—79	0.8	32.6
	1	3	70—76	2.0	35.9
n-C_6H_{13}	1	4	77—79	2.5	38.5
n-C_8H_{17}	1	4	90—92	1.5	19.1
n-$C_{12}H_{25}$	1	4	77	2.4	24.2

a) The product is bis(1-ethoxynaphthyl) disulfide.

109—110 °C). IR ($CHCl_3$) 2145 cm^{-1}. NMR ($CDCl_3$) δ= 1.08 (3H, t, J=7 Hz), 1.90 (2H, sex, J=7 Hz), 4.00 (2H, t, J=7 Hz, OCH_2), 6.65 (1H, d, J=8 Hz), 7.72 (1H, d, J=8 Hz), 7.3—7.8 (2H, m) 8.1—8.5 (2H, m). Found: S, 13.55%; M^+, 243. Calcd for $C_{14}H_{13}NOS$: S, 13.18%; M, 243. R=n-C_4H_9, mp 50—51.5 °C (methanol, lit,[6)] bp/6 Torr 127—130 °C). IR ($CHCl_3$) 2140 cm^{-1}. NMR ($CDCl_3$) δ=1.01 (3H, t, J=7 Hz), 1.3—2.1 (4H, m), 4.07 (2H, t, J=7 Hz), 6.66 (1H, d, J=8 Hz), 7.69 (1H, d, J=8 Hz), 7.3—7.7 (2H, m), 8.1—8.3 (2H, m). Found: C, 70.01; H, 5.87; N, 5.44; S, 12.46%; M^+, 257. Calcd for $C_{15}H_{15}NOS$: C, 70.30; H, 5.90; N, 5.65; S, 12.42%; M, 257. R=iso-C_5H_{11}, mp 40—41 °C (methanol, lit,[6)] bp/5 Torr 113—116 °C). IR (KBr) 2140 cm^{-1}. NMR ($CDCl_3$) δ=1.01 (6H, d, J=6 Hz, $(CH_3)_2$-C), 1.5—2.0 (3H, m), 4.18 (2H, t, J=6 Hz), 6.88 (1H, d, J=8.5 Hz), 7.91 (1H, d, J=8.5 Hz), 7.3—7.9 (2H, m), 8.2—8.6 (2H, m). Found: C, 70.58; H, 6.49; N, 5.22; S, 11.80%; M^+, 271. Calcd for $C_{16}H_{17}NOS$: C, 70.82; H, 6.31; N, 5.16; S, 11.81%; M, 271. R=n-C_6H_{13}, mp 41 °C (methanol-water). IR ($CHCl_3$) 2140 cm^{-1}. NMR ($CDCl_3$) δ=0.91 (3H, deformed t), 1.40 (8H, m), 4.08 (2H, t, J= 6 Hz), 6.70 (1H, d, J=8 Hz), 7.75 (1H, d, J=8 Hz), 7.2— 7.9 (2H, m), 8.1—8.5 (2H, m). Found: C, 71.45; H, 6.65; N, 4.90%; M^+, 285. Calcd for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71; N, 4.91%; M, 285. R=n-C_8H_{17}, mp 44 °C (methanol). IR (KBr) 2140 cm^{-1}. NMR ($CDCl_3$) δ=0.91 (3H, deformed t), 1.36 (12 H, m), 4.16 (2H, t, J=6 Hz), 6.82 (1H, d, J= 8 Hz), 7.87 (1H, d, J=8 Hz), 7.5—8.0 (2H, m), 8.2—8.5 (2H, m). Found: C, 72.31; H, 7.41; N, 4.52; S, 10.18%; M^+, 313. Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40; N, 4.47; S, 10.22%; M, 313. R=n-$C_{12}H_{25}$, mp 44.5—45 °C (acetone-methanol). IR (KBr) 2125 cm^{-1}. NMR ($CDCl_3$) δ=0.88 (3H, deformed t), 1.1—2.3 (20H, m), 4.16 (2H, t, J=6 Hz), 6.81 (1H, d, J=8 Hz), 7.86 (1H, d, J=8 Hz), 7.5—8.0 (2H, m), 8.2—8.5 (2H, m), Found: C, 74.90; H, 8.46; N, 3.65; S, 8.41%, M^+, 369. Calcd for $C_{23}H_{31}NOS$: C, 74.75; H, 8.45; N, 3.79; S, 8.68%; M, 369.

Bis(1-ethoxynaphthyl) disulfide, mp 144.5—145 °C (ethyl acetate). IR ($CHCl_3$) No characteristic band of νSCN. NMR ($CDCl_3$) δ=1.47 (3H, t, J=7 Hz), 4.07 (2H, q, J= 7 Hz), 6.46 (1H, d, J=8 Hz), 7.40 (1H, d, J=8 Hz), 7.2— 7.6 (2H, m), 8.1—8.4 (2H, m). Found: C, 70.94; H, 5.57; S, 15.75%; M^+, 406. Calcd for $C_{24}H_{22}O_2S_2$: C, 70.90, H, 5.46; S, 15.77%; M, 406.

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